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Application of the Freundlich Langmuir Temkin and Harkins-Jura adsorption isotherms for some amino acids and amino acids complexation with manganese ion(II) on carbon nanotube

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ABSTRACT

In this research, adsorption of some amino acids and their complexation with manganese (II) ion on carbon nanotube (MWCNT) by using of four relations Langmuir, Freundlich, Temkin and Harkins –Jura isotherms was investigated. From this relations, Freudlich and Trmkin relations predict good equilibrium diagram in isatherm condition. We could compute the theoretical constants by excel software. By considering these canstants, it is clear that among amino acids used and also amino acids were formed complex, L-phenylalanine and L-systeine in comparison with ather showed the most adsorption on carbon nanotube.

Keywords: Adsorption, Isotherm, Amino arids; Complexation; Carbon nanotube

INTRODUCTION

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 [1-5].
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 [6], the two fundamental articles by Sips [7] of 1948 and 1950, and the recurrence method proposed by Adamson and Ling[8] 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, Dubinin and Radushkevich, Temkin [9-10].

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.
The three classic overall isotherms are observed in adsorption on equilibrium surface [11, 12] The accounting of the solute or contaminant on the adsorbent are most often measured with batch equilibrium test. Varying solute concentrations are mixed with an adsorbent until equilibrium is achieved and the contaminant removed from the solution [14]. It is plotted as a function of the equilibrium contaminant concentration remaining in solution or as a function of initial contaminant concentration.
The initial concentration is useful for comparing contaminant uptake by different materials or uptake of a variety of contaminants on the same graph [15]. Note that when the equilibrium

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concentration is used it is more difficult to compare different adsorbents or contaminants since the range of equilibrium concentrations. may not correspond. Evaluation of the parameters in the isotherm is accomplished by obtaining a linear form of the isotherm and the best fitting line for the data is obtained by maximizing the coefficient of determination r^2. The r^2 value indicates the goodness of fit between the data and the isotherm but other error equations have also been used to evaluate the performance of adsorption models [16]. In this paper, the experimental adsorption data were tested with the Langmuir, Freundlich, Temkin and Harkins-Jura equations. The maximum adsorption capacity and the maximum bonded energy were determined from the Freundlich and Temkin isotherms.

EXPERIMENTAL

Apparatus

In this process we used ultraviolet-visible spectroscopy (UV/Vis) method to determine the concentratioo of amino acid solution and their complexatioo with manganese (II) iun. We used shaker-incubator apparatus infers model for solution stirring processes during equilibrium adsorption and at the end for 3 minutes then filtrated with filter paper and could measured the solution concentration with UV-Vis.

The effect of initial concentration

At first we prepared 0.01 M solution of amino acid and its complexation was measured with ultraviolet-visible spectroscopy. After prepared 1×10^{-3}, 1×10^{-4}, 1×10^{-5}, 1×10^{-6} and 5×10^{-6} of the above solutioo, 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-cysteine and L-phenylalanine that the amount of adsorption increases as a functioo 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 liocar by means of Excel software.

Freuodlich mndel

We often use this model for heterogeneous adsorpiion that has acceptable harmony with experimental data which expresses with n-order.

For commutating Freundlich equation constants we can design $\ln Q_e$ diagram based on $\ln C_e$ 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 [17-21].

$$Q_e=X/m=K_F*C_e^n \quad \ln Q_e=\ln K_F+n\ln C_e \qquad (1)$$

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 shnwn on tables (1, 2) which expresses amioo acids and their complexation.

Langmuir madel

This model is obtained from assiimption of similar energy of adsorption sites of absorbent surface, and expresses with below equation that has linear form. In this equation with attentinn to the equal amount of adsorption and repelling on surface, we can consider these velocities equal in each other and from this equivalent we can obtain equation 2 [21,22].

$$N=Q_e/Q_m=KLC_e/1+KLC_e \quad Q_mK_LC_e=Q_e+K_LC_eQ_e$$
$$C_e/Q_e=1/Q_mKL+C_e/Q_m \qquad (2)$$

k_l and Q_m parameters that we brought at tables (1,2) were computed with design nf diagram Cc based nn C_e/Q_m, slope of this diagram is $1/Q_m$ and intercept is $1/K_LQ_m$ which Q_m is maximum adsorptinn based on(mg/kg) and K_L constant depends on adsorption energy and is based on (L/mg)

Table 1. Calculated Langmuir, Freundlich, Temkin and Harkins-Jura isotherm parameters for amino acids adsorption on CNT

amino acids	Freundlich	Langmuir	Temkin	Harkins-Jura
Alanine	R^2=0.97 n=1.56 K_F=0.12	R^2=0.69 Q_m=-3.52 K_L=-0.05	R^2=0.99 B=0.28 K_T=47.62	R^2=0.76
Asparagine	R^2=0.97 n=1.53 K_F=0.024	R^2=8.66 Q_m=-1.77 K_L=-0.05	R^2=0.83 B=0.45 K_T=5.43	R^2=0.54
Cystein	R^2=0.85 n=0.96 K_F=0.58	R^2=0.42 Q_m=22.37 K_L=-0.01	R^2=0.91 B=0.26 K_T=1.69	R^2=0.44
Glycine	R^2= 0.99 n=1.88 K_F=0.10	R^2=0.90 Q_m=-0.78 K_L=-0.14	R^2=0.98 B=0.60 K_T=1.55	R^2=0.94
Histidin	R^2=0.96 n=1.5 K_F=0.007	R^2=0.68 Q_m=2.07 K_L=-5.13	R^2=0.99 B=0.73 K_T=0.64	R^2=0.87
Phenylalanine	R^2=0.90 n=0.54 K_F=1.40	R^2=0.69 Q_m=10.36 K_L=0.10	R^2=0.81 B=0.35 K_T=1.88	R^2=0.82
Proline	R^2=0.98 n=1.80 K_F=0.005	R^2=0.99 Q_m=-0.58 K_L=-0.03	R^2=1 B=-0.55 K_T=0.05	R^2=0.94
Threonine	R^2=1 n=1.13 K_F=0.50	R^2=0.89 Q_m=-0.44 K_L=-0.006	R^2=0.99 B=0.79 K_T=18.95	R^2=0.87
Valine	R^2=0.99 n=1.09 K_F=0.04	R^2=0.95 Q_m=-0.16 K_L=-0.1	R^2=0.96 B=1.31 K_T=2.83	R^2=0.89
Metionine	R^2=0.99 n=1.6 K_F=0.01	R^2=8.94 Q_m=-0.52 K_L=-0.05	R^2=0.81 B=1.09 K_T=2.87	R^2=0.90

Table 1. (continued)

amino acids	Freundlich	Langmuir	Temkin	Harkins-Jura
Valine	R^2=0.90 n=0.65 K_F=0.11	R^2=0.52 Qm=2.4 K_L=0.02	R^2=0.76 B=2.18 K_T=1.26	R^2=0.77 A=0.01 B=1.45
Arginine	R^2=0.68 n=1.10 K_F=0.04	R^2=0.04 Qm= -5 K_L= -0.008	R^2=0.86 B=1.14 K_T=3.8	R^2=0.46 A=0.03 B=1.38
Alanine	R^2=0.98 n=0.22 K_F=0.32	R^2=1 Qm= 0.81 K_L=0.20	R^2=0.99 B=7.05 K_T=0.80	R^2=0.96 A=0.34 B=2.17
Asparagine	R^2=0.94 n=2.07 K_F=0.001	R^2=0.42 Qm= -0.14 K_L= -0.02	R^2=0.95 B=1.43 K_T=2.96	R^2=0.44 A=1.43 B=2.96
Cystein	R^2=0.98 n=3.04 K_F=0.0001	R^2=0.43 Qm= -0.09 K_L= -0.03	R^2=0.82 B=0.34 KT=304.78	R^2=0.32 A=0.0001 B=1.38
Glycine	R^2=0.95 n=1.42 K_F=0.03	R^2=0.48 Qm= -3.21 K_L = -0.021	R^2=0.99 B=0.57 K_T=10.39	R^2=0.86 A=0.06 B=1.32
Histidin	R^2=0.91 n=0.99 K_F=0.03	R^2=0.008 Qm=34.72 K_L=0.001	R^2=0.98 B=1.09 K_T=6.25	R^2=0.61 A=0.10 B=1.65
Phenylalanine	R^2=0.93 n=1.47 K_F=0.01	R^2=0.47 Qm= -2.04 K_L= -0.01	R^2=0.77 B=0.38 KT=155.85	R^2=0.50 A=0.02 B=1.49
Proline	R^2=0.86 n=0.89 K_F=0.04	R^2=0.05 Qm=6.97 K_L=0.005	R^2=0.90 B=2.12 K_T=1.75	R^2=0.50 A=0.01 B=1.42
Threonine	R^2=0.99 n=1.75 K_F=0.06	R^2=0.97 Qm=2.5 K_L=0.01	R^2=0.97 B=2.25 K_T=1.78	R^2=0.90 A=0.06 B=1.56

Table 2. Complexation of :Catcutated Langmuir, Freundlich, Temkin and Harkins-Jura isotherm parameters for amino acids with Mn (II)

Complexion of Manganese (II) with amino acids	Freundlich	Langmuir	Temkin	Harkins-Jura
Valine	R^2=0.90 n=0.65 KF=0.11	R^2=0.52 Qm=2.4 KL=0.02	R^2=0.76 B=2.18 KT=1.26	R^2=0.77 A=0.01 B=1.45
Arginine	R^2=0.68 n=1.10 KF=0.04	R^2=0.04 Qm=-5 KL= -0.008	R^2=0.86 B=1.14 KT=3.8	R^2=0.46 A=0.03 B=1.38
Alanine	R^2=0.98 n=0.22 KF=0.32	R^2=1 Qm= 0.81 KL=0.20	R^2=0.99 B=7.05 KT=0.80	R^2=0.96 A=0.34 B=2.17
Asparagine	R^2=0.94 n=2.07 KF=0.001	R^2=0.42 Qm= -0.14 KL= -0.02	R^2=0.95 B=1.43 KT=2.96	R^2=0.44 A=1.43 B=2.96
Cystein	R^2=0.98 n=3.04 KF=0.0001	R^2=0.43 Qm= -0.09 KL= -0.03	R^2=0.82 B=0.34 KT=304.78	R^2=0.32 A=0.0001 B=1.38
Glycine	R^2=0.95 n=1.42 KF=0.03	R^2=0.48 Qm= -3.21 KL = -0.021	R^2=0.99 B=0.57 KT=10.39	R^2=0.86 A=0.06 B=1.32
Histidin	R^2=0.91 n=0.99 KF=0.03	R^2=0.008 Qm=34.72 KL=0.001	R^2=0.98 B=1.09 KT=6.25	R^2=0.61 A=0.10 B=1.65
Phenylalanine	R^2=0.93 n=1.47 KF=0.01	R^2=0.47 Qm= -2.04 KL= -0.01	R^2=0.77 B=0.38 KT=155.85	R^2=0.50 A=0.02 B=1.49
Proline	R^2=0.86 n=0.89 KF=0.04	R^2=0.85 Qm=6.97 KL=0.005	R^2=0.98 B=2.12 KT=1.75	R^2=0.80 A=0.01 B=1.42
Threonine	R^2=0.99 n=1.75 KF=0.06	R^2=0.97 Qm=2.5 KL=0.01	R^2=0.97 B=2.25 KT=1.78	R^2=0.90 A=0.06 B=1.56

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 [23].

Temkin model

The linear form of this model is shown in Fig. 3. This model was obtained with consideration of adsorption interaction and adsorption substances which was attained with designing diagram LnC_e based on Q_e. We could measure K_f and B parameters that were shown in table 1 and 2 [24-26]. With considering the correlation coefficient in Figures (1, 2), we observe that there is an accessible competition between this model and Freundlich model.

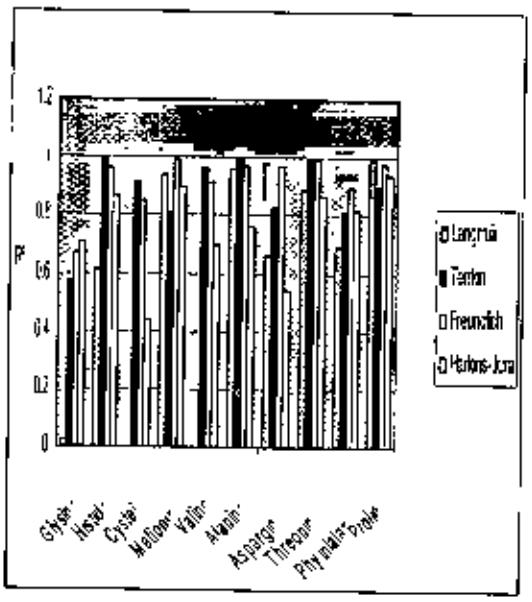

Fig. 1. The correlation coefficients of amino acids.

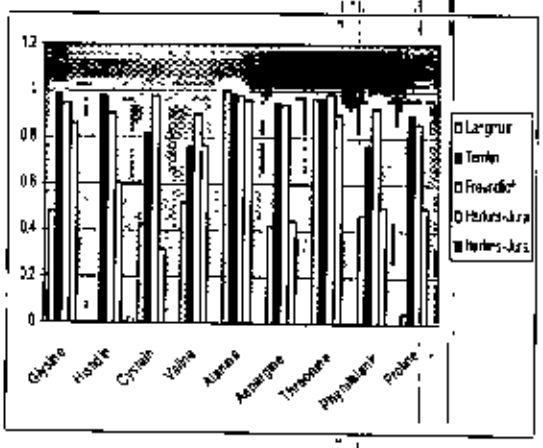

Fig. 2. The correlation coefficients of complexation of amino acids with Mn (II).

Harkins-Jura model

We discuss this model with equilibrium 3:

$$1/Q_e^2 = [B/A]-[1/A]\log C_e \quad (3)$$

with designing diagram $\log C_e$ based on $1/Q_e^2$ with considering A parameter slope and with attention to intercept we can compute B parameter that we could observe the data at tables (1, 2) [27].

By considering Figures (1, 2), it was observed that correlation coefficient in this model has not a good correlation with experimental data. We ignored studying of Henderson and Bet models because of multilayer adsorption and sigmodial Langmuir model which is diagram 1/Q based on 1/C and this is because of nonlinear figures [28] With attention to expand of designing adsorption isotherm for amino acid and their complexation with manganese (II) ion, we just presented models for L-cystein and L-phenylalanine amino acids Figures (3,4) and their complexation with manganese (II) ion Figures (5,6).

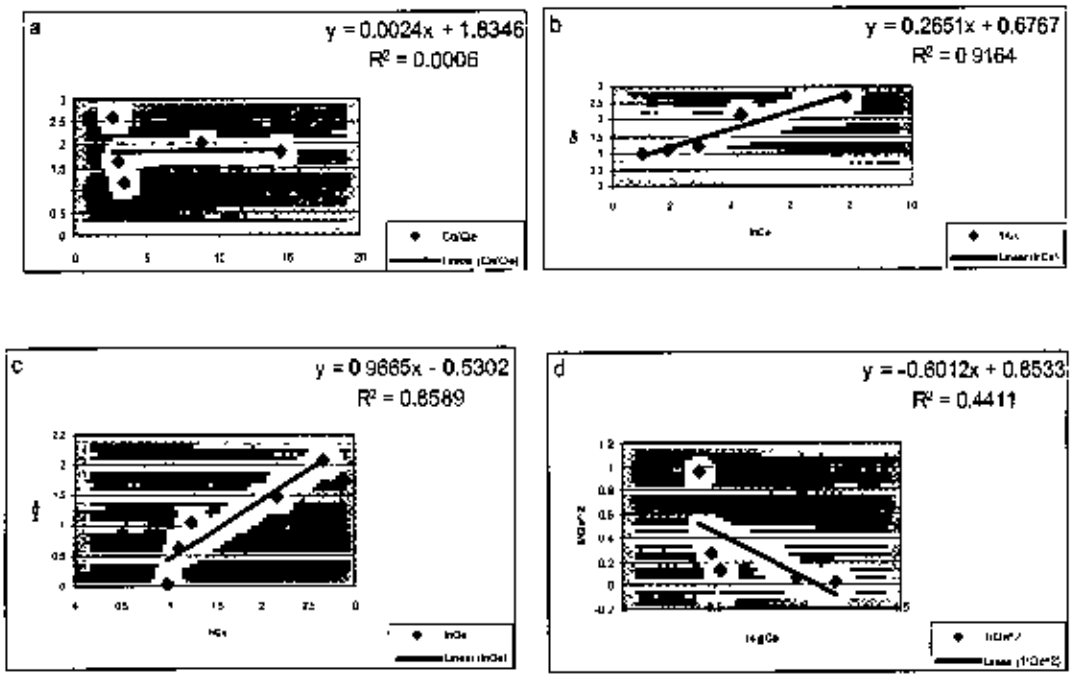

Fig. 3. Adsorption isotherms of L-cysteine with models a) Langmuir b) Temkin c) Freundlich d) Harkins-Jura.

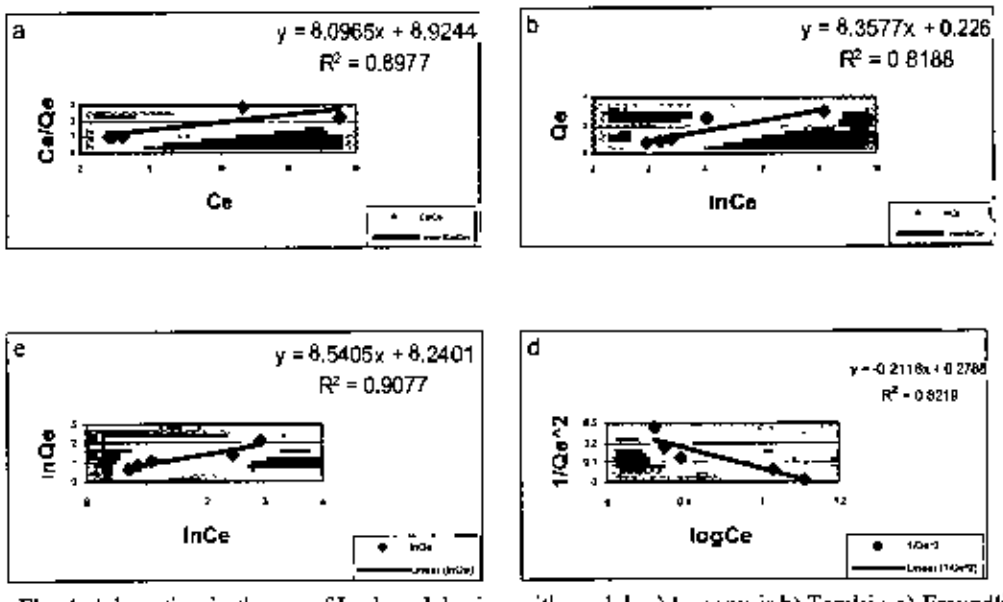

Fig. 4. Adsorption isotherms of L-phenylalanine with models a) Langmuir b) Temkin c) Freundlich d) Harkins-Jura.

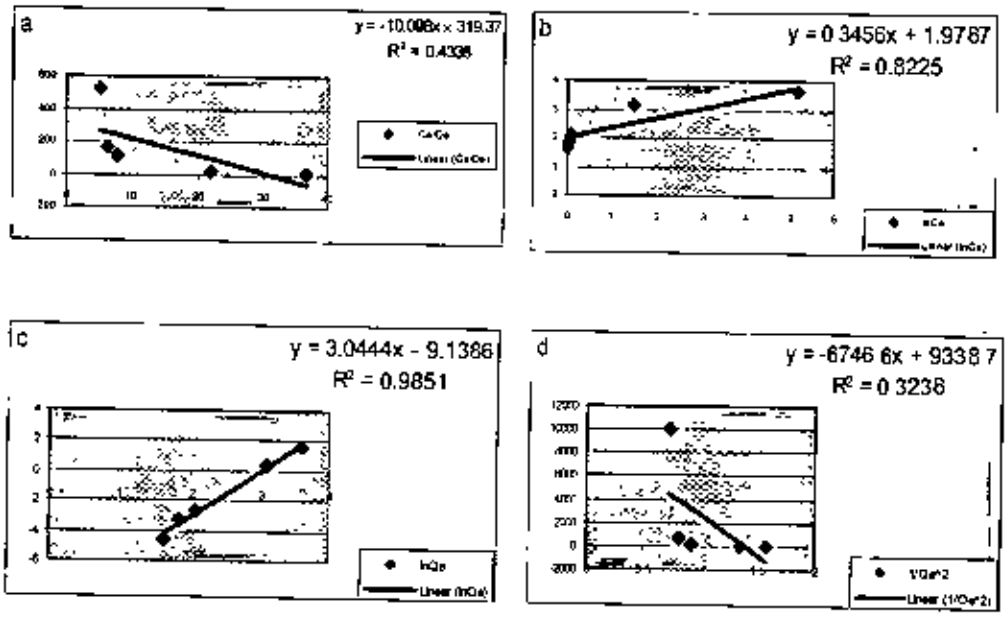

Fig. 5. Adsorption isotherms of complexation of L-cysteine with Mn (II) with models a) Langmuir b) Temkin c) Freundlich d) Harkins-Jura.

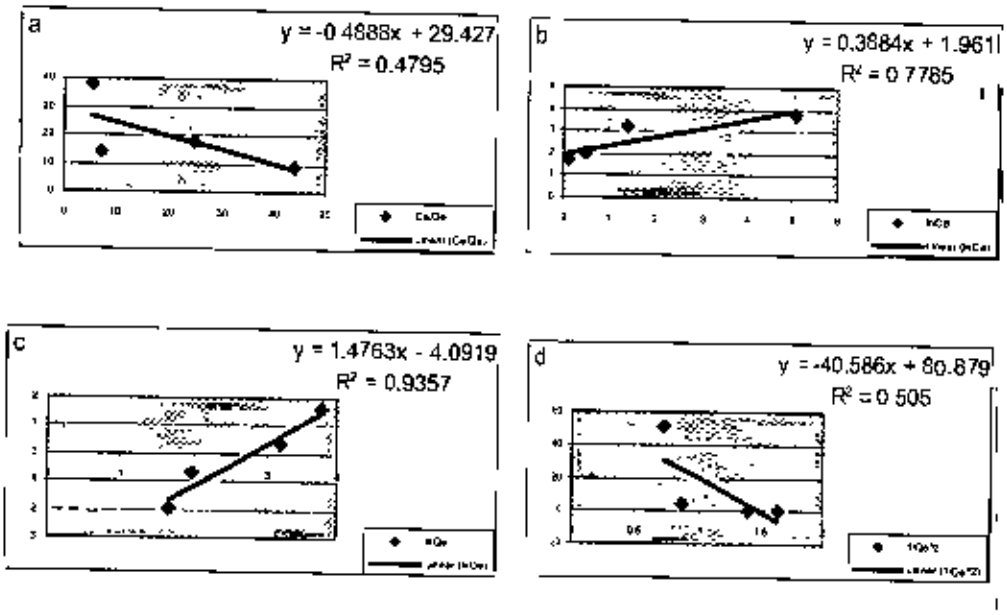

Fig. 6. Adsorption isotherms of complexation of L- phenylalanine with Mn (II) with models a) Langmuir b) Temkin c) Freundlich d) Harkins-Jura.

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-cysteine and L-phenylalanine adsorption was higher than the others, which table 1 shows this.

K_L or b: Langmuir equilibrium constant. Our reason from computing b is obtaining R_L 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 [29,30].

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

1/n and K_F 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-systeine and L-phenylalanine. 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. We can see that in table 1 [11, 31-35].

B and K_L are Temkin equation parameters and respectively adequate with adsorption condescended and boundary constant adequate with maximum of boundary energy Amount of B is RT/b and b is based on Temkin isotherm constant [25, 26]. By observing table 2 we can see the maximum amount adsorption of K_L for two complexes allude to L-systeine and L-phenylalanine amino acids.

CONCLUSION

The study that was accomplished on liquid-solid system adsorption affected separating amino acids and dissolved dependant complexity from dilution on carbon nanotube surface till dissolved residue in dilution on solid surface is 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 designing adsorption system. With attention to the correlation coefficient R^2 Frundlich and Temkin isotherms displayed a good accommodation with experimental data that was used respectively for computation thermodynamic and kinetic parameters but altogether we could consider Frundlich model as the best model for amino acids and their complex with manganese (II) ion. Although in this study with attention to the adsorption capacity of L-cystein and L-phenylalanine that was greater on carbon nanotube adsorption, their complexation adsorption was done with greater power that was dependant to the maximum bonded energy between complexity with their adsorption.

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