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Mercury(II) removal from aqueous solutions by adsorption on multi-walled carbon nanotubes

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Abstract−Our aim was to test how MWCNTs can be used as a new adsorbent for mercury(II). Multi-walled carbon nanotubes (MWCNTs) have been used for removal of mercury from aqueous solutions. Mercury removal from aqueous solutions by batch adsorption was investigated. Equilibrium isotherms, such as Freundlich, Langmuir, Temkin, Harkins-Jura, were tested. Kinetic studies based on Lagergren first-order, pseudo-second-order and Elovich rate expressions were done. The batch experiments were conducted at three different temperatures (17, 27 and 37 °C) and different pHs of the initial solution. Error function analysis shows that mercury(II) removal obeys pseudo-second order kinetics and Freundlich isotherm equation. Finally, the effects of solution pH and temperature on the adsorption were studied.

Key words: Adsorption, Kinetic, Mercury, Multi-walled Carbon Nanotubes, Equilibrium Isotherms

INTRODUCTION

Mercury(II) is one of the most toxic contaminants affecting the environment. Increasing mercury in both anthropogenic and biogenic emissions of mercury over the last fifty years has resulted in serious potential health risks [1]. A global mercury mass balancing model showed that 34% of the atmospheric mercury originates from coal burning [2]. Consequently, removal of mercury in water and wastewater is important.

Among several methods for the removal of heavy metals from solutions such as precipitation, evaporation, electroplating, ion exchange and membrane separation, adsorption proves to be an efficient and cost-effective method strongly recommended for low concentration [3], Many adsorbents such as hollow fiber supported liquid membranes (HFSLM) [4], biomaterials [5-8], Xanthate [9], Zeolites [10], low cost natural materials [11,12], activated carbon [13-15] were used for heavy metal removal from solutions. During the last few years, there has been a growing interest in the use of nanomaterials for the sorption and preconcentration of heavy metals from water. Multi walled carbon nanotubes (MWCNTs) are one of the new adsorbents with high capacity for metal sorption due to large specific area.

The MWCNTs can be thought of as cylindrical hollow microcrystals of graphite with have strong adsorption ability, exceptional mechanical properties, a unique electrical property, high chemical stability, a large specific surface area [16,17], and high adsorption capacity. With such unique characteristics, MWCNTs have attracted researchers' interest as a new type of adsorbent and have offered an attractive option for the removal of organic and inorganic contaminants from water [18]. The highly developed hydrophobic surface of CNTs exhibits strong sorption properties toward various compounds.

However, studies on the adsorption of heavy metals with MWCNTs are still very limited in the literature [19]. Tawabini et al. [20], with limited data, recently studied the efficiency of mercury(II) removal by multi-walled carbon nanotubes. They showed that mercury adsorption by MWCNTs follows a pseudo-second-order reaction and it is well described by the Langmuir isotherm. In this work, a detailed study was performed, including the equilibrium, kinetics and thermodynamics of batch adsorption for mercury(II) removal from aqueous solutions by MWCNTs in three different temperatures. The effect of initial pH of mercury(II) solution was also investigated [20].

METHODOLOGY

1. Materials

Multi-walled carbon nanotubes, which were produced by chemical vapor deposition (CVD) of methane at the Research Institute of the Petroleum Industry, Iran, at a temperature of 1,000 °C using cobalt-molybdenum supported on magnesium oxide (Co-Mo/MgO), specific surface area of 280 m^2/g, and purity above 95% with no additional groups, were selected as an adsorbent. The SEM photograph of MWCNT is shown in Fig. 1. As one can see, the outer diameter of MWCNT (d_p) is less than 10 nm (average d_p=8 nm), the length

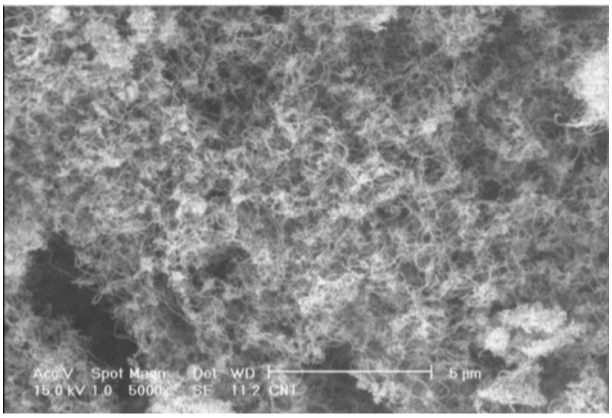

Fig. 1. SEM photograph of MWCNT.

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of MWCNTs is in the range of 5 to 15 μm. The MWCNTs were kept dry in a glass bottle at room temperature of 25 °C.

The chemicals used were mercury(II) chloride (Merck), hydrochloric acid (Merck), which was used due to decreasing effect of other ions, sodium hydroxide (Merck) and deionized water. A Spectra AA 220 Atomic Absorption Spectrophotometer was used to determine mercury(II) concentration in solution phase. The detection limit of FAAS for mercury(II) is higher than the alleged remaining concentration in solution phase in several experiments, but because of limited facilities and financial resources, for concentration analysis we have to use this technique. For some experiments, which remaining concentrations are less than the detection limits of FAAS, a trick was used. By evaporating the solution, Hg concentration was increased and this technique was operational.

2. Adsorption Experiments

By increasing initial concentration of mercury solution, it is clear that percentage of mercury removal was increased due to increase in mass transfer driving force. The mercury removal was increased to a maximum point and after that point, by increasing the concentration, for a certain adsorbent dosage, the percentage of mercury removal was decreased due to limiting capacity of the adsorbent. In this work, optimum concentration for initial solutions was suggested at about 50 mg/*l* of mercury(II).

2-1. Equilibrium Studies

For equilibrium studies, 100 mL solutions with mercury(II) concentration of 50 mg/L were prepared and each solution was treated with 15, 25, 40, 60, 85, 100, 125, and 145 mg of MWCNTs, respectively. All mixtures equilibrated for a period of 24 h for three temperatures of 17, 27 and 37 °C and at pH 6.7±0.2 of the solution in an orbital flask shaker. Finally, adsorbents were separated from the solutions by both micro filters and centrifugal force, and mercury(II) concentration was measured by atomic absorption spectrophotometer.

2-2. Effect of Contact Time

In this study, eight sets of experiment in three temperatures were designed, that in each of them 100 mL solutions with mercury(II) concentration of 50 mg/L mercury(II) were treated with 90 mg of MWCNTs for 5, 15, 25, 35, 45, 60, 75 and 90 minutes at 17, 27 and 37 °C. The solutions were also shaken in a flask shaker. Then, adsorbents were separated from the solutions by both micro filters and centrifugal force, and the concentration of final solutions was measured by atomic absorption spectrophotometer.

2-3. Initial pH

To study the effect of initial pH of the solutions, 100 mL solutions with mercury(II) concentration of 50 mg/L were treated with 65 mg of MWCNTs at desired pH between 2 and 12.5. Finally, adsorbents were separated from the solutions by both micro filters and centrifugal force. Then the concentration was determined by atomic absorption spectrophotometer.

2-4. Natural Sample

For investigating of application on natural waters, a sample of polluted water from the river next to the Shiraz Petrochemical Complex Co., Iran was gained with initial mercury(II) concentration about 37.4 ppm and pH about 6.5. For equilibrium studies, 100 mL solution was treated with 60, 75, 100 mg of MWCNTs. All mixtures equilibrated for a period of 24 h at temperature of 27 °C in an orbital flask shaker. Finally, adsorbents were separated from the solutions by both micro filters and centrifugal force and mercury(II) concentration was measured by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

1. Adsorption Isotherm Studies

The batch experimental data on equilibrium studies are given in Table 1. These data were tested to fit the various adsorption isotherm models. Four models are tested in this study.

First model is the Freundlich isotherm given by the following equation [21]:

$$Q=K_F C^{1/n} \tag{1}$$

where, K_F and n are the Freundlich empirical constants, C is the equilibrium liquid phase ion concentration (mg/L) and Q is the equilibrium solid phase ion concentration (mg/g). Q is related to C by:

$$Q=\frac{V}{m}(C_0-C)+Q_0 \tag{2}$$

where V is the volume of solution (L), m is the mass (g) of adsorbent and Q_0 (mg/g) is the concentration of the compound initially retained by the solid, which must be measured or shown to be negligible. The plot for the adsorption of mercury(II) on MWCNTs by the Freundlich isotherm is shown in Fig. 2. This figure shows a good fit with R-squared value of 0.998.

The second model is the Langmuir isotherm. The equation of this model is as follows [22]:

$$Q=\frac{Q_m K_L C}{1+K_L C} \tag{3}$$

Table 1. Batch experimental data for the adsorption of Mercury(II) on MWCNT, at normal pH and at three temperatures

T (°C)	17		27		37	
X (mg)	C (mg/L)	Q (mg/g)	C (mg/L)	Q (mg/g)	C (mg/L)	Q (mg/g)
15	38.6	76	37.4	84	36.6	89.33
25	32.1	71.6	30.1	79.6	28.9	84.4
40	23.2	67	20.5	73.75	18.7	78.25
60	13.8	66.33	11.4	64.33	10.6	65.66
85	6.3	51.41	5	52.94	4.6	53.41
100	4.1	45.9	3.1	46.9	2.8	47.2
125	1.9	38.48	1.5	38.72	1.4	38.88
145	1	33.79	0.9	33.86	0.7	34

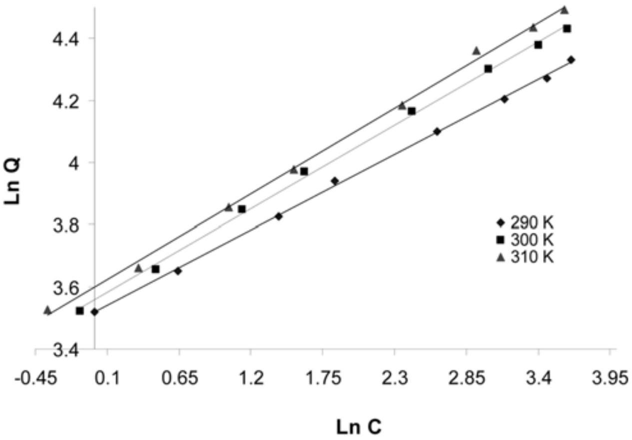

Fig. 2. Freundlich plot.

In this model, Q_m (mg/g) is the amount of adsorption corresponding to complete monolayer coverage, i.e., the maximum adsorption capacity and K_L (L/mg) is the Langmuir constant.

The third model is the Temkin isotherm that was expressed by the following equation [23]:

$$Q=B_1Ln(K_TC) \tag{4}$$

where B_1=RT/b. R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K), K_T is equilibrium binding constant (L/g) and b is related to heat of adsorption (J/mol).

The last model is the Harkins–Jura model; it is represented by the following equation [3]:

$$\frac{1}{Q^2}=\left[\frac{B}{A}\right]-\left[\frac{1}{A}\right]\log C \tag{5}$$

where A and B are model constants. Applied forms of the various adsorption isotherms, the values of parameters involved and the R-squared values are given in Table 2.

2. Best-fit Isotherm Model

All the isotherms studied in this work were in their linear form. Because of the inherent bias resulting from linearization, to find the best-fit isotherm model to the experimental equilibrium data, the hybrid fractional error function of non-linear regression is employed [24]. The hybrid error is given as:

$$HY\ BRID=\frac{100}{N-p}\sum\left[\frac{(Q_{exp}-Q_{calc})^2}{Q_{exp}}\right] \tag{6}$$

where N is the number of data points and p is the number of parameters in the isotherm model. The hybrid error is the lowest value for the Freundlich model for mercury adsorption on MWCNTs. This error was about 0.6 for all temperatures. Hybrid fractional error function values for other models are also given in Table 3. Tawabini et al. [20] showed that the Langmuir isotherm model with correlation coefficient of 0.9999 better described mercury adsorption on the MWCNTs than the Frendlich model with correlation coefficient of 0.9994 [20]. On the other hand, they also showed the linear Freundlich isotherm plot for their experiments had a better fit with experimental data than the Langmuir isotherm. This finding confirms the results of this work. Moreover, Tawabini et al. [20] used only three experimental data points in one temperature for fitting of isotherm models; whereas, in this study, eight data points in three temperatures were used. Therefore, it is clear that the accuracy of the present work is greater than that work.

Table 3. Hybrid error function values for different isotherm models

Model		290 K	300 K	310 K
Freundlich	$LnQ=LnK_F+\frac{1}{n}LnC$	0.6	0.6	0.6
Langmuir	$\frac{C}{Q}=\frac{1}{K_LQ_m}+\frac{C}{Q_m}$	0.71	0.7	0.68
Temkin	$Q=B_1\ln K_T+B_1\ln C$	0.75	0.71	0.79
Harkins-Jura	$\frac{1}{Q^2}=\left[\frac{B}{A}\right]-\left[\frac{1}{A}\right]\log C$	1.28	1.6	1.4

3. Effect of Contact Time

The kinetics of the mercury ions adsorption was studied over 90 min for different temperatures. The data for the effect of contact time is interpreted under rate constant study. Three kinetic models-pseudo-first order, pseudo-second order and Elovich equations-were used to test experimental data to examine the adsorption kinetics.

The pseudo-first order model [25] can be expressed by the equation below:

$$\log[Q-Q_t]=\log Q-\frac{k_1}{2.303}t \tag{7}$$

Table 2. Adsorption isotherm models and parameter values of the isotherms for the adsorption of Mercury(II) on MWCNTs

Model		290 K	300 K	310 K
Freundlich	$LnQ=LnK_F+\frac{1}{n}LnC$ $\frac{C}{Q}=\frac{1}{K_LQ_m}+\frac{C}{Q_m}$	R^2=0.999; K_F=33.73 n=4.54	R^2=0.998; K_F=35.4 n=4.09	R^2=0.998; K_F=36.5 n=3.99
Langmuir	$Q=B_1\ln K_T+B_1\ln C$	R^2=0.991; Q_m=78.125; K_L=2.71	R^2=0.991; Q_m=87.72; K_L=2.72	R^2=0.993; Q_m=93.45; K_L=2.36
Temkin	$\frac{1}{Q^2}=\left[\frac{B}{A}\right]-\left[\frac{1}{A}\right]\log C$	R^2=0.989; B_1=11.51 K_T=15.33	R^2=0.991; B_1=13.62 K_T=11.04	R^2=0.982; B_1=14.46 K_T=10.98
Harkins-Jura		R^2=0.9516; A=2500 B=2	R^2=0.928; A=2500 B=1.75	R^2=0.941; A=2500 B=1.75

Table 4. Adsorption kinetics models and parameter values of the models for the adsorption of Mercury(II) on MWCNTs

Model	290 K	300 K	310 K
Pseudo First order	k=0.02 R^2=0.936	k=0.021 R^2=0.924	k=0.023 R^2=0.917
Pseudo Second order	k_2=0.0015 R^2=0.9995	k_2=0.0018 R^2=0.9995	k_2=0.002 R^2=0.9997
Elovich	α=0.093 β=9.582 R^2=0.982	α=0.095 β=12.517 R^2=0.98	α=0.093 β=13.905 R^2=0.981

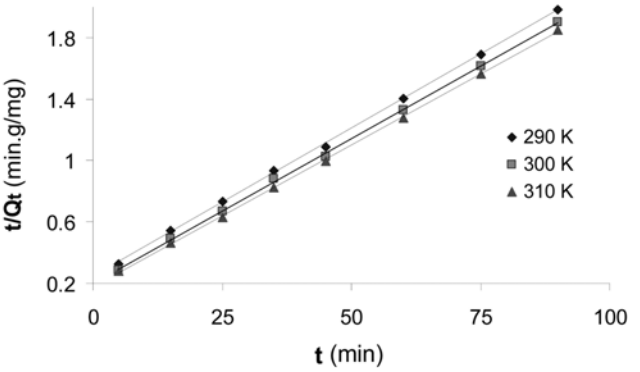

Fig. 3. Pseudo-second-order kinetic plots.

where Q and Q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t, respectively. k_1 (min^{-1}) is the rate constant of pseudo-first order adsorption.

The next model is the pseudo-second-order rate equation [26]:

$$\frac{t}{Q_t}=\frac{1}{k_2Q^2}+\frac{t}{Q} \tag{8}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order adsorption. A linear plot of t/Q_t versus t (see Fig. 3) was done and the k_2 values were calculated from the slopes and intercepts, which are summarized in Table 4. As Fig. 3 shows, there is a very good agreement between the results of this model and the experimental data (also, see Table 4 for R-squared values).

The last kinetic model is Elovich's equation [27]:

$$Q=\frac{1}{\alpha}\ln(\beta\alpha)+\frac{1}{\alpha}\ln t \tag{9}$$

where α the is the initial adsorption rate and β is the desorption constant during each experiment.

By comparing R-squared values for different models in Table 4, it is seen that the best adsorption kinetics model for mercury removal on MWCNTs is pseudo-second order.

4. The Effect of Temperature and Thermodynamic Parameters

The thermodynamic parameters such as enthalpy, ΔH^o, entropy, ΔS^o and Gibbs free energy, ΔG^o, of the sorption are useful in defining whether the sorption reaction is endothermic or exothermic and the spontaneity of the adsorption process. The effect of temperature on mercury(II) adsorption by MWCNT revealed the adsorption to be endothermic, as the adsorption capacity increased with increasing the temperature of the system (see Table 4). In this study, thermodynamic parameters were calculated to predict the process of adsorption (i.e., inherent energetic changes associated with adsorption). The Freundlich isotherm was used to calculate thermodynamic parameters using the following equation [28,29]:

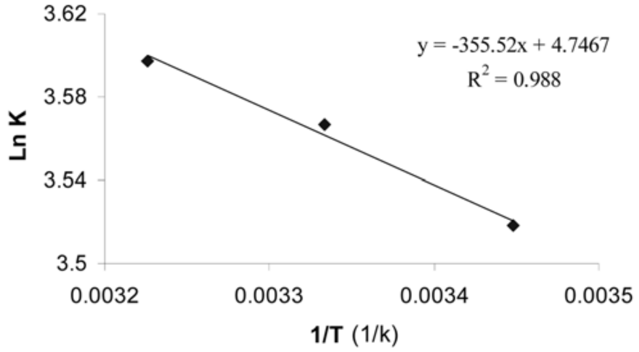

Fig. 4. Plot of Ln K versus 1/T.

Table 5. Thermodynamic parameters of MWCNTs at various temperatures

	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/mol K)
290 K	−8.483	2.956	39.464
300 K	−8.776		
310 K	−9.068		

$$\Delta G^o=-RT\mathrm{Ln}K_F \tag{10}$$

$$\mathrm{Ln}K_F=\frac{\Delta S^o}{R}-\frac{\Delta H^o}{RT} \tag{11}$$

where K_F is the Freundlich equilibrium constant, R is the gas constant (8.314 J/mol·K) and T is the temperature (K). Fig. 4 shows a plot of LnK versus 1/T. ΔH^o and ΔS^o values were calculated from the slope and intercept of the plot, respectively. Results are summarized in Table 5. Positive ΔH^o and ΔS^o values suggest that the adsorption of mercury(II) onto MWCNTs is endothermic, which fact is supported by the increase in the adsorption of mercury(II) with temperature. Moreover, the positive ΔS^o indicated that the degrees of freedom increased at the solid-liquid interface during the adsorption of mercury(II) onto MWCNTs. A more negative ΔG^o implied a greater driving force of adsorption, resulting in a higher adsorption capacity. When the temperature was increased from 290 to 310 K, ΔG^o became a high negative value, suggesting that adsorption was more spontaneous at high temperature.

5. The Effect of pH

The pH of the aqueous solution is an important variable that controls the adsorption of the metal at the MWCNTs-water interfaces. Hence, the effect of pH on the adsorption of mercury(II) onto MWCNTs was investigated in the pH range of 2-12.5. This study gives information on optimum pH. It can be observed from the results that the adsorption of mercury(II) increases with an increase in pH of the solution to a maximum around a neutral pH or slightly basic pH, and then decreases as the pH becomes more basic. According to the following reaction:

$$\mathrm{Mercury(II)}+2OH^-\rightarrow Hg(OH)_2 \qquad K_{sp}=3.6\times10^{-26} \tag{12}$$

with increasing of pH, the formation of $Hg(OH)_2$ was increased and the sorption of mercuric hydroxide on the surface of MWCNTs increased, but in pH higher than 7 the complex formation of $Hg(OH)_3^-$ and $Hg(OH)_4^-$ could be happening and these complex could not be retained on the CNTs surface because they are soluble in water as the following reactions [30]:

$$Hg(OH)_2+OH^- \rightarrow Hg(OH)_3^-, \qquad \mathrm{Log}K_1=10.6 \tag{13}$$

$$Hg(OH)_3^-+OH^- \rightarrow Hg(OH)_4^{2-}, \qquad \mathrm{Log}K_2=11.2 \tag{14}$$

Fig. 5 shows that maximum removal of mercury(II) is at normal pH (6.5-7.5). Finally, Table 6 shows a comparison between the amounts of different adsorbents needed for 90% removal from mercury solution with initial concentration of 50 mg/*l* in 1 hour.

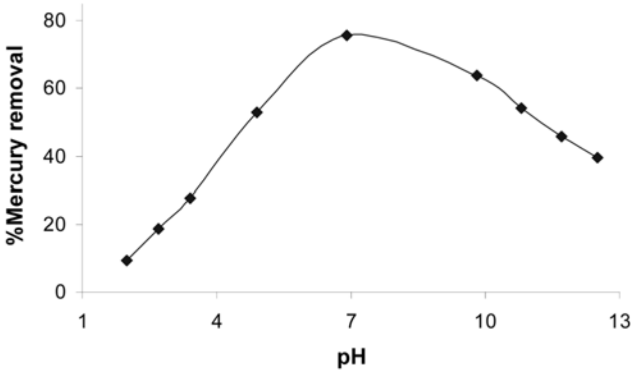

Fig. 5. Effect of pH on adsorption of Hg(II) onto MWCNTs.

Table 6. Comparison between the amount of different adsorbents for removing 90% mercury from a solution with initial concentration of 50 mg/*l* in 1 hour

Adsorbent	Amounts of adsorbent (gr)
Activated carbon [3]	0.40
Fuller's earth [3]	9.5
Keratin powder [31]	1.9
MWCNT	0.09

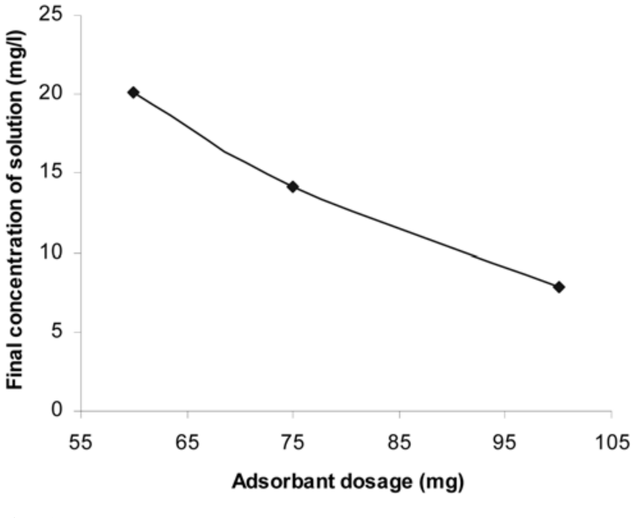

Fig. 6. Naturtal sample results.

6. Natural Sample Results

As shown in Fig. 6, by an increase in adsorbant dosage, the final concentration of solution was decreased. But compared to a synthetic solution, the final concentration of solutions with the same adsorbant dosage was relatively high due to presence of other ions in the solution. For an alternative, additional groups on the MWCNT can make it a selective adsorbant.

CONCLUSIONS

Batch adsorption equilibrium and kinetics of mercury onto MWCNTs at various pH values and temperatures have been investigated. The present work clearly finds that MWCNTs are very effective adsorbents for mercury(II) removal from aqueous solutions. The adsorption was found to be dependent on time, pH and temperature of the system. The best fit of the equilibrium data with the lowest value of hybrid error was obtained for the Freundlich adsorption isotherm for all temperatures. The kinetics data shows that the removal of Mercury(II) on MWCNTs follows a pseudo second order model. The adsorption of Mercury(II) on MWCNTs was found to be endothermic in nature and increases with increase in temperature. By increasing pH of initial solution, the removal percentage of mercury increases to a maximum and then it decreases. The optimum pH for removal of mercury by MWCNTs was near the neutral pH (6.5-7.5).

Moreover, a comparison of the results of mercury adsorption on MWCNTs in this study with the other sorbents shows that the adsorption capacity for removing mercury on MWCNTs is about 440% greater than the activated carbon**.** In fact, if only the price of adsorbent is considered, it will not be an economical decision to replace activated carbon by MWCNTs, but it will be explainable when it is considered at the industrial scale; the cost of equipment in the separation process will be sharply decreased due to decrease in mass of adsorbent. Finally, natural sample testing (gained from Shiraz Petrochemical Complex Co.) showed that multiple adsorption decreased capacity mercury adsorption on MWCNTs.

NOMENCLATURE

A : Harkins-Jura model constant [$mg^2 \cdot g^{-2}$]
B : Harkins-Jura model constant
b : related to heat of adsorption [J/mol]
C : equilibrium liquid phase ion concentration [mg/L]
C_0 : initial liquid phase ion concentration [mg/L]
k_1 : rate constant of pseudo-first order adsorption [min^{-1}]
k_2 : Rate constant of pseudo-second order adsorption [$g \cdot mg^{-1} \cdot min^{-1}$]
K_L : Langmuir constant [L/mg]
K_F : Freundlich empirical constants
K_T : equilibrium binding constant [L/g]
m : mass [gr]
n : Freundlich empirical constants
N : number of data points
p : number of parameters in the isotherm model
Q : concentration of the compound [$mg \cdot g^{-1}$]
Q_0 : concentration of the compound initially retained by the solid [$mg \cdot g^{-1}$]

R : gas constant [J/mol·K]
t : time [min]
T : temperature [K]
V : volume of solution [L]
α : initial adsorption rate [$g\cdot mg^{-1}$]
β : desorption constant [$mg\cdot g^{-1}$]
ΔG^o : Gibbs free energy [J/mol]
ΔH^o : enthalpy [J/mol]
ΔS^o : entropy [J/mol]

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