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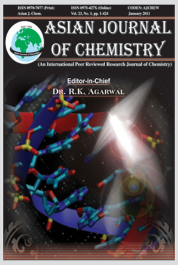

Adsorption Isotherms of Alkali Metal and Alkaline Earth Metal Ions on Multiwall Carbon Nanotube

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In this paper, adsorption isotherms of alkali metal and alkaline earth metal ions on multiwall carbon nanotubes were studied for three common adsorption isotherm models: Langmuir, Freundlich and Temkin. For each of these models determined different parameters for carbon nanotube adsorbent. The experimental results were fitted to the Langmuir, Freundlich and Temkin isotherms to obtain the characteristic parameters of each model. The Langmuir isotherm was found to well represent the measured sorption data for alkaline earth metal and both the Freundlich and Temkin isotherms were found to well represent the measured sorption data for alkali metal. According to the evaluation using the Langmuir equation, the maximum sorption capacities of metal ions onto multiwall carbon nanotube.

Key Words: Adsorption isotherm, Alkali metal, Alkaline earth metal, Multiwall carbon nanotube.

INTRODUCTION

The removal of metal ions from effluents is of importance to many countries both environmentally and for water re-use. The investigation in this area were performed not only for unique structure and properties of carbon nanotube but also for its high potential in technical applications.

The application of low-cost sorbents including carbonaceous materials, agricultural products and waste by-products has been investigated[1]. In recent years, agricultural by-products have been widely studied for removal of metal ions from water. These include peat[2], wood[3], pine bark[4], banana pith[5], rice bran, soybean and cottonseed hulls[6], peanut shells[7], hazelnut shell[8], rice husk[9], sawdust[10], wool[11], orange peel and compost[12] and leaves[13]. Most of this work has shown that natural products can be good sorbents for heavy metals.

Indeed, it could be argued that many of these natural sorbents remove metals more by ion exchange than by adsorption. Nevertheless, many previous workers tend to base their analyses on sorption theories. These include the acidic properties of carboxylic and phenolic functional groups present in humic substances[14,15]. Some ion exchange reactions, *e.g.* proton release when metal cations bind to peat[11].

Carbon nanotubes (CNTs) had been discovered by Iijima[16] has led research to new area in many interdisciplinary investigations. The advantages of carbon nanotubes are due to unique structural, electronic, optoelectronic, semiconductor, mechanical, chemical and physical properties[17]. Carbon nanotube would impact future nanoscience and nanotechnology since it is a highly potential material and has become available in macroscopic quantities[18-21].

Presently three main methods employed for carbon nanotubes synthesis are arc-discharge, laser ablation and chemical vapour deposition (CVD)[22]. Carbon nanotubes are divided into two types: (1) single-walled carbon nanotubes (SWCNTs) and (2) multi-walled carbon nanotubes (MWCNTs)[23,24]. Carbon nanotubes walls are not reactive, but their fullerene-like tips are known to be more reactive, so end functionalization of carbon nanotubes is used relatively often to generate functional groups (*e.g.*, -COOH, -OH or -CO)[24,25].

Carbon nanotubes have been proven to possess great potential as superior adsorbents for removing many kinds of organic and inorganic pollutants such as dioxin[26], volatile organic compounds[27,28] from air stream or fluoride[29], 1,2-dichlorobenzene[30], trihalomethanes[31], soil organic matters[32] and various divalent metal ions from aqueous solution[33,34].

The result of present studies is important for biologist, pharmcistant and physicians to cure cancers and cartilages. In each system the isotherm constants for the Langmuir, Freundlich and Temkin isotherms have been determined. The utilization of carbon nanotubes for the treatment of water and wastewater containing divalent metal ions is gaining more attention as a simple and effective means of pollution control. Future research works on developing a cost-effective way of carbon nanotube production and testing the toxicity of carbon nanotubes and carbon nanotube-related materials are recommend.

EXPERIMENTAL

Multiwall carbon nanotubes (produced by catalytic vapour decomposition) were purchased from Aldrich, with 5-10 nm in outer diameter, surface area of 40-600 m^2/g and purity above 95 %.

The metal solutions were prepared from 1000 mg/L stock solutions containing nitrate salts (Merck). The concentrations of metals were performed by atomic absorption spectrometry using a Perkin-Elmer 3110 apparatus.

Batch adsorption experiments: In adsorption experiments 0.05 mg of carbon nanotubes were mixed with 10 mL of appropriate metal ion solution. The initial metal concentration was increased from 5 to 30 mg/L, while pH of all solutions were maintained at optimize pH. After shaking for 4 h, the metal concentration in the aqueous solutions was determined by atomic absorption spectrophotometer. The adsorption capacity q (mg/g CNTs) were obtained as follows: $q = [(C_o - C_f)V/m]$; where C_o and C_f are the initial and final concentrations (mg/L) of metal ion in the aqueous solution, respectively, V the volume of metal ion solution and m is the weight of carbon nanotubes.

Effect of pH on metal ions adsorption on carbon nanotubes: To study the effects of pH on metal ions adsorption, 0. 05 mg of carbon nanotubes were dispersed into 10 mL of solutions containing 30 mg/L of each of metal ion. The initial pH values were adjusted from 2.0 to 11 using various phosphate buffers. After the suspensions were shaken for 4 h at room temperature, they were filtered through 0.45 µm membrane filters. The amounts of metal ions adsorbed on carbon nanotubes were calculated as the difference between initial and final concentration at equilibrium.

RESULTS AND DISCUSSION

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies in sorption give the capacity of the sorbent. It is described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium (Fig. 1).

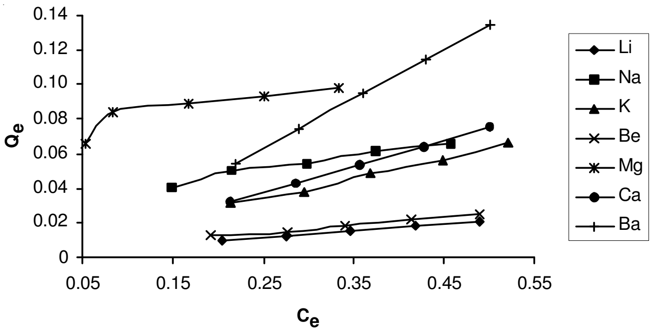


Fig. 1. Adsorption capacity of carbon nanotube for the initial concentration metal ions

The metal ion sorption equilibrium data are commonly correlated with the Langmuir or the Freundlich equations. The Langmuir equation is valid for dynamic equilibrium sorption process on completely homogenous surfaces while the Freundlich equation is applicable to heterogeneous surface. Several researchers reported that the metal ion sorption onto carbon nanotubes can be described by both Langmuir and Freundlich equations[34].

In order to investigate the sorption isotherm, three equilibrium models were analyzed. These included the Langmuir, the Freundlich and the Temkin isotherms.

Langmuir isotherm: The Langmuir sorption isotherm[35] has been successfully applied to many pollutants sorption processes and has been the most widely used for the sorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. It is then assumed that once a metal ion occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force which times an area. The driving force is the concentration in the solution and the area is the amount of bare surface. If the fraction of covered surface is ϕ, the rate per unit of surface is:

$$r_a = k_aC(1-j) \tag{1}$$

The desorption from the surface is proportional to the amount of surface covered:

$$r_d = k_d\phi \tag{2}$$

where K_a and K_d are rate coefficients, r_a is sorption rate, r_d is desorption rate, C is concentration in the solution and ϕ is fraction of the surface covered. At equilibrium, the two rates are equal and:

$$\phi = \frac{k_aC_e}{k_d + k_aC_e} \tag{3}$$

and

$$K_a = \frac{k_a}{k_d} \tag{4}$$

Since q_e is proportional to ϕ:

$$\phi = \frac{q_e}{q_m} \tag{5}$$

The saturated monolayer sorption capacity, q_m, can be obtained. When ϕ approaches 1, then $q_e = q_m$

The saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_mK_aC_e}{1 + K_aC_e} \tag{6}$$

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_aq_m} + \frac{1}{q_m}C_e \tag{7}$$

where C_e is the equilibrium concentration (mg/dm^3); q_e is the amount of metal ion sorbed (mg/g); q_m is q_e for a complete monolayer (mg/g); K_a is sorption equilibrium constant (dm^3/mg). A plot of C_e/q_e *versus* C_e should indicate a straight line of slope $1/q_m$ and an intercept of 1/Kaqm (Fig. 2).

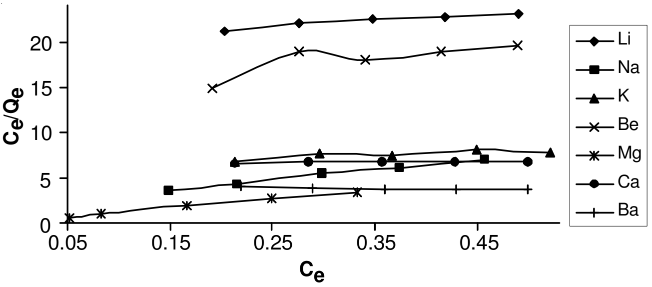


Fig. 2. Langmuir isotherms of metal ions sorbed on multiwall carbon nanotubes

Freundlich isotherm: Freundlich[36] found that if the concentration of solute in the solution at equilibrium, C_e, was raised to the power 1/n, the amount of solute sorbed being q_e, then $C_e^{1/n}/q_e$ was a constant at a given temperature.

This fairly satisfactory empirical isotherm can be used for non ideal sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \qquad (8)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (9)$$

The applicability of the Freundlich sorption isotherm is also analyzed by plotting log q_e *versus* log C_e (Fig.3). Table-1 shows the Freundlich sorption isotherm constants and the correlation coefficients. Fig. 2 shows the linear plot of C_e/q_e *versus* C_e gives a straight line of slope $1/q_m$ and intercepts 1/Kaqm. The values of the Langmuir constants q_m and K_a are presented in Table-1 for the seven metal/carbon nanotubes sorption systems. These values of the correlation coefficients indicate that there is not a strong positive relationship for the data and that the metal/carbon nanotubes sorption data follows the Langmuir sorption isotherm.

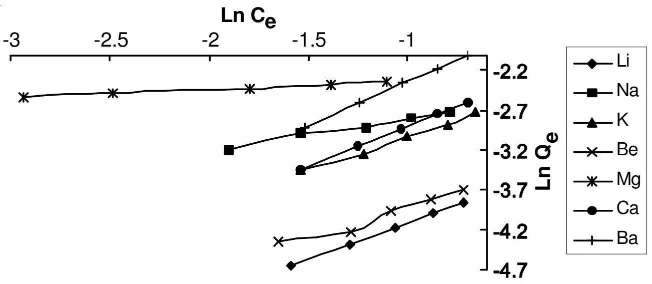


Fig. 3. Freundlich isotherms of metal ions sorbed on multiwall carbon nanotubes

The monolayer saturation capacities, q_m, for the seven metal ions are 0.14482, 0.091651, 0.298481, 0.075712, 0.101377, 44.84305, 0.912409 and 0.912409 mg/g carbon nanotube for Li, Na, K, Be, Mg, Ca and Ba, respectively.

Temkin isotherm: Temkin isotherm equation assumes that the 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:

$$Qe = (RT/\Delta Q) \ln K_T C_e$$

$$B = RT/\Delta Q$$

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

R the universal gas constant (Kg mol^{-1} K^{-1}), T the temperature (K), $\Delta Q = -\Delta H$

The variation of adsorption energy (Kg 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 from the slope and the intercept of the plot θ *versus* ln C_e that are presented in Fig. 4. It is observed that there is an accessible competition between this model and Freundlich model.

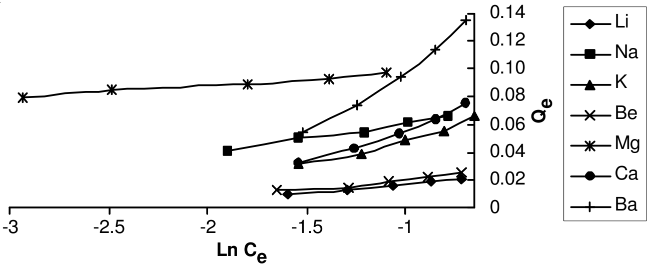


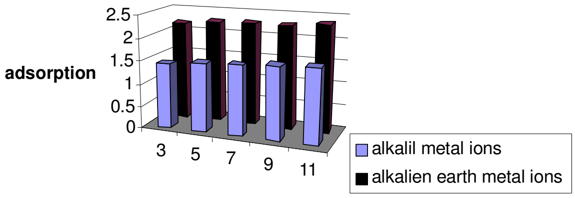
Fig. 4. Temkin isotherms of metal ions sorbed on multiwall carbon nanotubes

Effect of pH: In order to evaluate the effect of pH on the adsorption of metal ions on carbon nanotubes, prepared in different ways, a series of sample solutions containing single component at concentration of 10 mg/L were adjusted to a pH range of 2-11 with phosphate buffers and processed according

TABLE-1
ISOTHERM CONSTANTS FOR METAL IONS SORPTION ONTO CARBON NANOTUBES

	Li	Na	K	Be	Mg	Ca	Ba
Langmuir							
q_m, (mg/g)	0.14482	0.091651	0.298481	0.075712	0.101377	44.84305	0.912409
K_a, (dm^3/mg)	0.346591	5.320103	0.527797	0.976851	55.69848	0.003344	0.258631
r^2	0.9444	0.9932	0.669	0.6767	0.9983	0.4859	0.932
Frendlich							
Kf, (mg/g)(dm^3/mg)$^{1/n}$	25.03062	10.96491	9.007882	24.08044	9.247932	6.684557	3.458379
1/n	0.8957	0.4141	0.8335	0.7387	0.1032	0.9988	1.0989
r^2	0.9998	0.9842	0.9869	0.9612	0.9852	1	0.9999
Temkin							
Kt, (Lmg^{-1})	9.897752	44.74259	9.943062	12.50734	47.79834	8.497063	7.701775
B1	0.013	0.0216	0.0384	0.0133	0.0091	0.0501	0.0965
r^2	0.9833	0.9882	0.9609	0.9406	0.9799	0.9845	0.9854

to the recommended procedure. The adsorption percentage was calculated as a difference between the initial and final concentration of a given metal ion (Fig. 5).



pH	3	5	7	9	11
□ alkalil metal ions	1.44	1.52	1.55	1.61	1.65
■ alkalien earth metal ions	2.184	2.256	2.279	2.299	2.376

Fig. 5

Conclusion

The experimental results were fitted to the Langmuir, Freundlich and Temkin isotherms to obtain the characteristic parameters of each model. The Langmuir isotherm was found to well represent the measured sorption data for alkalis earth metals. Both the Freundlich and Temkin isotherms were found to well represent the measured sorption data for alkali metal. According to the evaluation using the Langmuir equation, the maximum sorption capacities of metal ions onto multiwall carbon nanotube. The adsorption properties of carbon nanotubes depend significantly on the pH value of the solution. The decrease of pH leads to neutralization of surface charge, thus, the adsorption of cations should decrease.

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