Determining the Best Isotherm Equation for the Surface Absorption of the Pb^{2+} and Cd^{2+} Ions from Aqueous Solutions Using Multi-walled Carbon Nanotubes

Aliasghar Rohani, Aliakbar Bastami, Alireza shakeri, Khashayar sharifi

***Abstract*— this article aims at investigating the lead and cadmium heavy metal ions (bivalent Pb^2 and Cd^2 cathions from wastewaters, using simple multi-walled carbon nanotubes (MWCNT) with carboxyl content (MWCNT-COOH). The 95% carboxyl agent was produced by CVD method (chemical vapor deposition). On the other hand, ion absorption changes were investigated for lead and cadmium metal ions with different contents (30, 40, 50 and 60 mg/lit) while the other variables was constant (PH=6, t=60min, carbon nanoabsorbent content of 1g/li, T=300±1K). Then, atomic spectrometry system (AAS) was applied for determining the final content of the remaining metal ions in the solution. It was revealed that absorption rate and qe rate (filtering capacity) of lead and cadmium ions from the solution b carbon nanotubes increases with the number of metal cathions in the solution. Comparing the obtained results from Langmuir and Freundlich models, the best equation for metal ions absorption by multi-walled carbon nanotubes was determined.**

***Index Terms*— multi-walled carbon nanotubes, Pb^{2+}, $Cd^{2+,}$ aqueous solution**

I. 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 most harmful metals for 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, cathions 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 [5, 1]. 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]. In this method, CNTs are exposed to oxidation agents such as HNO3 solution, KMno4 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 cathions are absorbed [8, 1].

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.

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II. MATERIALS AND METHOD

SOLUTION PROCESS STUDY

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 were changed during different experimental stages.

Cadmium and lead nitrate salts were utilized for producing heavy metal cathions and deionized purified water. Due to the fact that 50ml of the solution was used at each experimental stage, 98% Pb $(NO3)_2$ and cd (NO3)2 .4H2O400cc-made by Aldrich Company- was added to 400cc of deionized purified water to increase the initial ion content to 30mg/li in 100cc. At the next three stages, ions content was increased to 40, 50 and 60mg/li respectively. To filter metal cathions, 95% simple multi-walled carbon nanotubes with sectional area of 110 m^2 /g and diameter of 5-15 nm- produced in US Nano Company and purchased from Iranian Materials Nanopioneers Company- and 95% multi-walled carbon nanotubes with sectional area of 233 m^2 /g and diameter of 20-30 nm were applied.

In this method, 50cc of the solution with specific contents (30, 40, 50 and 60 mg/li) was poured into erlen. Having added 500mr of the absorbent, the experiment was performed at the temperature of 300K. Carbon nanotubes were not completely intermingled with wastewater due to their hydrophobic behavior. Ultrasonic wave's producer system (up200s-hielscher model) was applied for 5 minutes for intermingling heavy metal ions and nanotubes powders. The, solution was poured into erlen. To adjust initial ph rate of the solution, 0/1 moll of hydrochloric acid and 0/1 moll of sodium hydroxide was applied.

The solution containing erlen was closed with wooden top. The solution was stirred with magnetic stirring device (Heidolph MR 3001 K model) at 700rpm rate for one hour. Then, solution passed through filtering paper Whatman Grade6 and its content was measured using atomic absorption system (AAS: GBC 932 plus model).

III. DISCUSSION

Confirming the previous results, our findings reveal that ions absorption rate is dependent on their initial content in the aqueous solution [9].

In this study, different contents were selected for lead and cadmium metal ions (30, 40, 50 and 60 mg/li). The other reaction parameters were considered constant during the reaction (PH=6, t=60 minutes, carbon nanoabsorbent content of 1g/li, T=300±1K). Absorption rate increases with ions content. As the initial content of metal ions rises, more ions compete to react with active groups to the absorbent surface. As a result, active absorption sites are more rapidly saturated. Higher metal ions content increases the contacts between metal ions and absorbents which accelerates absorption process [10]. Filtering/absorption rate of metal ions is obtained from equation (1):

$$\text{Filtering percent} = [(co - cf) / (co)] *100 \qquad (1)$$

On the other hand, absorption capacity of metal ions is calculated by equation (2):

$$qe = (co - cf) * v / w \qquad (2)$$

V= solution volume (li);
W: absorbent mass (gr);
C_0 = the initial content of ions in the solution (mg/li);
C_f = the final content of ions in the solution (mg/li);

As demonstrated in figure (1), Pb^2 and Cd^2 Ions absorption is a function of the ions initial contents of absorbents surfaces. It was revealed that with the ions content increase (to 60 mg/li), metal ions absorption rate on MWCNT-COOH decreases to 80 and 68/2 for Pb (II) and Cd (II), respectively. Ions' absorption rate on MWCNT surface increases to 69/8 and 56/2- for Pb (II) and Cd (II) - respectively.

Based on figure (2) and the obtained results, absorption capacity of both ions on MWCNT-COOH carbon nanotubes is more than MWCNTs. As metal ion/absorbent ratio increases, most absorption sites on nanotubes surfaces are saturated and absorption is accelerated on less active sites. This leads to higher absorption capacity of metal ions [1]. The highest absorption capacity for lead metal was achieved by multi carbon nanotubes with carboxyl content of 46/4 mgr/gr.

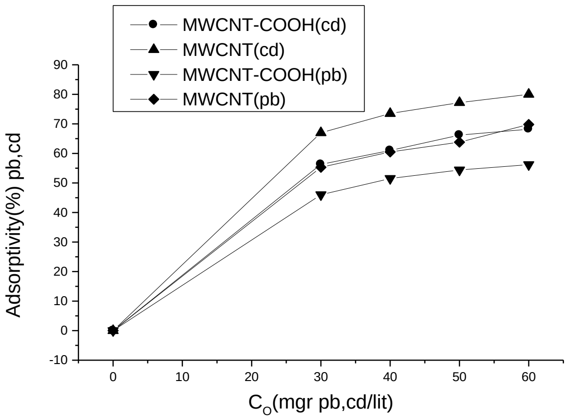

Fig. 1, lead and cadmium filtering percent by MWCNT and MWCNT-COOH based on the initial content of metal ions in the solution

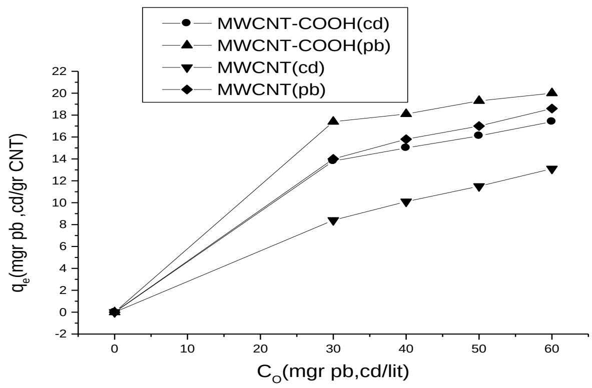

Fig. 2, lead and cadmium absorption capacity of MWCNT and MWCNT-COOH based on the initial content of metal ions in the solution

Equivalent data analysis is necessary for proposing an appropriate equation and explaining the obtained results. Data analysis is necessary for determining isothermal equations and modeling absorption equivalents. Equivalence data of metal ions absorption are related to Langmuir and Freundlich equations. These two equations are applied for investigating equivalence absorption on homogenous or inhomogeneous surfaces, respectively.

An absorption isotherm (isothermal line) is defined based on constants related to surface features and inclination to be combined with absorbents. It is an index of the absorbent's absorption capacity. Langmuir and Freundlich equations are applied for isotherm modeling of the absorption of lead and cadmium metal ions on MWCNT and MWCNT-COOH absorbents. Langmuir isotherm absorption model is applied to uni-layer absorption. This model assumes that the absorption surface has multiple sites with equal energy. Each individual molecule is absorbed at a specific site (among equal sites) [11]. Langmuir equation is demonstrated as follows:

qe = qm × b × Ce / 1 + b × Ce (3)

Where;

C_e = equivalent content of metal ions (mgr/li);
Q_e = amount of absorbed ions (mgr/li);
Q_m = maximum capacity of metal ions absorption (mgr/li);
B= Langmuir equivalent constant (li/mgr);

A fundamental feature of Langmuir equation is that it might be expressed with a non-dimension constant called equivalent parameter and expressed through the following equation:

R_L = 1/1+b$C_{0\ (4)}$

Where; b is Langmuir constant and C_0 is the maximum initial content of heavy metal ions (mgr/li). R_L value implies that isotherm type is isothermal or inappropriate (R_L >1), linear (R_L =0), appropriate (0<R_L <1) or irreversible (R_L =0).

Multilayer absorption isotherm for inhomogeneous surfaces is defined by Freundlich isotherm as follows:

qe = Kf × $Ce^{1/n}$ (5)

Where;

$C_{e:}$ equivalent content of metal ions (mgr/li);
qe: the amount of absorbed ions(mgr/gr);
$K_{f:}$ Freundlich equation constant indicating absorption intensity on homogenous surfaces;
n: Freundlich equation constant indicating absorption intensity on inhomogeneous surfaces.

Freundlich absorption isotherm (isotherm line) is widely applied in information mathematics to explain the proportionate content of the empirical data. This isotherm (isotherm line) reveals heterogeneousness of the surfaces, relative distribution of active sites and their energy levels.

To compare empirical data during metal ions absorption process and select the best governing model, constants of the two equations must be determined. In this regard, Langmuir equation is turned into a linear equation. The linear form used for depicting diagram is shown through equation (6):

Ce/qe=۱/(qmon.b)+Ce/qmon (6)

For linear reactions performed under different contents of Pb and Cd ions (30, 40, 50 and 60 mgr/li) and constant conditions (T=30K, PH=6 and constant content of 1gr/li in the solution), b and q_{mon} are obtained by considering equivalent contents and depicting Ce/qe based on C_e data in Table (1).

The Freundlich isotherm absorption is used for filtering Cd^2 and Pb^2 cathions by multi-walled carbon nanotubes. So, Freundlich equation is turned into a linear equation and the linear form is used for depicting a diagram based on the following equation:

$$\ln qe=\ln K_f+(1/n)\ln C_e \quad (7)$$

For linear reactions performed under different contents of Pb and Cd ions (30, 40, 50 and 60 mgr/li) and constant conditions (T=30K, PH=6 and constant content of 1gr/li in the solution), K_f and n are obtained by considering equivalent contents and depicting ln qe based on lnCe data in Table (1). The numerical value of 1/n<1 implies that absorption capacity of metal ions by MWCNTs is favorable [12].

Table (1): numerical value of equivalent contents and absorption capacity rates on absorbent surfaces

Nano tubes type	Metal ion content	Lead metal cathion(pb)					Cadmium metal cathion(cd)				
		Ce	qe	ln/qe	ln/Ce	Ce/qe	Ce	qe	ln/ qe	ln/Ce	Ce/qe
MWCNT	30 mgr	13.4	14	2.64	2.6	0.95	16.2	8.4	2.13	2.79	1.92
	40 mgr	15.7	15.9	2.71	2.76	0.99	19.6	10.1	2.31	2.98	1.94
	50 mgr	18.1	17	2.83	2.89	1.06	22.8	11.5	2.44	3.13	1.98
	60 mgr	21.1	18.6	2.92	3.04	1.13	26.3	13.1	2.57	3.27	2.00
		Ce	qe	ln/qe	ln/Ce	Ce/qe	Ce	qe	ln/ qe	ln/Ce	Ce/qe
MWCNT-COOH	30 mgr	9.90	17.4	2.85	2.29	0.57	13.1	13.8	2.62	2.57	0.95
	40 mgr	10.6	18.1	2.90	2.36	0.58	15.6	15	2.70	2.74	1.02
	50 mgr	11.4	19.3	2.96	2.43	0.59	16.9	16.1	2.78	2.83	1.05
	60 mgr	12	20	3.00	2.48	0.60	19.1	17.4	2.86	2.95	1.10

Isotherm absorption Linear equation was depicted for Pb^2 and Cd^2 based on Langmuir (equation Ce/qe based on Ce) at whole content range. Figures (3) and (4) are depicted for simple carbon nanotubes absorbent and figures (5) and (6) are depicted for the carbon nanotubes used for filtering lead and cadmium ions.

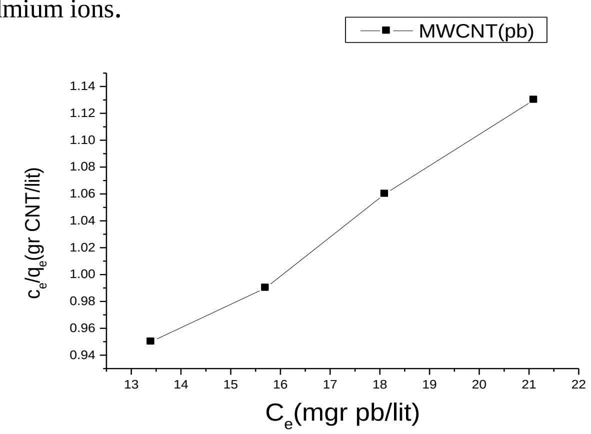

Fig. 3, Langmuir model for absorbing lead ions (MWCNT)

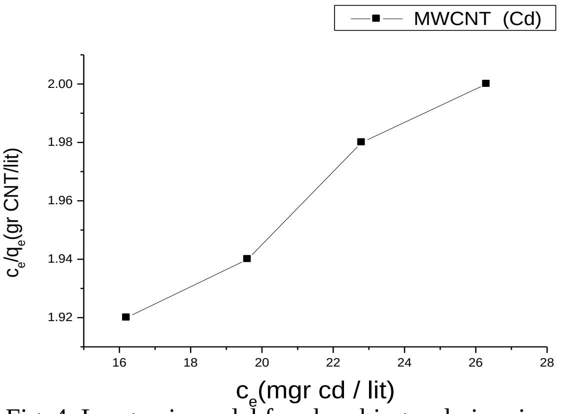

Fig. 4, Langmuir model for absorbing cadmium ions (MWCNT)

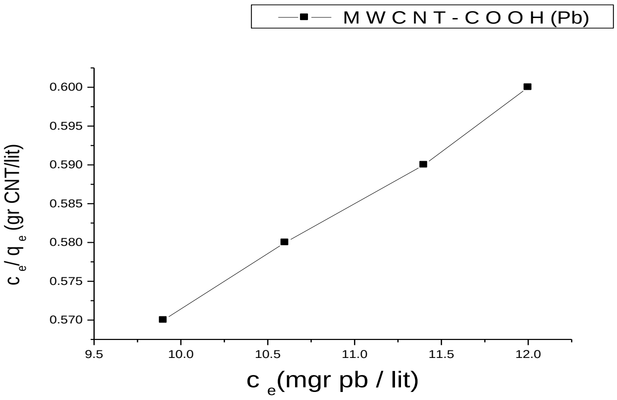

Fig. 5, Langmuir model for absorbing lead ions (MWCNT-COOH)

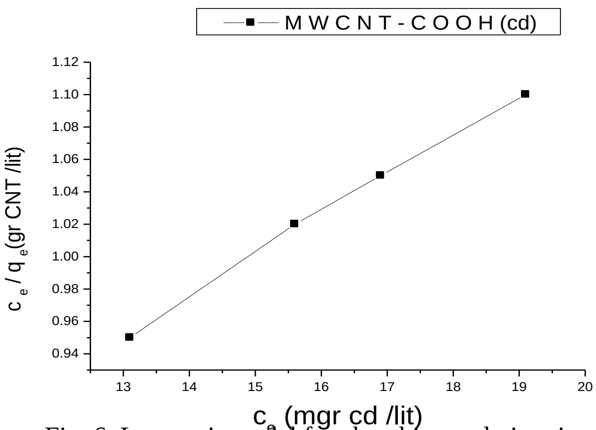

Fig. 6, Langmuir model for absorbing cadmium ions (MWCNT-COOH)

Figures (7) and (8) demonstrate isotherm absorption diagrams for Pb^2 and Cd^2 ions on simple multi-walleds carbon nanotubes surfaces. Figures (9) and (10) show absorption diagram for multi-carbon nanotubes with agent, based on Freundlich equation.

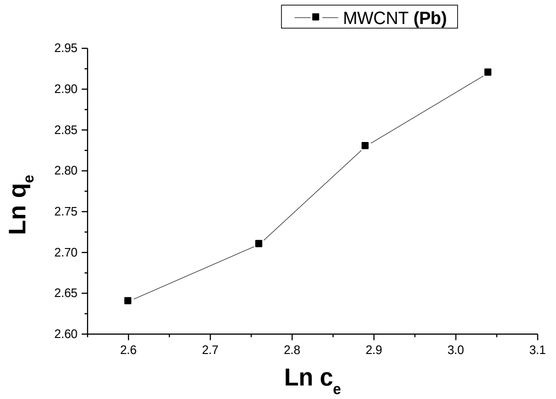

Fig. 7, Freundlich model for absorbing lead ions (MWCNT)

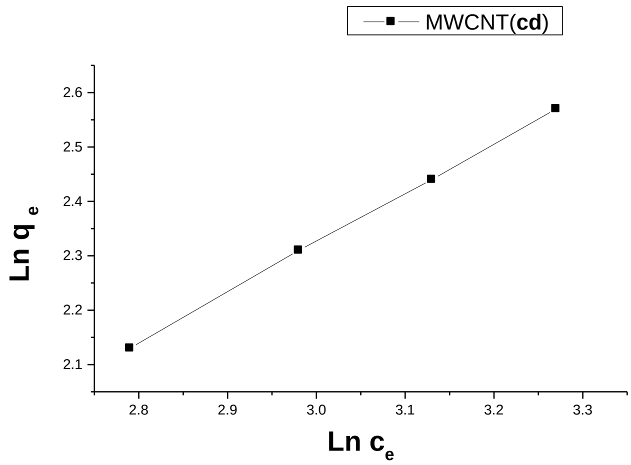

Fig. 8, Freundlich model for absorbing cadmium ions (MWCNT)

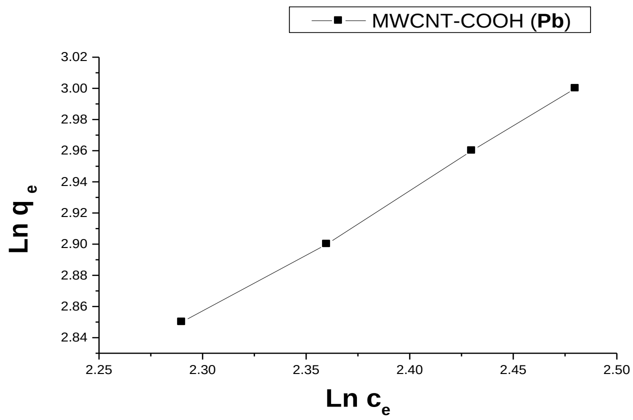

Fig. 9, Freundlich model for absorbing lead ions (MWCNT-COOH)

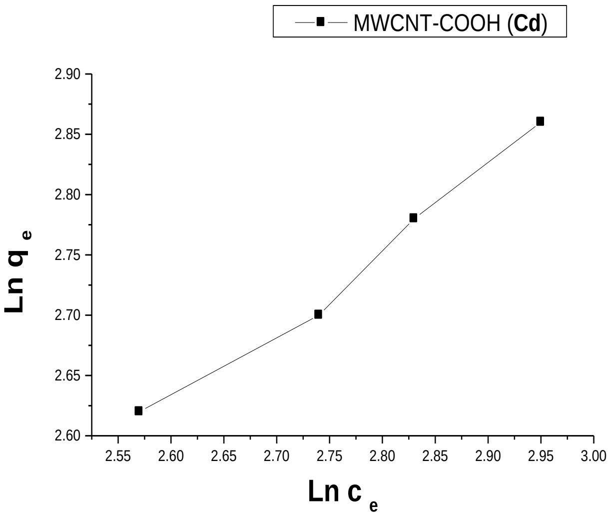

Fig. 10, Freundlich model for absorbing cadmium ions (MWCNT-COOH)

Table (2): surface absorption parameters in filtering metal cathions by multi-walled carbon nanotubes

Metal cathion type	Multi-walled nanotubes type	Langmuir				Freundlich		
		b(l/mg)	Qm(mg r/gr)	RL	R^2	KF	n	R^2
Pb(II)	MWCNT	0.443	47.52	0.037	0.9760	18.69	3.10	0.9982
	MWCNT-COOH	1.33	90.33	0.012	0.9813	45.43	1.83	0.9962
Cd(II)	MWCNT	0.141	33.71	0.105	0.9737	6.959	3.22	0.9929
	MWCNT-COOH	0.736	52.38	0.022	0.9924	22.23	1.05	0.9942

IV. Conclusion

Our findings revealed that filtering rate increases with the initial ions contents. Due to their vast contact zones, the multi-walled carbon nanotubes with carboxyl agent have higher capacity in filtering heavy metal ions from wastewaters. In Table (2), RL, as a non-dimensional Langmuir parameter, varies from 0 to 1 for simple and agented carbon nanotubes. In this regard, Langmuir might be assumed as an appropriate isotherm absorption model. But, linear absorption coefficient (R^2 or R correlation coefficient) is less than its similar situation in Freundlich equation. So, Freundlich equation is considered to be more appropriate for justifying metal cathions isotherm equation. N value-Freundlich equation constant and indicator of absorption intensity on inhomogeneous surfaces- is always more than 1 which reveals the favorable absorption capacity of metal ions by MWCNTs and MWCNT-COOH. As a result, numerical value of the metal ions maximum absorption capacity in Freundlich equation is more than Langmuir. Based on equations (3) and (5) and surface absorption parameters (Table-2), qe might be calculated based on Ce equivalent contents for agented nanotubes (with the initial ion content of 50mgr/li). Maximum absorption capacity for Pb2 and Cd2 calculated by Langmuir equation is 48/8 and 84/87 mgr/li, respectively. The same values calculated by Freundlich equation are 88/35 and 171/7 lgr/li, respectively.

It might be concluded that agented multi-walled carbon nanotubes are appropriate for filtering metal ions from industrial wastewaters. They can be resumed and reused after filtering process.

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