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The study of lead adsorption from aqueous solution by carbon nanotubes (CNTs): Adsorption equilibrium and kinetics

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ABSTRACT

Adsorption is a method for removing heavy metals from wastewater. The adsorption of lead from aqueous solution on multiwall carbon nanotubes (CNTs) has been investigated using a series of batch adsorption methods. In this work, adsorption rate was studied experimentally at various temperatures (283,298 and 303K), contact time, initial pH and initial lead concentration. It was observed that the lead adsorption rates increased dramatically in the initial times of experiment and reached equilibrium after 6 hrs. The optimum pH was six. Adsorption isotherm, the experimental data have been analyzed by four two-parameter isotherms (Langmuir, Frendhich, Temkin and Dubinin-Radushkevich) and four three-parameter isotherms (Redhich-Peterson, Sips, Toth and Khan). The data was fitted by linear and non-linear regression and three error functions were used to evaluate the goodness of the fitting. Four kinds of kinetic models were used to test the experimental data, which were intraparticular diffusion, Lagergren-first-order, second-order and the Elovich equation. The results showed that the second-order kinetic model was the best model. Thermodynamic parameters (DGp, DHp, and DSp) were determined in the temperature range of 283 to 308 K. These parameters showed that the adsorption of Pb (II) onto CNTs was a spontaneous and endothermic process.

KEYWORDS

Carbon nanotubes;
Lead;
Adsorption isotherm;
Kinetics;
Thermodynamic parameter.

INTRODUCTION

Lead is one of the common heavy metals that exists in industrial wastewater and mineral water. Lead is a poisonous metal that can damage nervous connection (especially in young children) and cause blood and brain disorders. Many industries such as the petrochemical, painting and coating, newsprint, smelting, metal electroplating, mining, plumbing and battery industries discharge lead into the environment[1].Generally removal and recovery of heavy metals from wastewater is important for environmental protection and human health. There are several methods for removing heavy metals from wastewater such as chemical precipitation, solvent extraction, reverses osmosis, ion-exchange, evaporation, air stripping, flotation and adsorption[2]. The adsorption technique is one of the preferred methods for removal of heavy metals because of its high efficiency and simple procedure.

In recent years, various adsorbents have been used for removing metals from aqueous solution. Ahmet Sari et al. used expanded perlit (EP) for removal Cu (II) and Pb (II) from solution[3]. Adsorption characteristics were studied with respect to the changes in pH solution, adsorbent dosage, contact time and temperature of solution. They calculated Thermodynamic functions, the change of free energy, enthalpy and entropy of adsorption[3].

Zhai et al. used sawdust and modified peanut husk as adsorbent to remove Pb (II), Cr (II) and Cu (II) from aqueous solution[2]. The capacity of sawdust and modified peanut husk in adsorption of Pb (II), Cr (II) and Cu (II) have been obtained.

In other work, natural and pretreated Clinoptilohte has been used for adsorption of lead from aqueous solution[4]. Adsorption characteristics were obtained to evaluate the effects of contact time, initial concentration and pretreatment of clinoptilolite on the removal of Pb (II).

Another adsorbent that was used in recent years for heavy metal removal from wastewater are bioadsorbents. Deng et al. used green alga *Cladophora fascicularis* as bioadsorpent for adsorption of lead (II) from wastewater[5]. In another work *Agave Lechuguilla* has been also used as bioadsorbent for removing Cr (V^2) from aqueous solution[6]. Results show that *Agave Lechuguilla* can be considered as an effective biomaterial for Cr (V^2) removal from aqueous solution[6]. Activated carbon is also an effective adsorbent for heavy metal removal. Demirbas et al. used activated carbon that was prepared from agricultural waste used for removing chromium from aqueous solution[7].

After the discovery of carbon nanotubes (CNTs) by Ijima, a new member of the carbon family, many researchers have been attracted to these materials for the removal of organic and inorganic contaminants from water, because they have a large specific surface area, small size and hollow and layer structures. As an instance, in some works adsorption of lead and also zinc on carbon nanotubes have been studied[8,9].

The present work described the adsorption characteristics of lead on carbon nanotubes against several parameters including time, initial pH, initial lead concentration and temperature. The experimental data have been analyzed by adsorption isotherm and kinetic models and finally the thermodynamic parameters of adsorption were obtained.

MATERIALS AND METHODS

Preparation of adsorbent

Carbon nanotubes (CNTs) can be classified into two types: one is multi-walled CNTs (MWCNTs) and the other single-walled CNTs (SWCNTs)[10]. In this work, multi-walled CNTs which produced in Iranian Research Institute of Petroleum Industry (R.I.P.I) were used as adsorbent.

Chemicals

All chemicals used in this work were of analytical grade and the solutions were prepared using distillated water. Analytical-grade Lead(II) Nitrate (Merck Ltd., CAS-No. 10099-74-8, EC-No. 233-245-9, 99.5% purity) was employed to prepare a stock solution of Pb(II) (1000 mg/l) which was further diluted with distilled water to desired lead concentration.

In this study, we prepared various solutions with initial lead concentrations ranging from 10 to 80 mg/l. To adjust the pH, solutions of HCl and NaOH were used.

Adsorption equilibrium experiments

For equilibrium studies, batch adsorption experiments were performed. First 100 ml of solution were prepared with initial lead concentration ranging from 10 to 80 mg/l (10, 20, 30, 40, 50, 60, 70 and 80 mg/l), next 50 mg CNTs was added to each solution into 250 ml glass flasks[8,9]. The mixtures were agitated on shaker incubator (Amperetabelle Multitrun II) continuously for 6 hrs at 283,298 and 308 K, respectively.

After 6 hrs, the suspension was filtered using a 0.2μm Millipore filter (Schleicher and Schuell, Ref. No. 104 62 200) and the filtrates were analyzed for residual lead concentration by a flame atomic absorption spectrometer (Varian, Spectra AA 220). The amount of lead uptake by CNTs in each flask was calculated using the mass balance equation:

$$\mathbf{q} = \frac{(\mathbf{C_0} - \mathbf{C_t})\mathbf{V}}{\mathbf{M}} \qquad \mathbf{(1)}$$

Where q is the amount of lead adsorbed by CNTs (mg/g); C_0 is the initial lead concentrations (mg/l); C_t is the lead concentrations contained in the original solution after time t (min) (mg/l); V is the initial solution volume (l) and M is the CNTs dosage (g).

Kinetic experiments

Kinetic studies were carried out in an agitated batch sorption system. At 298 K, we prepared several solutions of lead concentrations with 50 and 80 mg/l, respectively. The pH was that of the initial solution pH. In all case, the working pH was that of the solution and was not controlled. At predetermined time intervals, samples were collected, using a 0.2 μm membrane filter and then analyzed for residual lead concentration by flame atomic absorption spectrometry. The lead adsorption amount at time t was calculated by equations (1).

THEORY

Equilibrium isotherm models

In this work, two-parameter and three-parameter isotherms were considered for analyzing the experimental data.

1.1. Two-parameter isotherm

1.1.1. Freundlich isotherm[4,11]

Freundlich isotherm assumes heterogeneous surface with a nonuniform distribution of heat of adsorption. The Freundlich equation is given by:

$$q_e = k_F C_e^{1/n} \tag{2}$$

k_F and n are Freundlich constants related to the characteristics of the system, which are indicators of adsorption capacity and adsorption intensity, respectively.Eq (2) can be linearized in logarithmic form and Freundlich constants can be determined.

1.1.2. Langmuir isotherm[12]

The Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites is given by:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \tag{3}$$

Where q_m and k_L are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. Langmuir constants can be determined from the linear plot C_e/q_e versus C_e.

1.1.3. Temkin isotherm[4]

Temkin isotherm assumes that the any decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm takes the following form:

$$q_e = \frac{RT}{b}\ln(k_T C_e) \tag{4}$$

Where k_T is the equilibrium binding constant (l/g), b is related to heat adsorption (J/mol), R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). b and k_T can be determined by plotting q_e vs. $\ln C_e$ from slope and intercept, respectively.

1.1.4. Dubinin-radushkevich isotherm[3,4]

D-R isotherm is applied to find out the adsorption mechanism based on the potential theory assuming heterogeneous surface. This model indicated that adsorption occurred by physical or chemical processes. D-R is expressed as follows:

$$q_e = q_m \exp\left(\frac{\left(RT\ln\left(1 + \frac{1}{C_e}\right)\right)^2}{-2E} \right) \tag{5}$$

If ε is the Polanyi potential:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

Then equations (5) and (6) become:

$$q_e = q_m \exp\left(\frac{\varepsilon^2}{-2E^2}\right) \tag{7}$$

Where q_m is the maximum adsorption capacity (mg/g), E is the energy of adsorption (KJ/mol), R is the universal gas constant (8.314×10^{-3} KJ/mol K) and T is the absolute temperature (K). If the E value is between 8 and 16 KJ/mol, the adsorption process follows chemical ion-exchange and if E<8 KJ/mol, the adsorption process is of a physical nature[3].

1.2. Three-parameter isotherm

1.2.1. Redlich-Peterson isotherm[11,17]

The Redlich-Peterson isotherm was proposed to improve the fit by the Langmuir and Freundlich equations and is given by:

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{8}$$

Where A and B are isotherm constants, g is the exponent which lies between 0 and 1.

1.2.2. Sips isotherm[4,11]

The model is a combination of the Langmuir and Frendlich isotherm type models. The Sips model takes the following form:

$$q_e = \frac{q_m a_S C_e^{\frac{1}{n}}}{1 + a_S C_e^{\frac{1}{n}}} \qquad (9)$$

Where q_m is monolayer adsorption capacity (mg/g) and a_S is Sips constant related to energy of adsorption.

1.2.3. Toth isotherm[4]

Toth isotherm is langmuir-based isotherm and considers a continues distribution of site affinities. The Toth model takes the following form:

$$q_e = \frac{q_m C_e}{(k_{To} + C_e^n)^{\frac{1}{n}}} \qquad (10)$$

Where k_{To} is the Toth model constant and n is the Toth model exponent ($0<n=1$). For $n=1$ this isotherm reduces to the Langmuir equation.

1.2.4. Khan isotherm[4]

Khan et al. have suggested a generalized isotherm with temperature for the equilibrium adsorption of pure solution. Khan isotherm is given as:

$$q_e = \frac{q_m b_K C_e}{(1 + b_K C_e)^{a_K}} \qquad (11)$$

q_m and b_K are the Khan model constants and a_K is the Khan model exponent.

2. Kinetic model

Four kinds of kinetic models were used to test the experimental data. These are Lagergren-first-order equation, second-order equation, Elovich equation and intraparticular equation. The conformity between experimental data and model predicted values were expressed by the correlation coefficient (R^2). A relatively high R^2 value indicates that the model successfully described the kinetics of Pb (II) adsorption.

2.1. Lagergren-first-order equation[2]

Lagergren-first-order equation is one of the most popular kinetics equations. Lagergren-first-order equation (Lagergren, 1898) is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (12)$$

Where q_e and q_t (mg/g) are the amount of sorbed lead at equilibrium and time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the Lagergren-first-order equation. After definite integration by applying the condition $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, the equation becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (13)$$

k_1 and q_e can be determined experimentally by plotting ln(q_e - q_t) against t from the slope and intercept of the plot, respectively.

2.2. Second-order equation[2]

The second-order equation is in the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (14)$$

Integration of this equation for the boundary conditions ($q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$), gives:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (15)$$

k_2 is the rate constant of second-order equation (g/mg/min). A plot of (t/qt) against t should give a linear relationship form which q_e and k_2 can be determined from the slope and intercept. If the initial adsorption rate, h (mg/g/min) is:

$$h = k_2 q_e^2 \qquad (16)$$

Then equations (15) and (16) become:

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}t \qquad (17)$$

2.3. Elovich equation[2,4,11]

The Elovich equation is of general application to chemisorptions kinetics. Adsorption rate decreases with time due to increased surface coverage. The Elovich equation is generally expressed as (Chien and Clayton, 1980; Sparks, 1986):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \qquad (18)$$

Where α is the initial adsorption rate (mg/g/min) and β is related to the extent of surface coverage and the activation energy involved in chemisorptions (g/mg).

Integration of this equation for the boundary conditions ($q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$), gives:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (19)$$

2.4. Intraparticular diffusion equation[2,13]

The intraparticular mass transfer diffusion model (Weber and Morris, 1963; Srivastava et al. 1989) is given as:

$$q_t = k_{id}\sqrt{t} + C \qquad (20)$$

Where C is the intercept and k_{id} is the intraparticle diffusion rate constant (mg/g/min$^{1/2}$), which can be calculated from the slope of linear plot of q_t versus $t^{1/2}$.

In this model, the fractional approach to the equilibrium changes according to a function of $(Dt/r^2)^{0.5}$, where D is the diffusion coefficient within the solid adsorbent and r is the particle radius.

3. Adjusting the models parameters by the experimental data

The adsorption isotherm or adsorption kinetic models with two parameters can be transformed into linear forms to obtain an adjustable parameter by linear regression analysis. But the models with more than two parameters are not fitted to the experimental data by linear regression. In this case it is necessary to apply non-linear least square analysis. For the non-linear method, a trial and error procedure, which is applicable to computer operation, was developed to determine the isotherm parameter by minimizing the respective coefficient of determination between experimental data and isotherm.

3.1 Coefficient of determination

Coefficient of determination (R^2) was also used to evaluate the comparison of isotherm model with experimental data. Coefficient of determination is given as:

$$R^2 = 1 - \frac{SSE}{SST} \qquad (21)$$

$$SST = \sum q_{exp.}^2 - \frac{\left(\sum q_{exp.}\right)^2}{p} \qquad (22)$$

$$SSE = \sum \left(q_{exp.} - q_{cal.}\right)^2 \qquad (23)$$

Where q_{exp} (mg/g) is the equilibrium value obtained from the experimental data, q_{cal} is calculated by isotherm model and p is the number of data points.

The error functions employed were as follows:

3.2 The sum of the square of the error (SSE)

This error function is the one which is widely used. SSE provides best fit at the higher concentration data as magnitude of the error.

$$SSE = \sum_{i=1}^{p} \left(q_{exp.} - q_{cal.}\right)^2 \qquad (24)$$

3.3 The hybrid fractional error function (HYBRID)

The hybrid error function was developed by Porter et al. in order to improve the fit of the SSE function at low concentration.

$$HYBRID = \frac{100}{p-n} \sum_{i=1}^{p} \left[\frac{\left(q_{exp.} - q_{cal.}\right)^2}{q_{exp.}}\right] \qquad (25)$$

Where p is the number of data points and n is the number of parameter within the equation.

3.4 The average relation error (ARE)

$$ARE = \frac{100}{p} \sum_{i=1}^{p} \left(\frac{\left|q_{exp.} - q_{cal.}\right|}{q_{exp.}}\right) \qquad (26)$$

Where p is the number of data points.

RESULTS AND DISCUSSION

1. Effect of experimental conditions on adsorption

The effect of contact time on the adsorption rate of Lead by CNTs for different initial concentrations can be seen in figure 1. It is seen from this figure that the adsorption rate increased dramatically in the first 5 minutes of contact time for various initial concentrations.

The effect of initial lead concentration on the removal of Pb2+ by CNTs is shown in figure 1. This figure shows that when the initial lead concentration is in-

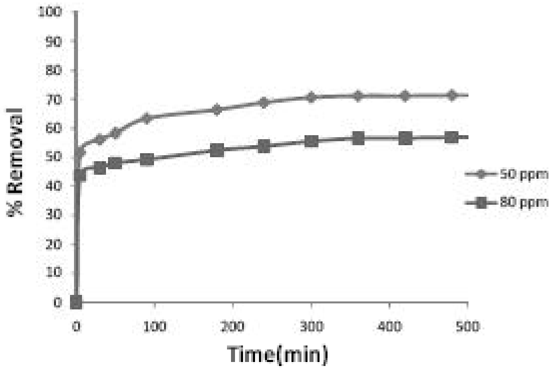

Figure 1: Effect of contact time on lead adsorption for different initial concentration (Initial pH, T=298 K)

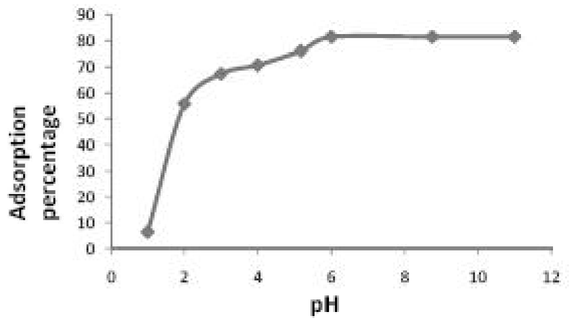

Figure 2 : Influence of the pH on adsorption percentage of lead onto CNTs (C0=50 mg/l, T=298 K)

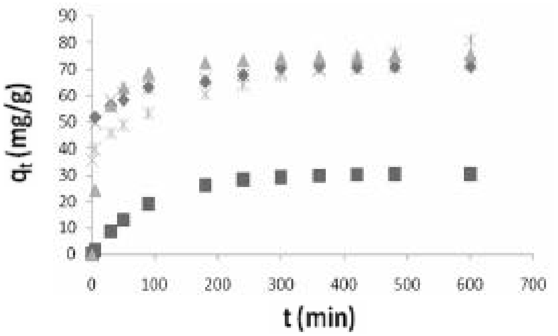

Figure 3 : Effect of agitation time and initial concentration lead on the adsorption of lead. (Initial pH, C_0=50 mg/l)

creased the percentage of adsorption decreased. This is obvious from the fact that, for constant dosage of adsorbent, equilibrium concentration of lead increase with the increasing the initial concentration of lead, then the adsorption percent decreases. Generally, the pH of solution is the most important variable that affects the metal ions adsorption. The effect of solution pH on lead adsorption is illustrated in figure 2. It can be seen that the adsorption capacity of lead by CNTs is clearly affected by the solution pH. The initial concentration of lead ion was 50 mg/l. It was apparent that the lead adsorption percentage increases with the pH value from 1 to 6. Precipitation will occur between lead and OH– as the pH exceed to six, so our experiments were carried out only under acidic condition. At pH values below the point after which the hydroxide precipitation begin to formulate, the decreased adsorption with the decrease of pH maybe is due to competition for sorption sites between lead and proton.

2. Adsorption kinetics

Figure 3 shows the kinetics of lead ion adsorption onto the CNTs. Four kinetic models, Lagergren-first order equation, second order equation, Elovich equation and intraparticle diffusion equation were used to fit the experimental data by linear regression. For comparison of kinetic models, we used correlation coefficient (R^2). The value of parameters and correlation coefficients for each model are presented in TABLE 2.

The Lagergren first order equation was used to correlate the experimental data based on the following mechanistic scheme:

$$M_{sol} + Pb^{+2}_{aq} \rightarrow MPb^{+2}_{sol.phase} \qquad (27)$$

One lead ion was assumed to sorb onto one adsorption site of the CNTs surface. As can be seen in figure 3.and TABLE 1, the calculated amount of adsorption equilibrium is far from the actual amount of adsorption equilibrium. Hence, this equation cannot provide an accurate fit of the experimental data[11] the second order model assumes that lead is sorbed onto two active sites:

$$2M_{sol} + Pb^{+2}_{aq} \rightarrow M_2Pb^{+2}_{sol.phase} \qquad (28)$$

The second order equation appeared to be the better fitting model than the Lagergren-first-order equation because it had a higher R^2. The calculated amount of adsorption equilibrium is similar to the actual amount

TABLE 1 : Comparison of adsorption kinetics constant

Temperature = 298 K			Temperature = 298 K		
	C_0=50 ppm	C_0=80 ppm		C_0=50 ppm	C_0=80 ppm
qe,exp. (mg/g)	71.1	130.58	qe,exp. (mg/g)	71.1	130.58
Lagergren-first-order			Elovich		
Qe,cal. (mg/g)	30.51	43.42	α (mg/g/min)	41649	1734127
k_1 (1/min)	0.011	0.01	β (g/mg)	0.215	0.142
R^2(Linear)	0.958	0.816	R^2(Linear)	0.959	0.983
Second-order			Intraparticular diffusion		
Qe,cal. (mg/g)	76.92	142.86			
k_2 (1/min)	0.0012	0.0013	k_{id} (mg/g/h0.5)	1.86	3.4
h (mg/g/min)	7.09	27.027	C (mg/g)	35.52	65.52
R^2(Linear)	0.999	0.999	R^2(Linear)	0.567	0.532

TABLE 2(a): Two-parameter isotherm constant and statistical comparison values

Adsorption isotherm	Temperature		
(two-parameter)	T=283	T=298	T=308
Freundlich			
k_F	34.226	34.329	39.845
1/n	0.245	0.29	0.244
R^2(linear)	0.982	0.926	0.991
ERRSQ	65.7	239.88	46.86
HYBRID	22.56	78.86	14.06
ARE	5.15	11.32	3.24
Langmuir			
q_m	90.909	90.909	100
k_L	0.297	0.611	0.5
R^2(linear)	0.984	0.994	0.99
ERRSQ	487.03	295.1	713.22
HYBRID	311.97	95.78	339.63
ARE	16.93	11.73	18.54
Temkin			
k_T	3.2441	17.737	52.131
B	132.93	185.586	219.239
R^2(linear)	0.992	0.988	0.958
ERRSQ	14.71	36.93	188.77
HYBRID	4.51	13.68	85.17
ARE	2.16	4.32	9.85
Dubinin-Radushkevich			
q_m	78.335	68.374	78.81
E	0.4093	2.27	1.3533
R^2(linear)	0.82	0.899	0.835
ERRSQ	197.6	569.94	506.54
HYBRID	46.65	156.87	128.87
ARE	6.95	13.139	11.15

TABLE 2(b): Three-parameter isotherm constant and statistical comparison values

Adsorption isotherm	Temperature		
(Three-parameter)	T=283	T=298	T=308
Redlich-Petrson			
A	46.792	74.031	69.542
B	1	1	1
g	0.82	0.967	0.919
R^2(nonlinear)	0.994	0.979	0.929
ERRSQ	283.53	65.82	320.72
HYBRID	278.74	32.43	275.65
ARE	11.93	5.7	13.83
Sips			
q_m	179.998	92.453	291.186
a_S	0.157	0.699	0.163
1/n	0.498	0.676	0.297
R^2(nonlinear)	1	0.986	0.992
ERRSQ	161.26	44.37	36.39
HYBRID	154.25	20.1	14.62
ARE	9.625	4.52	3.41
Toth			
q_m	100.005	98.261	106.546
k_{To}	0.941	0.652	1
n	0.529	0.533	0.614
R^2(nonlinear)	0.907	0.989	0.934
ERRSQ	352.16	38.45	296.78
HYBRID	247.76	17.12	247.08
ARE	14.6	4.12	13.53
Khan			
q_m	40.616	48.589	65.129
b_K	1	2.251	1
a_K	0.788	0.871	0.903
R^2(nonlinear)	0.997	0.993	0.928
ERRSQ	290.457	21.8	321.94
HYBRID	286.941	8.94	279.98
ARE	11.93	2.67	13.81

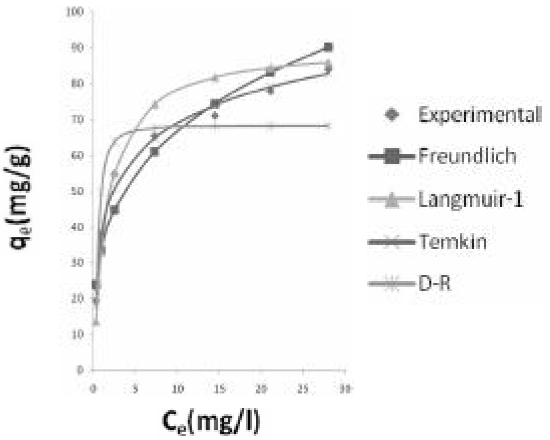

Figure 4 : Comparison of two-parameter isotherm models with experimental data (T=298 K)

of adsorption. The Elovich equation assumes that the active sites of the sorbent are heterogeneous and therefore exhibit different activation energies for chemisorp tions[4]. The value of the initial adsorption rate constant α, was found to increase with the increase in initial lead concentration but constant β decreased with the increase in initial lead concentration[11]. The Elovich equation is based on a general second-order reaction mechanism for heterogeneous adsorption processes. The Elovich model provides a good fitting to the experimental data. The intraparticle equation does not provide a good fit to the experimental data.

3. Adsorption isotherm

For the results presented in figure 4, the two-parameter isotherm provided accurate fit to the experimental data. Figure 5 shows comparison of three-parameter isotherm models with experimental data. Comparing the values of SSE, HYBRID, ARE and R^2 obtained from the adsorption models show that the fitness between the experimental values and the predicted val-

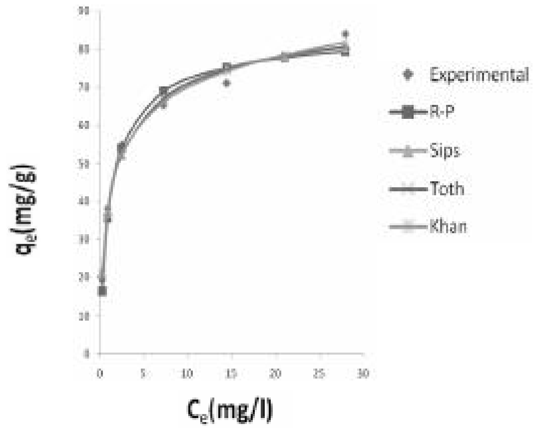

Figure 5 : Comparison of three-parameter isotherm models with experimental data (T=298 K)

ues using the models were generally very suitable for all three-parameter isotherm models. The value of parameter, correlation coefficient and error function were presented in TABLE 2.

The results obtained with the Langmuir isotherm show that the maximum adsorption capacity increased with increasing temperature. Also results have been obtained from Freundlich isotherm that the 1/n value was between 0 and 1 indicating that the adsorption of lead onto CNTs was favorable at studied conditions. The Sips model provided high values of q_{max} than those obtained with the Langmuir model. The Redlich-Peterson isotherm shows that the value of g approaches unity, indicating that the Redlich-Peterson isotherm tends towards a Langmuir isotherm.

4. Thermodynamic analysis[3,6,14]

Thermodynamic parameters including the change in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S\pi$) were calculated from the following equation:

$$K_D = \frac{q_e}{C_e} \qquad (27)$$

$$\Delta G° = -RT \ln K_D \qquad (28)$$

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (29)$$

$\Delta H\pi$ and $\Delta S\pi$ parameters can be calculated from the slope and intercept of the plot $\ln K_D$ vs. 1/T, respectively. From Eq (28), $\Delta G°$ was calculated using $\ln K_D$ values for different temperatures. It was found as and -3.486, -3.947 and -4.484 KJ/mol at 283, 298 and 308 K, respectively. The $\Delta H°$ parameter had a value of 7.555 KJ/mol. The $\Delta S°$ parameter was found to be 0.038893 KJ/mol K.

CONCLUSIONS

Based on the present study, the following conclusions can be drawn:

- In general, the adsorption of Lead onto CNTs increases with the increase of pH in the range of 1-6.
- The contact time to reach equilibrium is 6 hrs for CNTs.
- The second-order equation is the best choice for describing the adsorption kinetic of lead ions onto CNTs.
- Comparison of eleven isotherm models was made using three error functions. Three-parameter isotherm models resulted in better performance than two parameters model.
- The mean adsorption energy (E) was calculated E<8 KJ/mol. These results indicate that the adsorption process of the lead ions onto CNTs may be carried out via physical natural mechanism.
- The negative adsorption standard free energy changes and the positive standard entropy changes indicate that the adsorption reaction is a spontaneous process.
- A positive value for the standard enthalpy change indicates that the interaction of lead adsorbed by CNTs is endothermic.

Nomenclature

A: Redlich-Petrson constant; a_e: the activity of the solute in solution at equilibrium; a_K : Khan model exponent; a_S: Sips Constant; a_s: the activity of adsorbed solute; B : Redlich-Petrson constant; b : Temkin constant (J/mol); b_K : Khan model constant; C_0 : initial leadconcentration (mg/l); C_t : leadcon centrations at any time t (mg/l); D: diffusion coefficient ; E : energy of adsorption (KJ/mol); $\Delta G\pi$: the change in free energy; g : Redlich-Petrson constant; $\Delta H\pi$: the change in enthalpy; h : initial adsorption rate (mg/g/min) ; k_1: the rate constant of first-order equation (1/min); k_2 : the rate constant of second-order equation (g/mg/min); k_D : distribution coefficient; k_F : Freundlich Constant (l/g); k_{id} : intraparticle diffusion coefficient (mg/g $min^{0.5}$); k_L : Langmuir constant (l/mg): k_T : Temkin constant (l/g); k_{To} : Toth model constant; M : Carbon nanotubes dosage (g); n: Freundlich constant; q: Amount of lead adsorbed (mg/g); q_{cal} : calculated value (mg/g); q_{exp} : experimental value (mg/g): q_m : Langmuir constant (mg/g); R: universal gas constant ; R^2 : Coefficient of determination; r: particle radius ; ?Sπ

: the change in entropy; V: initial solution volume (l)

Greek Symbols

α : the rate constant of Elovich equation (mg/g/min); β: Elovich constant (g/mg); ε :Polanyi potential; ν_e : the activity coefficient of the solute in solution ; ν_s : the activity coefficient of the adsorbed solute

REFERENCES

[1] X.M.Zhan, X.Zhao, Water Res., **37**, 3905 **(2003)**.

[2] Q.L.J.Zhai, W.Zhang, M.Wang, J.Zhou; J.Hazard. Mater., **141**, 163 **(2007)**.

[3] A.Sary, M.Tuzen, D.Cýtak, M.Soylak; J.Hazard. Mater., **148**, 387 **(2007)**.

[4] A.Gunay, E.Arslankaya, I.Tosun; J.Hazard.Mater., **146**, 362 **(2007)**.

[5] L.Deng, Y.Su, H.Su, X.Wang, X.Zhu; J.Hazard. Mater., **143**, 220 **(2007)**.

[6] J.R.Gonzlez, J.R.P.Videa, E.R.Rodrguez, S.L. Ramirez, J.L.G.Torresdey; J.Chem.Thermo., **37**, 343 **(2005)**.

[7] E.Demirbas, M.Kobya, E.Senturk, T.Ozkan; Water SA, **30**, 533 **(2004)**.

[8] Y.H.Li, Z.Di, J.Ding, D.Wu, Z.Luan, Y.Zhu; Water Res., **39**, 605 **(2005)**.

[9] C.Lu, H.Chiu; Chem.Eng.Sc., **61**, 1138 **(2006)**.

[10] T.Kazuyoshi, V.Tokio, F.Kenichi; 'The Science and Technology of Carbon Nanotubes', Elsevier Science Ltd.; Netherlands, **(1999)**.

[11] A.B.P.Marín, V.M.Zapata, J.F.Ortuno; J.Hazard. Mater., **139**, 122 **(2007)**.

[12] K.Kumar, S.Sivanesan; J.Hazard.Mater., **B123**, 288 **(2005)**.

[13] Y.S.Al-Degs, M.I.El-Barghouthi, A.A.Issa, M.A. Khraisheh, G.M.Walker; Water Res., **40**, 2645 **(2006)**.

[14] R.Niwas, U.Gupta, A.A.Khan, K.G.Varshney; Coll.Surfa.A, **164**, 115 **(2000)**.