Examination of Surface Adsorption Isotherms of the Complex of some Amino acids with Cr (III) ion by Carbon Nanotubes

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ABSTRACT

The purpose of this research work, review Adsorption isotherms of complexes of some amino acids Glycine, Glutamine, Glutamic, Tryptophan and Tyrosine with chromium ion by Single–walled carbon Nanotubes (SWCNT) is a discontinuous method. By using on spectrophotometer (UV / VIS) adsorption of each complex were obtained and the relevant graph has been drawn. Review the results of experiments with models of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich performed and various parameters of these models is obtained. Experimental results obtained in the temperature 295 K showed that experimental data well by these models provided and model acceptable was Freundlich model.

Key words: Adsorption, Isotherm, Amino acid, Complexe, Carbon nanotube, Chromium.

INTRODUCTION

Proteins are macromolecules with molecular weight of 5000 Dalton, consisting of covalent bonds between a series of structural units called amino acids. Number, nature, and the way these units are placed along the protein chain determine their particular structure and specific behavior. Every amino acid is composed of an asymmetric carbon called α-carbon that forms bonds with four different groups: a carboxyl group (-COOH), a hydrogen atom, an alkaline amino group (NH$_2$-), and a side-chain (-R). The *R*- root can be a carbon chain or a carbon ring. Other factors such as alcohol, amine, carboxyl, and also sulfur may be present in the structure of *R*- root. The side-chain itself has several carbon atoms, shown by β, γ, and δ, depending on their distance from α-carbon.

If the –COOH group is bonded to α-carbon while the -NH$_2$ group is attached to non-α carbons, then the amino acid will be of β, γ, or δ type. There is a trace amount of free amino acids in cells. Most α-amino acids take part in protein synthesis, while β-, γ-, and δ-amino acids are chemical mediators. At pH = 7 most amino acids become bipolar; that is, the –NH$_2$ group picks up a proton and the –COOH group loses a proton and takes the form of –COO.

Amino acid adsorption on to solid surfaces is important in biomaterials such as artificial tissues[1] and contact surfaces[2]. Adsorption rate of amino

acids depends on several factors including the effects of surface charge[3], pH[4], ionic strength[5], and temperature[6].

Nanotubes are considered as an important discovery in the field of nano-technology. Nanotubes are sheet of carbon atoms moving in a roller-like (cylindrical) chamber, and apparently look like a wire lattice covered on one side. Carbon nanotubes are hollow carbon tubes. Carbon nanotubes are created from sources of carbon, like graphite or hydrocarbon gases, through methods such as arc discharge, CVD (chemical vapor deposition or vapor phase), and laser ablation. Due to properties like large specific surface (700-1000 gr/m^3), considerable rigidity (approximately 50 times that of steel), and unique electric and electronic characteristics, these substances have a wide variety of applications such as catalyst support, mechanical enhancement of polymers and composites, and manufacturing of electronic pieces.

Carbon nanotubes are divided into two general categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNT, discovered in 1991, consists of elongated fullerene fibers[7-8] or wrapped graphene sheets[9-10]. Its density is 0.8 gr/cm^3 and has a uniform diameter on the order of 1 to a few nanometers; but while being formed, it has a great tendency to become compressed and create larger bundles.

MATERIAL AND METHODS

Instruments

In this study a Perkin-Elmer 3110 spectrophotometer, centrifuge machine, magnetic stirrer, 120-degree oven, and a Mettler H30 analytical scale with the precision of 0.0001 were used to determine concentration.

Chemical substances

Single-walled carbon nanotubes with percentage purity of more than 95% were purchased from Aldrich. In order to prepare solutions, acids from Merck Company were used. And in all experiments solutions were made using distilled water.

RESULTS AND DISCUSSION

Equilibrium isotherms of surface adsorption

Equilibrium relations between the adsorbent and adsorbate are defined by adsorption isotherms which show the relation between the amount of the absorbed substance and the amount of it still left in equilibrium state.

Langmuir model

This model of surface adsorption is used for monolayer adsorptions. The Langmuir model is obtained on the basis of this assumption that the energy in all adsorption sites on the adsorption surface is the same, and is shown by the linear equation given below[11]:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e , \qquad ...(1)$$

where q_e is the amount of solute absorbed on the surface (mgg^{-1}), C_e is the solute equilibrium concentration (mgL^{-1}), and q_m and b are Langmuir constants indicating surface adsorption equilibrium constant and surface adsorption capacity of a saturated layer, respectively.

Freundlich model

Freundlich isotherm is an empirical equation that is used mainly to better understand the adsorption of metal ions on a heterogeneous surface with multilayer surface adsorption, and that the amount of solute absorbed on the surface is infinitely increased as the concentration increases[12]. Freundlich isotherm is expressed by the following equation:

$$Lnq_e = Lnk_f + \frac{1}{n} LnC_e . \qquad ...(2)$$

In this equation q_e is the amount of solute absorbed on the surface (mgg^{-1}), C_e is the equilibrium concentration of the solute (mgL^{-1}), and n and k_f constants indicate surface adsorption rate and surface adsorption capacity, respectively[13-14].

Temkin model

Temkin isotherm includes a factor that clearly shows the interactions between the adsorbent and absorbed particles. The linear form of Temkin isotherm is as follows:

$$q_e = B Ln A + B Ln C_e \qquad ...(3)$$

where

$$B = \frac{RT}{b}$$

In this equation, *A* (L/mg) is equal to the constant of the bond associated with maximum bond energy, *b* (J/mol) is the Temkin isotherm constant, and *B* (with no unit) is proportionate to the heat of surface adsorption.

Dubinin-Radushkevich model

Dubinin-Radushkevich Model is more comprehensive than Langmuir equation in that it does not require uniform surface adsorption sites. This model is explained by the following equation:

$$Lnq_e = Lnq_m + K\varepsilon^2 \cdot \qquad ...(4)$$

In this equation *k* is the Dubinin-Radushkevich surface adsorption constant, and *å* is Polanyi Potential explained by the function below:

$$\varepsilon = RT \, ln(1 + \frac{1}{C_e}) \qquad ...(5)$$

Here, *R* is the gas constant, *T* is Kelvin temperature, and C_e is the equilibrium concentration of the solute in solution. Using the relation given below it is possible to gain some information concerning the energy of surface adsorption:

$$E = (2K)^{-1/2} \qquad ...(6)$$

where *E* is given in KJ/mol.

Isotherms of amino acid adsorption on carbon nanotubes are shown in figures 1 to 4, and parameters of these models are calculated and given in table 1.

Table 1: Parameters and correlation of isotherms models

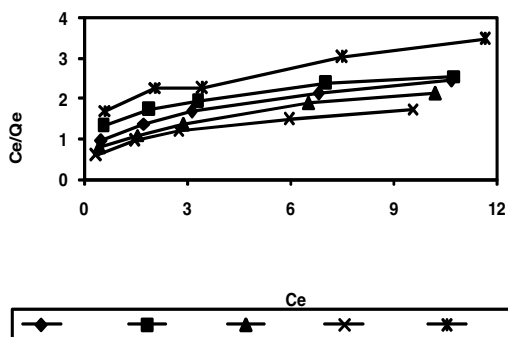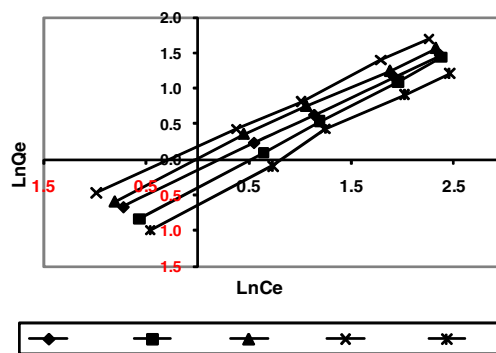| Langmuir model			Freundlich model			Temkin model				Dabinin-Radushkevich			
b (L/mg)	q (mg/g)	R²	n	K (mg/g)	R² (L/mg)	A	B (J/mol)	b (mg/g)	R² (Kj/mol)	q_m	K	E	R²
0.154	8.74	0.908	1.49	1.19	0.999	2.65	1.45	16.62	0.898	3.35	-0.0018	-16.66	0.780
0.154	7.42	0.935	1.47	1.00	0.997	2.97	1.30	18.60	0.925	3.05	-0.0022	-15.07	0.822
0.130	7.12	0.937	1.45	0.85	0.999	3.45	1.20	20.07	0.914	2.72	-0.0024	-14.43	0.796
0.079	8.75	0.911	1.29	0.67	0.999	6.01	1.24	19.45	0.899	2.55	-0.0025	-12.70	0.792
0.086	6.51	0.958	1.31	0.53	0.999	6.94	1.00	16.62	0.929	2.14	-0.0035	-11.95	0.809

Fig. 1: Adsorption of Langmuir model
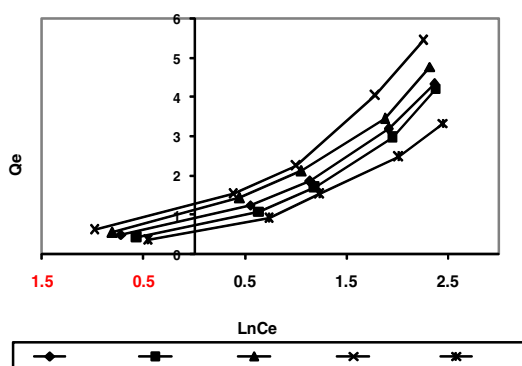

Fig. 2: Adsorption of Freundlich model
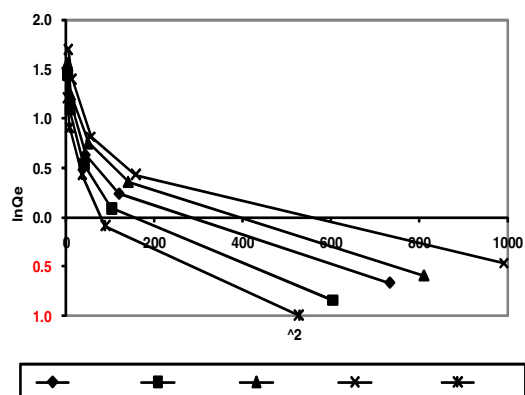

Fig. 3: Adsorption of Temkin model

Fig. 4: Adsorption of Dubinin-Radushkevich model

Application of Duclaux-Traube rule

Adsorption capacity of amino acids is examined by the connection between Q (the ratio of the amount of amino acid adsorbed onto the carbon nanotube (mg) and the adsorbent's mass (g)) and C_f (equilibrium concentration in mg/g).

With the increase in the length of the chain, the adsorption capacity of amino acid complexes on the surface of carbon nanotube also increased. Based on the behavior observed in 5 amino acids under study, the amount of absorbed substance became more as the $-CH_2$ group and benzene ring increased. In this examination, a greater adsorption rate was observed in amino acid tryptophan, shown by the relation between Q and C_f on the basis of Duclaux-Traube rule.

In figure 5 the behavior of Q is shown as a function of C_f for the adsorption of amino acid complexes on carbon nanotubes.

CONCLUSION

In this research we considered the factors affecting the adsorption of amino acids onto carbon nanotubes; namely, spatial inhibition, Lewis Base Power (ligand nucleophilicity), and the effect of chelate (multidentate ligands). The results suggested that when the volume of ligand (amino acid) is smaller, its alkaline power is greater, and the chelate cycles formed by ligand "teeth" are smaller, then the resulting complexes are more stable and have greater adsorption rate on carbon nanotubes. Considering the results obtained from the five amino

acids studied in this research, amino acid tryptophan showed the greatest adsorption rate on carbon nanotubes. Moreover, the results suggested that surface adsorption of amino acid complexes correspond to Freundlich model with a stronger correlation, and this finding expresses heterogeneity of adsorption and non-uniformity of adsorption bonds between the adsorbent and adsorbate.

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