

Mathematical modeling and thermodynamic study of copper (II) removal from aqueous solution by *Coriandrum Sativum* seeds

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Abstract: *Coriandrum Sativum* seeds (CSS), were tested as a new eco-friendly adsorbent of copper ions from aqueous solutions. Hence, the effect of the most influencing experimental parameters such as initial concentration of Cu (II) and the temperature was studied upon the adsorption process in order to use its results in following studies. Lagergren pseudo-first-order, pseudo-second-order, and Intraparticle diffusion models were used to describe the biosorption kinetics. The adsorption process was also analyzed by Langmuir, Freundlich and Temkin models and the maximum monolayer biosorption capacity of CSS was found to be 33,5 mg. g⁻¹ by using the Langmuir model. So as to investigate the thermodynamic properties of the adsorption process, the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) values in the temperature range of 25-55 C ° were also calculated in order to conclude the process characteristics. SEM and EDAX analysis were effectuated in order to study the surface morphology of CSS before and after the adsorption process.

Keywords: *Coriandrum Sativum*, Cu (II), adsorption, thermodynamic, mathematic modelling, SEM and EDAX.

Introduction

Industry development has produced large volumes of wastewaters coming from the new manufacturing processes. Some of them contain pesticides, dyes, heavy metals and other toxic substances¹. In some cases, these toxic substances could be degraded by biological treatment, but concerning heavy metals, they remain in the sediments and are slowly released and rejected into the water body, which causes serious and dangerous health problems to living species, even to human health¹⁻⁴.

Several methods and techniques such as ion exchange, precipitation, reverse osmosis, filtration, electrochemical treatments, solvent extraction, membrane processes, and adsorption, were developed for removal of organic and inorganic pollutants from aquatic environment⁵⁻⁷.

The biosorption or the investigation of natural adsorbents as removal of heavy metal ions from contaminated aqueous solutions is an essential field of research due to being environmentally friendly and low cost^{8,9}. These biosorbents contain different biopolymers responsible for biosorption process such as cellulose, hemicelluloses, lignin, polyphenols, etc.

Many natural substances were employed in this context, such as lentil husks¹⁰, orange peel¹¹,

cucumber peel¹², *Sargassum filipendula*¹³, jatropha fruit¹⁴, etc.

Coriander seed (*Coriandrum Sativum*) is an abundant spice¹⁵, a major ingredient of curry powder, an effective antioxidant^{16,17} and a drug for indigestion¹⁸ against worms¹⁹, rheumatism^{20, 21}. They have also several properties such as antimicrobial activity²², insecticidal effect, hypolipidemic activity²³, hypoglycemic action²⁴. Coriander seeds extracts were also investigated as an efficient low-cost inhibitor from mild steel corrosion in 1,0 M hydrochloric acid and 0,5 M sulfuric acid in previous work by the same authors²⁵.

The purpose of the present work is to complete previous works, which were interested to study the possible use of *Coriandrum Sativum* seeds²⁶, after its characterization²⁷, as removal of copper ions from contaminated solutions. The adsorption parameters, such as initial ions concentration and temperature, were investigated using AAS and ICP techniques to evaluate the possible adsorbent-metal ion interactions and to use its results in mathematical modeling of adsorption process by kinetic models (pseudo first order, pseudo-second order) and isotherm models (Langmuir, Freundlich and Temkin) and thermodynamic studies. Finally, the analysis of CSS surface was realized through SEM and EDAX techniques.

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Material and Methods

Preparation of adsorbent

The coriander seeds (*Coriandrum Sativum*) were collected from the west of Morocco (Kenitra), washed with double distilled water to remove impurities such as sand and dust, dried in air at 50 °C for 24 hours, ground using mortar, and then sieved, until the grain-size of particles was lower than 250 µm. The obtained powder was washed by double distilled water and filtrated several times in order to obtain a clean powder. The resulted material was stored in a desiccator to prevent it from moisture in order to keep the constant mass of the dry adsorbent ²⁷.

Fourier Transform Infrared (FTIR)

The Fourier Transform Infrared (FTIR) of Coriander seeds samples before and after adsorption was carried out at Center of analysis and characterization in Faculty of sciences, Marrakech, using a Perkin Elmer Spectrum apparatus version 10.03.07 ATR. It was carried out using a device of type VERTEX 70 in the range of wavelengths of 400 to 4000 cm⁻¹. The spectral resolution is 4,0 cm⁻¹. The pellets were conducted from an intimate mixture of the sifted sample (0,01 g) and potassium bromide KBr (0,99 g) under a pressure of 4,5 Pa.

Preparation of aqueous solution

Aqueous solutions were prepared from copper sulfate salt (purchased from Sigma Aldrich). The stock solutions were then used to obtain the working solutions through dilution with double distilled water. Fresh dilutions were prepared and used for each experiment. 10⁻¹ mol /L HNO₃ or NaOH solutions were used to adjust the initial pH of working solutions at pH = 5,5 ^{28,29}.

Adsorption experiments

The adsorption experiments were realized by adding 0,1 g of adsorbent to 100 mL of aqueous solution with known heavy metal ion concentration and pH equal to 5,5, in 200 mL conical flask. The flask was intermittently stirred for an adequate period of time, depending on the purpose of the experiment. Samples were collected after filtration by Buchner. Concerning the study of the concentration effect towards the adsorption process, all experiments were studied at room temperature (25 °C) with different concentrations (10, 30, 75 and 150 ppm) for 4 hours, while the study of temperature effect was realized at different temperature values (25, 35, 45 and 55 °C) for just one hour. After adsorption, samples were analyzed using the Atomic Adsorption Spectroscopy (AAS) for high concentration values and Inductively

Coupled Plasma (ICP) for low concentrations which need precision. All analysis were realized in the University Center for Analysis, Expertise, Transfer of Technology and Incubation, Ibn Tofail University, Kenitra, Morocco.

Data evaluation

The adsorption process was evaluated by calculating the amount of adsorption from experimental results using the following Eq. (1) ^{30,31}:

$$Q_e = \frac{C_0 - C_e}{m} * V \quad (1)$$

C_0 is the initial concentration of Cu (II) in the solution (ppm), C_e is the equilibrium concentration of Cu (II) in the solution (ppm), V is solution volume (L) and m is the mass of coriander seeds (g).

All the data are the mean values of three replicate measurements, and the standard deviation calculated in each case was lower than ± 1,0%.

Results and discussion

Adsorbent experiments

Effect of Cu²⁺ initial concentration

The effect of initial copper ions concentration on the adsorption performance of coriander seeds CSS, under defined experimental conditions (0,1 g of adsorbent; initial solution pH of 5,5 and 4 hours of contact time) was illustrated in [Figure 1](#). The study was carried out at several concentrations ranging from 10 to 150 ppm. It can be seen that the adsorption capacity of coriander seeds increases with the increase of initial copper ions concentration from 5 to 31 mg/g. This significant increase of the amount values was expected as a result of the correlation between the high initial copper ions concentrations correlate and the higher probability of collisions between Cu²⁺ and superficial functional groups of the adsorbent (-COOH, -OH) ³².

Effect of temperature

The effect of temperature on the adsorption of Cu (II) by CSS was also studied. Four different temperatures of 298, 308, 318 and 328 K were considered. From [Figure 2](#), the amount of copper ions removed by coriander seeds decreases slightly from 7,82 to 6,70 mg/g, when the temperature increase from 298 to 328 K. These results indicate that adsorption may be exothermic ³³ and the increase of temperature may not be in favor of any agglomeration of copper ions on the solid surface.

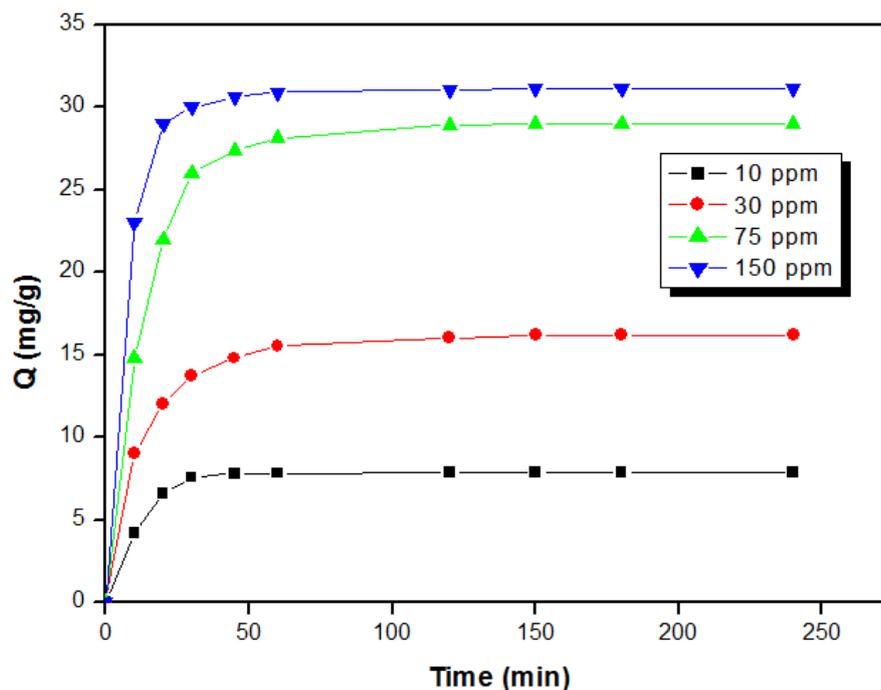


Figure 1. Effect of initial concentration of Cu^{2+} on the adsorption kinetic by CSS

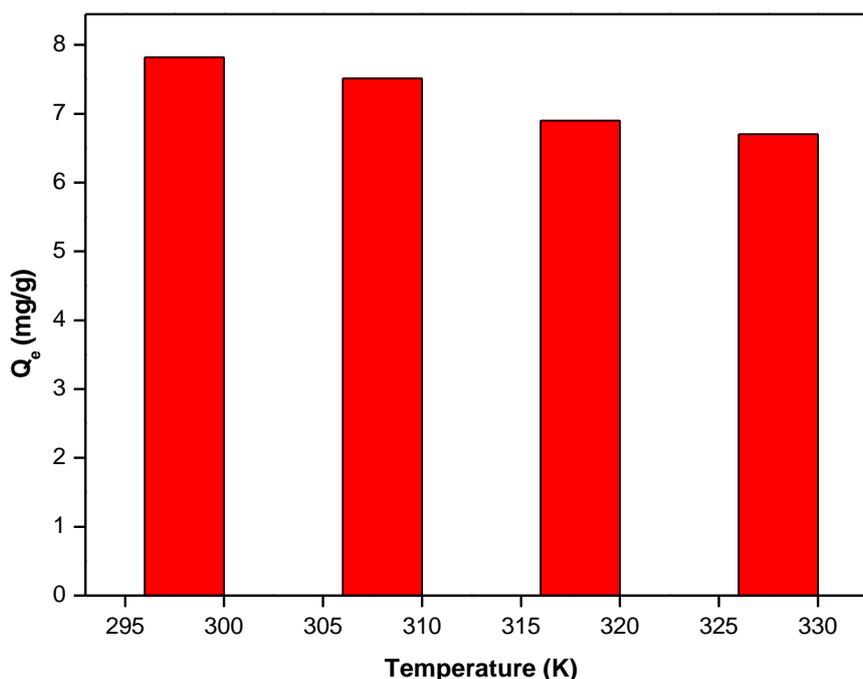


Figure 2. Effect of temperature on the adsorption of copper ions by CSS

Adsorption kinetics

The kinetic study reveals how fast an adsorbate adsorbed on the surface of an adsorbent. The adsorption process usually completes in two different stages: fast phase followed by a slight phase. It was observed that adsorption of copper ions by CSS occurred at a high speed for all four concentrations and most of Cu (II) was removed within initial 15 min and equilibrium was obtained at 30 min (Figure 1). To more explain the adsorption process, two kinetic

models were considered: pseudo first order, pseudo-second order.

Lagergren pseudo-first-order

The experimental measurements were analyzed using linear forms of Lagergren pseudo-first order³⁴ eq. (2):

$$\log(Q_e - Q_t) = \ln(Q_e) - \frac{K_1}{2.303}t \quad (2)$$

Q_e (mg/g) is the equilibrium amount of adsorption, Q_t (mg/g) is the amount of adsorption of CSS at time t (min) and K_1 (min^{-1}) is the rate constant.

The Figure 3 has shown the pseudo first-order model corresponding to the adsorption of copper ions on CSS.

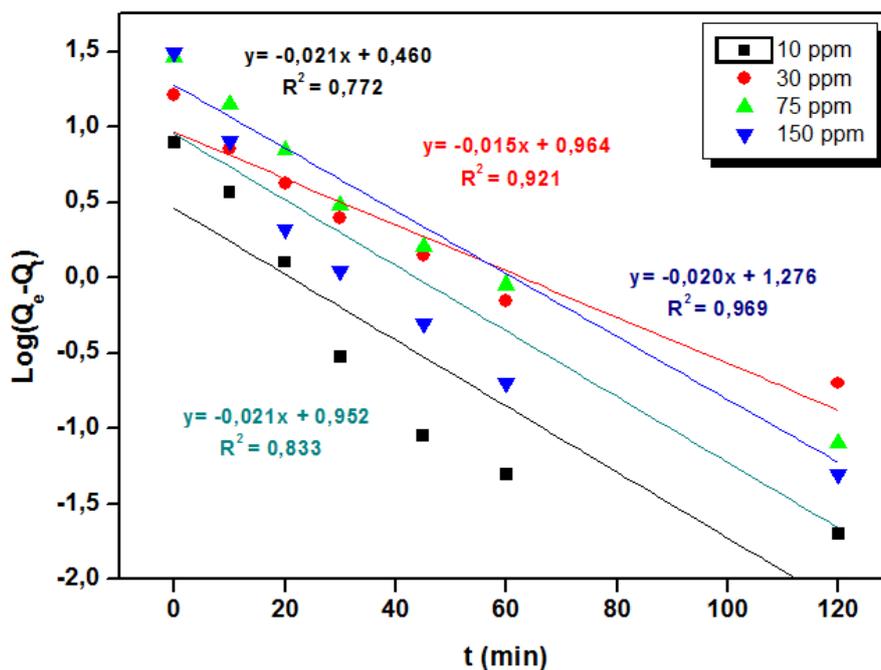


Figure 3. Pseudo-first-order model

Pseudo-second order

The pseudo-second-order kinetic model is expressed in the linear form as the following equation (3) ^{35,36}:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{(K_2 \cdot Q_e)^2} \tag{3}$$

Q_e (mg/g) is the equilibrium amount of adsorption, Q_t (mg/g) is the amount of adsorption of CSS at time t (min) and K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the rate constant. The Figure 4 represents the pseudo second-order model.

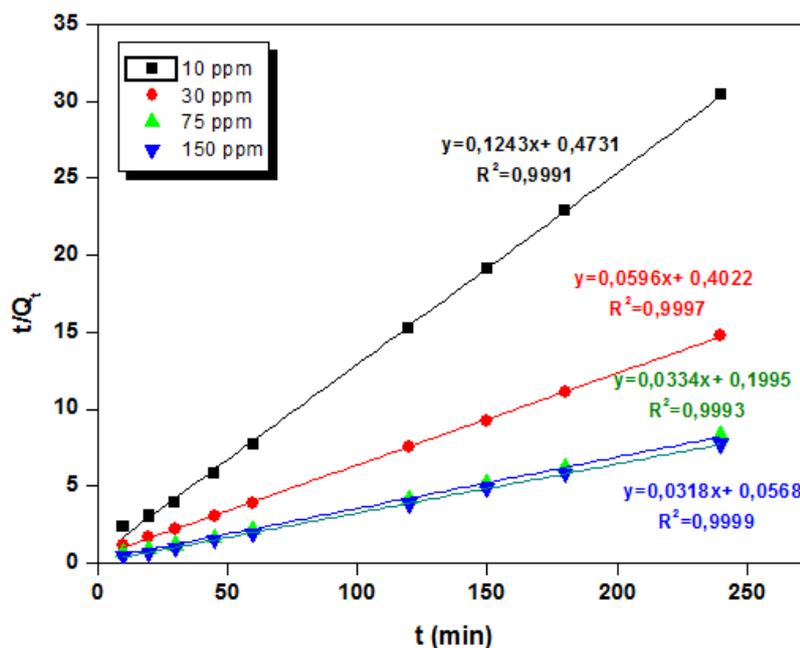


Figure 4. Pseudo-second-order model

Table 1 represents the reported parameters characterizing both of Lagergren models (pseudo first

order and pseudo second order) obtained from Figures (3 and 4).

Table 1. Adsorption kinetic model parameters.

Models	[Cu ²⁺] (ppm)	Q _{exp} (mg/g)	Q _e (mg/g)	R ²	Constants	
Pseudo first order	10	7.87	0.62	0.0838	K ₁ (min ⁻¹)	0.0078
	30	16.2	9.20	0.6897		0.0397
	75	29	5.98	0.3971		0.0128
	150	31.1	43.26	0.9317		0.0797
Pseudo second order	10	7.87	8.04	0.9991	K ₂ (g.mg ⁻¹ .min ⁻¹)	0.1807
	30	16.2	16.7	0.9997		0.0939
	75	29	29.9	0.9993		0.0747
	150	31.1	31.4	0.9999		0.1334

According to Table 1, the determination coefficient R² values corresponding to pseudo second-order model of adsorption process at different concentrations are close to unity (>0,999). In addition, the difference between the experimental and calculated values of adsorption amount is very low in comparison with pseudo first-order ones which confirms that the adsorption of copper ions by CSS from aqueous solution followed the pseudo second-order model³⁷. It was clear that the rate constant of the pseudo second-order model decreases gradually with the increase of Cu²⁺ concentration. This can be due to competition between higher levels of metal ions and CSS active sites. In fact, K₂ values suggest that adsorption systems with low concentrations have

required a short time to achieve a specific fractional uptake.

To sum up, the adsorption process depends on the concentration of ions on the adsorbent surface in accordance with the nature of chemisorption.

Adsorption isotherms

The adsorption isotherm models are often applied in order to analyze experimental adsorption equilibrium results and studying the surface properties of the adsorbent and its affinity, especially for the adsorption of heavy metal ions.

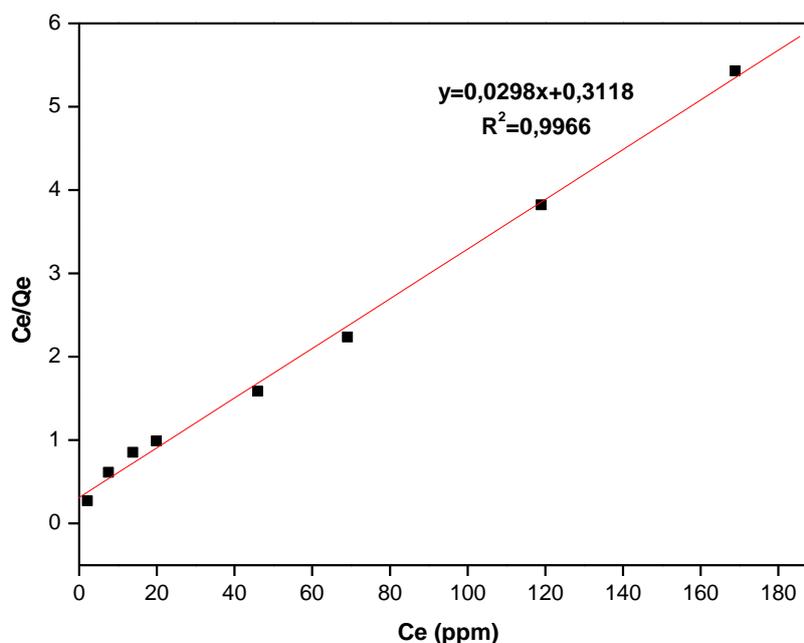


Figure 5. Langmuir isotherm model

Langmuir model

Langmuir isotherm model supposes that the adsorption amount reached the maximum when a

saturated monolayer was formed on the adsorbent surface, also the energy of adsorption is constant and there is no migration of molecules in the adsorbent

surface³⁸. The linear form is expressed by equation (4):

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (4)$$

C_e (ppm) is the equilibrium concentration value of copper ions, Q_e (mg/g) is the equilibrium amount of adsorption, Q_m (mg/g) is the initial amount of adsorption and K_L (L/g) is the Langmuir constant which related with the affinity of the binding sites. Figure 5 represents the Langmuir isotherm model.

Freundlich

The linear form of Freundlich model equation that is an empirical equation which can be applied to

adsorption processes on heterogeneous surfaces as well as multilayer adsorption is expressed by equation (5)³⁹:

$$\log(Q_e) = \log(K_F) + \frac{1}{n} \log(C_e) \quad (5)$$

Q_e (mg/g) is the equilibrium amount of adsorption, K_F (L/g) is the Freundlich constant, and C_e (ppm) is the equilibrium concentration value of copper ions. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption, $n > 1$ represent favorable adsorption condition. Values of K_F and n are calculated from the intercept and slope of the Freundlich isotherm plot represented in Figure 6 and listed in Table 2.

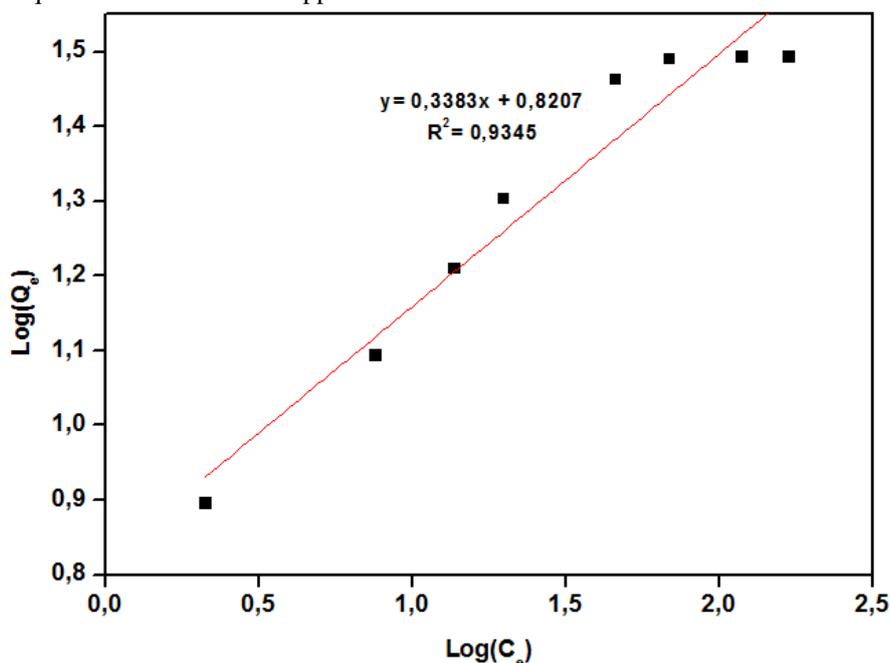


Figure 6. Freundlich isotherm model

Temkin

The Temkin isotherm was generally expressed in the linear form as following equation (6)⁴⁰:

$$Q_e = B \ln(A) + B \ln(C_e) \quad (6)$$

Where $B = \frac{RT}{\Delta Q}$, ΔQ (J/mol) is the variation of the adsorption energy; A (L/g) is the Temkin isotherm constant, R the gas constant (8.314 J/mol.K) and T (K) the absolute temperature. Therefore, by plotting Q_e versus $\ln(C_e)$ in Figure 7 the constants A and B can be determined and then listed in Table 2.

Figures 5, 6 and 7 have shown, respectively, the Langmuir, Freundlich and Temkin adsorption isotherms of Cu (II) on CSS at 298 K. All parameters characterizing each isotherm model were represented

in Table 2. According to the obtained values. Determination coefficient values which correspond to all studied isotherms indicate that Langmuir describes well the adsorption of copper ions on CSS surface. These results were concluded through the determination coefficient value which is close to unity (0,9966), also the calculated amount value (33,55 mg/g).

The Langmuir isotherm assumes monolayer coverage of copper ions over the homogeneous surface of CSS. The adsorption of each molecule onto the surface has the same adsorption activation energy¹¹, while Temkin model assumes that the heat of adsorption of Cu^{2+} in the layer decreases linearly with increasing coverage which is caused by adsorbent-adsorbate interactions⁴¹.

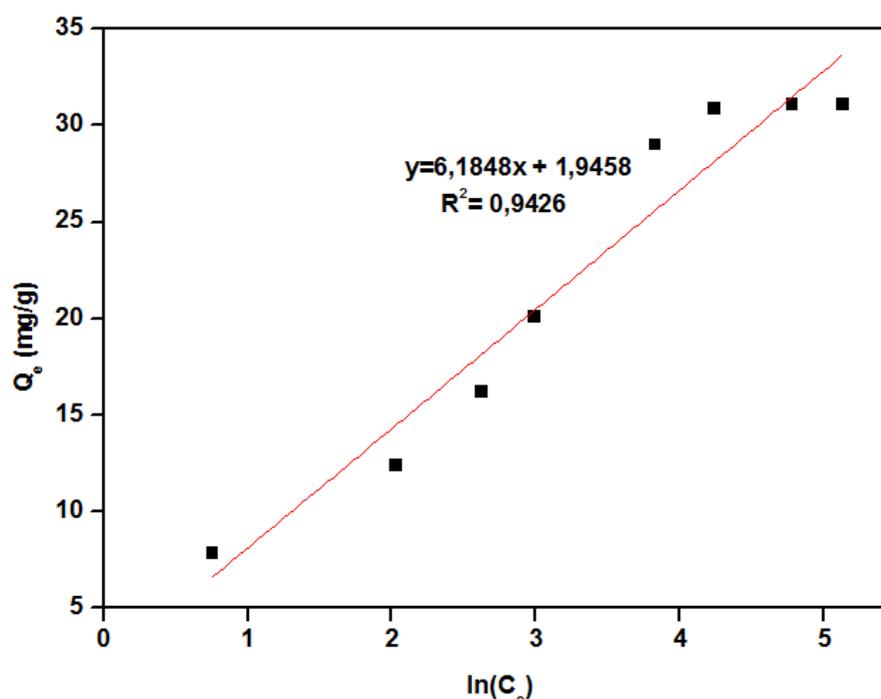


Figure 7. Temkin isotherm model

Table 2. Parameters corresponding to Langmuir, Freundlich, and Temkin models.

Isotherms	Parameters			
Freundlich	K_F (mg.g⁻¹)		n	R²
	0.1511		2.95	0.9345
Langmuir	Q_{exp} (mg/g)	Q_m (mg/g)	K_L	R²
	31.1	33.55	0.0956	0.9966
Temkin	A (L/mg)	B (mg/g)	ΔQ (Kj/mol)	R²
	1.3697	6.1848	392.21	0.9426

Thermodynamic studies

The thermodynamic study is necessary to describe the adsorption process (type, spontaneity...). Thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) changes can be estimated using equilibrium constants changing as a function of temperature.

ΔG^0 is the standard free energy change (J) is calculated by the following equation (7) ⁴²:

$$\Delta G^0 = -RT \ln (K_D) \quad (7)$$

R is the universal gas constant, 8.314 J/mol K and T (K) is the absolute temperature and K_D (L/g) is the thermodynamic equilibrium constant that can be expressed as equation (8):

$$K_D = \frac{Q_e}{C_e} \quad (8)$$

Where Q_e (mg/g) is the amount of metal ion adsorbed at equilibrium, C_e (mg/L) is the concentration of heavy metal ions at the system equilibrium. The values of ΔH^0 and ΔS^0 were calculated from the slope and the intercept of the plot of $\ln (K_D)$ versus $1/T$ by the equation (9):

$$\ln (K_D) = - \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (9)$$

ΔG^0 , ΔH^0 and ΔS^0 are related by the following equation (10):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

The Van'tHoff plot, which corresponds to the adsorption process of copper ions by CSS, is illustrated in Figure 8.

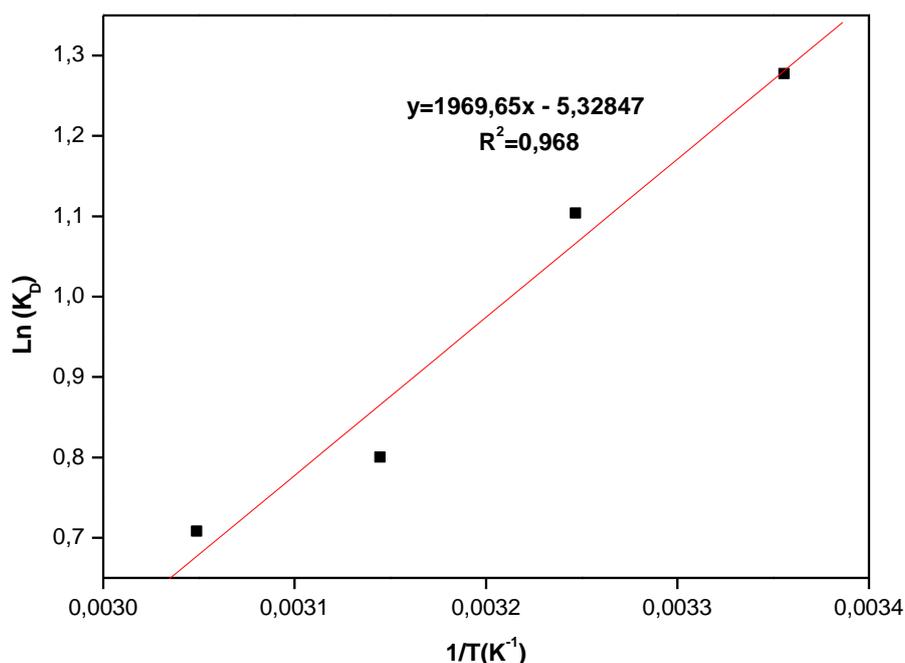


Figure 8. Van'tHoff curve corresponding to the adsorption of Cu²⁺ by CSS

All thermodynamic parameters were listed in [Table 3](#).

Table 3. Thermodynamic parameters of the adsorption process.

Temperature (K)	K _D	ΔG ⁰ (KJ/mol)	ΔH ⁰ (KJ/mol)	ΔS ⁰ (KJ/mol)
298	3.59	-3.16	-16.37	-44.30
308	3.02	-2.82		
318	2.22	-2.11		
328	2.03	-1.93		

The ΔH⁰, ΔG⁰, and ΔS⁰ values were calculated and listed in [Table 3](#). These values confirm the exothermic type process, also the stability and spontaneity of the studied process⁴³. In fact, these values imply that the retention process of copper by CSS is an adsorption process⁴⁴. It was found that Gibbs free energy (ΔG⁰) and enthalpy (ΔH⁰) were negative at all temperatures associating the exothermic and spontaneous nature of the process. While the negative value of the entropy (ΔS⁰) probably indicates that the adsorption of Cu²⁺ increases randomly.

FTIR characterization of CSS

The pattern of sorption of heavy metals ions by natural adsorbents is generally attributed to the active groups and bonds present on them⁴⁵. FTIR spectroscopy was, therefore, done for preliminary quantitative analysis of major functional groups present in CSS before and after using as an adsorbent of Cu²⁺ ions. The FTIR spectra of coriander seeds

before “C₁” and after adsorption of copper ions “C₂” was effectuated by studying the evolution of transmittance (%) versus wavenumber (cm⁻¹). This analysis was studied to determine the correspondence metal adsorption to the deformation of active groups in CSS [Figure 9](#).

The spectra C₁ corresponding to CSS before adsorption of copper ions contain a peak at 3443,07 cm⁻¹ associated to the O–H stretching vibrations of phenol, cellulose, and lignin. The peaks observed at 2925,9 cm⁻¹ can be attributed to the C–H stretching vibrations of methyl and methylene groups. The peak observed at 1745,74 cm⁻¹ is the stretching vibration of C–O bond due to non-ionic carboxyl groups (–COOH, –COOCH₃), and may be assigned to carboxylic acids or their esters⁴⁶. Symmetric stretching vibrations of ionic carboxylic groups (–COO–), appeared 1460,06 cm⁻¹⁴⁷. The bands in the range 1300–1000 cm⁻¹ can be assigned to the C–O stretching vibration of carboxylic acids and alcohols. It is well indicated by FTIR spectrum of CSS that carboxyl, hydroxyl groups and cellulose were present in abundance. These

groups in biopolymers may function as proton donors; hence deprotonated hydroxyl and carboxyl groups may be involved in coordination with metal ions^{30, 31}.

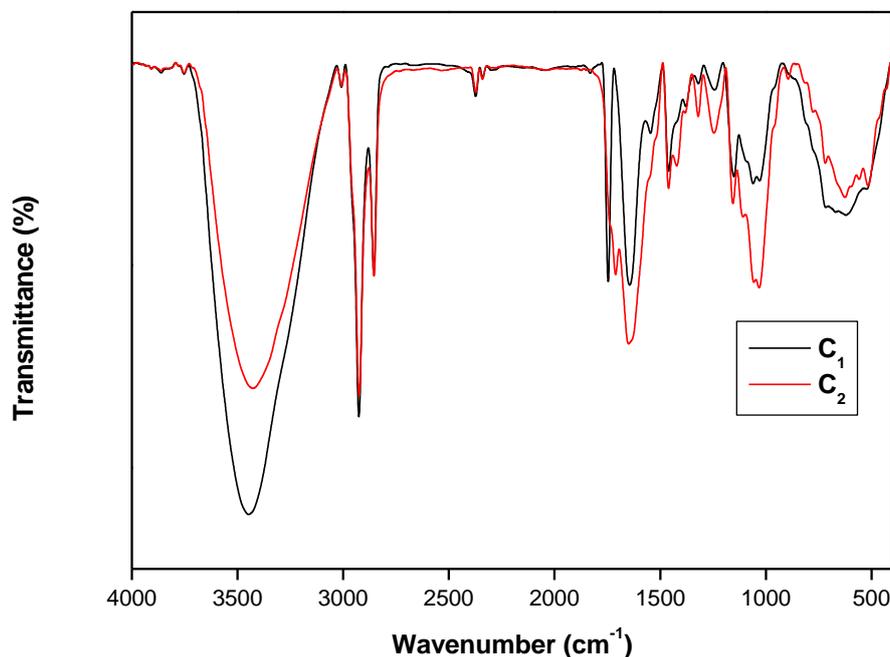


Figure 9. FTIR spectra of Coriander seeds before “C₁” and after adsorption of copper ions “C₂”

The comparison of both of spectra before C₁ and after C₂ adsorption of copper ions shows a slight increase in the transmittance values. For the C=O band of the acidic groups of the support and also for the C-O-C band corresponds to the ether function. This may be due to the changes in ions associated with carboxylate and hydroxylate anions, suggesting that acidic groups, carboxyl, and hydroxyl, are predominant contributors in metal ion uptake, then the adsorption of Cu²⁺ ions

by the support. All other peaks are, however, retained as such.

Scanning Electron Microscopy (SEM)

Figures 10a and 10b show the scanned morphology of coriander seeds, respectively, before and after copper (II) adsorption. It's clear from sample constituted by CSS charged in Cu (II), surface cavities were completed due to the adsorption of Cu²⁺ on the adsorbent surface, which confirms all previous results.

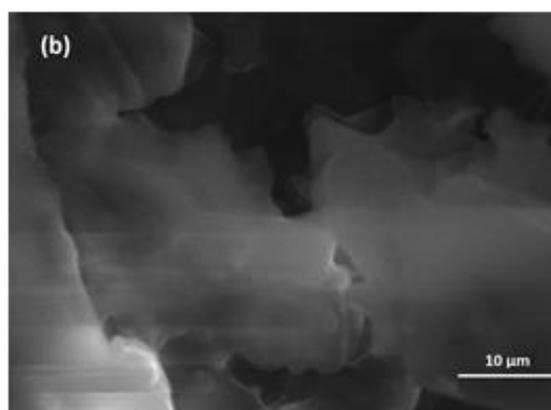
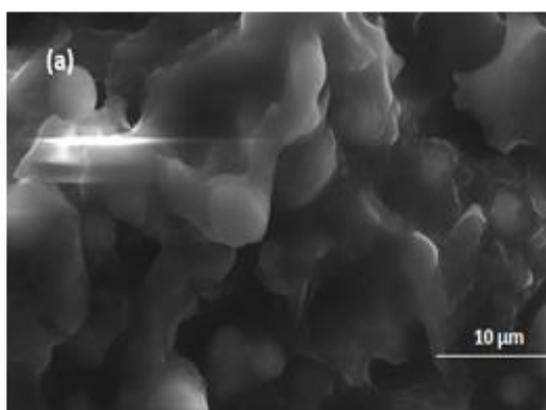


Figure 10. SEM micrographs of CSS before (a) and after (b) adsorption of copper ions

The EDAX analysis of coriander seeds before and after adsorption of copper ions were established. The obtained results were figured out in Figures 11a and 11b. The EDAX spectrum of coriander seeds before adsorption Figure 11a has shown the presence of C, O,

P, S, Na, Mg and Ca. However, the additional peak corresponding to Cu element was observed in Figure 11b with a reduction of elements found previously in Figure 11a, which confirm the adsorption process²⁹.

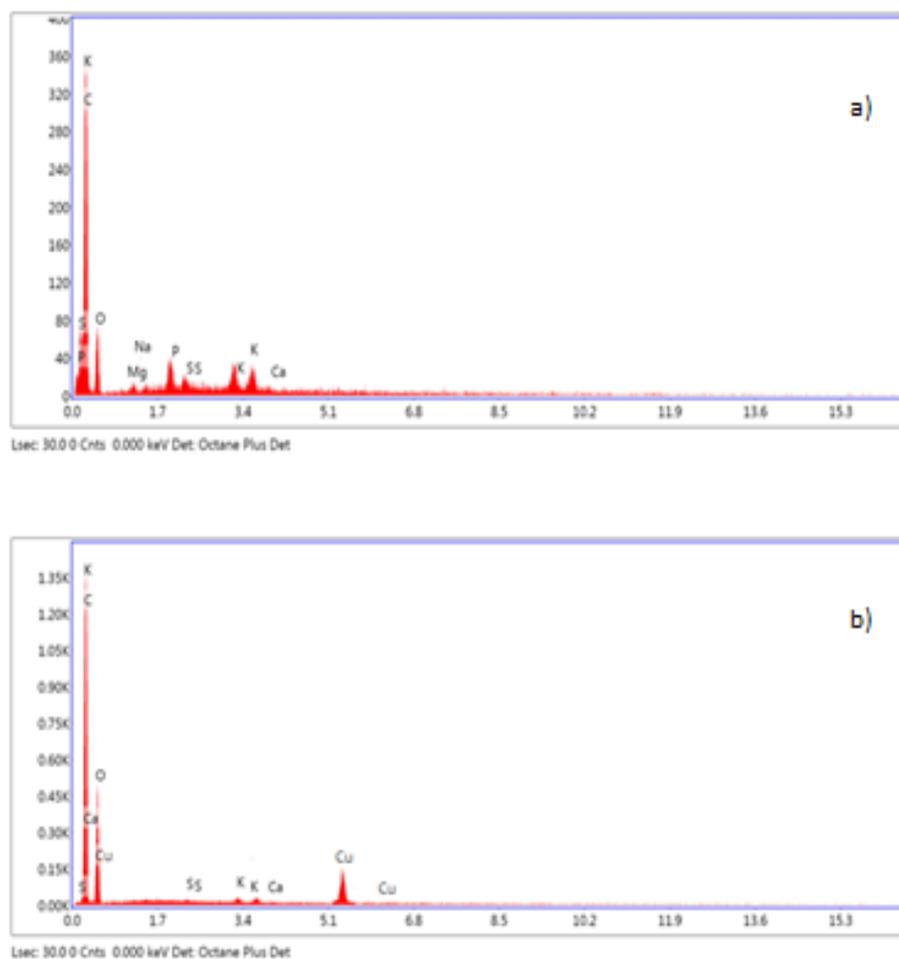


Figure 11. EDAX spectrum of CSS before (a) and after (b) adsorption of copper ions

Table 4. Comparative study of the adsorption of Cu^{2+} by different materials.

Adsorbent	Adsorption capacity (mg/g)	Reference
Fly ash	8.10	32
Green Macroalga	5.57	48
<i>Pseudomonas aeruginosa</i> (bacteria)	0.29	49
Tea	11.35	50
Turkish coals	1.62	51
Herbaceous peat	4.84	52
<i>Coriandrum Sativum</i> seeds	31.1	Present study

Comparison with other adsorbents

Table 4 shown various adsorbents that were studied previously for copper ions removal. It was found that the adsorption amount of *Coriandrum Sativum* seeds is the highest capacities of natural adsorbents. All results encourage to apply CSS for

copper ions removal from industrial wastewaters, which implicates that CSS is an efficient low-cost adsorbent for the removal of Cu (II) from wastewaters.

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Conclusion

This work clearly indicates the potential of using coriander seeds as an excellent adsorbent for the removal of Cu (II) from aqueous solutions. The study of the effect of initial copper ions concentration has revealed that CSS is able to remove the heavy metal ions at low and high concentrations from aqueous solution. The kinetic measurements show that the process follows the pseudo-second-order model. The adsorption process was described through Langmuir isotherm (R^2 close to unity) which suggest that the studied process is monolayer adsorption. The ΔS° , ΔH° and ΔG° values obtained through thermodynamic study indicate the adsorption process is exothermic, stable and spontaneous on CSS surface. In addition, the FTIR, MEB and EDAX analysis confirm all previous results. Finally, the study has revealed that *Coriandrum Sativum* seed is a low-cost, eco-friendly and available adsorbent for copper removal found in industrial effluents.

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