Effect of Temperature on Sequestration of Cu(II) from Aqueous Solution onto Turmeric Powder

[1]AMTUL QAYOOM* AND [2]SYED ARIF KAZMI
[1]*Department of Mathematics and Basic Sciences, NED University of Engineering and Technology, Karachi, Pakistan.*
[2]*H.E. J. Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi, Pakistan.*

(Received on 19th October 2009, accepted in revised form 6th April 2010)

Summary: In this work effect of temperature on adsorption of Cu(II) onto turmeric powder was investigated in order to understand sequestrating behavior of turmeric powder. Langmuir, Freundlich and D-R equilibrium models were employed and changes in equilibrium parameters with changing temperature have been discussed. Various thermodynamic parameters such as ΔH°, ΔG° and ΔS° have been calculated. It was found that with increase in temperature maximum adsorption capacities of Cu(II) increase which showed that the adsorption of Cu(II) onto turmeric powder is endothermic. ΔH° and E_a values also confirmed the same trend. Entropy values showed increased in randomness with increasing temperature. Gibbs free energies were non spontaneous at all the temperatures studied. E values were in the range of 2.89-3.53KJmol^{-1}, which indicated that adsorption is essentially of physical nature. The value of S^* is much less than 1 indicating favourable sticking of adsorbate to adsorbent with physiosorption mechanism predominant.

Introduction

Fruits and vegetables are consumed enormously in many countries and thus constitute one of the most important food supplies. Owing to their traditional food habit and economic consideration, a significant amount of vegetables are consumed by people in Asia belonging to middle and low income groups. Sewage, often untreated, is used to irrigate 10 % of the world's crops [1]. Although this treatment generally increase crop production, it results in the accumulation of toxic substances in soil and in the crop as sewage is usually contaminated with pollutants such as heavy metals from domestic and industrial wastes that enter into the sewer system [2, 3]. Through foodstuffs, these toxic metals may accumulate in the human body. Inside the body they compete with and displace essential metals and interfere with organ system functions and may introduce serious diseases such as hypertension, abdominal pain, skin eruptions, intestinal ulcer and different types of cancer [4]. Copper is generally known to deposit in brain, skin, liver, pancreas, and myocardium [5].

Turmeric is considered to be one of the most widely used spices in Asian region. It is used as a safe food colour in cheese, spices, mustard, cereal products, pickles, potato flakes, soups, ice creams, yogurt etc, in Asian countries, including China and South East Asia. Studies have indicated that turmeric is non toxic to human even at a dose of 8000 mg/day taken continuously [6]. Due to the presence of curcuminoids, proteins, carbohydrates etc, turmeric powder has a strong potential to bind toxic metal ions through different processes in gastrointestinal tract, which may include physical and/or chemical adsorption, ion exchange, coordination, complexation, chelation and micro precipitation, Cu(II) may have strong interactions with turmeric powder. Sequestering these toxic metals from food, drinks, or biosystem can result in detoxification and therefore turmeric powder may be used in medicines. Cumin, another important spice, is also tested and found capable to bind toxic metals by similar processes [7]. Milk protein (casein) is also found to exhibit biosorptive properties for toxic metal ions in biosystem [8].

The object of the present work was to study the effect of temperature and to determine thermodynamic parameters for the removal of Cu(II) by turmeric powder because if the thermodynamic parameters were properly assessed they could provide in depth information regarding the inherent energy and structural changes after adsorption.

*To whom all correspondence should be addressed.

Results and Discussions

Equilibrium Parameters of Adsorption

Equilibrium data, generally known as adsorption isotherms are basic requirement to understand the mechanism of the adsorption. Classical adsorption isotherm models, Langmuir, Freundlich and Dubinin-Radushkevish (D-R) were used to describe equilibrium between adsorbed metal(II) ions and turmeric powder at different temperatures.

The Langmuir adsorption isotherm assumes that the adsorption occur at specific homogenous sites within the adsorbent and has found successful application in many monolayer adsorption process. The linear form of the Langmuir isotherm equation is [9].

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \tag{1}$$

where q_e is the maximum equilibrium metal(II) concentration on the adsorbent ($mmolg^{-1}$); C_e is the equilibrium metal(II) concentration in the solution ($mmolL^{-1}$), q_{max} the monolayer adsorption capacity of the adsorbent($mmolg^{-1}$) and b, the Langmuir adsorption constant ($Lmmol^{-1}$) related to the free energy of adsorption. A high value of b indicates the high affinity of the sorbents for the sorbate. A plot of $1/q_e$ verses $1/C_e$ for the adsorption gives a straight line of slope $1/(q_{max}b)$ and intercept $1/q_{max}$ (Fig. 1). The essential feature of Langmuir isotherm can be expressed by means of 'R_L' a dimensionless constant referred to as separation factor or equilibrium parameter. R_L is calculated using the following equation where b is the Langmuir adsorption constant ($Lmmol^{-1}$) and C_o is the highest initial metal (II) concentration ($mmol\ L^{-1}$) (eq. 2).

$$R_L = \frac{1}{1 + bC_o} \tag{2}$$

The maximum sorption capacity, q_{max}, was found to increase from 0.053 – 0.15 $mmolL^{-1}$ when temperature was raised from 298K to 303K but further rise in temperature increased adsorption capacities to lesser extent. The other Langmuir constant, b, indicates the affinity of sorbent for the binding of Cu(II) ions. The values of b were found to be maximum *i.e.* 2.5 $Lmmol^{-1}$ at 298K and minimum *i.e.* 0.85 $L\ mmol^{-1}$ at 303K. The increase in the values of Langmuir constants with increasing temperature may indicate chemisorptions and the reverse is generally true for physical adsorption. However, there are a number of contradictory cases in the literature [10]. The effect of temperature was insignificant in the range of 303K-313K and the values of adsorption isotherms parameters lie quite close together. Probably the removal of Cu(II) ions from the solution takes place through more than one mechanisms. As the R_L values lie between 0 and 1 for the adsorption of Cu(II) by turmeric powder, the adsorption process is favorable [11, 12].

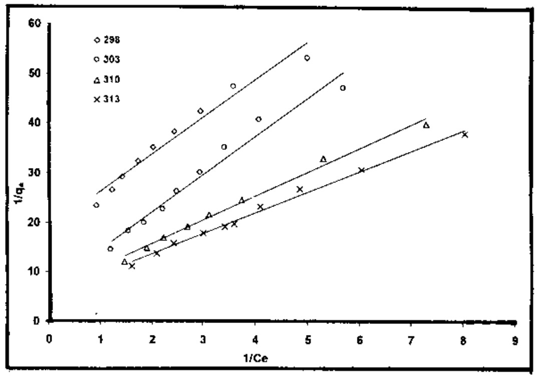

Fig. 1: Langmuir isotherm for the adsorption of Cu(II) onto turmeric powder. (Contact time 50 min, Initial pH 6, temperature 298-310K,turmeric dose 10 g/L, [Cu(II)] 0.38 $mmolL^{-1}$-1.51 $mmolL^{-1}$).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous system. A linear form of Freundlich equation is [13]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where K_F($mmolg^{-1}$) and n are Freundlich adsorption isotherm constants, being indicative of the extent of adsorption and adsorption intensity between solution concentration and adsorption, respectively. A relatively slight slope (and hence a high value of n) indicates that adsorption is good over the entire range of concentrations studied, while a steep slope (and hence small n) means that adsorption is good at high concentrations but much less at lower concentrations [14]. The plot of logq_e verses logC_e for the adsorption was employed to generate K_F and n from the intercept and slope values, respectively. The value of K_F increased with the rise in temperature. The value of n is slightly greater than 1 at all temperatures, indicating that the process is favorable at relatively higher concentrations [15] (Fig. 2).

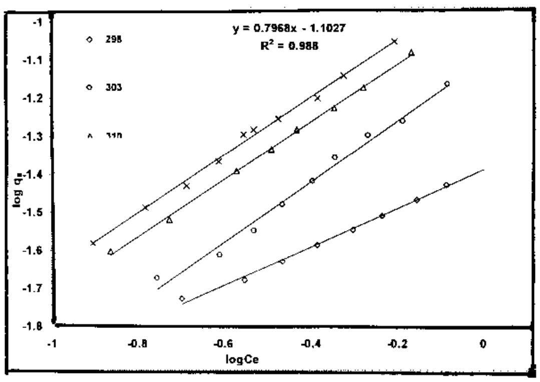

Fig. 2: Freundlich isotherm for the adsorption of Cu(II) onto turmeric powder. (Contact time 50 min, Initial pH 6, temperature 298-310K,turmeric dose 10 g/L, [Cu(II)] 0.38 mmolL^{-1}-1.51 mmolL^{-1}).

The Dubinin-Radhushkevich (D-R) isotherm is more general than the Langmuir isotherm because it does not assume a homogenous surface, constant adsorption potential or absence of stoic hindrance between sorbed and incoming particles. It was applied to distinguish between physical and chemical adsorption. The linear form of (D-R) isotherm equation is [16]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (4)$$

where β is a constant related to mean energy of adsorption per mole of the adsorbate (mol^2J^{-2}); q_m, the theoretical saturation capacity, and ε is the Polanyi potential which is equal to $RT\ln\left(1+\frac{1}{C_e}\right)$, where R ($Jmol^{-1}K^{-1}$) is the gas constant; and T(K), the absolute temperature. Hence, by plotting lnq_e verses ε^2 it is possible to generate the value of q_m ($mmolg^{-1}$) from the intercept, and the value of β from the slope (Fig. 3).

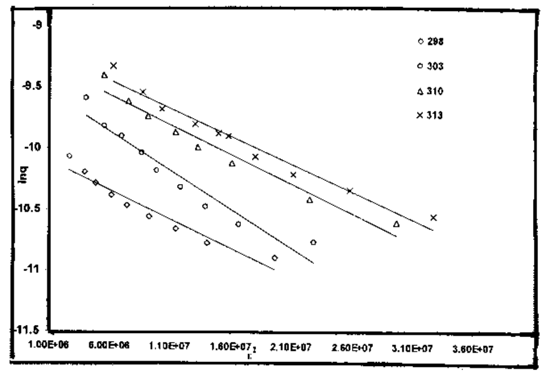

Fig. 3: D-R parameters for the adsorption of Cu(II) onto turmeric powder. (Contact time 50 min, Initial pH 6, temperature 298-310K, turmeric dose 10 g/L, [Cu(II)] 0.38 mmolL^{-1}-1.51 mmolL^{-1}).

If a very small sub-region of the adsorbent surface is chosen and assumed to be approximation of Langmuir isotherm, the quantity $\beta^{1/2}$ can be related to the mean sorption energy, E ($Kjmol^{-1}$), when 1 mol of solute is transferred to the surface of the solid from infinity (in solution) (eq. 5). This parameter gives information about adsorption mechanism as chemical ion exchange or physical adsorption and can be calculated using the relationship [17].

$$E = \frac{1}{\sqrt{-2\beta}} \quad (5)$$

The difference in the free energy between the adsorbed phase and the saturated liquid adsorbate is referred to as the potential [18, 19]. Thus the sorption space in the vicinity of the solid surface may be characterized by a series of equipotential surfaces with a given sorption potential. The sorption potential is independent of temperature but varies according to the nature of the adsorbent and adsorbate [20]. The magnitude of E was in the range of 2.89-3.53 $Kjmol^{-1}$ which is too small for any chemical ion exchange mechanism therefore it can be concluded that sorption of Cu(II) onto turmeric powder is essentially of physical nature due to weak Vander Waals forces.

In addition to the R^2 value, the mean percentage error (%) was used to evaluate the model's goodness of fit as following (eq. 6):

$$Error(\%) = \frac{100}{N}\sum_{i=1}^{n}\frac{|q_{mod} - q_{exp}|}{q_{exp}} \quad (6)$$

where q_{mod} and q_{exp} are the model prediction and the experimental data respectively and N is the number of data points (Table-1).

Table-1: Isotherm model parameters for the adsorption of Cu(II) onto turmeric powder.

Isotherm model	Temp. (K)	Cu(II)			
		298	303	310	313
Langmuir	q_{max} $mmolg^{-1}$	0.053	0.15	0.16	0.19
	b $Lmmol^{-1}$	2.5	0.87	1.25	1.27
	R_L	0.21	0.43	0.35	0.34
	R^2	0.96	0.96	0.99	0.99
	%error	4.18	6.57	2.58	2.39
Freundlich	n	1.99	1.25	1.33	1.32
	K_F $mmolg^{-1}$	0.041	0.079	0.11	0.13
	R^2	0.99	0.99	0.99	0.99
	%error	2.75	1.93	1.17	1.46
D-R	q_m $mmolg^{-1}$	0. 043	0.077	0.094	0.10
	β mol^2J^{-2}	5E-08	6E-08	5E-08	4E-08
	E $Kjmol^{-1}$	3.16	2.89	3.16	3.53
	R^2	0.93	0.93	0.95	0.97
	%error	3.74	9.72	5.60	10.47

On the basis of values of R^2 and mean percent error(%), It was found that the fruendlich isotherm model provided better fit for adsorption data at all the temperatures as compared to Langmuir and D-R isotherm models.

Thermodynamic Parameters

Thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were determined using the following equations:

$$K_d = q_e / C_e \quad (7)$$

$$\Delta G^o = -RT \ln K_d \quad (8)$$

$$\ln K_d = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (9)$$

where K_d is the distribution coefficient, q_e is the amount of solute (mmol) adsorbed on the adsorbent (g) of the solution at equilibrium and C_e is the equilibrium concentration ($mmolL^{-1}$) of the solute in solution. T is the temperature in Kelvin and R is the gas constant. ΔH° and ΔS° were obtained from the slope and intercept of the Van't Hoff plot of $\ln K_d$ verses 1/T.

Sticking Probability

The surface coverage (θ) for studying the sticking probability was calculated from the relation

$$\theta = 1 - \frac{C_e}{C_o} \quad (10)$$

where C_o and C_e are the initial and equilibrium metal ion concentrations respectively. In order to further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage as expressed in the equation:

$$S^* = (1-\theta)\exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

The sticking probability, S^*, is a function of the adsorbate/adsorbent system under consideration but must lie in the range $0 < S^* < 1$ and is dependent on the temperature of the system. The parameter S^* indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely.

The effect of temperature on the sticking probability was evaluated throughout the temperature range from 20°C to 40°C by calculating the surface coverage at the various temperatures. The plot of $\ln(1-\theta)$ against 1/T gave linear plots with intercept of $\ln S^*$ and slope of E_a/R (Figs. 4 and 5).

Table-2 shows the calculated values of the thermodynamic parameters for the adsorption of Cu(II) by turmeric powder from aqueous solutions. Values of ΔH° for the adsorption of Cu(II) are positive indicating that the process was endothermic in the given conditions. These results can be explained by considering that adsorption of metal ions from aqueous solutions needs metal ion to lose its hydration sheath before getting attached to the sorbent surface and this dehydration process requires energy [21]. In case of Cu(II) energy of dehydration exceeds the exothermicity of the ions attaching to the

Table-2: Thermodynamic parameters for the adsorption of Cu(II) onto turmeric Powder.

Conc. $mmolL^{-1}$	ΔH° $KJmole^{-1}$	ΔS° $jmol^{-1}K^{-1}$	ΔG° $KJmol^{-1}$ T=298K	T=303K	T=310K	T=313K	E_a $KJmol^{-1}$	S^{*}
0.38	42.96	124.34	5.88	5.34	4.39	4.05	25.04	2.14E-05
0.78	57.80	170.49	7.10	5.95	5.01	4.44	29.17	4.87E-06
1.19	60.22	177.10.	7.66	6.23	5.32	4.91	27.61	9.76E-06

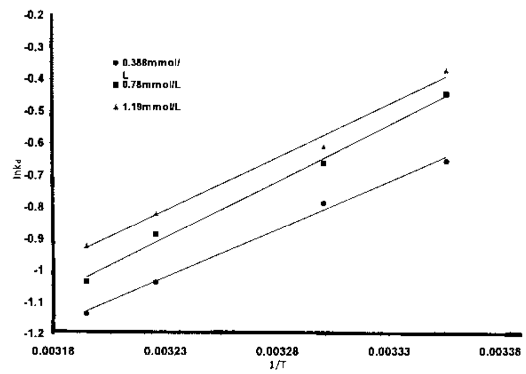

Fig. 4: The plot of lnkd Vs 1/T for the adsorption of Cu(II) onto turmeric powder. (Contact time 50 min, Initial pH 6, temperature 298-310K, turmeric dose 10 g/L, [Cu(II)] $mmolL^{-1}$-1.19 $mmolL^{-1}$).

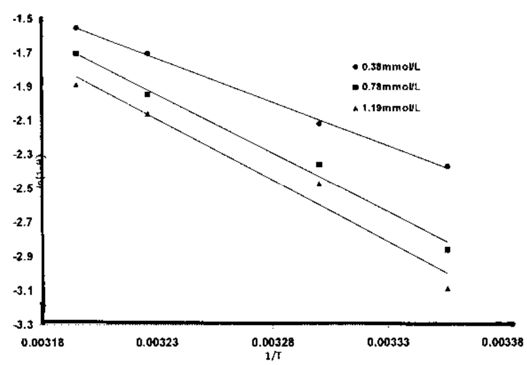

Fig. 5: Sticking Probability for the adsorption of Cu(II) onto turmeric powder. (Contact time 50 min, Initial pH 6, temperature 298-310K,turmeric dose 10 g/L, [Cu(II)] 0.38 $mmolL^{-1}$-1.19 $mmolL^{-1}$).

sorbent surface. Values of ΔG° were positive and weak, which indicate the presence of an energy barrier in the adsorption process. Moreover, increasing the temperature decreased ΔG° values possibly due to the loss of its hydration sheath at higher temperatures. Such dehydration process promoted diffusion into adsorbent channels and provided the achievement of less accessible sites [22]. The positive values of entropy show increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent [23].This increase in randomness can also be attributed to the release of water molecules due to dehydration of metal ions. Another reason of increase in entropy values could be the exchange of the metal ions with more mobile ions present on the sorbent [24]. The E_a values calculated from the slope of the plot of $\ln(1-\theta)$ vs 1/T and were found to be 25.04-27.61 $KJmol^{-1}$ .The positive values of E_a indicate that higher solution temperatures favour metal ion removal by adsorption onto the turmeric powder. These values of S* was less than 1 which indicates favorable sticking of adsorbate to adsorbent with physiosorption mechanism predominant [25].

Experimental

Adsorbent

Commercially available turmeric powder (Shan food limited, Pakistan) was purchased and used without further purification.

Metal Solutions

Stock solutions of Cu(II) were prepared by dissolving appropriate amount of $CuSO_4.5H_2O$ in deionized water. The stock solutions were used to prepare dilute solutions of different working concentrations. All the solutions were prepared in deionized water, which was obtained by passing double distilled water through a column of cation exchanger (Amberlite resin IRA-401 from BDH).

All the glass wares were of standard quality. Special care was taken to wash them thoroughly before use. The glassware were washed with detergent solution followed by tap water and then soaked in dilute nitric acid prior to several times rinsing with deionized water.

Batch Experiment

A volume of 50 mL of metal ion solution with varying initial Cu(II) concentration (0.38 $mmolL^{-1}$-1.51 $mmolL^{-1}$) was placed in a specially designed double jacketed 100 mL container with a supply of water circulation at constant temperatures. An accurately weighed turmeric powder (0.500 ± 0.001 g) was then added to the solution to obtain a suspension. The suspension was adjusted to pH 6±0.1 by adding required volume of 0.1M HNO_3 and NaOH solutions.

A series of such suspensions were shaken at a constant speed at temperatures 298, 303, 310, 313K for 60 minutes. The contents were then suction filtered. Equilibrium concentrations of Cu(II) solutions were determined by Atomic Absorption Spectrophotometry. The amount of metal ions adsorbed was calculated by subtracting final concentration from initial concentration. All the experiments were carried out in triplicate and mean concentration was calculated by averaging them

Analysis of Metal Ions

A PerkinElmer Model Analyst 700 atomic absorption spectrophotometer equipped with air-acetylene flame atomizer and fully computer controlled operating system was used for quantitative analysis of metal ions.

Metal uptake (q) is determined as follows:

$$q_e = V \times (C_i - C_e)/S \quad (12)$$

where q_e (metal uptake $mmolg^{-1}$) is the amount of metal ions adsorbed on the biosorbent, V (L) is the volume of the metal containing solution in contact with the biosorbent. C_i and C_e ($mmolL^{-1}$) are the initial and equilibrium concentrations of metal ions in the solution, respectively, and S(g) is the amount of added biosorbent on a dry basis.

Conclusions

The aim of this work was to investigate the sequestering behavior of turmeric powder as a function of temperature. The equilibrium data were described more satisfactorily Freundlich model than Langmuir and D-R isotherm models. Maximum adsorption capacities obtained from Langmuir was 0.13 $mmolg^{-1}$ at 313K. The magnitude of E is in the range of 2.89-3.53KJ therefore the process is of physical nature. The positive values ΔS° indicated increased in randomness. ΔG° values were found to be positive at all the temperatures which indicated the presenence of energy barrier in adsorption process. The positive values of E_a further confirmed endothermic nature of the process. These values of S* is much less than 1 which indicated favorable sticking of adsorbate to adsorbent with physiosorption mechanism predominant.

Thus turmeric powder has metal sequestering properties and can decrease the soluble concentration of heavy metal ions. They can effectively sequester dissolved metal ions from aqueous solutions and can be recommended for deeper studies of their sequestering behavior in bio systems.

References

1. C. Scott, N. Faruqui, and L. Raschid-Sally. (Eds), Wastewater use in irrigated agriculture: Confronting the livelihood and environmental realities. CAB International (2004).
2. A. Aleem, J. Israr, and A. Malik, *Bioresource Technology*, **86**, 7(2003).
3. R. K. Rattan, S. P. Datta, S. Chandra, and N. Saharan, *Fertil. News*, **11**, 21 (2002).
4. J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th Edition, Pearson Education Inc., USA (2000).
5. T. A. Davis, B. Volesky, and R. H. S. Vieira, *Water Research*, **34**, 4270 (2000).
6. A. L. Cheng, C. H. Hsu, J. K. Lin, M. M. Hsu, Y. F. Ho, T. S. Shen, J. Y. Ko, J. T. Lin, B. R. Lin, M. S. Wu, H. S. Yu, S. H. Jee, G. S. Chen, T. M. Chen, C. A. Chen, M. K. Lai, T. S. Pu, M. H. Pan, Y. J. Wang, C. C. Tsai, and C. Y. Hsieh, *Anti Cancer Research*, **21**, 2895 (2001).
7. Z. R. Komy, *Journal of Colloid and Interface Science*, **270**, 281 (2004).
8. S. P. Mishra, D. Tiwari, R. S. Dubey, and M. Mishrah, *Bioresource Technology*, **63**, 1 (1998)
9. Langmuir, *Journal of American Chemical Society*, **40**, 1361 (1918).
10. D. Norman, S. Ndur, and R. Nartey, *Journal of Colloid and Interface Science*, **321**, 493 (2008).
11. K. R. Hall, L. C. Eagleton, A. Acrivos, and T. Vermeulen, *Industrial and Engineering*

Chemistry Fundamentals, **5**, 212 (1966).
12. V. B. H. Dang, H. D. Doan, T. Dang-Vu, and A. Lohi, *Bioresource Technology*, **100**, 211 (2009).
13. H. M. F. Freunlich, *Journal of Physical Chemistry*, **57**, 385 (1906).
14. R. Donat, A. Akdogan, E. Erdem, and H. Cetisli, *Journal of Colloid and Interface Science*, **286**, 43 (2005).
15. J. E. Eren, and B. Afsin, *Journal of Hazardous Materials*, **151**, 682 (2008).
16. M. M. Dubinin, and L. V. Radhushkevich, *Proceedings* of *the* Academy *of Sciences Physical Chemistry Section U.S.S.R.*, **57**, 385 (1906).
17. S. M. Hasany, and M. H. Chaudary, *Applied Radiation* and Isotopes, **47**, 467 (1996).
18. M. Polanyi, *Transactions of the Faraday Society*, **28**, 316 (1932).
19. M. M. Dubinin, E. D. Zaverin, and L. V. Radushkevich, *Z. Fizicheskoi Khimii*, **21**, 1351 (1947)
20. T. K. Naiya, P. Chowdhury, A. K. Bhattacharya, and S. K. Das, *Chemical Engineering Journal*, **148**, 68 (2009).
21. S. S. Tahir, and N. Rauf, *Journal of Chemical Thermodynamics*, **35**, 2003 (2003).
22. R. M. Schneider, C. F. Cavalin, M. A. S. D. Barros, and C. R. G. Tavares, *Chemical Engineering Journal*, **132**, 355 (2007).
23. V. K. Gupta, *Industrial and Engineering Chemistry Research*, **37**, 192 (1998).
24. N. Unlu, and M. Ersoz, *Journal of Hazardous Materials*, **B136**, 272 (2006).
25. M. Horsfall, and A. I. Spiff, *Electronic Journal of Biotechnology*, **8**, 162 (2005).