**ADSORPTION OF AQUEOUS Cd (II) IONS ONTO TURMERIC POWDER: KINETIC MODELLING**

Amtul Qayoom**1\***, Syed A. Kazmi**2**, Saeeda Nadir Ali**1**

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

2H.E.J. Research Institute of Chemistry, International Center for Chemical

Biological Sciences, University of Karachi, Karachi, Pakistan

Corresponding author: Amtul Qayoom,

Phone: 00-92-03008267181

(Email: [amtulq@neduet.edu.pk](mailto:amtulq@neduet.edu.pk))

*In previous studies, turmeric was found to sequester metal ions from their aqueous solutions. In present work, various kinetic models were applied on experimental data to evaluate adsorption efficiency of turmeric to sequester aqueous Cd (II) ions. The rate constants and the reaction order have also been determined. The obtained kinetic parameters suggested that adsorption of aqueous Cd (II) onto turmeric is a chemisorption process following the pseudo-second-order and Elovich kinetics. On raising temperature from 298K to 313K, the values of metal uptake (qe) and Initial sorption rate (ho) decreased from 0.032to 0.023 mmol g‑1 and 0.0038 to 0.0020 g mmol-1min-1, respectively indicating exothermic nature of the Cd (II)-turmeric interaction. These results were in accordance with thermodynamic parameters obtained for Cd (II) adsorption onto turmeric powder. Due to low activation energy, the affinity of turmeric powder for Cd (II) ions may be attributed to electrostatic attractions/ Van der Waals forces*

**Keywords:** cadmium, kinetic, adsorption, intraparticle diffusion, turmeric

# **INTRODUCTION**

In many developing countries, agricultural land is often irrigated with raw sewage as a supplement of essential plant nutrients. Industrial and domestic sewage is also disposed of into fresh water systems which again can be used to irrigate agricultural land [1-3]. In Pakistan, it is common practice to use water resources loaded with untreated industrial effluents and raw sewage for vegetable cultivation around the urban areas of Pakistan [4]**.** Although crop production is usually increased by irrigation with sewage and industrial effluents, it results in the contamination of soil and crops with harmful pollutants e.g. polychlorinated substances and heavy metals [5, 6]. Food is the key source of toxic metals intake by human beings [7]. Moreover, Atmospheric deposition also add toxic metals to surface waters, used for drinking in many parts of the world [8].

Cadmium is a non-essential and extremely toxic metal perhaps because of its ability to bond itself with sulfur and thus replace essential metals, i.e. Zn2+ and Ca2+ from certain enzymes [9]. IARC has identified cadmium and cadmium compound as human carcinogens [10]. Cadmium is present in at least 1,014 of the 1,669 hazardous sites that have been identified by US-EPA for inclusion in the National Priorities List (NPL) [11].

High intake of cadmium for long term exposure can cause diseases such as kidney disorder (Fanconi syndrome) [12], anaemia [13], acute, chronic metabolic disorders, emphysema, hypertension [14], osteomalacia (‘Itai –itai’ syndrome) [15], blood and liver damage etc. [16]. Cadmium accumulates in bones and may interfere with calcification, decalcification, and bone remodelling [16]. Majority of the cadmium in the diet usually comes from leafy vegetables, potatoes, wheat, rice and other grains [17]. Various researchers estimated concentration of cadmium in raw municipal sewage and in sewage-irrigated soils, vegetables and fruits grown in different areas of Pakistan [18-21]. The concentration of cadmium in municipal sewage was found threefold (0.03 mg L–1) it’s acceptable concentration (0.01mg L–1) in irrigation water. These studies found that almost all the sampled vegetables contain higher cadmium concentration in their fruits and leaves [22].

The practice of using certain plants or their parts as natural chelates for detoxification of living organisms is quite topical. Many researchers explored the properties of local food and herbs for heavy metal detoxification [23-25]. Turmeric has been used over 6000 years as herbal medicines. From ancient time, it is utilized as a spice, colouring agent, food preservative, and cosmetic and as medicinal herb. Presence of curcuminoids, carbohydrates, proteins etc. suggests its capability to fight metal toxicity by interacting and binding with toxic metals through chemical and/or physical adsorption, ion exchange, complexation, coordination etc.. In previous work, effects of varying experimental conditions on aqueous Cd (II) adsorption onto turmeric powder were evaluated. Equilibrium and thermodynamic parameter were also determined [26, 27]. The application of kinetic models on experimental data and their thorough analysis would further be helpful in understanding possible interaction mechanisms between Cd (II) ions and turmeric surface.

The main objective of present study was to understand adsorption mechanism by applying various reactions and diffusion based kinetic models on experimental data. The relationship between temperature and various kinetic parameters were also explored.

1. **MATERIALS & METHODS**
   1. **Experimental**

Batch biosorption experiments were conducted at different biosorption time intervals using initial Cd (II) concentration as 0.53 mmol L-1. Turmeric dose was adjusted to 10 g L-1. Temperature of solution was varied in the range of 298-313K. The samples were taken at different time intervals (1–100 min) at the end of each agitation period and the mixtures were suction filtered.

A PerkinElmer Model Analyst 700 atomic absorption spectrophotometer was employed for quantitative analysis of metal ions. The adsorbed metal ions concentration was computed by subtracting final concentration from initial concentration. Batch adsorption tests were conducted in triplicate and average concentration was calculated by taking their mean values.

Metal uptake (qe) and percent adsorption are determined as follows:

(1)

(2)

Where concentration of adsorbed Cd (II) ions is represented as qe (mmol g-1), volume of the adsorbate solution as V (L), amount of turmeric powder added as m (g) and Cd (II) ions concentration in the solution in the beginning, at equilibrium and at time t as Ci (mmol L-1), C e(mmol L-1), Ct (mmol L-1), respectively.

* 1. **Kinetic modelling**

Kinetic models can be categorized into two major classes: reaction and diffusion-based models.

### Reaction-based Models

***Pseudo-second order model***

Legergren equation for pseudo-first order is given as [28] :

(03)

At the initial conditions *qt* =0 at *t* = 0, hence, integrating equation (03) results into:

(04)

Where equilibrium concentration of adsorbed Cd (II) ions is taken as qe (mmol g-1and the same at time t (min) is represented as qt (mmolg-1); Pseudo-first order rate constant is taken as k1 (min−1). Log (qe-qt) was plotted versus t to assess the pseudo-first order kinetic model.

***Pseudo-second order model***

Equation (5) is used to describe Pseudo-second order kinetic model [29]:

(05)

Where pseudo-second order rate constant is represented as k2 (g mmol-1min-1). Rearranging variables and integrating Eq. (4) at qt =0 to qt = qt and t=0 to t = t gives following equation.

(06)

Linearizing Eq. (5) results in:

(07)

Eq. (7) results in straight line when t/qt is plotted versus t. Slope and intercept of the plot were used to estimate values of parameters, qe and k2, respectively. Initial sorption rate ho (mmol g-1 min-1) can be determined from the value of rate constant (k2) using Eq. (8)

(08)

***Elovich model***

Elovich equation explains 2nd order kinetics by considering actual adsorbent surfaces as energetically heterogeneous [30]. Eq. (09) represents Elovich equation [31]:

(09)

Where initial adsorption rate (mmol g-1 min‑1) is represented as α, and βE is associated with the activation energy for chemisorption and degree of surface coverage (g mmol-1). Assuming that α βE t >>1 and qt =0 at t = 0, Elvoich equation is simplified as follows:

(10)

Plot of qt versus lnt is used to assess validity of Elovich equation. The intercept and slope of the resulted straight line is used to estimate α and βE, respectively. Validity of Elovich equation favours the assumption that adsorption rate can be described by chemisorption mechanism [32].

### Diffusion-based model

Adsorption kinetics depends on various independent processes occurring simultaneously or in series. Usually adsorbate uptake on porous adsorbents occurs in following four steps [33].

* Bulk diffusion: movement of sorbate from bulk solution to the boundary layer at liquid-sorbent junction.
* Film diffusion: adsorbate transfer from the boundary layer to the external adsorbent surface.
* Intraparticular diffusion: surface diffusion and/or pore diffusion of sorbate from the external surface of adsorbent to the intraparticular active sites.
* Sorbate uptake by the active sites present on adsorbent surface.

Adsorption rate may depend on one or more of these steps. Bulk diffusion and sorbate adsorption on adsorbent surface occur almost instantaneously therefore overall adsorption kinetics is usually independent of these steps [34]. Film diffusion and intraparticle diffusion act in parallel and slowest of these steps will govern overall sorption rate. Though, the rate-determining step might be distributed between film diffusion and intraparticle diffusion.

### *Intraparticle diffusion (Weber–Morris model)*

If adsorption rate is determined by intra-particle diffusion step, adsorption is directly related to the square root of contact time. Therefore, adsorption capacities as a function of t1/2 are often employed to calculate adsorption rates. Following equation represents Weber and Morris Intraparticle diffusion model [35]:

(11)

Where intraparticle diffusion constant is represented by ki and C gives an idea of the degree of the boundary layer thickness.

## Activation parameters

Arrhenius equation was used to calculate activation energy for adsorption of Cd (II) ions onto turmeric:

(12)

Where second-order adsorption rate constant (g mmol-1s-1) is represented as k2, activation energy (J mol-1) as EA, Arrhenius factor (g mmol-1 s-1) as k0, gas constant (J K-1 mol-1) and temperature (K) of adsorbate solution as R and T, respectively.

1. RESULT & DISCUSSION
   1. Kinetic modelling

Efficiency of adsorbents can be assessed by studying adsorption kinetics because diffusion process and the residence time of adsorbate uptake at the sorbent–solution interface usually depend upon adsorbate uptake rate. Table 1 represents kinetic modelling parameters for the adsorption of aqueous Cd (II) onto turmeric.

Table 1. Effect of temperature on kinetic modelling parameters for the adsorption of aqueous

Cd (II) onto turmeric

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Kinetic Model** | **Temp. (K)** | **298** | **303** | **310** | **313** |
| **Qe (mmol g-1) (exp)** | **0.030** | **0.026** | **0.023** | **0.021** |
| Pseudo-first order | Qe (mmol g-1) | 0.022 | 0.017 | 0.016 | 0.0154 |
| k1 (min-1) | 0.046 | 0.025 | 0.030 | 0.030 |
| R2 | 0.98 | 0.92 | 0.98 | 0.98 |
| Pseudo-second order | Qe (mmol g-1) | 0.032 | 0.028 | 0.024 | 0.023 |
| k2 (g mmol-1 min-1) | 3.65 | 3.71 | 3.84 | 3.86 |
| ho(mmol g-1 min-1) | 0.0038 | 0.0028 | 0.0023 | 0.0020 |
| R2 | 0.99 | 0.99 | 0.99 | 0.99 |
| Elovich | α (mmol g-1 min‑1) | 0.016 | 0.011 | 0.0082 | 0.0058 |
| β (g mmol-1) | 200 | 227.27 | 256.41 | 263.16 |
| R2 | 0.93 | 0.93 | 0.95 | 0.97 |
| Intraparticle diffusion | Ki1(x103) | 1.10 | 1.15 | 1.03 | 0.97 |
| C | 0.0098 | 0.0066 | 0.0055 | 0.0047 |
| R2 | 0.98 | 0.99 | 0.99 | 0.96 |
| Ki2(x103) | 0.13 | 0.15 | 0.18 | 0.178 |
| R2 | 0.93 | 0.97 | 0.96 | 0.92 |

* + 1. **Reaction-based Models**

Fig. 1 Pseudo-first order plot for the adsorption of aqueous Cd (II) onto turmeric powder at different temperatures

**Fig. 2 Pseudo-second order plot for the adsorption of aqueous Cd (II) onto turmeric powder at different temperatures.**

Fig. 3 Elovich plot for the adsorption of aqueous Cd (II) onto turmeric powder at different temperatures

Figure 1-3 represent linear regression plots of pseudo-first order, pseudo-second order and Elovich models, respectively. For pseudo-first order model, coefficients of correlations were low and experimental and theoretical qe values were very different from each other. Thus, the results indicated that the adsorption of aqueous Cd (II) by turmeric powder was not Pseudo-first order reaction. Pseudo-secondorder and Elovich kinetic equations provided better for the experimental data. The pseudo-second order model assumes that biosorption follows a second order mechanism and the metal uptake rate is directly proportional to the square of the number of available (unoccupied) sites while Elovich equation is used to describe second order kinetics which is based on the assumption that the actual sorbent surfaces are energetically heterogeneous [36].

The value of qe (theoretical) calculated from pseudo-second order model and qe (experimental) were quite close to each other. Moreover, higher value coefficient of correlation for pseudo-second order kinetic and Elovich kinetic models suggested that the rate limiting step may be chemical adsorption. This result can be expected because most probably the surface of turmeric powder behaved like a chelate exchanger due to the presence of curcuminoids, protein and carbohydrates and therefore Cd (II) sorption by turmeric powder followed Elovich and second-order kinetic model.

The values of k2 and ho decreased from 0.034 to 0.023mmolg‑1 and0.0031 to 0.0018 g mmol-1min-1, respectively fortemperature variation from 298K to 313K which indicated exothermic nature of the Cd(II)-turmeric interaction. Initial adsorption rate, α (mmolg-1min-1), estimated from Elovich model showed the same trend. These results were in accordance with thermodynamic parameters obtained for Cd (II) adsorption onto turmeric powder.

* + 1. **Diffusion-based Model**

**Intraparticle diffusion**

Figure 4 presents intrapartilce diffusion plot for adsorption of aqueous Cd (II) onto turmeric powder.

Fig. 4 **Intrapartilce diffusion plot for the adsorption of aqueous Cd (II) onto** turmeric powder at different temperatures

Multilinearity in the qt versus t1/2 plot showed two separate regions which indicated that the sorption process followed two phases i.e. at least two steps were involved in the intraparticle diffusion process. If the external mass transfer resistance is ignored then first linear portion represented macropore diffusion and the second linear region showed micropore diffusion to less accessible sites until equilibrium was reached.

Since slopes for first linear portion of plot were steep i.e. higher ki1 values, this step was rapid and hence not rate limiting step. The ki2 (mmol g-1 min-0.5) represented slope of second linear region in the plot and it had been taken as the intraparticle diffusion constant. The intercept of the first linear part, C, was taken as the boundary layer thickness. Value of the intercept is a measure of the extent of surface sorption i.e. larger intercept suggests greater role of surface sorption in the rate-determining step [37]. The values of intraparticle diffusion coefficients, ki1 and ki2, and boundary layer thickness constants, C, at different temperatures are given in Table 1. The values of ki1 and ki2 represent diffusion rates of the surface adsorption and intraparticle diffusion stages, respectively. Initially, Cd (II) ions uptake by the exterior surface of turmeric powder was rapid. Followed by saturation of exterior surface, the Cd (II) ions were adsorbed by the interior particle surfaces by entering into the adsorbent particles through the pores within the particles. Gradually, the diffusion rate became slower with decrease in the adsorbate concentration and eventually diffusion equilibrium was attained. Low ki2 values suggest that intraparticle diffusion is the rate-limiting step in adsorption process but the plot of qt versus t1/2 did not yield a straight line passing through the origin. Therefore the adsorption rate for the Cd (II) adsorption onto turmeric powder is not solely pore diffusion controlled.

* + 1. **Activation Energy**

The values of activation energies were calculated from the slope of plot of lnk2 versus 1/T (Figure 5), which was found to be 0.82 kJ mol-1 for aqueous Cd (II) adsorption onto turmeric powder. The rate controlling step can be characterized partly by its activation energy. Values of activation energy can provide information about the type of adsorption. Low activation energies (5–40 kJ mol-1) are associated with physisorption, whereas higher activation energies (40–800 kJ mol-1) are indicative of chemisorption [38].

Fig. 5 lnk2 versus 1/T for the activation parameter for Cd(II) adsorption onto turmeric powder

The results obtained for the adsorption of aqueous Cd(II) onto turmeric powder indicated low energy requirements and can be associated with physisorption because weak attractive forces were involved in physical adsorption. Therefore, the affinity of turmeric powder for Cd(II) ions may be attributed to Van der Waals forces or electrostatic attractions.

1. **CONCLUSION**

Present work was aimed at to understand kinetics mechanism of the adsorption of aqueous Cd (II) onto turmeric because it would be useful in determination and evaluation of turmeric’s adsorption efficiency. Various reaction and diffusion based models were applied on experimental data. It was found that aqueous Cd (II) adsorption onto turmeric followed pseudo-second order and Elovich kinetic models. Moreover, the values of activation energies for adsorption of aqueous Cd (II) onto turmeric were also determined using slope of the lnk2 versus 1/T plot, which was found to be 10.82 kJ mol-1 suggesting weak van der Waals interactions between Cd (II) and turmeric.

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