ISSN: 0970-020 X; CODEN: OJCHEG
Oriental Journal of Chemistry
2011, Vol. 27, No. (2): Pg. 545-551

http://www.orientjchem.org

Study of the Freundlich, Langmuir and Temkin Adsorption Isotherms for some Amino Acids and their Complexation with Lanthanum(III) on Multi-wall Carbon Nanotube (MWCNT)

MEHDI VADI[1]* and FATEMEH TOLOU[2]

[1]Department of Chemistry, Fasa Branch, Islamic Azad University, Fasa (Iran).
[2]Department of Chemistry, Firoozabad Branch, Islamic Azad University, Firoozabad (Iran).
E-mail: mahdi_vadi@iaufasa.ac.ir

(Received: May 06, 2011; Accepted: June 14, 2011)

ABSTRACT

In this article, adsorption of some amino acids and their complexation with lanthanum(III) ion on carbon nanotube (MWCNT) by using of three relations Langmuir, Freundlich and Temkin isotherms was investigated. From this relations, Freudlich and Temkin relations predict good equilibrium diagram in isotherm condition. We could compute the theoretical constants by excel software. By considering these constants, it is clear that among amino acids used and also amino acids were formed complex,l-arginine in comparison with other showed the most adsorption on carbon nanotube.

Key words: Adsorption; Isotherm; Amino acids; Complexation; lanthanum; Carbon nanotube.

INTRODUCTION

Lanthanum is a soft, malleable, silvery white metal which has hexagonal crystal structure at room temperature. At 310 °C, lanthanum changes to a face-centered cubic structure, and at 865 °C into a body-centered cubic structure[1]. Lanthanum easily oxidizes (a centimeter-sized sample will completely oxidize within a year[2]) and is therefore used as in elemental form only for research purposes. For example, single La atoms have been isolated by implanting them into fullerene molecules[3]. If carbon nanotubes are filled with those lanthanum-encapsulated fullerenes and annealed, metallic nanochains of lanthanum are produced inside carbon nanotubes[4]. Although lanthanum belongs to the element group called rare earth metals, it is not rare at all. Lanthanum is available in relatively large quantities (32 ppm in Earth's crust). "Rare earths" got their name because they were indeed rare as compared to the "common" earths such as lime or magnesia, and historically only a few deposits were known[5].

Monazite (Ce, La, Th, Nd, Y)PO_4, and bastnäsite (Ce, La, Y)CO_3F, are the principal ores in which lanthanum occurs, in percentages of up to 25 to 38 percent of the total lanthanide content. In general, there is more lanthanum in bastnäsite than in monazite. Until 1949, bastnäsite was a rare and

obscure mineral, not even remotely contemplated as a potential commercial source for lanthanides. In that year, the large deposit at the Mountain Pass rare earth mine in California was discovered. This discovery alerted geologists to the existence of a new class of rare earth deposit, the rare-earth bearing carbonatite, other examples of which soon surfaced, particularly in Africa and China.

Basic nitrogen-containing compounds, amino acids, are formed in plant microbial, and animal cells under the action of microorganisms. These are biologically important compounds, and the formation of many of them precedes the synthesis of alkaloids and hormones, neuromediators, phospholipids and vitamin components, and initiators of numerous enzymatic reactions[6-10]. Here we would like to show that amino acids could be adsorbed on carbon nanotubes. The problem of evaluating the surface heterogeneity of adsorbents from the experimental overall isotherm has a long history in physical chemistry. It suffices to recall Langmuir's work of 1918 [11], the two fundamental articles by Sips[12] of 1948 and 1950, and the recurrence method proposed by Adamson and Ling[13] in 1961. Of all the "classic isotherms" only some of them can be explained or have been proposed on statistical mechanical grounds, others on the contrary, can not be justified by simple models. This is the case of the important isotherms empirically proposed by Freundlich, Temkin[14-15]. These isotherms are usually ascribed to the heterogeneity of the surface. It allows the computation of the adsorption-energy distribution associated with each type of experimental behavior.

EXPERIMENTAL

Apparatus

In this process we used ultraviolet-visible spectroscopy (UV/Vis) method to determine the concentration of amino acid solution and their complexation with lanthanum(III) ion.

We used shaker-incubator apparatus infers model for solution stirring processes during equilibrium adsorption and at the end for 5 minutes then filtrated with filter paper and could measured the solution concentration with UV-Vis.

The effect of initial concentration

At first we prepared 1000ppm solution of amino acid and its complexation was measured with ultraviolet-visible spectroscopy. After prepared,10 , 15 , 25 and 50ppm of the above solution, their adsorption were measured with UV-vis. Then they added to 0.01 g CNT and after 24 h agitation with shaker-incubator they filtered by filter paper. Then, the adsorption of the filtered solution was measured with spectrophotometer. Finally, the amount of adsorbed complex on 100 g CNT was calculated. The maximum gram of adsorbed complex was found to be L-Arginine that the amount of adsorption increases as a function of initial concentrations.

RESULTS AND DISCUSSION

Study of equilibrium

We can compute experimental results from equilibrium experiences by several adsorption isotherm models that were the linear by means of Excel software.

Freundlich model

We often use this model for heterogeneous adsorption that has acceptable harmony with experimental data which expresses with n-order. For commutating Freundlich equation constants we can design lnQe diagram based on lnCe the slope of this diagram is n and the intercept is $\ln K_f$. Distribution coefficient K_f displays ion adsorption addiction and with increase in K_f amount adsorption amount will be increase and vice versa.This relation is expressed by equation 1 [16-20].

$$Q_e = X/m = K_F * C_e^{\,n} \quad \ln Q_e = \ln K_f + n \ln C_e \quad \ldots(1)$$

With attention to the correlation coefficient from data that we could observe from Figures 1 and 2 that have acceptable accommodation between data and models. Model parameters that obtained from diagram were shown on tables (1, 2) which express amino acids and their complexation.

Langmuir model

This model is obtained from assumption of similar energy of adsorption sites of absorbent surface, and expresses with below equation that has linear form. In this equation with attention to the equal amount of adsorption and repelling on surface,

we can consider these velocities equal to each other and from this equivalent we can obtain eq. 2 [20,21].

$$N=Q_e/Q_m=K_l\ C_e/1+K_l\ C_e$$
$$Q_m\ K_l\ C_e=Q_e+K_l\ C_eQ_e$$
$$C_e/Q_e=1/Q_m\ K_l+C_e/Q_m \quad ...(2)$$

K_l and Q_m parameters that we brought at tables (1,2) were computed with design of diagram C_e based on C_e/Q_m, slope of this diagram is $1/Q_m$ and intercept is $1/K_lQ_m$ which Q_m is maximum adsorption based on(mg/kg) and K_l constant depends on adsorption energy and is based on (L/mg).

This model hasn't a good corresponding with attention to the correlation coefficient that was mentioned in figures (1, 2), but commutating the parameters has a good application for expressing several adsorption.

Temkin model

The linear form of this model is shown in Fig. 3. This model was obtained with consideration

Table 1. Calculated Langmuir, Freundlich, Temkin isotherm parameters for amino acidsadsorption on CNT

Amino acids	freundlich	Langmuir	Temkin
methionine	R^2=0.982	R^2=0.727	R^2=0.971
	n=1.44	Q_m=22.7	B=4.18
	K_F=2.001	K_L=0.022	K_T=0.295
Arginine	R^2=0.802	R^2=0.316	R^2=0.705
	n=1.7KF=1.8	Q_m=37.03KL=0.035	B=7.4KT=0.46
Valine	R^2=0.623	R^2=0.619	R^2=0.521
	n=3.4	Q_m=32.25	B=4.21
	K_F=1.28	K_L=0.16	K_T=9.63
Glutamic acid	R^2=0.878	R^2=0.999	R^2=0.878
	n=4.38	Q_m=3.96	B= -1.426
	K_F=0.796	K_L= -3.1	$K_T=2.49\times10^{-3}$

Table 2: Complexation of : Calculated Langmuir, Freundlich, Temkin isotherm parameters for amino acids with La(III)

Complexion oflanthanum (III) with amino acids	freundlich	Langmuir	Temkin
methionine	R^2=0.926	R^2=0.742	R^2=0.967
	n=3.62	Q_m= -23.8	B=1.5
	K_F=1.3	K_L= -0.02	K_T=3.42
Arginine	R^2=0.997	R^2=0.919	R^2=0.966
	n= -2.15	Q_m=1.43	B= -2.019
	K_F=0.62	K_L= -0.17	K_T=0.01
Valine	R^2=0.968	R^2=0.699	R^2=0.909
	n=0.54	Q_m= -11.49	B=21.69
	K_F=6.3	K_L= -0.035	K_T=0.15
Glutamic acid	R^2=0.965	R^2=0.711	R^2=0.935
	n=0.33	Q_m= -0.98	B=10.55
	K_F=20.1	K_L= -0.028	K_T=0.088

of adsorption interaction and adsorption substances which was attained with designing diagram LnC_e based on Q_e. We could measure K_T and B parameters that were shown in table 1 and 2 [22-24].

With considering the correlation coefficient in Figs. 1,2, we observe that there is an accessible competition between this model and Freundlich model.

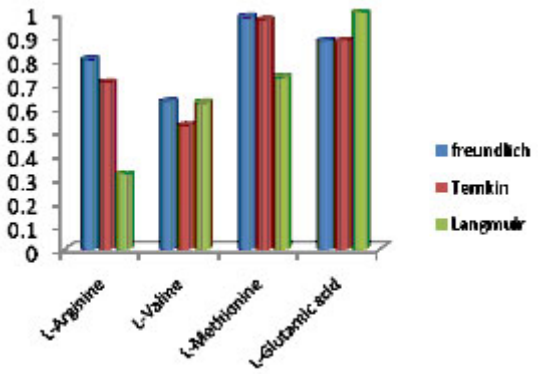

Fig1: The correlation coefficients of amino acids.

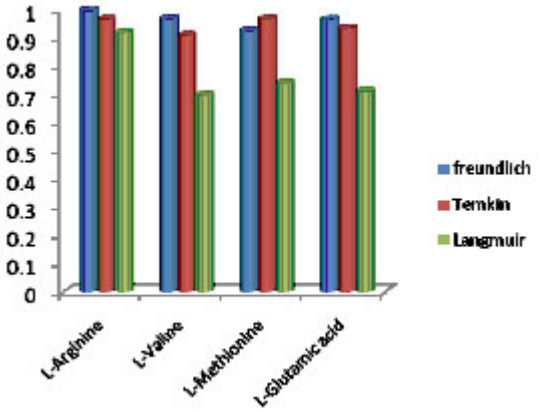

Fig. 2: The correlation coefficients of complexation of amino acids with La (III).

Q_m Langmuir constant is related to maximum adsorption capacity: Q_m amounts that were obtained from Langmuir model were necessary amino acid amounts for single layer constituent at amino acid adsorption. This amount was higher than Q_m amount at their complexation adsorption to amino acids and among amino acids adsorption capacity L-arginine adsorption was higher than the others, which table 1 shows this. KL or b: Langmuir equilibrium constant. Our reason from computing b is obtaining RL that is equilibrium parameter and we can express following equation for it and we can use it to indicate isotherm kinds. If $R_L=0$, isotherm is irreversible , if $0<R_L<1$, isotherm is desirable, if $R_L=1$ isotherm is linear and if $R_L>1$ isotherm is undesirable[25,26].

$$R_L=1/1+bc \qquad ...(4)$$

1/n and KF are Frundlich constants theory which is introduced intension of adsorption amount and adsorption capacity. At Frundlich isotherm when K_F increases adsorption energy will increase too and that causes to increase L-arginine The amount of n between 1-10 displays acceptable adsorption processes. If n=1 heterogen of the surface is less significant and if n=10 it is more significant (Table 1) [27-32].

B and KL are Temkin equation parameters and respectively adequate with adsorption condescended and boundary constant adequate with maximum of boundary energy. Amount of B is R_T/b and b is based on Temkin isotherm constant[23,24]. By observing table 2 we can see the maximum amount adsorption of KL for complexe of L-arginine amino acid.

CONCLUSION

We could observe the adsorption increase when we increased the concentration solutes.

This was true about the complexes adsorption on carbon nanotube . In this research, we realized that Freundlich isotherm showed the best accommodation with the experimental data.

Q_m Langmuir constant is related to maximum adsorption capacity on carbon nanotube, that L-Arginine had the maximum value. It is an alkaline amino acid with an extra group of amine. This amino acid can be found in some proteins such as Histone and Protamine the statement of adsorbent and adsorbate material, their being reversible or irreversible process concentration and adsorption process are of the main factors effecting

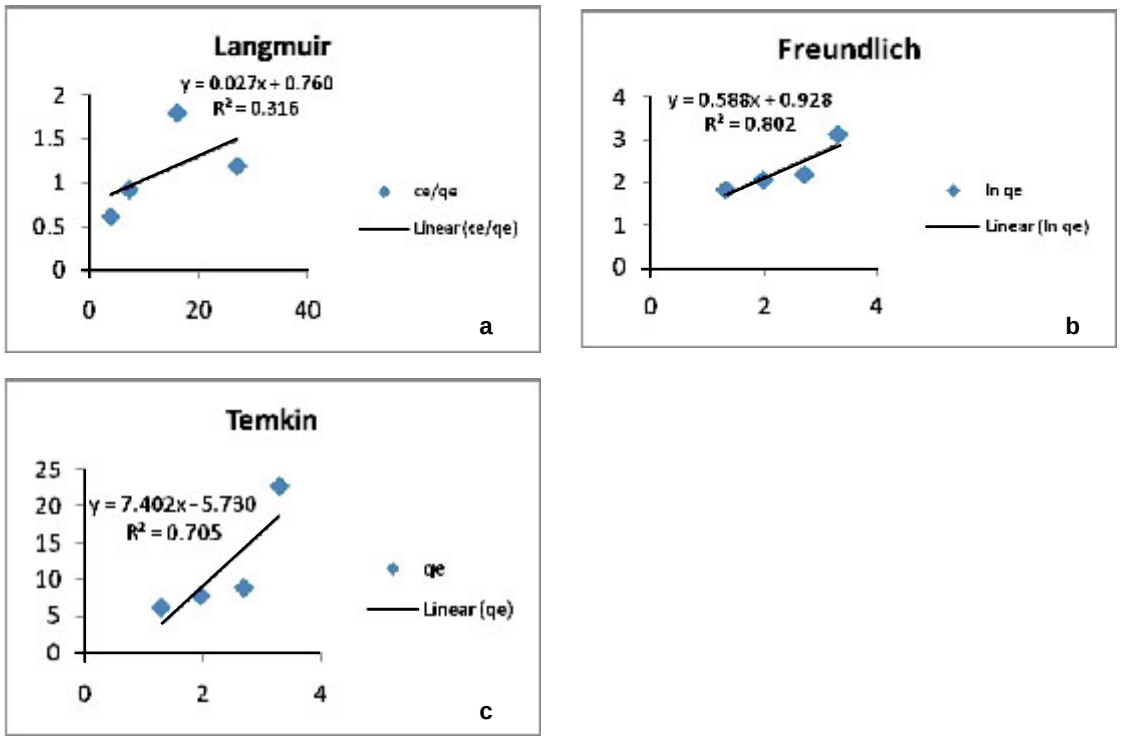

Fig. 3. Adsorption isotherms of L-Arginine with models a) Langmuir b) b) Freundlich c)Temkin

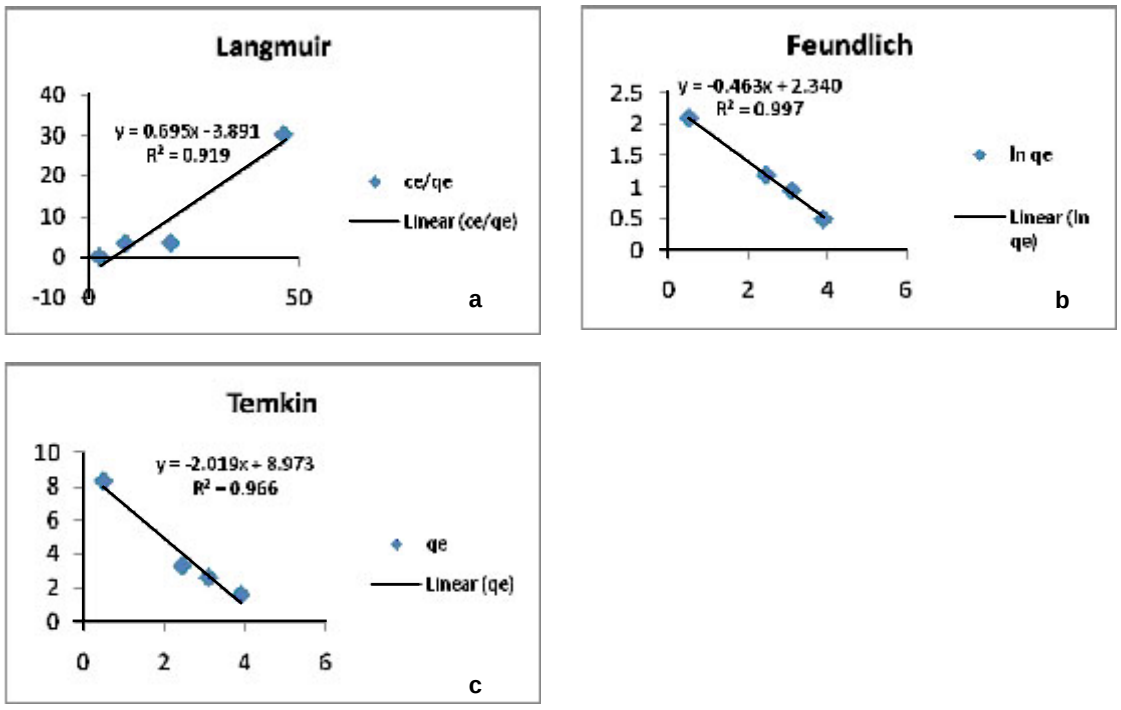

Fig. 4: Adsorption isotherms of complexation of L-arginine with La (III) with models a) Langmuir b) Freundlich c) Temkin

adsorption , this could be proved obtaining the parameters for adsorption isotherm. This study that was accomplished on liquid-solid system adsorption effected separating amino acids and dissolved residue in dilution on solid surface in arranged in dynamic equilibrium. At equilibrium state there is a limitation on dissolved distribution between liquid and solid phases and by means of isotherms we described adsorption capacity of them for analysis and drawing adsorption system.

Steric hindrance, ligand alkalinity and chelate impression can effect the adsorption amino acids on carbon nanotube. Also, the aut comes signifies that the amino acid with little ligand and more alkalinity and smaller chelate ring , will produce more stable comlex, in addition to that they help to better adsorption, its complexation adsorption was done with greater power that was dependant to the maximum bonded energy between other complexes adsorption.

REFERENCES

1. R. Hammond. *The Elements, in Handbook of Chemistry and Physics 81st edition*. CRC press. ISBN 0849304814 (2000).
2. "Rare-Earth Metal Long Term Air Exposure Test". http://www.elementsales.com/re_exp/index.htm. Retrieved 2009-08-08.
3. Tsuchiya, T; Kumashiro, R; Tanigaki, K; Matsunaga, Y; Ishitsuka, Mo; Wakahara, T; Maeda, Y; Takano, Y et al., "Nanorods of endohedral metallofullerene derivative.". *Journal of the American Chemical Society* **130** (2): 450-1 (2008). doi:10.1021/ja710396n. ISSN 0002-7863. PMID 18095695.
4. Guan, L; Suenaga, K; Okubo, S; Okazaki, T; Iijima, S. "Metallic Wires of Lanthanum Atoms Inside Carbon Nanotubes". *Journal of the American Chemical Society* **130** (7): 2162-3 (2008). doi:10.1021/ja7103069. ISSN 0002-7863. PMID 18225905.
5. Patnaik, Pradyot. Handbook of Inorganic Chemical Compounds. McGraw-Hill. pp. 444–446. ISBN 0070494398. http://books.google.com/?id=Xqj-TTzkvTEC&pg=PA243. Retrieved 2009-06-06 (2003).
6. K. Bradlay, M. Briman, A. Star and G.Gruner; Charge transfer from adsorbed proteins Nano Lett. **4**: 253-6 (2004).
7. A. Star, J C P. Gabriel, K .Bradley and G.Gruner Electronic detection of specific protein binding using nanotube FET devices Nano Lett. 34 (2003)59-63.
8. A. Bianco, K. Kostarelos and M. Prato; Applications of carbon nanotubes in drug delivery *Curr. Opin. Chem. Biol*. **9**: 674-9 (2005).
9. K. K. Jain. Drug Discovery Today: *Technologies* **1**(2): 75-78 (2004).
10. A. Bianco, J. Hoebeke, S. Godefrog, O. Chaloin, D. Pantarotto J. Briand, S. Muller, M. Prato, C. D. Partidos, *J. Amer. Chem. Soc*. **127**(1): 58-59 (2005).
11. I. Langmuir, *J. Amer. Chem. Soc*. **40**: 1361 (1918).
12. R. Sips, *J. Chem. Phys*. **18**: 1024 (1950).
13. A. W. Adamson, and I. Ling, *Advan. Chem. Ser*. **33**: 51 (1961).
14. M. I. Temkin, *J. Phys. Chem*. **14**: 1153 (1940).
15. H. Freundlich, *Trans. Faraday Soc*. **28**: 195 (1932).
16. K. Kadirvelu, C. Namasivaryam, Aricultural by-products as metal adsorptions: sorption of lead () from aqueous solutions onto coir-pith carbon, *J. Membr. Sci*. **165**: 156-167 (2000).
17. R. Sips, *J. Chem. Phys*. **16**: 490 (1948).
18. R. Sips, *J. Chem. Phys*. **18**: 1024 (1950).
19. Y.S.Ho, J.F. Porter, G. McKay. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, water Air Soil Pollut.**141**: 1-33 (2002).
20. Inge Daems, Philibrt Leflative,Alain Methivier,Gino V.Baron,.Microporous and Mesoporous Materials, **30**.: 149-156 (2006).
21. Inge Daems, Philibrt Leflative, Alain Methivier, Gino V. Baron, Microporous and Mesoporous Materials, **30**: 191-199 (2005).
22. U. John, Kennedy oubagaranadin, N.

Sathyamuthy, Evaluation of Fuller's earth for the adsorption of mercury from aqueous solutions: A comparative study with actived carbon, *Journal of Hazardous Materials* **142**: 165-174 (2007).

23. M. Ozacar, I.A.S engil, *Bioresour. Tecnol*., **96**: 791-795 (2005).
24. I.D. mall, V.C. Srivastava, N.K. Agarwall, I.M. Mishra. Chemosphere, **61**: 492-501 (2005).
25. T.W. Weber, R. K. Chakraborty, Pore and diffusion models for fixed bed adsorbents, *J. Am. Inst. Chem. Eng*. **20**: 2228- 2238 (1974).
26. N. Ahalya, R. D. Kanamadi, T. V. Ramachandra, Biosorption of chromium (V) from aqueous solutions by the husk of Bengal gram (Cicerarientium), *Elec. J. Biotechnol*. **8**(3): 258-264 (2005).
27. G. F. Cerofalini, *Chem Phys.* **33**: 423 (1978).
28. A.S. Ozcan, B. Erdem, A. Ozcan, *J. Colloid Interface Sci*. **280**: 44 (2004).
29. P. Wick, P .Manser, L. K. Limbach, U. Dettla – Weglikowska, F. Krumeich, S. Roth, W.J. Stark, A. Bruinink. *Toxicology Letters* **168**(2): 121-131 (2007).
30. P .Nednoor, V.G .Gavalas, N .Chopra, B. J. Hinds, L .G .Bachas. *Journal of Materials Chemistry* **17**(18): 1755- 1757 (2007).
31. M. R .Babaa, I .Stepanek, K. Masenelli – Varlot, N. Dupont – Pavlovsky, E .McRae, P. Bernier. Surface Science **531**(1): 86-92 (2003).
32. Y. Xie, Y. Kong, A .K. Soh, H .Gao. *Journal of Chemical Physics* **127**(22): 225101 (2007).