

Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of *Capsicum annuum*

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Abstract

Adsorption of copper ions onto *Capsicum annuum* (red pepper) seeds was investigated with the variation in the parameters of pH, contact time, adsorbent and copper(II) concentrations and temperature. The nature of the possible adsorbent and metal ion interactions was examined by the FTIR technique. The copper(II) adsorption equilibrium was attained within 60 min. Adsorption of copper(II) ions onto *C. annuum* seeds followed by the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. Maximum adsorption capacity (q_{\max}) of copper(II) ions onto red pepper seeds was $4.47 \times 10^{-4} \text{ mol g}^{-1}$ at 50°C . Three kinetic models including the pseudo-first-order, pseudo-second-order and intraparticle diffusion equations were selected to follow the adsorption process. Kinetic parameters such as rate constants, equilibrium adsorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. It was indicated that the adsorption of copper(II) ions onto *C. annuum* seeds could be described by the pseudo-second-order kinetic model and also followed the intraparticle diffusion model up to 60 min, but diffusion is not only the rate controlling step. Thermodynamics parameters such as the change of free energy, enthalpy and entropy were also evaluated for the adsorption of copper(II) ions onto *C. annuum* seeds.

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1. Introduction

As a result of industrial activities, many chemical substances such as heavy metals, organic and synthetic compounds generate pollution in the environment and result in deterioration of some ecosystems. Unlike other pollutants, heavy metal contamination in the environment poses a serious health problems due to their accumulation in living tissues throughout the food chain as a nonbiodegradable pollutants [1]. The main sources of heavy metal pollution include textile, electroplating, painting, dyeing, surface treatment industry, etc. [2].

The commonly used traditional methods for the treatment of metal bearing effluents include chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, solvent extraction, ion exchange and evaporation, all show several disadvantages, such as high cost, incomplete metal removal, low selectivity, high energy requirements, the generation of toxic slurries that are difficult to be eliminated [3]. In recent years, there has been considerable interest in the use of agricultural by-products as adsorbents to remove toxic metals from aqueous solution by adsorption since they are cheap and have high efficiency adsorbents for adsorption of pollutants [4–6].

The removal of copper(II) ions from industrial wastewaters has received considerable attention in recent years [7]. Agricultural wastes such as tree fern [5], soybean hulls [8], cotton seed hulls [8], spagnum most peat [9], banana pith [10], apple wastes [11], sawdust [12], sunflower stalks [13], pine bark [14], carrot residues [15], cork biomass [16], groundnut

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shells [17], wheat shell [18], grape stalks [19] and tea waste [20] have been used to remove copper(II) ions from water solution by adsorption, but new, locally available, highly effective and economical adsorbent materials are still needed. One of the agricultural by-products from waste of pepper paste factory is *Capsicum annuum* seeds, which are an abundant, cheap and readily available residue. To our knowledge, they have not been used for heavy metal ions removal from aqueous solutions.

The characteristics of the adsorption behavior are generally inferred in terms of both adsorption kinetics and equilibrium isotherms. They are also an important tool to understand the adsorption mechanism for the theoretical evaluation and interpretation of thermodynamic parameters [21,22].

The objective of this study was to investigate the possible use of *C. annuum* seeds as an alternative adsorbent material for removal of copper(II) ions from aqueous solutions. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) equations were used to fit the equilibrium isotherm. The adsorption capacity was determined using various kinetic models. The dynamic behavior of the adsorption was investigated on the effect of concentration, temperature and pH. The thermodynamic parameters were also evaluated from the adsorption measurements.

1.1. Equilibrium parameters of adsorption

Equilibrium data, generally known as adsorption isotherms, are basic requirements to understand the mechanism of the adsorption. Classical adsorption isotherm models, Langmuir, Freundlich and Dubinin–Radushkevich (D–R), are used to describe the equilibrium between adsorbed copper(II) ions on *C. annuum* seeds (q_e) and copper(II) ions in solution (C_e) at a constant temperature.

The Langmuir adsorption isotherm assumes that adsorption occur at specific homogeneous sites within the adsorbent and has found successful application in many monolayer adsorption process. The linear form of the Langmuir isotherm equation is [23]:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max} K_L} \right) \frac{1}{C_e}, \quad (1)$$

where q_e is the equilibrium copper(II) concentration on the adsorbent (mol g^{-1}); C_e , the equilibrium copper(II) concentration in the solution (mol dm^{-3}); q_{\max} , the monolayer adsorption capacity of the adsorbent (mol g^{-1}); and K_L , the Langmuir adsorption constant ($\text{dm}^3 \text{mol}^{-1}$) related to the free energy of adsorption. A plot of $1/q_e$ versus $1/C_e$ for the adsorption gives a straight line of slope $1/(q_{\max} K_L)$ and intercept $1/q_{\max}$.

The effect of isotherm shape has been discussed [24] with a view to predict whether an adsorption system is favorable or unfavorable. The essential feature of the 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,

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

where K_L is the Langmuir constant ($\text{dm}^3 \text{mol}^{-1}$) and C_o the highest initial copper(II) concentration (mol dm^{-3}).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. A linear form of the Freundlich equation is [25].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (3)$$

where K_F and n are Freundlich adsorption isotherm constants ($\text{dm}^3 \text{g}^{-1}$), being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. The plot of $\ln q_e$ versus $\ln C_e$ for the adsorption was employed to generate K_F and n from the intercept and the slope values, respectively.

The Dubinin–Radushkevich (D–R) isotherm is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant adsorption potential. It was applied to distinguish between the physical and chemical adsorption [26] of copper(II) ions. The linear form of (D–R) isotherm equation [27] is

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

where β is a constant related to the mean free 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 $RT \ln(1 + (1/C_e))$, where R ($\text{J mol}^{-1} \text{K}^{-1}$) is the gas constant; and T (K), the absolute temperature. Hence, by plotting $\ln q_e$ against ε^2 it is possible to generate the value of q_m (mol g^{-1}) from the intercept, and the value of β from the slope.

The constant β gives an idea about the mean free energy E (kJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship [28–30]:

$$E = \frac{1}{(2\beta)^{1/2}}. \quad (5)$$

1.2. Kinetic parameters of adsorption

Kinetics of adsorption is one of the most important characteristics to be responsible for the efficiency of adsorption. Various kinetic models including the pseudo-first-order, pseudo-second-order and intraparticle diffusion have been applied for the experimental data to predict the adsorption kinetics. Among them pseudo-first-order rate equation is [31,32],

$$\frac{1}{q_t} = \frac{1}{q_1} + \frac{k_1}{q_1 t}, \quad (6)$$

where q_1 and q_t are the amounts of the copper(II) ions adsorbed at equilibrium and at time t (mg g^{-1}) and k_1 is the

pseudo-first-order rate constant (min^{-1}) of adsorption. Values of k_1 can be calculated from the slope of the plots of $1/q_t$ versus $1/t$.

The pseudo-second-order kinetic model [33] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t, \quad (7)$$

where q_2 is the maximum adsorption capacity (mg g^{-1}) for the pseudo-second-order adsorption; q_t , the amount of copper(II) ions adsorbed at equilibrium at time t (mg g^{-1}); k_2 , the equilibrium rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). Values of k_2 and q_2 can be calculated from the plot of t/q_t against t .

The intraparticle diffusion equation [34] can be written as follows:

$$q_t = k_p t^{1/2} + C, \quad (8)$$

where C is the intercept and k_p , the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$).

The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism and the kinetic results were then analyzed by using the intraparticle diffusion model. According to this model, the plot of uptake, q_t , versus the square root of time ($t^{1/2}$) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate-controlling step [35–37]. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and these further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The slope of linear portion from the figure can be used to derive values for the rate parameter, k_p , for the intraparticle diffusion.

1.3. Thermodynamic parameters of adsorption

Because K_L is equilibrium constant, its dependence with temperature can be used to predict thermodynamic parameters including change in the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated to the adsorption process and were determined by using following equations:

$$\Delta G^\circ = -RT \ln K_L, \quad (9)$$

$$\ln K_L = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

The plot of $\ln K_L$ as a function of $1/T$ yields a straight line from which ΔH° and ΔS° can be calculated from the slope and intercept, respectively.

2. Experimental

2.1. Preparation of the adsorbent material

The *C. annuum* used in this study were purchased from a local market. The seeds were separated and extensively washed with pure water followed by drying at 80°C in an oven. Dried adsorbent was crushed and sieved to select particle size of $300 \mu\text{m}$ by using ASTM standard sieve and stored for further use.

2.2. Copper(II) solutions

A stock solution of copper(II) was prepared by dissolving an accurate quantity of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in deionized water. Other concentrations prepared from stock solution by dilution varied between 75 and 250 mg dm^{-3} and the pH of the working solutions was adjusted to desired values with 0.1 M HNO_3 or 0.1 M NaOH . Fresh dilutions were used for each experiment. All the chemicals used were in analytical grade.

2.3. Batch adsorption studies

All batch experiments were conducted with adsorbent samples in a beaker on a magnetic stirrer at 200 rpm to elucidate the optimum conditions of pH, adsorbent and copper(II) ion concentrations.

The effect of pH on the adsorption rate of copper(II) onto *C. annuum* by-product was determined by equilibrating the adsorption mixture with dried adsorbent and 50 ml of 100 mg dm^{-3} copper(II) solution at different pH values between 1 and 6 . The effect of adsorbent concentration was studied by using adsorbent sample ranging from 0.4 to 4.0 g dm^{-3} .

For the assessment of the effect of metal ion concentration on adsorption, metal solutions ranging from 75 to 250 mg dm^{-3} were prepared and used. The optimum pH and adsorbent concentration were then determined as 5 and 1.2 g dm^{-3} , respectively used throughout all adsorption experiments, which were conducted at various time intervals between 5 and 120 min and temperatures of 20 – 50°C . When the adsorption procedure completed, the solutions were centrifuged at 4500 rpm for 2 min and the supernatants were then analyzed for residual copper(II) ion concentrations.

The adsorption of copper(II) onto *C. annuum* seeds was evaluated at constant temperatures of 20 – 50°C for the adsorption isotherms as well as pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models.

2.4. Analytical methods

The final copper(II) concentrations of the solutions were determined by using an atomic absorption spectrophotometer (Hitachi 180-70, Japan) with an air-acetylene flame. Deuterium background correction was used. The spectral slit width, the working current and wavelength were 1.3 nm ,

7.5 mA and 324.8 nm, respectively. The instrument calibration was periodically checked by using standard metal solutions for every 10 reading. Infrared spectra of dried and copper(II) loaded *C. annuum* seeds prepared as KBr discs were recorded in a Bruker Tensor 27 infrared spectrophotometer.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra of dried unloaded and copper(II)-loaded *C. annuum* seeds in the range of 400–4000 cm^{-1} were taken and compared with each other to obtain information on the nature of the possible adsorbent-metal ion interactions and presented in Fig. 1. The broad stretching absorption bands at 3280–3303 cm^{-1} , representing –NH and bonded –OH groups. These bands intensities decreased only in the FTIR spectrum of copper(II)-loaded *C. annuum* seeds. The change in the intensities decrease of the amino and hydroxyl groups in FTIR spectrum indicated that these two groups possibly involved in the copper(II) adsorption. The bands observed at 2865 and 2932 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations of the –CH₃ and –CH₂ groups and their bending vibrations are 1371 and 1445 cm^{-1} for unloaded and copper(II)-loaded *C. annuum* seeds. Carbonyl stretching band of un-ionized carboxylates of adsorbent was observed at 1740 cm^{-1} . The bands at 1650 cm^{-1} and 1540 cm^{-1} correspond to carbonyl stretching vibration of amide considered to be due to the combined effect of double-bond stretching vibrations [38] and –NH deformation band

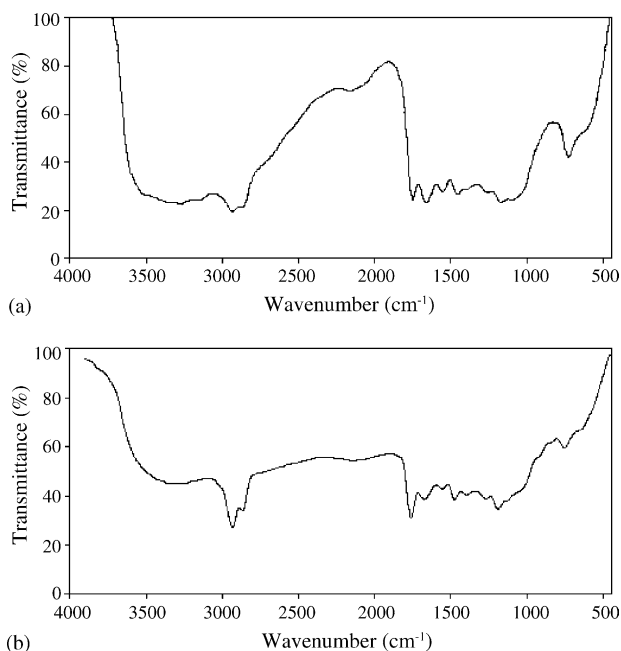


Fig. 1. FTIR spectra of (a) unloaded and (b) metal loaded copper(II) onto *C. annuum* seeds.

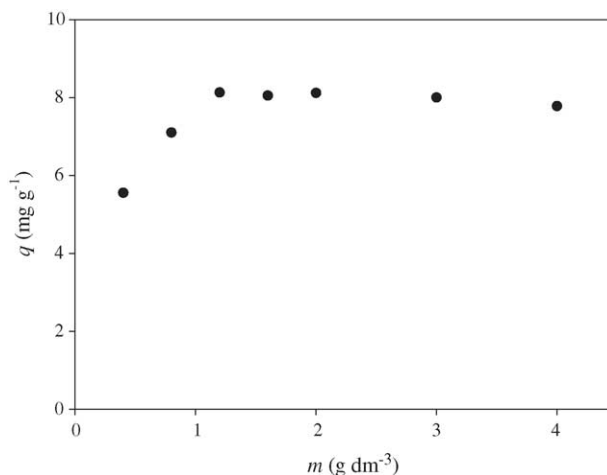


Fig. 2. Effect of adsorbent concentration for the adsorption of copper(II) onto *C. annuum* seeds at 20 °C.

for unloaded and copper(II)-loaded *C. annuum* seeds, respectively. Their intensities in the spectrum of unloaded biomass decreases and separately the –NH deformation band shifts to 1532 cm^{-1} in the copper(II)-loaded biomass. This behavior reflects the interaction between the amino groups and metal ions. Therefore, *C. annuum* seeds provide more adsorption sites for copper(II) ions.

The 1085 cm^{-1} band is due to C–O stretching of carbonyl groups and the bending vibration of hydroxyl groups for unloaded *C. annuum* seeds but the disappearance of this band after the copper(II)-loaded *C. annuum* seeds suggests that this type of functional groups is likely to participate in metal binding.

3.2. Effect of adsorbent concentration on metal removal

The results of the experiments with varying adsorbent concentrations are presented in Fig. 2. With increase in adsorbent concentration, from 0.4 to 2.0 g dm^{-3} the amount of adsorbed copper(II) removal increases from 5.55 to 8.12 mg g^{-1} , as the number of possible binding sites are increased. The amount of *C. annuum* seeds for further adsorption experiments was selected as 1.2 g dm^{-3} .

3.3. Effect of pH

The pH of solution has been identified as the most important variable governing metal adsorption on adsorbent. This is partly because hydrogen ions themselves are strongly competing with adsorbates. Fig. 3 indicates the effect of pH on the removal of copper(II) onto *C. annuum* seeds from aqueous solutions. It can be seen from Fig. 3 that adsorption capacity are very low at strong acidic medium (pH 1–3). After pH 3, uptakes increase sharply up to pH 5 since more metal binding sites could be exposed and carried negative charges, with subsequent attraction of metal ions with positive charge and adsorption onto the adsorbent surface. A decrease in adsorp-

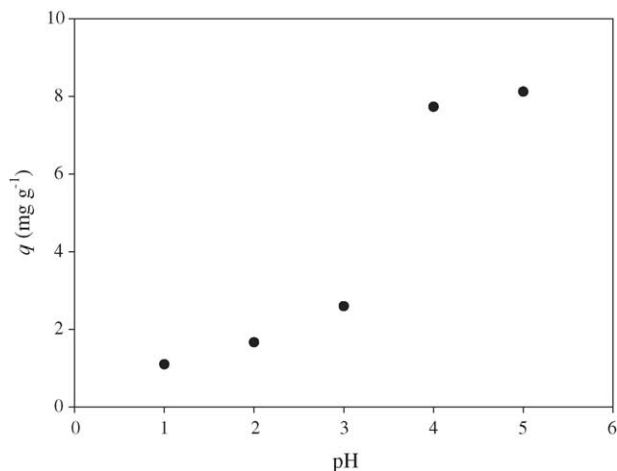


Fig. 3. Effect of pH for the adsorption of copper(II) onto *C. annuum* seeds at 20 °C.

tion of copper(II) was noticed above pH 5. Experiments were carried out with the pH values of up to 5 due to the fact that metal precipitation appeared at higher pH values and interfered with the accumulation or adsorbent deterioration [39–41].

3.4. Effect of equilibrium contact time

The adsorption capacity of copper(II) removed by *C. annuum* seeds versus contact time is illustrated in Fig. 4. It can be seen that the adsorbed amount of copper(II) ions increased with contact time up to 60 min, after that a maximum removal is attained. Therefore, 60 min was selected as the optimum contact time for all further experiments.

3.5. Effect of temperature on metal uptake

The equilibrium adsorption capacity of copper(II) onto *C. annuum* seeds was favored at higher temperatures. This

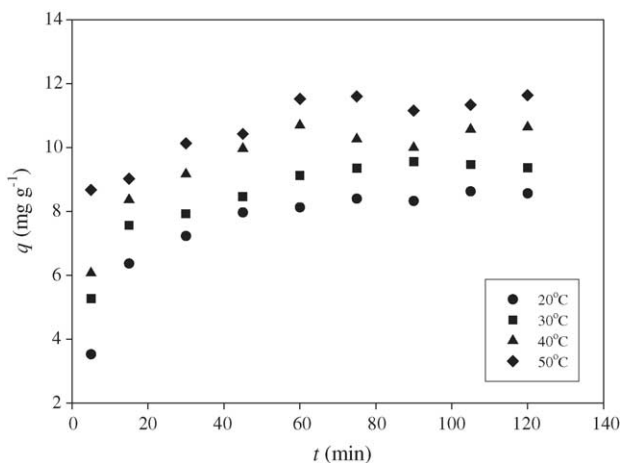


Fig. 4. The effect of contact time for the adsorption of copper(II) onto *C. annuum* seeds at various temperatures.

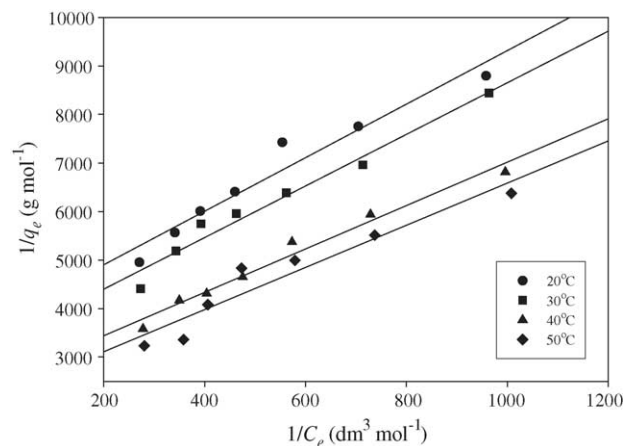


Fig. 5. Langmuir plots for the adsorption of copper(II) onto *C. annuum* seeds various temperatures.

may indicate that adsorption of copper(II) onto *C. annuum* seeds is chemical. An increase in the temperature from 20 to 50 °C leads to an increase in the adsorption capacity from 8.13 to 11.53 mg g⁻¹ at an equilibrium time of 60 min. Below equilibrium time, an increase in the temperature leads to an increase in the copper(II) adsorption, which indicates kinetically controlling process. After the equilibrium attained, the uptake increases with increasing temperature, this effect may be explained by availability of more active sites of adsorbent at higher temperatures.

3.6. Adsorption isotherms

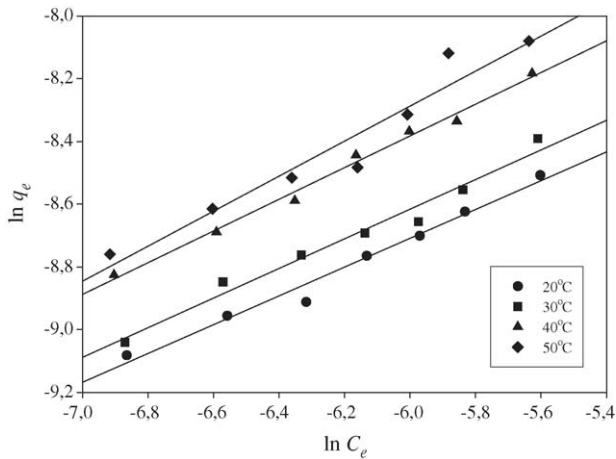
The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the adsorption. Several isotherm equations are available and three important isotherms are chosen in this study, which are namely the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms. The plots of linear form of Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption isotherms of copper(II) ions obtained at the temperatures of 20–50 °C are illustrated in Figs. 5–7. All of the isotherm model parameters for the adsorption of copper(II) onto *C. annuum* seeds are tabulated in Table 1. It is evident from these data that the surface of *C. annuum* seeds is made up of homogeneous and heterogeneous adsorption patches. In other words, all of the isotherm models fit very well when the r^2 values are compared in Table 1. It concluded that the adsorption of copper(II) ions onto *C. annuum* seeds is thus complex, involving more than one mechanism.

The maximum adsorption capacity (q_{\max}) of adsorbent calculated from Langmuir isotherm equation defines the total capacity of the adsorbent for copper(II). The adsorption capacity of adsorbent increased on increasing the temperature. The highest value of q_{\max} obtained at 50 °C is 4.47×10^{-4} mol g⁻¹. It appears to be the highest in comparison with the uptake obtained at the other temperatures (Table 1).

Table 1

Adsorption isotherm constants for the adsorption of copper(II) onto *C. annuum* seeds at various temperatures

t (°C)	Langmuir				Freundlich			Dubinin–Radushkevich (D–R)			
	q_{\max} (mol g ⁻¹)	K_L (dm ³ mol ⁻¹)	r_L^2	R_L	n	K_F (dm ³ g ⁻¹)	r_F^2	q_{\max} (mol g ⁻¹)	β (mol ² kJ ⁻²)	r_{D-R}^2	E (kJ mol ⁻¹)
20	2.63×10^{-4}	6.88×102	0.950	0.270	2.177	2.60×10^{-3}	0.982	6.23×10^{-4}	6.19×10^{-3}	0.975	8.99
30	3.00×10^{-4}	6.27×102	0.970	0.288	2.117	3.08×10^{-3}	0.975	7.10×10^{-4}	5.95×10^{-3}	0.972	9.17
40	3.93×10^{-4}	5.69×102	0.978	0.309	1.980	4.74×10^{-3}	0.992	9.80×10^{-4}	5.94×10^{-3}	0.989	9.17
50	4.47×10^{-4}	5.15×102	0.917	0.331	1.792	7.16×10^{-3}	0.936	1.24×10^{-3}	6.13×10^{-3}	0.928	9.03

Fig. 6. Freundlich plots for the adsorption of copper(II) onto *C. annuum* seeds various temperatures.

The value of R_L calculated from Eq. (2) is incorporated in Table 1. As the R_L values lie between 0 and 1, the adsorption process is favorable [24,42]. Further, the R_L values for this study at all temperatures studied are between 0.270 and 0.331, therefore, the adsorption is spontaneous.

One of the Freundlich constants K_F indicates the adsorption capacity of the adsorbent and the values of K_F at equilibrium at all temperatures lies a range of 2.60×10^{-3} to 7.16×10^{-3} dm³ g⁻¹. The other Freundlich constant n is a measure of the deviation from linearity of the adsorption and

the numerical values of n at all temperatures lies between 1.792 and 2.177 and is greater than unity, indicating that copper(II) ions are favorably adsorbed by *C. annuum* seeds at all the temperatures studied.

The mean free energy E (kJ mol⁻¹) of adsorption was connected with Dubinin–Radushkevich (D–R) adsorption isotherm and calculated from Eq. (5). This parameter gives information about adsorption mechanism as chemical ion-exchange or physical adsorption. The magnitude of E is between 8 and 16 kJ mol⁻¹, the adsorption process follows by chemical ion-exchange [43], while for the values of $E < 8$ kJ mol⁻¹, the adsorption process is of a physical nature [44]. The numerical value of adsorption of the mean free energies increased from 8.99 to 9.03 kJ mol⁻¹, when the temperature is increased at 20–50 °C, which may correspond to a chemical ion-exchange mechanism.

3.7. Kinetics of adsorption

In order to analyze the adsorption kinetics of copper(II) ions, three kinetic models, which are the pseudo-first-order, pseudo-second-order and intraparticle diffusion, have been applied for the experimental data. The plots of linear form of the pseudo-first-order, pseudo-second-order (Fig. 8) and intraparticle diffusion (Fig. 9) for the adsorption of copper(II) ions were obtained at the temperatures of 20–50 °C. The kinetic parameters for the adsorption of copper(II) onto *C. annuum* seeds are given in Table 2. The plots of $1/q_t$ ver-

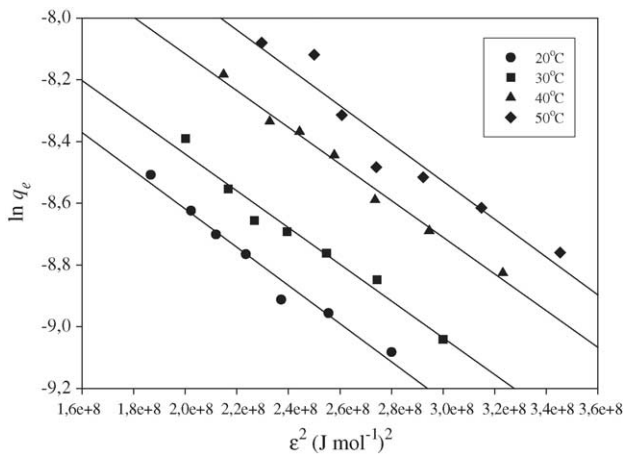
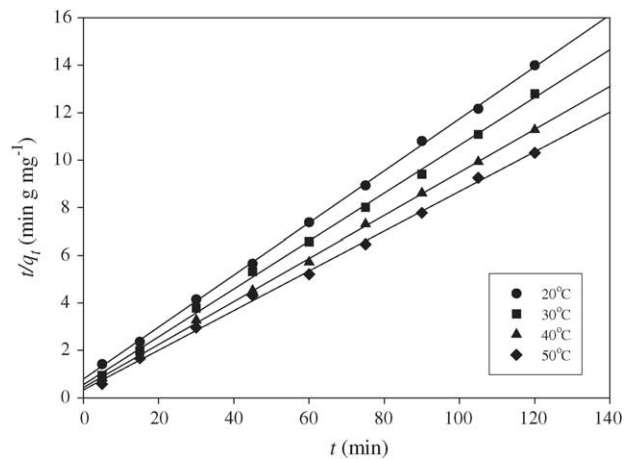
Fig. 7. Dubinin–Radushkevich (D–R) plots for the adsorption of copper(II) onto *C. annuum* seeds various temperatures.Fig. 8. Pseudo-second-order kinetic plots for the adsorption of copper(II) onto *C. annuum* seeds various temperatures.

Table 2

Kinetic parameters for the adsorption of copper(II) onto *C. annuum* seeds at various temperatures

t (°C)	k_1 (min ⁻¹)	q_1 (mg g ⁻¹)	r_1^2	k_2 (g mg ⁻¹ min ⁻¹)	q_2 (mg g ⁻¹)	r_2^2	k_p (mg g ⁻¹ min ^{-1/2})	C (mg g ⁻¹)	r_p^2
20	8.04	9.30	0.996	1.51×10^{-2}	9.13	0.999	0.802	2.47	0.885
30	4.18	9.62	0.982	1.83×10^{-2}	9.93	0.999	0.632	4.38	0.898
40	4.05	10.89	0.990	1.90×10^{-2}	11.04	0.999	0.767	4.82	0.947
50	1.76	11.32	0.723	2.06×10^{-2}	11.98	0.998	0.506	7.32	0.947

sus $1/t$ for the pseudo-first-order equation are not shown as a figure because the correlation coefficients for the pseudo-first-order model are lower than that of the pseudo-second-order model. Therefore, this implies that the adsorption of copper(II) onto *C. annuum* seeds does not follow the pseudo-first-order kinetic model.

The correlation coefficients obtained are greater than 0.998 for the pseudo-second-order model. These results imply that the adsorption system studied follows to the pseudo-second-order kinetic model at all time intervals.

The correlation coefficients for the intraparticle diffusion model are lower than that of the pseudo-second-order kinetic model but this model indicates that the adsorption of copper(II) *C. annuum* seeds may be followed by an intraparticle diffusion model up to 60 min.

The pseudo-second-order rate constants indicate a steady increase from 1.51×10^{-2} to 2.06×10^{-2} g mg⁻¹ min⁻¹ with an increase in the solution temperatures from 20 to 50 °C (Table 2), indicating that the adsorption of copper(II) ions onto *C. annuum* seeds is adsorption rate-controlled.

3.8. Thermodynamic parameters of adsorption

The thermodynamic parameters of ΔH° and ΔS° were obtained from the $\ln K_L$ versus $1/T$ plot (Fig. 10). The Gibbs free energies (ΔG°) were calculated from Eq. (9) and the results are given in Table 3. The negative values of ΔG° at all temperatures studied are due to the fact that adsorption process is spontaneous. The negative value of ΔH° suggests the

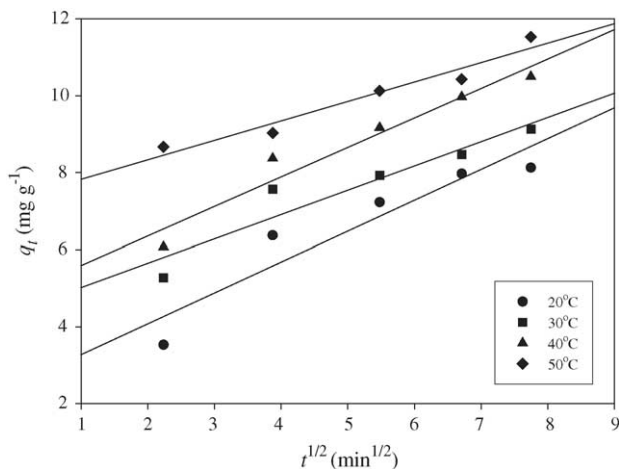


Fig. 9. Intraparticle diffusion plots for the adsorption of copper(II) onto *C. annuum* seeds various temperatures.

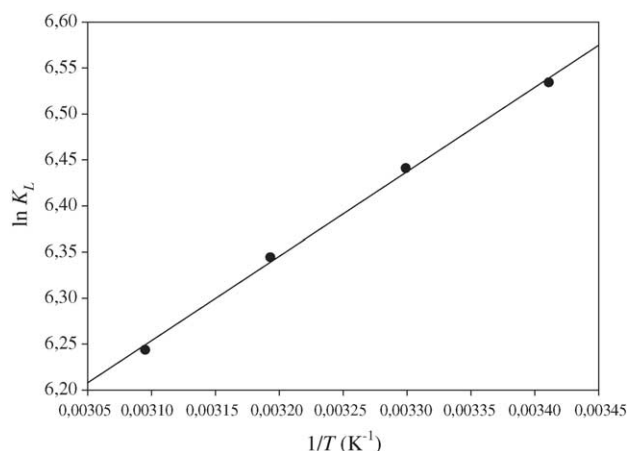


Fig. 10. Plot of K_L vs. $1/T$ for estimation of thermodynamic parameters for the adsorption of copper(II) onto *C. annuum* seeds.

Table 3

Thermodynamic parameters calculated from the Langmuir isotherm constant (K_L) for the adsorption of copper(II) onto *C. annuum* seeds

t (°C)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
20	-15.93		
30	-16.23	-7.63	28.35
40	-16.52		
50	-16.77		

exothermic nature of adsorption. The positive value of ΔS° suggests increased randomness at the solid/solution interface during the adsorption of copper(II) onto *C. annuum* seeds.

4. Conclusions

This study has revealed that one of the agricultural by-products *C. annuum* seeds, can be used to remove copper(II) ions from aqueous solution. The maximum adsorption capacity of *C. annuum* seeds for the removal of copper(II) was obtained at pH 5. Experiments were performed as a function of pH, contact time and temperature.

The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were used for the mathematical description of the adsorption of copper(II) ions onto *C. annuum* seeds depending on temperature and the isotherm constants were evaluated from these isotherms. Results indicated that the adsorption equilibrium data fitted very well to three isotherm models in the studied concentration range at all temperatures studied. The chemical ion-exchange

being important according to the values of mean free energies from D–R isotherm of adsorption were the range of 8.99–9.17 kJ mol⁻¹. The kinetics of copper(II) ions adsorption onto *C. annuum* seeds was based on the assumption of the pseudo-second-order mechanism and also followed the intraparticle diffusion model up to 60 min, whereas diffusion is not only the rate controlling step. The negative values of ΔG° confirm a favorable adsorption of copper(II) onto *C. annuum* seeds and the negative value of ΔH° leads to an exothermic nature of adsorption. It may be concluded from above results that *C. annuum* seeds can be used for elimination of heavy metal pollution from wastewater since it is a low-cost, abundant and locally available adsorbent.

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