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Thermodynamic Investigation of Pb^{2+} and Cd^{2+} Ions Absorption from Aqueous Solutions Using Multi-Walled Carbon Nanotubes

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

In this study, removal of heavy metal ions including cadmium and lead from wastewater were studied. Adsorption process was carried out using simple multiwalled carbon nanotubes (MWCNT) and functionalized MWCNT with the carboxyl agent (MWCNT-COOH) prepared by CVD (chemical vapor deposition) method with a purity of 95%. Furthermore, the effect of temperature at 27.32, 37 and 47°C on absorption rate was investigated, in terms of the other constant variables such as initial content of metal ions, solution pH, contact time and concentration of carbon nano absorbers. Final content of the metal ions remaining in the solution was measured by atomic absorption spectroscopy (AAS). It was revealed that there is a direct relationship between solution's temperature and cadmium and lead ions absorption rate on carbon nanotubes. Furthermore, thermodynamic calculations of absorption showed that Gibbs free energy (ΔG) of absorption process by MWCNT-COOH and MWCNT is negative. This result indicating the spontaneous absorption reaction and removal of metal cathion by carbon nanotubes. This reaction is endothermic and Positive ΔH confirms it.

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Keywords: Multi-Walled carbon nanotubes; cathion; lead; cadmium thermodynamic; aqueous solutions

1. INTRODUCTION

Water pollution, caused by metal ions disposal, is a universal concern. Wastewaters from metallurgical operations, chemical materials, batteries and metal mines contain one or several kinds of toxic metals [1]. To prevent the entrance of toxic materials into food cycles, metal ions must be filtered from wastewaters prior to being disposed in environment. Lead is a white-bluish metal element and one of the four metals that most of the effects on human health. Lead is naturally found in environment. It is also a by-product of petrol production by human. Lead causes poisoning, anemia, cerebral distortions and kidney inflation. Cadmium is a white metal element and a by-product of lead purification. Cadmium enters environment through mechanisms like stone weathering, disposal into rivers, firefighting and human activities such as manufactured phosphate composts or industrial waste streams. Cadmium has unfavorable effects on human body among which are diarrhea, stomachache, bone fracture, infertility, central cerebral system damage and immunity system damage. Huge amounts of lead and cadmium in drinking water and food, like many other elements in environment, can cause diseases in human. The maximum acceptable content of lead and cadmium in drinking water, proposed by WHO, is less than 0.5 and 0.003 mg/L, respectively. Due to these considerations and the huge consumption of the two elements in industrial world and inevitable pollute in water resources and industrial wastewaters, some policies must be regarded for removal of soluble lead and cadmium in the water [2-4].Different methods are studied for separation of metal ions from aqueous solutions including oxidation-reduction, precipitation, membrane filtration, cathion exchange and adsorption. Due to absorber retrieval capability in the adsorption, this method is economical and more regarded. In adsorption method, materials like activated carbon, Zeolite, synthetic resins and carbon nanotubes are used [1,5]. Carbon nanotubes (CNTs) were discovered by Injima in 1991 and widely applied in different fields. CVD (chemical vapor deposition) is a major method of producing carbon nanotubes [6]. Two main types of carbon nanotubes have been detected: single-Walled carbon nanotubes (SWCNTs) and multi-Walled carbon nanotubes (MWCNTs). Due to their high specific surface area, nanotubes are selected for metal ions absorbers. But the main problem for this application is the high cost of CNTs production. Several studies have been conducted in the last few years for lowering their production costs [7].

Carbon nanotubes are an effective adsorbent and have many applications in the reduction of various pollutants such as dioxin from air or lead, cadmium, fluoride, 1; 2-dichlorobenzene or THMs from water [7-12].

In this method, CNTs are exposed to oxidation agents such as HNO_3 solution, $KMnO_4$ and NaOCl. Functional bonds such as –COOH, OH and C=O are added to both ends of carbon nanotubes which are active and similar to Fullerenes. As a result, their reactivity is improved and more positive metal cathion are absorbed [1,7].

In this research, the main purpose is measuring the absorption percentage and calculating thermodynamic parameters in absorption process of lead and cadmium heavy metals from aqueous solutions using simple multi-walled carbon nanotubes. The result compared with modified multi-walled carbon nanotubes with temperature change during solution reaction.

2. MATERIALS AND METHODS

2.1 Sample Preparation

Due to unavailability of real wastewater or polluted water containing both cadmium and lead ions, wastewater solutions with specific contents of lead and cadmium were prepared under laboratory conditions. Metal ions contents and solution temperature were changed during different experimental stages.

Cadmium and lead nitrate salts were utilized for producing heavy metal cathion and deionized purified water were utilized for solution samples. In this regard, $Pb(NO_3)_2$ and $Cd(NO_3)_2$ $.4H_2O$ produced in Aldrich company were added to 400mL of 98% deionized purified water to increase initial ions concentration in the equivalent solution to 50mg/L. Also for removal of metal cathion utilized from 95% simple multi-walled carbon nanotubes with specific surface area of 233 m^2/g (with a diameter of 5-15 nm) and 95% functionalized multi-walled carbon nanotubes with specific surface area of 233 m^2/g (with a diameter of 5-15 nm). This material produced in US NANO Company and purchased from Iranian nano materials Company.

2.2 Experimental Procedure

In this method, absorbers were added to 50mL of the sample solution. Amount of absorber in each stage was specified and all experiments were carried out in different temperature including 300, 310, 315, and 320 K. Each step was carried out in 60 minutes. Carbon nanotubes were not completely intermingled with wastewater due to their hydrophobic feature. Ultrasonic wave's producer system (up200s-hielscher model) was applied for 5 minutes for intermingling heavy metal ions and nanotubes powders. Then, the solution was poured into laboratory Erlenmeyer flask. To adjust initial pH of the solution, hydrochloric acid and sodium hydroxide was applied with 0.1M concentrations.

The solution containing Erlenmeyer flask was closed with cork cap. The solution was stirred with magnetic stirring device (Heidolph MR 3001 K model) at 700 rpm rate for one hour. Then, solution passed through filter paper (Whatman Grade 6) and its concentration was measured using atomic absorption spectography (AAS: GBC 932 plus model).

3. RESULTS AND DISCUSSION

The temperature of the absorption process influences on final absorption rate and temperature change is effective on absorber yield [1].

Based on the obtained results, ion absorption is dependent on aqueous solutions temperature. The temperature (300, 310, 315, and 320 K) of metal ions containing solution was repeatedly changed during absorption process. The other reaction parameters were considered constant during the reaction (pH=6, t=60 minutes, C_0= 50 mg/l).

Removal rate increases with temperature as shown in Figs. 1 and 2. The relationship between increasing of ion absorption rate in higher temperature is due to the fact that absorption sites in carbon nanotubes (points on nanotubes with absorption capability) are more active at higher temperatures. Cathion kinetic energy increases with temperature. At higher temperatures, ions and absorption points are more in contact with each other. So, absorption coefficient increases with temperature. Absorption reaction is more physical than chemical. Also at higher temperatures, size of the pores of carbon nanotubes somewhat increased and can absorb more metal cathion [1-7,13,14].

Metal ions removal/absorption rate is calculated by equation (1):

$$\text{Removal percent} = [(c_0 - c_f) / (c_0)] * 100 \quad (1)$$

Furthermore, metal ions absorption capacity (q_e) is calculated by equation (2):

$$q_e = (c_0 - c_f) * v/w \quad (2)$$

V: solution volume (L)
W: absorber mass (gr)
C_0: initial concentration of the metal ions in solution (mg/L)
C_f: final concentration of the metal ions in solution (mg/L)

As shown in Fig. 1, absorption percent of Pb^{2+} and Cd^{2+} ions are a function of temperature on the absorbers surfaces. When temperate is increased to 320 K, maximum absorption percents per metal ion on MWCNT-COOH are 71.6 and 91.5 for Cd^{2+} and Pb^{2+}, respectively and for MWCNT are 62.9 and 78.3, respectively.

According to Fig. 2, when functional carbon nanotubes are used, metal ions absorption capacity is higher than MWCNT.

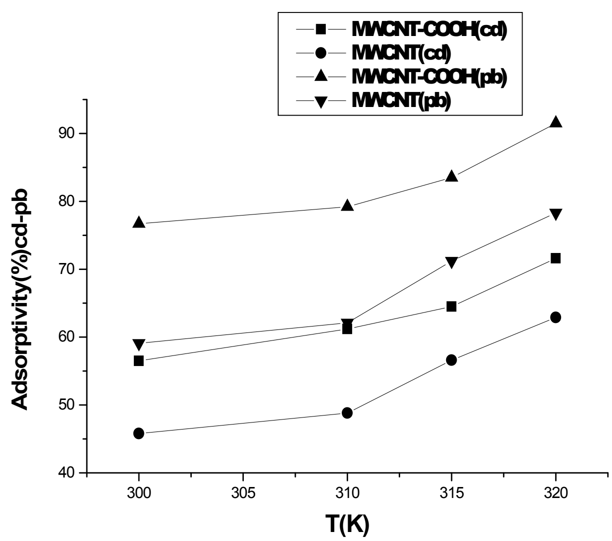

Fig. 1. Cadmium and lead removal percent by MWCNT and MWCNT-COOH in terms of solution temperature rat

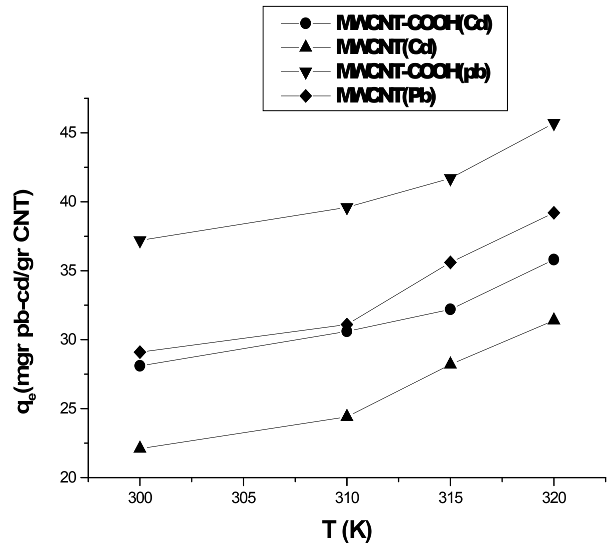

Fig. 2. Changes in Cadmium and lead absorption capacity with solution temperature

3.1 Absorption Thermodynamics

Thermodynamic parameters provide additional information concerning internal energy change during absorption process. Thermodynamic parameters such as ΔG (Gibbs free standard energy of absorption), ΔS (standard entropy) and ΔH (standard enthalpy) during metal ions absorption by carbon multi-walled nanotubes are investigated based on data Tables. Two types of nanotubes (MWCNT and MWCNT-COOH) were applied at different temperatures (300, 310, 315, and 320 K). Concentration of lead and cadmium metal ions are same 50 (mg/L) and final concentration after reactions was consider equivalent while thermodynamic parameters changes were measured. Thermodynamic constant (K_0), also called distribution ratio, is defined in equivalent absorption reaction as follows [15].

$$K_0 = a_s/a_e = (\gamma_s.q_e) / (\gamma_e.C_e) \qquad (3)$$

In the above equation, a_s is the absorbed ions activity coefficient on absorber surface and a_e is the ion activity coefficient in the equivalent solution. γ_s and γ_e are activity coefficients of the absorbed salts and metal ions at equivalence stage. For example, when salts concentration in the solution is almost zero, activity coefficients (γ_s and γ_e) are inclined to 1. Finally, the above equation turns into equation (4).

$$K_0 = a_s/a_e = q_e/ C_e \qquad (4)$$

q_e: absorbed ion concentration on the absorber surface (mg/L);
C_e: metal ion concentration at equivalence time (mg/L).

According to equation (4), distribution ratio (K_0) reveals the shares of solution and absorber of metal cathion after reaction. So, we can write:

$$K_0= (\text{solution metal content/ absorber metal content}) * (V/m) \qquad (5)$$

V: solution volume at each reaction stage (ml);
M: absorber's weight at each reaction container (g);

Absorber metal content is part of lead and cadmium metal cathion absorbed from solution by carbon nanotubes. Solution metal content is some metal ions remain in the wastewater solution after reaction.

K_0 parameters calculated during absorption reaction are demonstrated in Table 1.

ΔG is obtained from equation (6) at various temperatures:

$$\Delta G = - RT \ln(K_0) \tag{6}$$

Where R is the universal constant of gases(R=8.314(J/mol.K)) and T is temperature (K).
On the other hand, we can write:

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \tag{7}$$

Because the left side of Equations 6 and 7 are equal, so we have:

$$- RT \ln(K_0) = \Delta H_0 - T\Delta S_0 \tag{8}$$

$$\ln(K_0) = (-\Delta H_0/R)*(1/T) + (\Delta S_0 / R) \tag{9}$$

On the other hand, equation (9) reveals that K_0 equivalence constant changes with absolute temperature in an equivalence system. In Table. 1, in (K_0) and ΔG^0 have been measured for both absorbents based on equations (5) and (6).

Sign of Gibbs free energy is negative which reveals the automatic nature of lead and cadmium ions absorption on MWCNTs and MWCNT-COOH surfaces and its amount increases with temperature. It is confirm because the Gibbs free energy becomes more negative as the temperature increases.

Also, ln (K_0) versus (1/T) was depicted for reversible absorption of ions on MWCNTs and MWCNT-COOH surfaces at different temperatures in Table. 1. Curve slope numerical value determines ($-\Delta H^0/R$) and introduce standard enthalpy and intercept numerical value determines ($\Delta S^0/ R$) and introduce standard entropy in equivalent absorption reaction.

Figs. 3 and 4 demonstrate distribution ratio changes (ln (K_0)) versus 1/T for removal lead and cadmium metal cathion by simple multi-walled carbon nanotubes. Distribution ratio change is directly related to Gibbs free energy and increases with temperature. Distribution ratio change in lead ions is higher than cadmium ions. This is due to the fact that carbon nanotubes reaction with the metal ion containing solution on nanotubes surfaces is more spontaneous for Pb(II). So that in the competition to absorption Pb(II)>Cd(II). This reveals the higher charge level of Pb^{2+} compared to Cd^{2+}. Charge density is proportionate to cathion size. Since lead cathion size is larger, it is more easily involved in absorption active points on nanotubes surfaces [15].

Table 1. Calculating numerical value of the distribution ratio (Ln (K_0)) and ΔG^0

Nanotubes type	Temperature(K)	Remaining metal ion amount in solution		Metal ion amount absorbed by the absorbent		Ln(K_0)		ΔG^0 (KJ/Mol)		1/T (K^{-1})
		Cd(II) (mg/L)	Pb(II) (mg/L)	Cd(II) (mg/L)	Pb(II) (mg/L)	Cd(II)	Pb(II)	Cd(II)	Pb(II)	
MWCNT	300	27.10	20.60	22.9	29.4	6.74	7.29	-16.8	-18.2	0.00333
	310	25.60	18.94	24.40	31.06	6.86	7.40	-17.7	-19.1	0.00322
	315	21.72	14.40	28.3	35.6	7.17	7.81	-18.8	-20.5	0.00317
	320	18.55	10.83	31.45	39.17	7.44	8.19	-19.8	-21.8	0.00313
MWCNT-COOH	300	21.7	13.10	28.30	36.9	7.22	7.9	-18.0	-19.7	0.00333
	310	18.4	14.25	31.6	35.75	7.45	7.83	-19.5	-20.2	0.00322
	315	13.75	10.26	36.25	39.74	7.88	8.26	-20.6	-21.6	0.00317
	320	10.18	6.15	39.82	43.85	8.27	8.87	-22.0	-21.6	0.00313

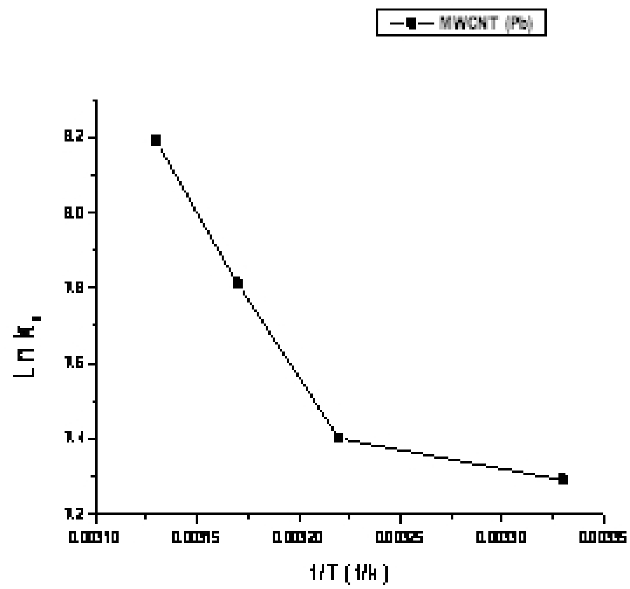

Fig. 3. Cadmium distribution ratio changes with temperature

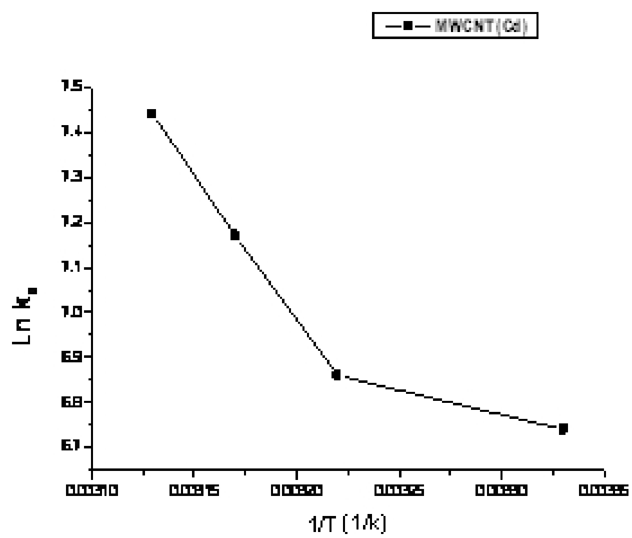

Fig. 4. Lead distribution ratio changes with temperature

Figs. 5 and 6 demonstrate distribution ratio (ln (K_0)) versus (1/T) for removal of lead and cadmium metal cathion by functional multi-walled carbon nanotubes.

Calculating thermodynamic parameters for absorbing Pb and Cd ions on MWCNTs and MWCNT-COOH surfaces provides us with useful information concerning energy changes during surface adsorption. It was revealed that an enthalpy change during absorption reaction is positive which reveals the endothermic feature of absorption reaction [16]. This fact is demonstrated in the experimental data of Table. 2 as shown that absorption of Pb and

Cd ions on nanotubes surfaces increases with temperature. On the other hand, entropy changes positivity might have originated from water molecules formation due to cathion exchange reaction between metal ions and MWCNTs and MWCNT-COOH surfaces. This fact reveals the high absorption rate of Pb and Cd metal ions from MWCNT surface [17,18].
Both ions absorption reactions are endothermic in this work. This process is considered to two parts. In the first part, multi-walled carbon nanotubes are combined with water (an endothermic reaction) and in the second part metal ions are absorbed on absorbent surfaces (an exothermic reaction). Due to the higher probability of the carbon nanotubes hydration compared to metal ions absorption on absorbent surfaces, the first reaction part has more frequency than the second one and the reaction might be assumed as endothermic.

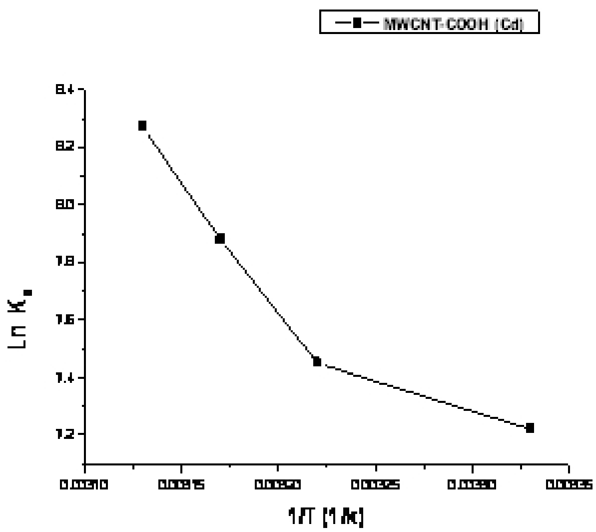

Fig. 5. Cadmium distribution ratio changes with temperature

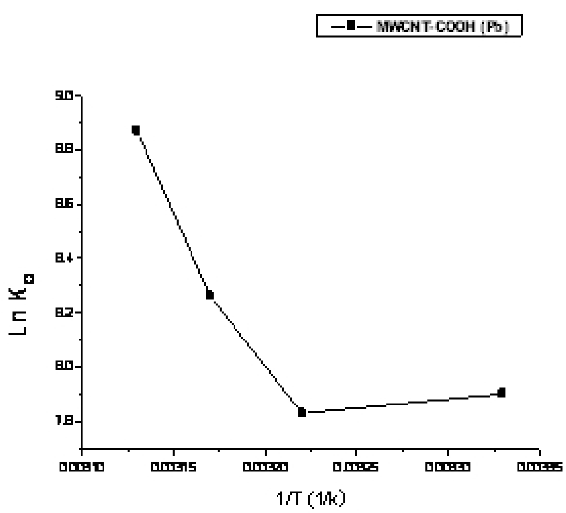

Fig. 6. Lead distribution ratio changes with temperature

Table 2. Determining thermodynamic parameters of absorption process by multi-walled carbon nanotubes

Metal cathion	**Carbon nanotubes**	**Temperature** (K)	**ΔG^0** (kJ/mol)	**ΔH^0** (kJ/mol)	**ΔS^0** (J/molK)	**Straight line equation**	**Regression coefficient**
Pb(II)	MWCNT	300	-18.2	37.72	177.04	Y = -538.0710X + 21.2952	R^2 = 0.9235
		310	-19.1				
		315	-20.5				
		320	-21.8				
	MWCNT-COOH	300	-19.7	44.99	213.91	Y = -411.1675X + 25.73102	R^2 =0.8775
		310	-20.2				
		315	-21.6				
		320	-23.6				
Cd(II)	MWCNT	300	-16.8	40.56	187.10	Y = -879.6903X + 22.5034	R^2 =0.9602
		310	-17.7				
		315	-18.8				
		320	-19.8				
	MWCNT-COOH	300	-18.0	43.82	205.80	Y = -271.0659X + 24.7541	R^2 =0.96142
		310	-19.5				
		315	-20.6				
		320	-22.0				

4. CONCLUSION

Temperature effect on Cd^{2+} and Pb^{2+} ions absorption from aqueous solution by multi-walled carbon nanotubes was investigated. It was revealed that with temperature increase from 27°C to 47°C, each metal ion's absorption percentage on each absorbent surface increased by 20%, in average. A maximum removal rate of 91.5% was recorded for Pb^{2+} metal cathion in touch with functional multi-Walled carbon nanotubes.

On the other hand, the positive sign of enthalpy proves endothermic essence of the absorption process. Based on thermodynamic calculations, negative sign of Gibbs free energy and regarding of the obtained value for the entropy of the absorption process, it might be concluded that the mentioned process is spontaneous and ΔG is directed dependent on temperature. Our results confirm the more negative amount of Gibbs free energy in high temperatures. In higher temperatures, reaction is more spontaneous. Also result shown whatever metal cathions absorption rate on nanotubes surfaces is higher, more thermal energy is needed for the reaction. This fact was revealed for Pb^{2+} metal cathion absorption with the reaction enthalpy rate of 44.99kJ/mol.

In this study, both ions absorption reactions are endothermic. This reaction is completed in two parts. In the first part, multi-walled carbon nanotubes are combined with water (an endothermic reaction) and in the second part metal ions are absorbed on absorbent surfaces (an exothermic reaction). Due to the higher probability of the carbon nanotubes hydration compared to metal ions absorption on absorbent surfaces, the first reaction part has more frequency than the second one and the reaction might be assumed as endothermic reaction

COMPETING INTERESTS

Authors have declared that there are no competing interests.

REFERENCES

1. Gadupudi Purnachadra Rao, Chungsying Lu, Fengsheng Su. Sorption of divalent metal ions from aqueous solution by carbon nanotubes. Separation and Purification Technology. 2007;58:224–231.
2. Anna Stafiej, Krystyna Pyrzynska. Solid phase extraction of metal ions using carbon nanotubes. Microchemical Journal. 2008;89:29–33
3. Yan-Hui Li et al. Competitive adsorption of Pb2+ , Cu2+ and Cd2+ ions from aqueous solutions by multiwalled carbon nanotubes. Carbon. 2003;41:2787–2792.
4. Zhuang HL, Zheng GP, Soh AK. Interactions between transition metals and defective carbon nanotubes. Computational Materials Science. 2008; 43:823–828.
5. Venkata K.K. Upadhyayula et al. Application of carbon nanotube technology for removal of contaminants in drinking Water. Science of the Total Environment. 2009;408:1–13.
6. Iijima S. Helical microtubes of graphitic carbon. Nature 354. 1991:56–58.
7. Li YH, Wang S, Wei J, Zhang X, Xu C, Luan Z, Wu D, Wei B. Lead adsorption on carbon nanotubes. Chem. Phys. Lett. 2002;357:263–266.
8. Li YH, Wang S, Luan Z, Ding J, Xu C, Wu D. Adsorption of cadmium (II) from aqueous solution by surface oxidized carbon nanotubes. Carbon. 2003;41:1057–1062.

9. Li YH, Wang S, Wei J, Zhang X, Wei J, Xu C, Luan Z, Wu D. Adsorption of fluoride from water by aligned carbon nanotubes. Material Research Bulletin. 2003;38:469–476.
10. Long RQ, Yang RT. Carbon nanotubes as superior sorbent for dioxin removal. Journal American Chemical Society. 2001;123:2058–2059.
11. Lu C, Chung YL, Chang KF. Adsorption of trihalomethanes from water with carbon nanotubes. Water Research. 2005;39:1183–1189.
12. Peng X, Li Y, Luan Z, Di Z, Wang H, Tian B, Jia Z. Adsorption of 1, 2-dichlorobenzene from water to carbon nanotubes. Chemical Physics Letters. 2003;376:154–158.
13. Lu C, Chiu H. Adsorption of zinc (II) from water with purified carbon Nanotubes. Chem. Eng. Sci. 2006;61:1138–1145.
14. Mobasherpour I, Salahi E, Ebrahimi M. Thermodynamics and kinetics of adsorption of Cu (II) from aqueous solutions onto multi-walled carbon nanotubes. Journal of Saudi Chemical Society. 2011.doi:10.1016/j.jscs.2011.09.006.
15. Moradi O, Zare K, Yari M. Interaction of some heavy metal ions with single walled carbon nanotube. Int.J.Nano.Dim. 2011;1(3):203–220.
16. Anna Stafiej, Krystyna Pyrzynska. Adsorption of heavy metal ions with carbon nanotubes. Separation and Purification Technology. 2007;58:49–52.
17. Lu C, Chiu H, Liu C. Removal of zinc (II) from aqueous solution by purified carbon nanotubes: kinetics and equilibrium studies. Ind. Eng. Chem. Res. 2006;45:2850–2855.
18. Li YH, Di Z, Ding J, Wu D, Luan Z, Zhu Y. Adsorption thermodynamic, kinetic and desorption studies of Pb2+ on carbon nanotubes. Wat. 2005;39:605–609.

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