

Effect of Temperature on Equilibrium and Thermodynamic Parameters of Cd (II) Adsorption onto Turmeric Powder

¹AMTUL QAYOOM* AND ²SYED ARIF KAZMI

¹Department of Chemistry, NED University of Engineering and Technology, Karachi-75270, Pakistan.

²H.E.J. Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi, Pakistan.
amtulq@gmail.com*

(Received on 05th January 2012, accepted in revised form 02nd May 2012)

Summary: Batch adsorption of Cd (II) onto turmeric powder was conducted as a function of temperature. Nonlinear Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin equilibrium models were employed. In addition to R², five different error functions were used to determine best fit equilibrium isotherm model. It was found that Freundlich isotherm model provided better fit for adsorption data at 298 and 303 K and Langmuir model was suitable for the experimental data obtained at 310 and 313 K. It was found that increase in temperature decreased maximum adsorption capacities, showing that the adsorption of Cd (II) onto turmeric powder is exothermic. Enthalpy values also confirmed the same trend. Entropy values were negative which means that randomness decreased on increasing temperature. Gibbs free energies were non spontaneous at all the temperatures studied. E values were in the range of 2.73-3.23 kJ mol⁻¹ which indicated that adsorption mechanism is essentially physical.

Keywords: Adsorption; Temperature; Isotherms; Thermodynamics.

Introduction

Rapid urbanization and industrialization all over the world has become an important concern because of increasing environmental pollution. In developing countries, farmlands around cities are often used for growing vegetables and fruits. Municipal wastes and industrial effluents are being used for irrigation, resulting in elevated level of toxic metals in the human food cycle [1]. Cadmium is among the most abundant of these heavy metals and is particularly toxic even at a low concentration. Cadmium is easily absorbed by plant roots and passes to edible seeds, leaves and fruits. It has the tendency to buildup in animal milk and fatty tissues [2]. Therefore, for people who do not smoke, food is the most common source of cadmium. The highest cadmium concentrations are found in wheat, oyster, shellfish, rice, mussels, liver and kidney cortex of adult animals [3]. Industrial effluents and atmospheric deposition also add cadmium to surface waters used for drinking in many parts of the world [4]. Eating lower level of cadmium for a long period can lead to its elevated level in the kidneys and may cause bone degeneration ('Itai-itai' syndrome), renal dysfunction (Fanconi syndrome), blood damage and liver damage [5, 6].

Some dietary fibers, including cellulose, lignin and pectin have been found to bind cadmium and decrease its renal accumulation in young rats [7-9]. It is assumed that cadmium might react with phytates present in the diet to form insoluble complexes [10].

Turmeric powder is one of the most widely used spices in Asia. It has been found to be non-toxic even at the dose of 8000 mg day⁻¹ taken continuously [11]. Due to the presence of curcuminoids, proteins, carbohydrates etc., turmeric powder has strong potential to act as a biosorbent and interact with toxic metals through a combination of different metal binding processes including ion exchange, physical adsorption, chemical adsorption, complexation, coordination, chelation and micro precipitation. This sequestering ability of turmeric powder may be used to remove toxic metals from foods, drinks and biosystems. Cumin, another important spice, is also tested and found capable of binding toxic metals by similar processes [12]. Milk protein (casein) is also found to exhibit biosorptive properties for toxic metal ions in biosystem [13].

The present study is conducted to evaluate the effect of temperature on equilibrium and determine thermodynamic parameters for the removal of Cd (II) onto turmeric powder because it might provide some insight into the processes involved in sequestration of Cd (II) onto turmeric powder.

Result and Discussion

Equilibrium Parameters of Adsorption

The distribution of adsorbate molecules between aqueous and the solid phases at equilibrium state is a measure of sorbate/sorbent affinity, which can be described by many isotherm models. The

*To whom all correspondence should be addressed.

shape of the isotherm depends on the sorption mechanism involved and associated sorption energy. The sorption data was analyzed in terms of nonlinear Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin models at different temperatures. Fig. 1 and 2 illustrate nonlinear Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin adsorption isotherms for the adsorption of Cd (II) ions onto turmeric powder at the temperature 298–313 K and isotherm model parameters obtained are listed in Table-1.

Table-1: Equilibrium parameters for the adsorption of Cd (II) onto turmeric powder.

Isotherm	Temp.(K)	298	303	310	313
Langmuir	q_{\max} (mmol g ⁻¹)	0.39	0.14	0.21	0.22
	b (L mmol ⁻¹)	0.34	0.62	0.38	0.32
	R_L	0.74	0.61	0.71	0.75
	R^2	0.99	0.99	0.99	0.99
	$1/n$	0.91	0.84	0.88	0.86
Freundlich	K_F (mmol g ⁻¹)	0.11	0.078	0.063	0.055
	R^2	0.09	0.99	0.99	1.00
	q_m (mmol g ⁻¹)	0.074	0.065	0.057	0.054
D-R	E_{DR} (KJ mol ⁻¹)	3.23	3.00	2.84	2.73
	R^2	0.09	0.99	0.99	0.99
	b_T (KJ mol ⁻¹)	83.07	101.99	111.93	136.93
Temkin	A_T (L g ⁻¹)	12.26	11.35	9.22	10.13
	R^2	0.99	0.99	0.99	0.99

The Langmuir adsorption isotherm is often used to describe adsorption at finite homogenous sites within the adsorbent and there is no interaction between the adsorbate molecules. Once all the sites are occupied by a monolayer of metal ions, no further adsorption can occur. Concentration of sorbate in the solution and bare surface available for adsorption are driving forces. Langmuir isotherm equation is [14].

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (1)$$

Where q_e is the maximum equilibrium metal (II) concentration on the adsorbent (mmol g⁻¹); C_e is the equilibrium metal (II) concentration in the solution (mmol L⁻¹), q_{\max} the monolayer adsorption capacity of the adsorbent (mmol g⁻¹) and b , the Langmuir adsorption constant (Lmmol⁻¹) associated with free energy of adsorption and affinity of the sorbent for the sorbate. Weber and Chakraborti expressed essential feature of Langmuir isotherm by ' R_L ', a dimensionless constant referred to as separation factor [15]. R_L is calculated using the following equation where b is the Langmuir adsorption constant (L mmol⁻¹) and C_o is the highest initial metal (II) concentration (mmol L⁻¹).

$$R_L = \frac{1}{1 + b C_o} \quad (2)$$

The maximum sorption capacity, q_{\max} , was found to decrease from 0.39 to 0.22 mmol L⁻¹, when temperature was raised from 298 K to 313 K. The

other Langmuir constant, b , indicates the affinity of sorbent for the binding of Cd (II) ions. The value of b was found to be maximum i.e. 0.62 L mmol⁻¹ at 303 K and minimum i.e. 0.32 L mmol⁻¹ at 313 K. The decrease in the values of Langmuir constants with increasing temperature suggests that the adsorption of Cd (II) onto turmeric powder is an exothermic process [16]. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). As the R_L values lie between 0 and 1 for the adsorption of Cd (II) by turmeric powder, the adsorption process is favorable [17, 18]. Comparison of the values of q_{\max} of turmeric powder with other adsorbents used for Cd (II) removal is given in Table-2. It shows that turmeric powder has a comparable adsorption capacity with other biosorbents.

Table-2: Values of q_{\max} for the adsorption of Cd (II) onto turmeric powder in comparison with different biosorbents.

biosorbent	q_{\max} (mmol g ⁻¹)	Reference
Turmeric powder	0.39	[this work]
Coconut copra meal	0.041	[19]
Degreased coffee beans	0.059	[20]
Areca, a chewing nut	0.099	[21]
Esterified lemon	0.99	[22]

The Freundlich isotherm model is used to describe heterogeneous system having different sites with different adsorption energies. Freundlich equation is [23]:

$$q_e = K_F C_e^{1/n} \quad (3)$$

K_F (mmol g⁻¹) is indicative of the extent of adsorption while n is related to the distribution of bonded ions on the sorbent surface and has been used as measure of adsorption intensity between solution concentration and adsorption. The value of K_F decreased with the rise in temperature, which indicates the preference of low temperature for adsorption. If the value of n is less than unity, it suggests that the adsorption process is chemical, and if n is above unity, it is physical adsorption [24]. The value of n is slightly greater than one at all temperatures, indicating that interaction of Cd (II) with adsorbent is of physical nature and hence of relatively low intensity.

The Dubinin-Radushkevich (D-R) isotherm, which is based on Polanyi theory, does not assume a homogenous surface, constant adsorption potential or absence of steric hindrance between sorbed and incoming particles. It was employed to make a distinction between physical and chemical adsorption. D-R isotherm equation is [25]:

$$Q_e = q_m \exp(-\beta \epsilon^2) \quad (4)$$

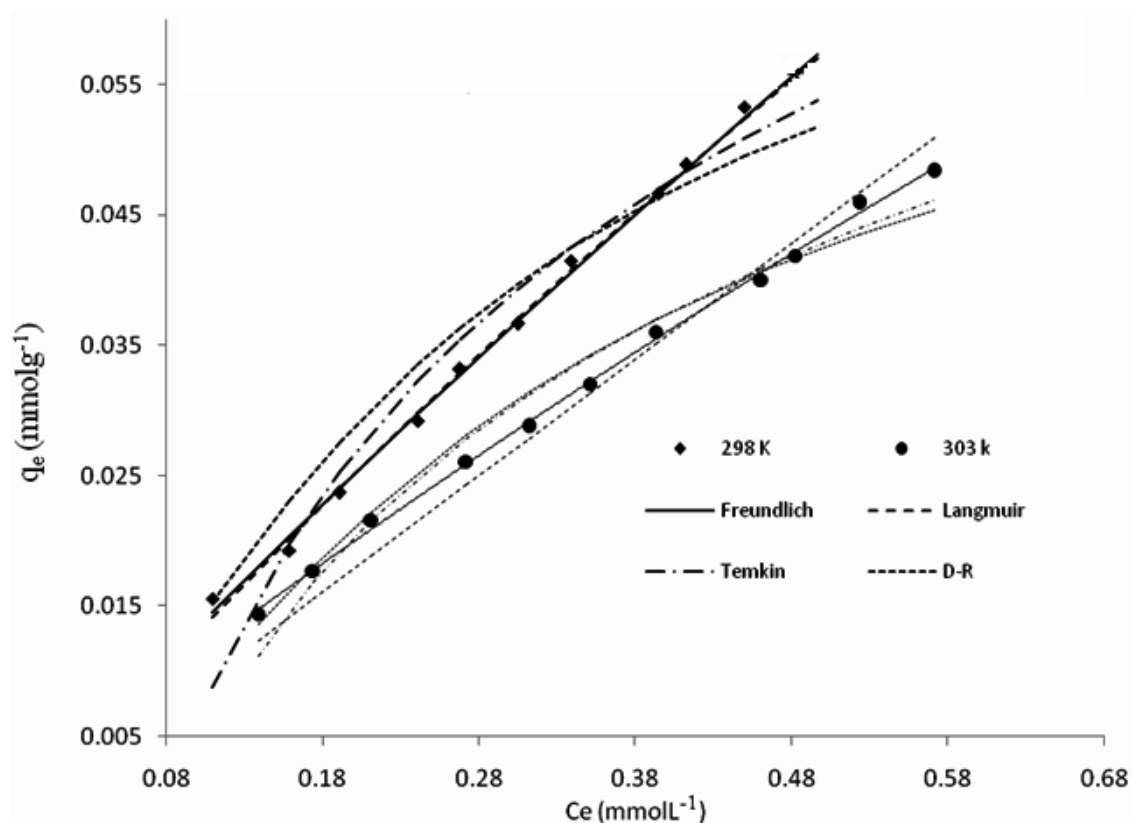


Fig. 1: Nonlinear equilibrium isotherms for the adsorption of Cd (II) onto turmeric powder at 298 and 303 K.

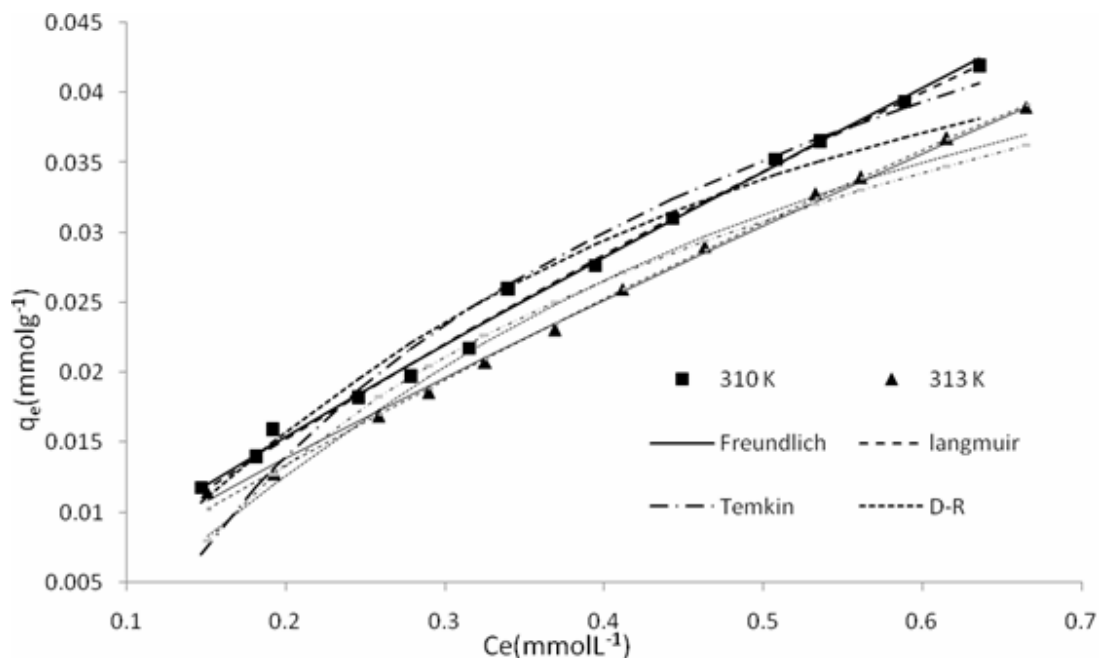


Fig. 2: Nonlinear equilibrium isotherms for the adsorption of Cd (II) onto turmeric powder at 310 and 313 K.

Where β is a constant associated with mean energy of adsorption per mole of the adsorbate ($\text{mol}^2 \text{J}^{-2}$); 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 ($\text{J mol}^{-1} \text{K}^{-1}$) is the gas constant; and $T(\text{K})$, the absolute temperature.

If a very small sub-region of the adsorbent surface is assumed to be approximation of Langmuir isotherm, $\beta^{1/2}$ can be associated with mean sorption energy, E_{DR} (KJ mol^{-1}), when 1 mol of solute is transferred to the surface of the solid from infinity (in solution). This magnitude of E_{DR} is used to distinguish among chemical, ion exchange or physical adsorption and can be calculated using the relationship [26].

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

The magnitude of E_{DR} was in the range of 2.73-3.23 KJ mol^{-1} which is too small for any chemical ion exchange mechanism therefore adsorption of Cd (II) onto turmeric powder is due to weak Vander Waals forces and hence of physical nature.

Temkin isotherm is based on the assumptions that binding energies are uniformly distributed and decrease in the heat of sorption due to the sorbate and sorbent interaction is linear with coverage rather than logarithmic [27]. Temkin isotherm model equation is:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (6)$$

Where b_T is the Temkin constant associated with sorption enthalpy (kJ mol^{-1}), R is the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), A_T is the Temkin equilibrium binding constant (L g^{-1}), and T the absolute temperature (K). On increasing temperature from 298 to 313K, values of b_T increased from 83.07 to 136.93 KJ mol^{-1} for the adsorption of Cd (II) onto turmeric powder. Values of A_T were found to decrease from 12.26 to 9.22 L g^{-1} on increasing temperature from 298 to 310 K.

It is not appropriate to compare the goodness of fit solely on the basis of R^2 . Therefore, in addition to nonlinear R^2 , five different error functions i.e. The sum of the absolute errors (SAE), The sum of the squares of the errors (SSE), Chi-square test (χ^2), Mean Percent Error, Marquardt's percent standard deviation (MPSD) were also determined to evaluate

the fit of the isotherm to the experimental results and a comparison of non linear regression error analysis is given in Table-3.

Table-3: Non linear regression error analysis for the equilibrium modelling of Cd (II) sorption onto turmeric powder.

Temp. (K)	Error Function	Langmuir	Freundlich	D-R	Temkin
298	SAE	0.044	0.0073	0.029	0.023
	SSE(x10 ⁵)	0.64	0.68	1.03	8.24
	χ^2 (x10 ³)	0.26	2.3	2.9	6.3
	% error	2.13	0.24	8.38	8.23
	MPSD	0.050	0.506	1.91	2.11
303	SAE	0.017	0.0040	0.048	0.016
	SSE(x10 ⁵)	3.18	0.195	0.34	3.5
	χ^2 (x10 ³)	1.4	0.062	0.96	1.6
	% error	5.56	1.21	4.56	5.75
	MPSD	1.15	0.26	1.04	1.28
310	SAE	0.0059	0.0066	0.36	0.021
	SSE(x10 ⁵)	0.622	0.57	0.33	5.55
	χ^2 (x10 ³)	0.31	0.4	1.5	5.0
	% error	2.40	2.56	6.25	9.17
	MPSD	0.53	0.67	1.21	1.81
313	SAE	0.0035	0.0047	0.31	0.019
	SSE(x10 ⁵)	0.21	0.23	0.25	3.91
	χ^2 (x10 ³)	0.17	0.12	1.8	2.5
	% error	1.72	2.05	6.14	7.47
	MPSD	0.39	0.35	1.20	1.44

$$SAE = \sum_{i=1}^n |q_{e,mod} - q_{e,exp}|_i \quad (7)$$

$$SSE = \sum_{i=1}^n (q_{e,mod} - q_{e,exp})_i^2 \quad (8)$$

$$\chi^2 = \frac{\sum_{i=1}^n (q_{e,mod} - q_{e,exp})_i^2}{q_{e,mod}} \quad (9)$$

$$Error (\%) = \frac{100}{n} \sum_{i=1}^n \frac{|q_{e,mod} - q_{e,exp}|}{q_{e,exp}} \quad (10)$$

$$MPSD = 100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{(q_{e,exp} - q_{e,mod})}{q_{e,exp}} \right)_i^2} \quad (11)$$

Where $q_{e,mod}$ and $q_{e,exp}$ are the model prediction and the experimental data, respectively and n is the number of observations and p is the number of parameters in the model. On the basis of R^2 and error analysis, it is concluded that Freundlich isotherm was the most suitable isotherm for predictions at 298 and 303K and Langmuir model provided best fit for the experimental data at 303K and 313K.

Thermodynamic Parameters

Thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) contribute to determine the driving force for

adsorption reactions. These parameters were determined using the following equations:

$$K_d = \frac{q_e}{C_e} \quad (12)$$

$$\Delta G^\circ = -RT \ln K_d \quad (13)$$

$$\ln K_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (14)$$

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 (mmol L^{-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 $\ln K_d$ versus $1/T$ (Fig. 3)

ΔH° values were found to be negative, indicating that the sorption was exothermic and a low temperature favored metal ion removal by sorption onto turmeric powder. The magnitude of adsorption enthalpy values also gives information about the type of biosorption. Enthalpy values less than 40 KJ mol^{-1} are associated with physisorption (electrostatic attraction), rather than chemical bonding [28]. In this

study, average enthalpy value was found to be $-33.55 \text{ KJ mol}^{-1}$; indicating a physical adsorption phenomenon. The negative values of ΔS° suggest decreased randomness at the solid-solution interface during biosorption [29]. The positive and low values of ΔG° indicate the presence of an energy barrier in the adsorption process. Moreover, increasing the temperature increased ΔG° values confirming exothermic nature of the adsorption [30].

Experimental

Adsorbent

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

Metal solutions

Stock solutions of Cd (II) were prepared by dissolving appropriate amount of

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in deionized water obtained by passing double distilled water through a column of cation exchanger (Amberlite resin IRA-401 from BDH). Dilute solutions of different working concentrations were prepared from stock solution.

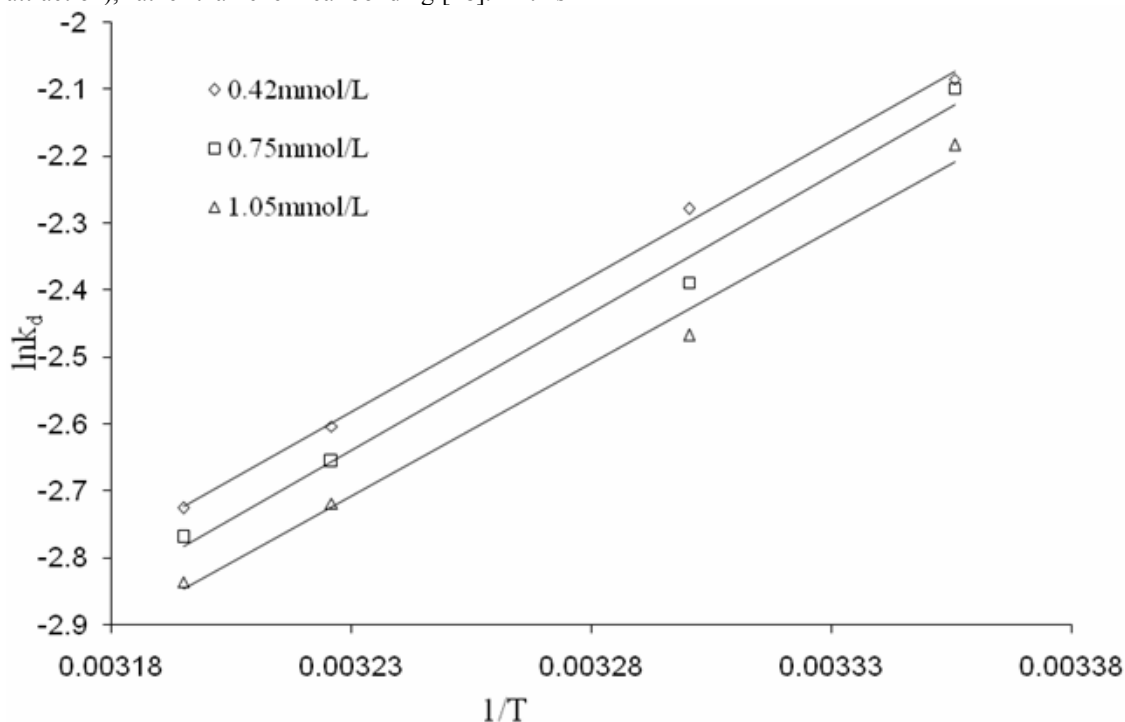


Fig. 3: Plot of $\ln K_d$ Vs $1/T$ for the adsorption of Cd (II) onto turmeric powder.

Batch Experiment

A volume of 50 ml of metal ion solution with varying initial Cd (II) concentration (0.26 mmol L⁻¹-1.05 mmol L⁻¹) was placed in a specially designed double jacketed 100 ml container with a supply of water circulation at constant temperatures. 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 7±0.1 by adding required volume of 0.1 M HNO₃ and NaOH solutions (In another study pH 7 was found to be optimum pH for the adsorption of Cd (II) onto turmeric powder).

A series of such suspensions was stirred at a constant stirring rate at temperatures 298, 303, 310, 313 K for 60 minutes. The contents were then suction filtered. Equilibrium concentrations of Cd (II) solutions were determined by Atomic Absorption Spectrophotometer.

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:

$$q_e = V \times \frac{C_i - C_e}{S} \quad (15)$$

Where q_e (metal uptake mmol g⁻¹) is the amount of adsorbed metal ions, V (L) is the volume of the metal solution in contact with the biosorbent, C_i and C_e (mmol L⁻¹) are the initial and equilibrium concentrations of metal ions in the solution, respectively and S (g) is the amount of biosorbent added in the solution.

Conclusion

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 by Freundlich model at 298 and 303 K and Langmuir model provided better fit at 310 and 313 K. Maximum adsorption capacities obtained from Langmuir isotherm models was 0.39 mmol g⁻¹ at 298 K. The magnitude of E_{DR} was in the range of 3.06-2.73 KJ mol⁻¹ therefore the adsorption of Cd (II) onto turmeric powder was of physical nature. The negative values ΔS° indicated decreased randomness at the solid–solution interface during

biosorption. ΔG° values were found to be positive at all the temperatures indicating presence of energy barrier in adsorption process.

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. V. P. Singh, *In Toxic Metals and Environmental Issues, Sarup and Sons, New Dehli*, p. 7 (2005).
2. M. Kaneta, H. Hikichi, S. Endo and N. Sugiyama, *Environment Health Perspect*, **65**, 33 (1986).
3. E. M. Gama, L. A. da Silva and V. A. Lemos, *Journal of Hazardous Materials*, **136**, 757 (2006).
4. J. D. Zuane, *In Handbook of Drinking Water Quality, 2nd Edition, John Wiley and Sons, Inc., USA*, p. 66 (1996).
5. ATSDR, *Draft Toxicological Profile for Cadmium*. US DHHS, Public Health Service, Atlanta GA, (2008). Available at <http://www.atsdr.cdc.gov/toxprofiles/tp.5.pdf>
6. L. Stayner, R. Smith, M. Thun, T. Schorr and R. Lemen, *Annals of Epidemiology*, **2**, 177 (1992).
7. M. Kiyozumi, M. Mishima, S. Noda, K. Miyata, Y. Takahashi, F. Mizunaga, M. Nakagawa and S. Kojima, *Chemical and Pharmaceutical Bulletin*, **30**, 4494 (1982).
8. M. Omori and Y. Muto, *Journal of Nutritional Science and Vitaminology*, **23**, 361 (1977).
9. M. Wing, *British Journal of Nutrition*, **69**, 199 (1993).
10. J. L. Schroder and N. T. Basta, J. Si, S. W. Casteel, T. Evans and M. Payton, *Environmental Science and Technology*, **37**, 1365 (2003).
11. 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, *Anticancer Research*, **21**, 2895 (2001).
12. Z. R. Komy, *Journal of Colloid and Interface Science*, **270**, 281 (2004).
13. S. P. Mishra, D. Tiwari, R. S. Dubey and M. Mishrah, *Bioresource Technology*, **63**, 1(1998).
14. Langmuir, *Journal of American Chemical Society*, **40**, 1361 (1918).

15. T. W. Weber and R. K. Chakraborti, *American Institute of Chemical Engineers Journal*, **20**, 228 (1974).
16. H. Baker and F. Khalili, *Analytica Chimica Acta*, **516**, 179 (2004).
17. K. R. Hall and L. C. Eagleton, A. Acrivos and T. Vermeulen, *Industrial and Engineering Chemistry Fundamentals*, **5**, 212 (1966).
18. V. B. H. Dang, H. D. Doan, T. Dang-Vu and A. Lohi, *Bioresource Technology*, **100**, 211 (2009).
19. Y. S. Ho and A. E. Ofomaja, *Biochemical Engineering Journal*, **30**, 117 (2006).
20. K. Kaikake, K. Hoaki, H. Sunada, R. P. Dhakal and Y. Baba, *Bioresource Technology*, **98**, 2787 (2007).
21. W. Zheng, X. Li, F. Wang, Q. Yang, P. Deng and G. Zeng, *Journal of Hazardous Materials*, **157**, 490 (2008).
22. H. Arslanoglu, H. S. Altundogan, and F. Tumen, *Journal of Hazardous Materials*, **164**, 1406 (2009).
23. H. M. F. Freunlich, *Zeitschrift fur Physikalische Chemie*, **57**, 385 (1906).
24. S. Veli and B. Alyuz, *Journal of Hazardous Materials*, **149**, 226 (2007).
25. M. M. Dubinin and L. V. Radhushkevich, *Proceedings of the Academy of Sciences Physical Chemistry*, U. S. S. R. **55**, 331 (1947).
26. S. M. Hasany and M. H. Chaudary, *Applied Radiation and Isotopes*, **47**, 467 (1996).
27. Y. Kim, C. Kim, I. Choi, S. Rengaraj and J. Yi, *Environmental science and Technology*, **38**, 294 (2004).
28. D. Ringot, B. Lerzy, J. P. Bonhoure, E. Auclair, Eric Oriol and Y. Larondelle, *Process Biochemistry*, **40**, 3008 (2005).
29. M. H. Khani, A. R. Keshtkar, M. Ghannadi and H. Pahlavanzadeh, *Journal of Hazardous Materials*, **150**, 612 (2008).
30. E. I. Unuabonah, K. O. Adebowale, B. I. Oluowolabi, L. Z. Yang and L. X. Kong, *Hydrometallurgy*, **93**, 1(2008).