Removal of Cu (II) Ions from Aqueous Solutions by Turmeric Powder

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Summary: Copper is an essential nutrient, but it is toxic at high intake levels. The presence of copper(II) ions causes serious toxicological concerns, it is usually known to deposit in brain, skin, liver, pancreas and myocardium. In this work the ability of turmeric to remove copper (II) ions from aqueous solution was studied. Adsorption of metals ions by turmeric powder may be used as a natural remedy for sequestration of toxic metals which are ingested through daily food intake. It was found that adsorption increased with increasing contact time, pH, temperature, adsorbent dose. The equilibrium data were satisfactorily described by Freundlich isotherm model. Adsorption of Cu (II) by turmeric powder was followed by pseudo 2[nd] order kinetics.

Introduction

Due to traditional food habits, a large amount of vegetables and fruits are consumed by Pakistani population in both raw and cooked form. Among different food systems, vegetables are most exposed food to environmental pollution. Untreated sewage and industrial water is commonly used for the cultivation of vegetable around the urban area of Pakistan [1]. Different studies have been carried out to estimate the heavy metals in vegetable grown in industrially polluted and non-polluted area [2-4]. Copper, one of these heavy metals, is an essential nutrient for various metabolic processes. Because it is required only in trace amounts, copper becomes toxic at high concentrations. Children under 10 years of age are more susceptible to copper toxicity [5]. It is generally known to deposit in brain, skin, liver, pancreas and myocardium [6].

Turmeric is widely used as spice in South Asian cookings. Sometimes it is also used as a coloring agent. It is used in canned beverages, baked products, dairy products, ice cream, yogurt, yellow cakes, orange juice, biscuits, popcorn-color, sweets, cake icings, cereals, sauces, gelatins, etc. It is an essential ingredient in most commercial curry powders. It contains protein (6.3 %), fat (5.1 %), minerals (3.5 %), carbohydrates (69.4 %), and moisture (13.1 %). Curcumin (3-4 %) is responsible for the yellow colour [7] and it is considered as most important chelating agent for toxic metals [8, 9]. The protective role of turmeric is mainly credited to the presence of curcumin. But poor bioavailability and rapid metabolism of curcumin could be a reason to question these studies [10]. Therefore there is a need to look for other factors playing their role to make turmeric powder a powerful remedy against toxic metal effects [11]. Due to the presence of curcuminoids, proteins, carbohydrates etc, turmeric powder may have a strong potential to sequester 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. Cumin, another important spice, is tested and found capable to bind toxic metals by similar processes [12]. Milk protein (casein) is also found to exhibit biosorptive properties for toxic metal ions in biosystem [13].

The objective of this research is to test the overall ability of turmeric as a sequestering substance for copper (II) ions from aqueous solution as a function of initial concentration, contact time, pH and temperature. It may be helpful to establish that turmeric powder can adsorb toxic metals and adsorption of metals ions by turmeric powder may be used as a natural remedy for sequestration of toxic metals which are ingested through daily food intake.

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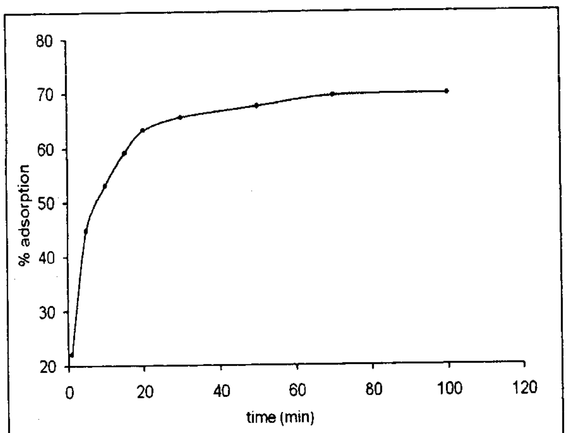
Results and Discussion

Effect of Contact Time

A plot of percentage adsorption versus adsorption time is shown in Fig. 1. It shows that the rate of metal uptake was rapid in the early stages but gradually decreased and becomes constant when equilibrium was reached. 65% of the metal was absorbed within initial 30 minutes. In the initial stages the removal efficiency by turmeric powder increased rapidly due to the abundant availability of active binding sites on the biomass, and with gradual occupancy of these sites, the sorption became less efficient in the later stages [14].

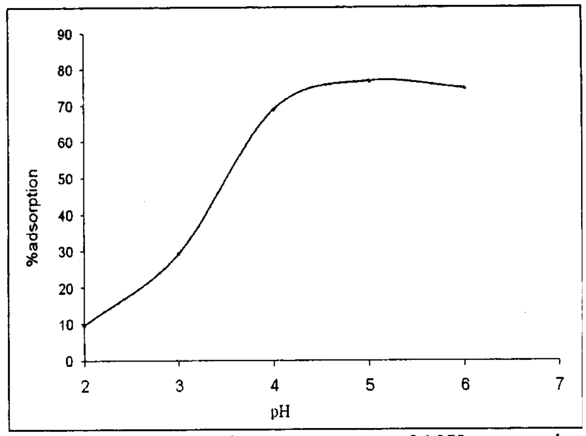


(Initial pH 6, temperature 310K, turmeric dose 10g/L, [Cu (II)] 0.67mmol/L)

Fig. 1: Effect of contact time on adsorption of Cu (II) by Turmeric Powder.

Effect of pH

pH of the solution influences electrostatic binding of metal ions to adsorbent functional groups and has been found as an important parameter governing metal adsorption on adsorbent. Fig. 2 shows the effect of pH on the removal of Cu (II) onto turmeric powder from aqueous solution. It can be seen that the adsorption is very low in strong acidic medium. After pH 3, uptake increases sharply up to pH 5 and a plateau was reached at around pH 5.0-6.0. At low pH the Cu (II) ions compete with the H^+ ions in the solution for the active sites and therefore less adsorption occurs. The surface charge of the biomass materials strongly depends upon pH. Therefore at



(Contact time 30 min, temperature 310K, turmeric dose 10g/L, [Cu (II)] 0.67mmol/L)

Fig. 2: Effect of pH on adsorption of Cu (II) by Turmeric Powder.

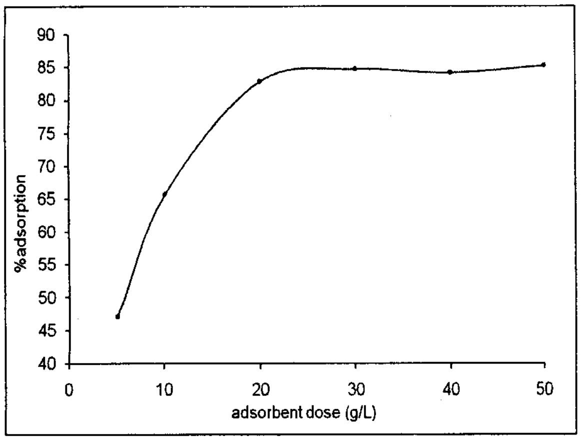
high pH values surface of the adsorbent has a higher negative charge which results higher attraction of Cu (II) ions. Experiments could not be conducted at higher pH values because metal precipitation appeared at higher pH values.

Effect of Adsorbent Dose

In another adsorption experiment all the variables were kept constants except the amount of adsorbent. 5g/l, 10g/l, 20g/l, 40g/l, 50g/l adsorbent dose was used to observe the effect of adsorbent amount on metal uptake and results are presented in Fig. 3. It was found that at lower doses metal uptake is directly proportional to the amount of adsorbent and percentage adsorption increases with increasing adsorbent amount but after a certain point metal adsorption becomes fairly constant and independent of the adsorbent amount. This might be due to the attainment of equilibrium between adsorbate concentration and adsorbent amount at existing temperature and pH which made adsorbent incapable of further adsorption. Increase in adsorption is because of an increase in number of metal binding sites of the adsorbent, which results in the high percent adsorption of Cu (II).

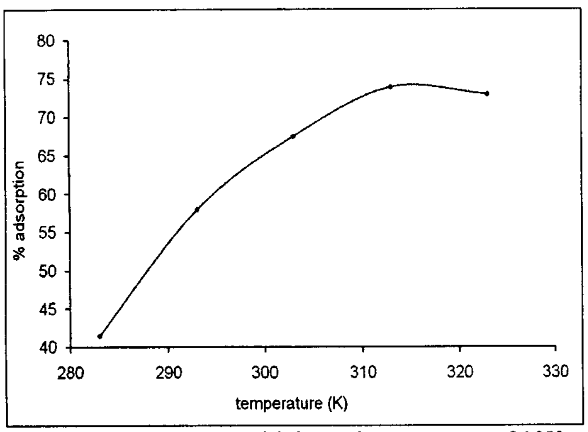
Effect of Temperature

Temperature is a crucial parameter in adsorption reactions. The data presented in Fig. 4 shows increase in adsorption at different



(Contact time 30min, Initial pH 6, temperature 310K, [Cu (II)] 0.67mmol/L).

Fig. 3: Effect of adsorbent dose on adsorption of Cu (II) by Turmeric Powder



(Contact time 30min, Initial pH 6, temperature 310K, turmeric dose 10g/L, [Cu (II)] 0.67mmol/L)

Fig. 4: Effect of temperature on adsorption of Cu (II) by Turmeric Powder.

temperatures (283 °C-323 °C).Increase in adsorption at high temperature could be due to an increase in collision frequency and greater mobility of Cu (II) ions with increase in temperature. There might be the availability of more active binding sites because of the bond rupture of functional groups onto the surface of turmeric powder at high temperatures [15, 16]. Increase in adsorption with increasing temperature can also lead to conclude that the sorption of Cu (II) onto turmeric powder is an endothermic process.

Equilibrium Parameters of Adsorption

In order to understand the effect of initial concentration another adsorption experiment was conducted with different initial concentration of adsorbate solutions keeping all other variables constant. Two adsorption models, the Langmuir model and Freundlich equation were applied to the experimental data.

The Freundlich equation deals with heterogeneous surface adsorption and can be expressed as follows [17]:

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

where q_e (metal uptake mmol/g) is the amount of Cu (II) ions adsorbed on the biosorbent at equilibrium C_e(mmol/L) is equilibrium concentration of Cu (II) in the solution. K_F is the relative indicator of adsorption capacity (mmol/g) and n indicates the intensity of adsorption [18, 19]. The values of K_F and n are presented in Table 1. n value is found to be greater than 1which indicates favorable sorption [20].

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

Langmuir					Freundlich			
q_o mmol g^{-1}	b L $mmol^{-1}$	R_L	R^2	Error (%)	n	K_F mmol g^{-1}	R^2	Error (%)
0.16	1.29	0.34	0.98	1.04	1.33	0.109	0.99	2.30

The Langmuir model, which was initially developed to study physical adsorption, is a useful tool for the interpretation of biosorption profiles. The Langmuir models can be expressed as follows[21]:

$$q_e = \frac{q_o b C_e}{1 + b C_e} \qquad (2)$$

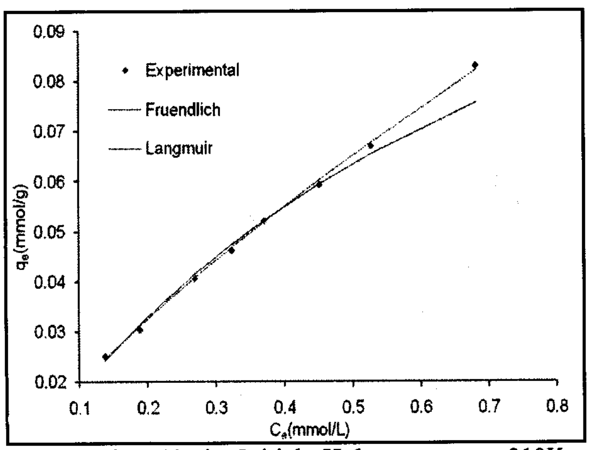
where q_o(mmol/g) is the maximum sorbate uptake under the given conditions and b (L/mmol) is the Langmuir constant related to the affinity between the sorbent and sorbate. The essential feature of Langmuir isotherm can be expressed by means of 'R_L' a dimensionless constant referred to as separation factor or equilibrium parameter R_L is calculated using the following equation where b is the Langmuir adsorption constant (L $mmol^{-1}$) and C_o is the highest initial metal (II) concentration (mmol L^{-1}).

$$R_L = \frac{1}{1 + b C_o} \qquad (3)$$

R_L is in the range of 0–1 which indicates favorable adsorption [22]. It was difficult to compare the maximum capacity with other reported studies due to differences in experimental conditions and models used to fit the data in each study. However, under similar conditions, a comparison of maximum adsorption capacities, q_o, of turmeric powder with those of some other biosorbents reported in literature is given in Table-2. It shows that turmeric powder has comparable adsorption capacity with other biosorbents.

Table-2: Values of q_o for the adsorption of Cu (II) onto turmeric powder in comparison with different biosorbents.

biosorbent	q_o (mmol/g)	Reference
Turmeric powder	0.13	This work
Seeds of capsicum annum	0.39	23
Carrot residues	0.49	18
Areca, a chewing nut	0.046	24
Grape stalks	0.16	25



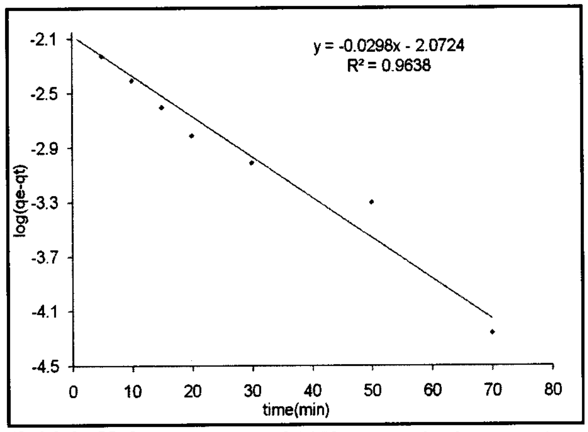
(Contact time 50min, Initial pH 6, temperature 310K, turmeric dose 10g/L, [Cu (II)] 0.38mmol/L-1.51mmol/L)

Fig. 5: Adsorption Isotherm Plot for the adsorption of Cu (II) by Turmeric Powder.

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

$$Error(\%) = \frac{100}{N}\sum_{i=1}^{n}\frac{|q_{\text{mod}} - q_{\text{exp}}|}{q_{\text{exp}}} \quad (4)$$

where q_{mod} and q_{exp} are the model prediction and the experimental data respectively and N is the number



(Initial pH 6, temperature 310K, turmeric dose 10g/L, [Cu (II)] 0.67mmol/L)

Fig. 6: Pseudo 1st order kinetics for the adsorption of Cu (II) by turmeric powder.

of data points. From the values of mean percentage error (%) and R^2 it can be concluded that Freundlich model better fitted on the experimental data.

Kinetic Modelling

The order of adsorbate-adsorbent interaction has been described by various kinetics models. The pseudo 1st order rate expression is generally described by the following expression [26].

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \quad (5)$$

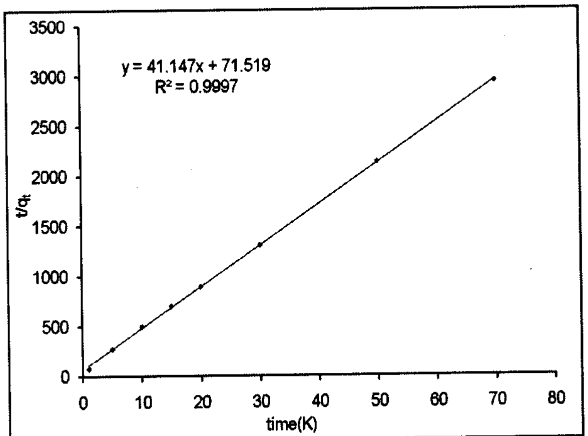
where q_e is the amount of Cu (II) adsorbed at equilibrium per unit weight of turmeric (mmol/g); q_t is the amount of copper adsorbed at any time (mmol/g); and k_1 is the rate constant (min^{-1}). Integrating and linearizing the above equation will take the form as following.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (6)$$

It is required that calculated equilibrium adsorption capacity values q_e(theoretical) should be in accordance with the q_e(experimental) values. For pseudo 1st order model, linear correlation coefficient and mean percentage error values are not good. Experimental and theoretical q_e values are also not in

Table-3: Pseudo 1st and 2nd order kinetic model parameters for the adsorption of Cu (II) by turmeric powder.

	Pseudo 2nd order kinetic model				Pseudo 1st order kinetic model			
q_e, (exp.) mmol/g	q_e (mmol/g)	k_2 (g/mmol min)	R^2	Error (%)	q_e (mmol/g)	k_1 (min^{-1})	R^2	Error (%)
0.0238	0.024	23.67	0.99	4.08	0.0085	0.067	0.96	4.66



(Initial pH 6, temperature 310K, turmeric dose 10g/L, [Cu (II)] 0.67mmol/L)

Fig. 7: Pseudo 2nd order kinetics for the removal of Cu (II) by turmeric powder

agreement with each other. So the results suggest that the adsorption of Cu (II) by turmeric powder in aqueous solutions is not Pseudo 1st order reaction.

The best fit for the experimental data of this study was achieved by the application of pseudo 2nd order kinetics equation. The pseudo 2nd order is based on the assumption that biosorption follows a 2nd order mechanism. So the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites [27].

$$\frac{t}{q}=\frac{1}{k_2 q_e^2}+\frac{1}{q_e}t \qquad (7)$$

where k_2 is the adsorption constant of pseudo 2nd order biosorption (g/mmolmin). Smaller values of mean percentage error (%) and coefficient of correlation for pseudo 2nd order kinetic model suggest that the rate limiting step may be chemical adsorption[28]. 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 sorption of Cu (II) by turmeric powder followed the second order kinetic model.

Experimental

Commercially available turmeric powder was used without further purification. Analytical grades of $CuSO_4.5H_2O$, HNO_3 and NaOH were used. 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 glass wares 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 adsorption experiments were conducted by varying initial concentration of adsorbate (0.38mmol/L-1.51mmol/L), contact time (1-100min), pH (2-6), adsorbent dose(5-50g/L) and temperature (283-323K).

The experiments were carried out in a specially designed double walled glass cell. The temperature was maintained by circulating water through a thermostat. 50 ml of adsorbate solutions were used. The pH of the solution was maintained at a desired value by adding 0.1M HNO_3 or NaOH. The contents were stirred for the required time period at constant stirring rate and then suction filtered. 3 ml of conc. HNO_3 is added to 25 ml of the filtrate and final volume made to 50 ml. Equilibrium concentrations of Cu (II) in the solutions were determined by Atomic Absorption Spectrophotometry.

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 Cu (II).
Metal uptake (q) is determined as follows

$$q_e = V \times \frac{C_i - C_e}{S} \qquad (8)$$

where q_e (metal uptake mmol/g) is the amount of Cu (II) 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 (mmol/L) are the initial and equilibrium concentrations of Cu (II) in the solution, respectively and S (g) is the amount of added biosorbent on a dry basis.

Conclusions

The present work evaluated the removal of copper (II) from aqueous solutions using turmeric powder. It was found that the adsorption of Cu (II) by turmeric powder is affected by contact time, pH, adsorbent dose and temperature. Biosorption efficiency increased with increasing contact time, pH, adsorbent dose and temperature. The equilibrium data was satisfactorily described by Freundlich isotherm model. The adsorption followed pseudo 2^{nd} order kinetics

The result of this studies have shown that turmeric powder can be used for the sequestration of Cu (II) from aqueous solutions and may be considered for deeper studies to see if it can decrease the bioavailability of toxic metals ingested with daily food intake.

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