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Catalytic Effects of Carbon Nanotubes on Complexation of Some Amino Acids via Cobalt Cation Catalyst

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Abstract

In this research, investigation of the adsorption isotherms and the effect of solution conditions such as pH and concentration of complexation of some amino acids with cobalt(II) nitrate six-hydrate upon multi-wall type carbon nanotube (CNT) were done. The adsorption capacity of complexation of amino acids onto the surface of carbon nanotube increased with the pH from acidic to alkaline. At pH = 9 the affinity order of the complexation of amino acids towards carbon nanotube is L-arginine > L-phenylalanine > L-asparagine > L-methionine > L-cysteine > glycine > L-alanine > L-valine > L-histidine. The curves have an important role in the design and optimization of the unit operations such as preservation, drying storing packaging and mixing. The adsorption equilibrium isotherms were fitted by Freundlich, Langmuir and Temkin models, but the Freundlich model is better than other models because is does not assume the surface as homogeneous with respect to adsorption energies and also the r^2 value indicates the goodness of fit between the data and the isotherm.

Keywords: Isotherm, Adsorption, Amino acid, Complexation, Co(II) ion, Carbon Nanotube

1. 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 hormones, neuromediators, phospholipids and vitamin components and initiators of numerous enzymatic reactions [1-6].

Here we would like to show that amino acids could be adsorption onto carbon nanotubes (without chemical reactions). 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 [7], the two fundamental articles by Sips [8] and the recurrence method proposed by Adamson and Ling [9]. Of all the "classic isotherms "only some can be explained or have been proposed on statistical mechanical grounds others, on the contrary, cannot be justified by simple models. This is the case of the important isotherms empirically proposed by Freundlich, Dubinin and Radushkevich, Temkin [10,11]. These isotherms are usually ascribed to the heterogeneity of the surface; his allows the computation of the adsorption-energy distribution associated with each type of experimental behaviour.

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The three classic overall isotherms, *i.e.*, are absorbed in adsorption on equilibrium surface [12,13]. Solute or contaminant uptake by an adsorbent is most often measured with batch equilibrium test [14]. Varying solute concentrations are mixed with an adsorbent until equilibrium is achieved and the contaminant removed from the solution [15] 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 as reported by Chen *et al.* [16].

It is noted that when the equilibrium 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 acomplished by obtaining a linear from 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 equatifiers have also been used to evaluate the performance of adsorption models [17].

In this paper, we describe adsorption isotherms of complexation of amino acids on multiwall carbon nanotube. The experimental adsorption data were tested with the Langmuir, Freundlich and Temkin equations. Three models matched the experimental data quite well and the Frundlich model had the highest correlation coefficient values. The Frundlich model is better than the Langmuir model because it does not assume the surface as homogeneous with respect to adsorption energies [1]. In fact, most carbon nanotube are of surface energy heterogeneity. The surface of carbon nanotube generally consists of two energy states of carbon (*i.e.*, graphite-like and disordered carbons) [18].

2. Materials and Methods

Mutiwalled carbon nanotubes (produced by catalytic vapour decomposition) were purchased from Aldrich, with 510 nm in outer diameter, surface area of 40-600 m^2/g and purity above 95 %. The content of acids and basic surface groups as well as pH were obtained by Boehm titration [19].

The complexation of amino acids solutions with cobalt(II) ion were prepared from 100 mg/L stock solutions containing $Co(NO_3)_2{\cdot}6H_2O$ (Merck) to added the solutions of amino acids from 200 mg/L that added them to 0.01 g carbon nanotube.

We used shaker incubator apparatus for solution stirring processes at the time of equilibrium adsorption and at the end filtration and separating the adsorbent from surrounding with paper filtered then measured the adsorption of complexation by ultraviolet-visible spectroscopy.

3. Results and Discussion

3.1 Adsorption isotherms study: Equilibrium studies that give the capacity of the adsorbent and asorbate are described by adsorption isotherms which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature. Freundlich, Langmuir and Temkin isotherms are the earliest and simplest known relationships describing the adsorption equation[20-22]. Adsorption isotherms are described in many mathematical forms, some of which are based on a simplified physical picture of adsorption, while others are purely empirical and intended to correlate the experimental data in simple equations with two or at most, three empirical parameters : the more the number of empirical parameters, the better the fit between experimental data[23,24]. The experimental data were correlated by Langmuir, Freundlich and Temkin models. The adsorption capacity of complexation of amino acids with cobalt on multiwall carbon nanotube increased with the increase of concentrations (Fig. 1). Based on those model equations, the adsorption parameters Q_{max}, K_L, K, n, K_T, B and the correlation

coefficient values (R^2) of complexation of amino acids on multiwall carbon nanotube were obtained (Table-1) (*i.e.*, graphite-like and disordered carbons).

3.2 Langmuir isotherm: The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface that is Q_{max} and K_L reflects the free energy of sorption and these parameters are given in Table-1. That the maximum adsorption capacity relation with complexation of L-phenylalanine and L-arginine with Co(II). The equation is expressed by:

$$Q_e = Q_{max}K_LC_e/1 + K_LC_e$$

The linearized from of the above equation after rearrangement is given by:

$$C_e/Q_e = 1/Q_{max}K_L + C_e/Q_{max}$$

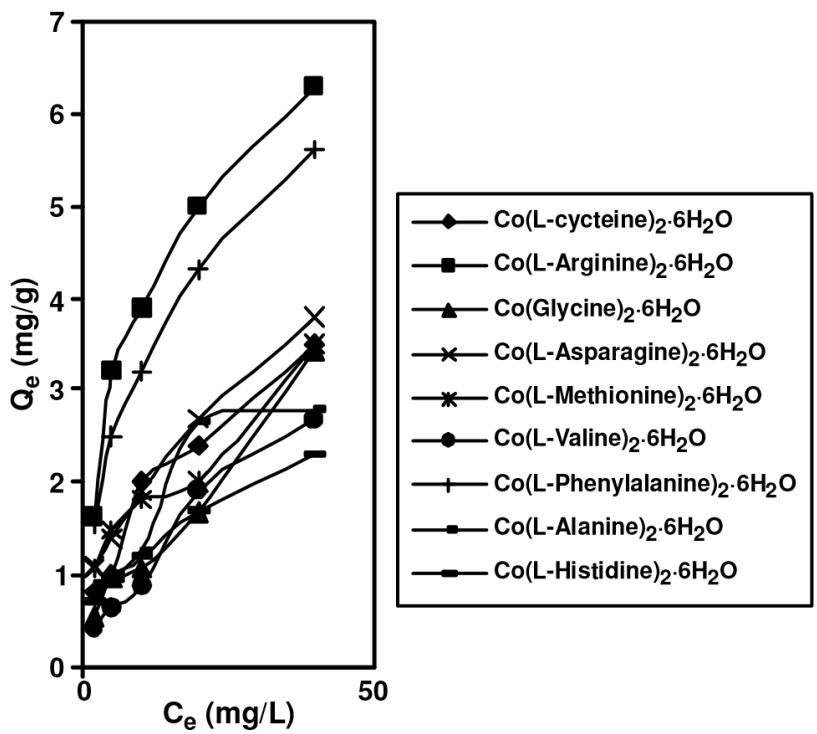


Figure 1. Adsorption capacity of carbon nanotube for the initial concentration of complxation of amino acids with Co(II) ion.

Table1. Calculated langmuir, freundlich, temkin isotherm parameters for complexations of amino acids with Co(II).

Complexion of cobalt(II) with amino acids	Temkin	Langmuir	Freundlich
Valine	$R^2 = 0.83$ $B = 0.66$ $K_T = 0.88$	$R^2 = 0.75$ $Q_m = 4.03$ $KL = 0.047$	$R^2 = 0.94$ $1/n = 0.55$ $K_F = 0.32$
Arginine	$R^2 = 0.95$ $B = 1.01$ $K_T = 9.37$	$R^2 = 0.97$ $Q_m = 6.57$ $KL = 0.30$	$R^2 = 0.98$ $1/n = 0.30$ $K_F = 2.16$
Alanine	$R^2 = 0.79$ $B = 0.60$ $K_T = 2.37$	$R^2 = .90$ $Q_m = 3.35$ $KL = 0.13$	$R^2 = 0.92$ $1/n = 0.36$ $K_F = 0.83$
Asparagine	$R^2 = 0.85$ $B = 0.70$ $K_T = 3.09$	$R^2 = 0.93$ $Q_m = 4.3$ $KL = 0.13$	$R^2 = 0.94$ $1/n = 0.33$ $K_F = 1.01$
Cystein	$R^2 = 0.94$ $B = 0.73$ $K_T = 2.07$	$R^2 = .94$ $Q_m = 3.90$ $KL = 0.14$	$R^2 = 0.99$ $1/n = 0.42$ $K_F = 0.75$
Glycine	$R^2 = 0.67$ $B = 0.55$ $K_T = 2.61$	$R^2 = 0.68$ $Q_m = 3.98$ $KL = 0.074$	$R^2 = 0.88$ $1/n = 0.38$ $K_F = 0.95$
Histidin	$R^2 = 0.90$ $B = 0.46$ $K_T = 2.47$	$R^2 = 0.95$ $Q_m = 2.63$ $KL = 0.13$	$R^2 = 0.97$ $1/n = 0.34$ $K_F = 0.61$
Phenylalanine	$R^2 = 0.93$ $B = 0.91$ $K_T = 8.10$	$R^2 = 0.98$ $Q_m = 6.06$ $KL = 0.25$	$R^2 = 0.99$ $1/n = 0.29$ $K_F = 1.90$
Methionine	$R^2 = 0.77$ $B = 0.56$ $K_T = 4.68$	$R^2 = 0.87$ $Q_m = 3.73$ $KL = 0.14$	$R^2 = 0.90$ $1/n = 0.28$ $K_F = 1.04$

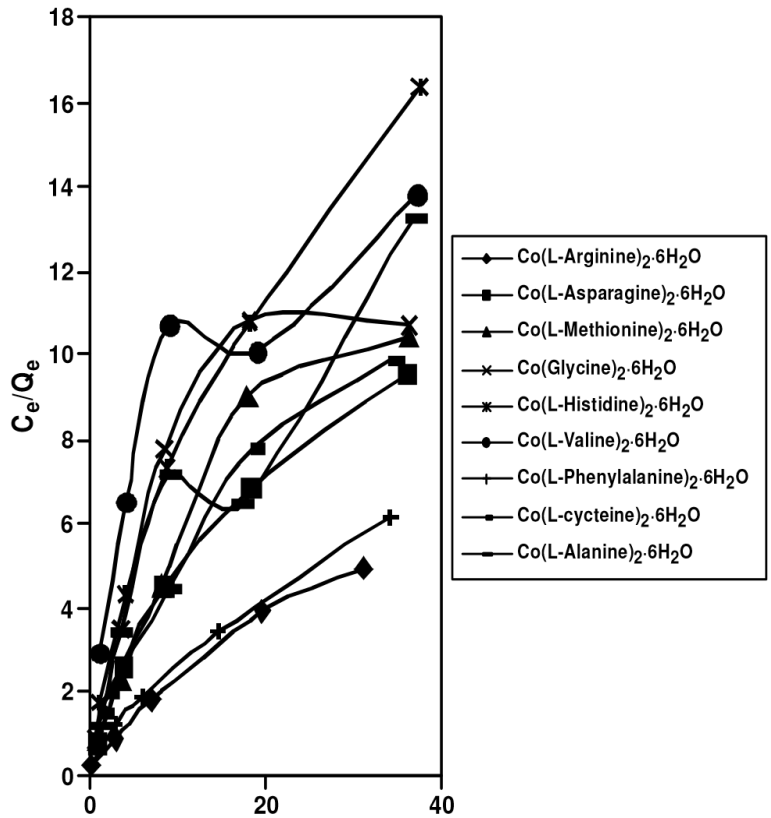


Figure 2. Langmuir adsorption isotherm for some complexations of amino acids.

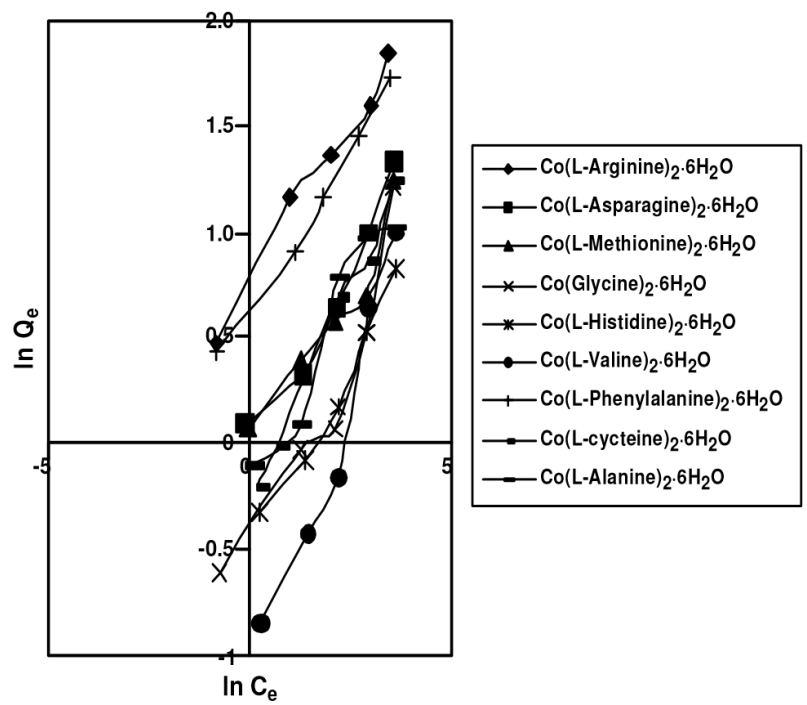


Figure 3. Freundich adsorption isotherm for some complexations of amino acids.

The experimental data is then fitted into the above equation for linearization by plotting C_e/Q_e against C_e that are presented in figure 2 [25-27].

3.3 Freundlich isotherm: After Freundlich is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by:

$$Q_e = K_F C_e 1/n$$

K_F also represents adsorption capacity of multiwall carbon nanotube and n is the adsorption intensity that are given in Table-1. The above equation is conveniently used in linear from as:

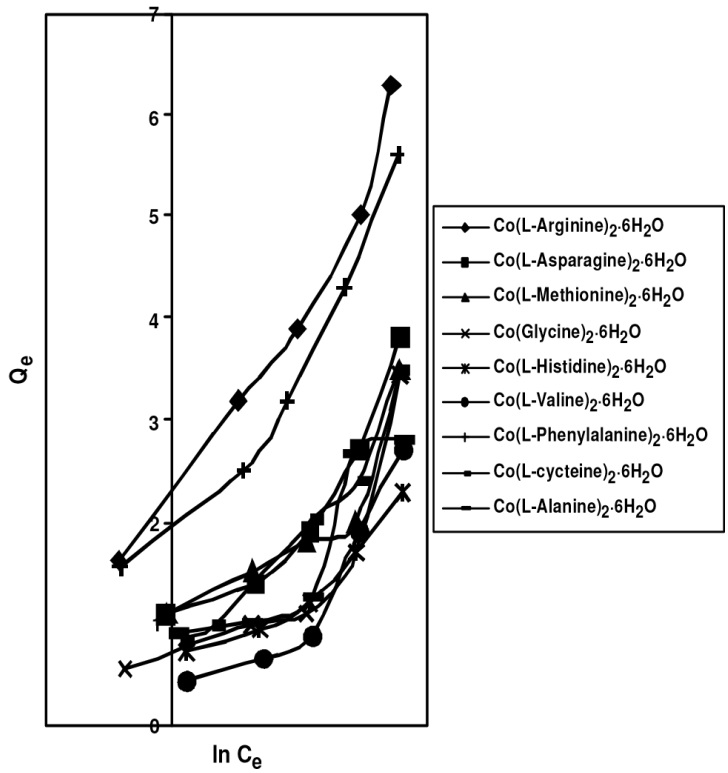


Figure 4. Temkine adsorption isotherm for complexation of amino acids.

$$\ln Q_e = \ln K_F + (1/n) \ln C_e$$

A plot of ln C_e against ln Q_e yielding a straight line indicates [28-30] the conformation of the Freundlich adsorption isotherm are presented in figure 3.

3.4 Temkin isotherm: The Temkin isotherm equation assumes that the heat at adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin model is given by:

$$Q_e = (RT/\Delta Q) \ln K_T C_e \; B = RT/\Delta Q$$

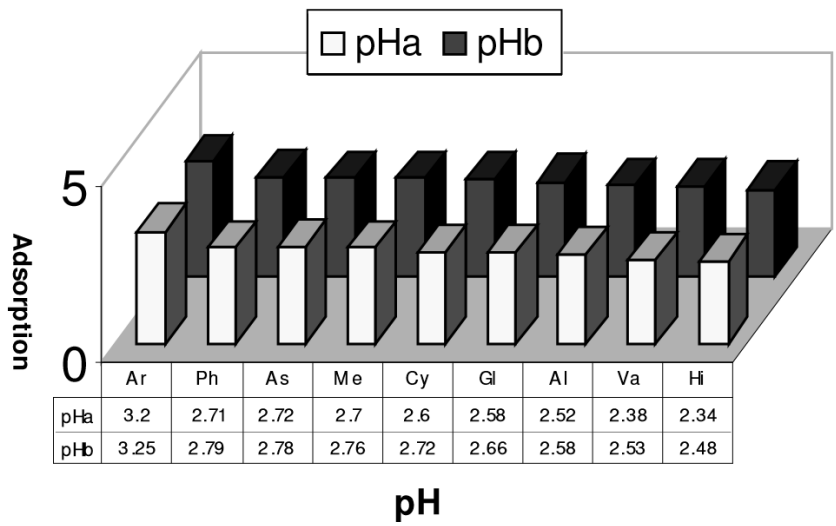
$$Q_e = B \ln K_T + B \ln C_e$$

That R is universal gas constant (J mol^{-1} K^{-1}), T the temperature (K)

$$\Delta Q = -\Delta H$$

The variation of adsorption energy (J mol^{-1}) and K_T is the Temkin equilibrium constant (L mg^{-1}) (table 1). If the adsorption obeys Temkin equation, the variation of adsorption energy and the Temkin equilibrium constant can be calculated [31-33] from the slope and the intercept of the plot Q_e *versus* ln C_e that are presented in figure 4.

3.5 Effect of pH: The pH value plays an important role with respect to the adsorption of particular ions on carbon nanotube [34,35]. When pH of the solution is higher than point of zero charge (pH_{pze}), the negative charge on the surface provides electrostatic interactions that are favourable for adsorbing cationic species. The decrease of pH leads to neutralization of surface charge, thus, the adsorption of cations should decrease. In order to evaluate the effect of pH on the adsorption of complexation of some amino acids on carbon nanotube, prepared in different ways, a series of sample solutions containing single component at concentration of 40 mg/L were adjusted to a pH rang of 2.3 - 9.0 (Figure 5) shows the effect of pH on the adsorption of complexation of amino acids on carbon nanotube. The adsorption of complexations increased with the increase of pH from 3.2 to 9, but more sharp increase was observed [36,37] for $Co(L\text{-}Arginine)_2{\cdot}6H_2O$ and the low adsorption that took place in acidic region was $Co(L\text{-}Histidine)_2{\cdot}6H_2O$.



	Ar	Ph	As	Me	Cy	Gl	Al	Va	Hi
pHa	3.2	2.71	2.72	2.7	2.6	2.58	2.52	2.38	2.34
pHb	3.25	2.79	2.78	2.76	2.72	2.66	2.58	2.53	2.48

Figure 5. Relationship between adsorption and pH.

4. Conclusions

The competitive adsorption isotherms of some complexation of amino acids with cobalt(II) ion by multiwall carbon nanotube was studied and showed that the adsorption affinity of complexation by carbon nanotube followed the order L-arginine > L-phenylalanine > L-asparagine > L-methionine > L-cysteine > glycine > L-alanine > L-valine > L-histidine.

The competitive adsorption capacities of complexations increased with increasing pH (rang of 2.3-9.0). The adsorption equilibrium isotherms were fitted by Freundlich, Langmuire and Temkin models but the Freundlich model is better than other models because the r^2 value indicates the goodness of fit between the data and the isotherm.

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