

Kinetic, Equilibrium and Thermodynamic Studies of the Biosorption of Heavy Metals by *Ceratonia Siliqua* Bark

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Abstract Biosorption of Zn(II), Ni(II), Cu(II) and Cd(II) ions from aqueous solutions onto *Ceratonia siliqua* (Carob tree) bark has been investigated in a batch biosorption process. The biosorption process was found to be dependent on pH of solution, initial metal ion concentration, biosorbent dose, contact time and temperature. The experimental equilibrium biosorption data were analyzed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The Langmuir model gave a better fit than the other three models by higher correlation coefficient, R^2 . The maximum biosorption capacity calculated from the Langmuir isotherm was 42.19 mg/g, 31.35 mg/g, 21.65 mg/g and 14.27 mg/g for Ni(II), Zn(II), Cu(II) and Cd(II), respectively at optimum conditions. The kinetic studies indicated that the biosorption process of the metal ions followed well pseudo-second-order model. The negative values of ΔG° and the positive ΔH° revealed that the biosorption process was spontaneous and endothermic. According to the biosorption capacity, *Ceratonia siliqua* bark considered as an effective, low cost, and environmentally friendly biosorbent for the removal of metal ions from aqueous solutions.

Keywords Biosorption, *Ceratonia siliqua* bark, Ni(II), Zn(II), Cd(II), Cu(II), Kinetic, Thermodynamic

1. Introduction

The major sources of Ni(II), Zn(II), Cu(II) and Cd(II) ions release into the environment by waste streams are electroplating, leather tanning, paint dyes and textiles industries. Different methods of treating effluents containing metals have been developed over years which include chemical precipitation, chemical oxidation or reduction, electrochemical treatment, ion exchange, reverse osmosis, filtration, evaporation recovery, adsorption, and electrocoagulation[1-8]. These methods have significant disadvantages, including high energy requirements, incomplete metal removal, generation toxic sludge needs treatment and expensive equipments. The search for novel technologies has recently been directed to the application of biosorption, which constitutes an attractive to common applied physical-chemical methods. The advantages of biosorption lie in the good performance in metal removal, cost-effectiveness and eco-friendly to environment. Many biomaterials have been investigated as biosorbents for removal of heavy metals such as leaf, stem and root phytomass of *Quercus ilex*[9], pomegranate peel[10], banana (*Musa paradisiaca*), lemon (*Citrus limonum*) and orange (*Citrus sinensis*) peel[11], rice husk[12], peanut

husk[13], neem leaf[14], hazelnut, walnut and almond shell [15], *Ulmus carinifolia* and *Fraxinus excelsior* leaves[16], processed walnut shell[17], sugar cane bagasse[18], walnut, hazelnut, almond, pistachio and apricot stone[19], *Lagenaria vulgaris* shell[20], olive leaves[21], *Eriobotrya japonica*[22], grape stalk waste[23], *Pinus sylvestris*[24], *Eucalyptus* bark saw dust, mango bark saw dust, and pineapple fruit peel[25]. *ceratonia siliqua* tree is native to the Mediterranean region and grows up to 10 meters tall. Its crown is broad and semi-spherical, supported by a thick trunk with brown rough bark.

The present study describes a new biosorbent *Ceratonia siliqua* bark (carob bark) for the biosorption of Ni(II), Zn(II), Cu(II) and Cd(II) ions from aqueous solutions. The effects of different parameters such as the pH of the solution, the initial metal concentration, the dose of the adsorbent, the contact time and temperature were investigated.

2. Materials and Methods

2.1. Adsorbent

Ceratonia siliqua bark was collected from a local carob trees at Royal Scientific Society Campus, Amman, Jordan. *C. siliqua* bark was thoroughly rinsed with distilled water to remove dust and soluble materials and then it was allowed to dry at room temperature. The dried *C. siliqua* was crushed

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and grounded to a fine powder in a grinding mill (Retsch RM 100) and sieved to get size fraction < 44 μm . The *C. siliqua* bark powder was dried in an oven at 60°C for 6 h and then stored in a desiccator to be used for the batch experiments.

2.2. Materials

All chemicals used were analytical grade purchased from Fluka AG. Stock solutions of 1000 mg/L were prepared by dissolving $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2$ in distilled deionized water. Desired test solutions of metal ions were prepared using appropriate subsequent dilutions of the stock solutions. The range of concentrations of metal ions prepared from standard solution varies between 5 and 100 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

2.3. Analysis

The concentrations of metal ions in the solutions before and after equilibrium were determined by atomic absorption spectrometer (AAS-6300, Shimadzu, Japan). The pH of the solution was measured with a WTW pH meter using a combined glass electrode. Fourier transform infrared spectroscopy, FT-IR (IR Prestige-21, Shimadzu, Japan) was used to identify the different chemical functional groups present in *C. siliqua* bark. FT-IR analysis also used to determine the functional groups which are responsible for the metal binding with *C. siliqua* bark. The analysis was carried out using KBr and the spectral range varying from 4000 to 400 cm^{-1} .

2.4. Batch Biosorption Experiments

Batch biosorption experiments were conducted by mixing biosorbent with metal ion solution with desired concentration in 250 mL glass flask. The glass flasks were stoppered during the equilibration period and placed on a temperature controlled shaker at a speed 120 r/min. The effect of pH on the equilibrium biosorption of Ni(II), Zn(II), Cu(II) and Cd(II) was investigated by mixing. The amount of biosorption was calculated based on the difference between the initial (C_o , mg/L) and final concentration (C_e , mg/L) in every flask, as follows:

$$q_e = \frac{C_o - C_e}{M} \times V \quad (1)$$

where q_e is the metal uptake capacity (mg/g), V the volume of the metal solution in the flask (L) and M is the dry mass of biosorbent (g). Percent removal (% R) of metal ions was calculated from the following equation:

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

3. Results and Discussion

3.1. Effect of pH

The effect of pH on the biosorption of metal ions onto *C. siliqua* bark was studied at pH 1.0–8.0. The maximum biosorption was observed at pH 5.0–6.0 for metal ions. Therefore, the remaining all biosorption experiments were carried out at this pH values.

3.2. Effect of Initial Metal Concentration

Ni(II), Zn(II), Cu(II) and Cd(II) ions biosorption by *C. siliqua* bark was studied in batch experiments (pH 5.0–6.0) using different initial metal concentrations of 5, 20, 40, 60, 80 and 100 mg/L. The equilibrium uptake of the biosorbent was observed increasing gradually with an increasing the initial concentration of metal ions. The increase of biosorption yield with the increase in metal ions concentration is probably due to higher interaction between the metal ions and sequestering sites of biosorbent

3.3. Effect of contact time

The rate of biosorption is important for designing batch biosorption experiments. Therefore, the effect of contact time on the biosorption of metal was investigated. The biosorption of Ni(II), Zn(II), Cu(II) and Cd(II) ions increased considerably until the contact time reached 80 min at 30°C. Further increase in contact time did not enhance the biosorption, so, the optimum contact time was selected as 80 min for further experiments.

3.4. Effect of adsorbent dose on biosorption

The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial metal concentration. The biosorption efficiency for Ni(II), Zn(II), Cu(II) and Cd(II) ions as a function of biosorbent dosage was investigated. The percentage of the metal biosorption steeply increases with the biosorbent loading up to 5 g/L. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption site increases by increasing the biosorbent dose. The maximum biosorption for Ni(II), Zn(II), Cu(II) and Cd(II) was attained at biosorbent dosage, 5 g/L. Therefore, the optimum biosorbent dosage was taken as 5 g/L for further experiments.

3.5. Biosorption Isotherms

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Biosorption of Ni(II), Zn(II), Cu(II) and Cd(II) ions onto *C. siliqua* bark powder was modeled using four adsorption isotherms.

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as [26]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \quad (3)$$

where K_L is the Langmuir constant related to the energy of adsorption and q_{\max} is the maximum biosorption capacity (mg/g). Values of Langmuir parameters q_{\max} and K_L were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e as shown in Figure 1. Values of q_{\max} , K_L and regression coefficient R^2 are listed in Table 1. These values for *C. siliqua* powder biosorbent indicated that Langmuir model describes the biosorption phenomena favorable. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L expressed as in the following equation:

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (4)$$

The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L was found to be 0.25 - 0.86 for concentration of 5–100 mg/L of metal ions. They are in the range of 0-1 which indicates the favorable biosorption.

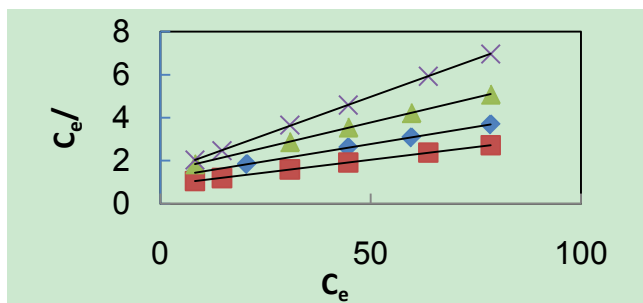


Figure 1. Langmuir isotherm for ■, Ni(II); ♦, Zn(II); ▲, Cu(II); X, Cd(II) ions biosorption onto *C. siliqua* bark

The Freundlich isotherm model is the well known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form[27]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where K_F is the Freundlich constant related to the bonding energy. $1/n$ is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined from the plot of $\ln q_e$ versus $\ln C_e$, Figure 2 on the basis of the linear of Freundlich equation. The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then

adsorption is a chemical process; if $n > 1$, then adsorption is a physical process. The n value in Freundlich equation was found to be 1.73 – 2.21 for *C. siliqua* bark powder, Table 1. Since n lie between 1 and 10, this indicate the physical biosorption of metal ions onto *C. siliqua* bark.

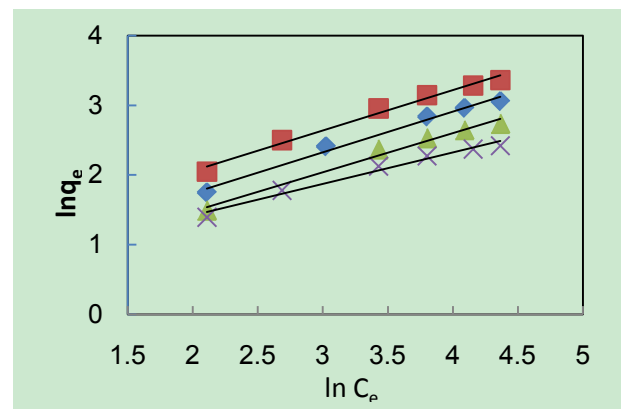


Figure 2. Freundlich isotherm for ■, Ni(II); ♦, Zn(II); ▲, Cu(II); X, Cd(II) ions biosorption onto *C. siliqua* bark

Temkin isotherm equation[28] assumes that the heat of biosorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy. The Temkin isotherm has been used in the linear form as follows:

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

A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants b_T and A_T obtained from the slope and the intercept, Figure 3. Where A_T (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy and constant b_T is related to the heat of biosorption, Table 1.

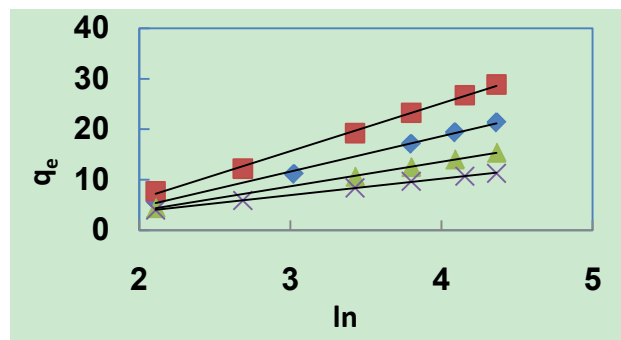


Figure 3. Temkin isotherm for ■, Ni(II); ♦, Zn(II); ▲, Cu(II); X, Cd(II) ions biosorption onto *C. siliqua* bark

Dubinin-Radushkevich (D-R) model, which does not assume a homogenous surface or a constant biosorption potential as the Langmuir model, was also used to test the experimental data[29].

$$\ln q_e = \ln q_d - \beta \epsilon^2 \quad (7)$$

Where ϵ can be correlated to C_e (mg/L) by the following equation:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (8)$$

Where R is the gas universal (8.314 J/mol K) and T is the absolute temperature (K). The D-R isotherm parameters β and q_d were obtained from the slope and intercept of the plot of $\ln q_e$ versus ε^2 , Figure 4. The calculated values are listed in Table 1. The values of correlation coefficient were lower than that of other three isotherm values. In all cases, the D-R model represents the least fit to experimental data than the other isotherms models.

Table 1. Langmuir, Freundlich, D-R and Temkin isotherm constants for biosorption of metal ions onto *Ceratonia siliqua* bark

Langmuir	$q_{\max}(\text{mg/g})$	$K_L(\text{L/mg})$	R^2
Ni(II)	42.19	0.03	0.9999
Zn(II)	31.35	0.03	0.9999
Cd(II)	21.65	0.031	0.9999
Cu(II)	14.27	0.048	0.9999
Temkin	$b_T(\text{J/mol})$	$K_T(\text{L/g})$	R^2
Ni(II)	265.82	0.995	0.9975
Zn(II)	298.55	0.995	0.9924
Cd(II)	586.69	0.998	0.9993
Cu(II)	775.84	0.999	0.9983
Freundlich	n	K_F	R^2
Ni(II)	1.73	2.46	0.9853
Zn(II)	1.71	1.77	0.9875
Cd(II)	1.77	1.76	0.9835
Cu(II)	2.21	1.68	0.9768
D-R	β	$q_d(\text{mg/g})$	R^2
Ni(II)	3.00E-05	2.309	0.7739
Zn(II)	4.00E-05	2.945	0.8702
Cd(II)	1.00E-04	5.49	0.9088
Cu(II)	3.00E-05	5.74	0.8031

The mean free energy of biosorption, E defined as the free energy change when 1 mole of ion is transferred to the surface of the solid from infinity in solution and calculated from the β value using the following equation:

$$\beta = \frac{1}{\sqrt{2E}} \quad (9)$$

If the magnitude of E is between 8 to 16 KJ/mol, then the sorption process is supposed to proceed via chemisorption reaction, while for values of E is less than 8 kJ/mol, the sorption process is of physical nature. The value of E calculated from equation (9) for the biosorption of metal ions by *C. siliqua* bark is 0.13 kJ/mol. This indicates that the biosorption process is of physical nature.

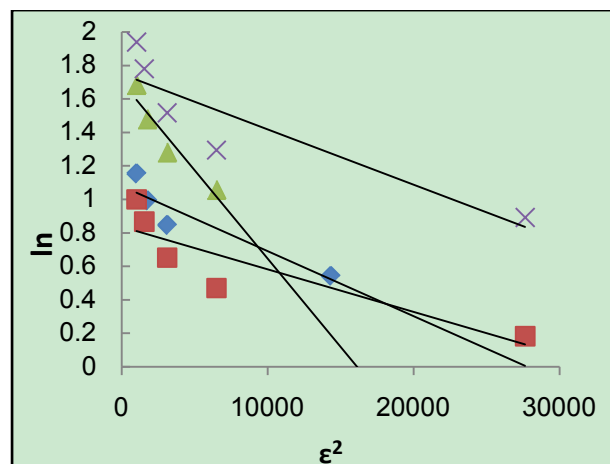


Figure 4. D-R isotherm for ■, Ni(II); ♦, Zn(II); ▲, Cu(II); X, Cd(II) ions biosorption onto *C. siliqua* bark

3.6. Biosorption Kinetics

Parameters from two kinetic models, pseudo first-order and pseudo second-order were fit to experimental data to examine the biosorption kinetics of metal uptake onto *C. siliqua* bark. The pseudo-first order equation of Lagergren [30] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (10)$$

Where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of pseudo-first order sorption, (1/min). After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$; the integrated form of equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (11)$$

The equation applicable to experimental results generally differs from a true first order equation in two ways: the parameter $k_1(q_e - q_t)$ does not represent the number of available sites; and the parameter $\log q_e$ is an adjustable parameter which is often not found equal to the intercept of a plot of $\log(q_e - q_t)$ against t , whereas in a true first order sorption reaction $\log q_e$ should be equal to the intercept of $\log(q_e - q_t)$ against t . In order to fit equation 11 to experimental data, the equilibrium sorption capacity, q_e must be known. In many cases is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 80 minutes of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, on treating q_e as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, in order to analyze the pseudo-first order model kinetics. The pseudo first order rate constant can be obtained from the slope of plot between $\log(q_e - q_t)$ against time (t), Figure 5.

The calculated values and their corresponding linear regression correlation coefficient values are listed in Table 2. R^2 was found to be 0.8718 - 0.9391, which shows that this model cannot be applied to predict the adsorption kinetic model.

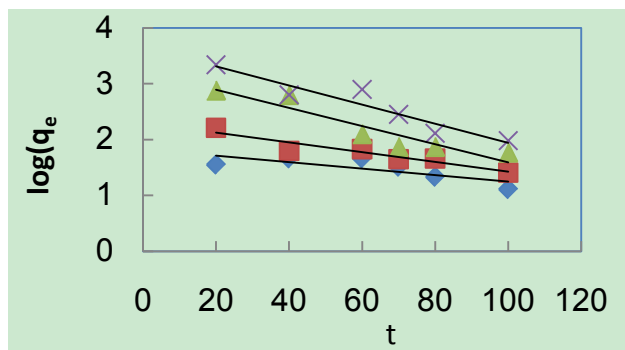


Figure 5. Pseudo-first order kinetics for ♦, Ni(II); ■, Zn(II); ▲, Cu(II); x, Cd(II) biosorption onto *C. siliqua* bark

The pseudo second-order rate expression, which has been applied for analyzing chemisorption kinetics rate, is expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (12)$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg/g) and k is the rate constant of pseudo-second order sorption, (g/mg min). For the boundary conditions to $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$; the integrated form of equation becomes:

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

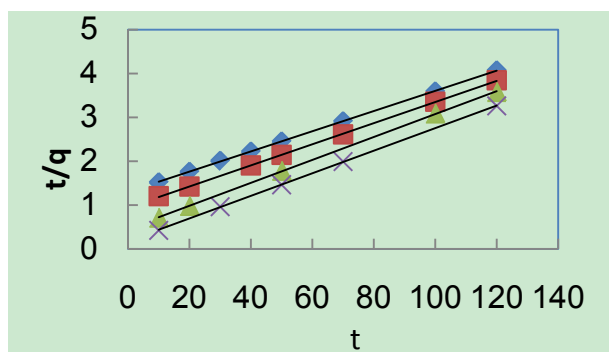


Figure 6. Pseudo-second order kinetics for ♦, Ni(II); ■, Zn(II); ▲, Cu(II); X, Cd(II) ions biosorption onto *C. siliqua* bark

Where t is the contact time (min), q_e (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t . If pseudo-second order kinetics is applicable, the plot of t/q_t versus t of the equation should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot, Figure 6. The pseudo-second order rate constant k_2 , the calculated q_e value and the corresponding linear regression correlation coefficient value are given in Table 2. At all initial metal concentrations, the linear regression correlation coefficient R^2 values were higher. The higher values confirm that the

adsorption data are well represented by pseudo-second order kinetics

Table 2. Kinetic parameters of metal ions biosorption onto *C. siliqua* bark

1st order	K_1	q_e (mg/g)	R^2
Ni(II)	0.0067	5.76	0.9391
Zn(II)	0.0064	4.53	0.8876
Cu(II)	0.0067	3.39	0.8963
Cd(II)	0.0111	3.95	0.8718
2nd order	K_2	q_e (mg/g)	R^2
Ni(II)	0.0005	43.48	0.9999
Zn(II)	0.0006	41.67	0.9998
Cu(II)	0.0022	35.21	0.9999
Cd(II)	0.0441	31.45	0.9999

3.7. Thermodynamic Parameters

In order to describe thermodynamic behaviour of the biosorption of metal ions onto *C. siliqua* bark, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from following equations[31,32]:

$$\Delta G^\circ = -RT \ln K_D \quad (14)$$

where R is the universal gas constant (8.314J/mol K), T (K) is the temperature and K_D is the distribution coefficient. The thermodynamic equilibrium constant (K_D) of the adsorption is defined as:

$$K_D = \frac{C_a}{C_e} \quad (15)$$

where, C_a is mg of adsorbate adsorbed per liter and C_e is the equilibrium concentration of solution, mg/L. According to thermodynamics, the Gibb's free energy change is also related to the enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by the Van't Hoff equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (16)$$

Equations (14) and (15) can be written as:

$$-RT \ln K_D = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (18)$$

According to the equation 18, the values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot of $\ln K_D$ vs. $1/T$. The calculated values of thermodynamic parameters ΔG° , ΔH° , and ΔS° for the biosorption of metal ions onto *C. siliqua* are reported in Table 3. A negative value of the free energy (ΔG°) indicated the spontaneous nature of the biosorption process. It was also noted that the change in free energy, increases with increase in which exhibits an increase in adsorption with rise in temperature. This could be possibly because of activation of more sites on the surface of *C. siliqua* bark with increase in temperature or

that the energy of biosorption sites has an exponential distribution and a higher temperature enables the energy barrier of biosorption to be overcome. The physical adsorption the free energy change (ΔG°) ranges from (–20 to 0) kJ/mol and for chemical adsorption it ranges between (–80 and –400) kJ/mol^{–1}. The ΔG° for metal ions biosorption onto *C. siliqua* was in the range of (–2.97 to –7.75) kJ/mol^{–1} and so the biosorption was predominantly physical biosorption. A positive value of ΔS° as 69.85–102.73 J/mol K showed increased randomness at solid solution interface during the adsorption of metal ions onto *C. siliqua* bark.

3.8. FT-IR Spectroscopy Analysis

FT-IR spectra of *C. siliqua* bark biosorbent, Figure 7 showed a number of absorption peaks reflecting its complex nature. A strong band at 3340 cm^{–1} results due to the stretching of the N-H bond of amino groups and also indicative of bonded hydroxyl groups O-H. The bands at 2916 cm^{–1} and 2846 cm^{–1} could be assigned to –CH stretching vibrations of –CH₃ and –CH₂ functional groups. The peak at 1612 cm^{–1} is due to C=O stretching mode of the primary and secondary amides. The bands at 1134 cm^{–1} to 1473 cm^{–1} are indicative of the N-H stretching of the primary and secondary amides and the presence of carboxylic acids. The strong band of C-O at 1026 cm^{–1} confirms the lignin structure of *C. siliqua* bark.

Table 3. Thermodynamic parameters of metal ions biosorption onto *C. siliqua* bark

T/K	LnK _d	ΔG°	ΔH°	ΔS°
Ni(II)				
293	1.22	-2.97	20.56	80.24
303	1.47	-3.71		
313	1.76	-4.56		
Zn(II)				
293	1.68	-4.09	16.38	69.85
303	1.89	-4.76		
313	2.11	-5.49		
Cu(II)				
293	1.98	-4.26	17.91	77.54
303	2.21	-5.57		
313	2.45	-6.38		
Cd(II)				
293	2.34	-5.72	24.39	102.73
303	2.67	-6.73		
313	2.98	-7.75		

Figure 8 shows the spectrum of *C. siliqua* bark after the sorption of metal. The peak at 3340 cm^{–1} corresponding to the stretching of N-H bond of amino group and bonded hydroxyl O-H group shifts to the lower frequency 3263 cm^{–1} after metal take up. Thus, it can be concluded that the amino groups may be the main biosorption site for metal attachment

on the *C. siliqua* bark. In addition the FT-IR spectrum shows the shift in peak at wavenumber 1612 cm^{–1} to 1604 cm^{–1} suggests that metal ions interact with the carbonyl functional group present in *C. siliqua* bark. Hence, FT-IR spectra indicated that the functional groups N-H, O-H and C=O present on *C. siliqua* bark surface are involved in metal biosorption process.

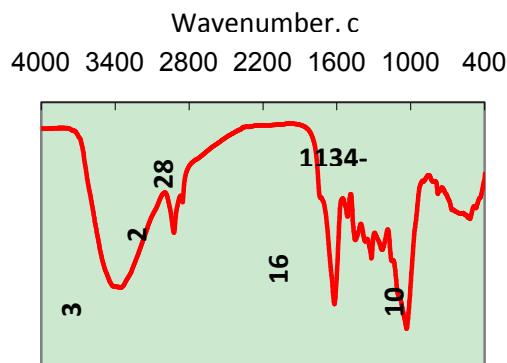


Figure 7. FT-IR of spectra of *C. siliqua* bark before biosorption of metals

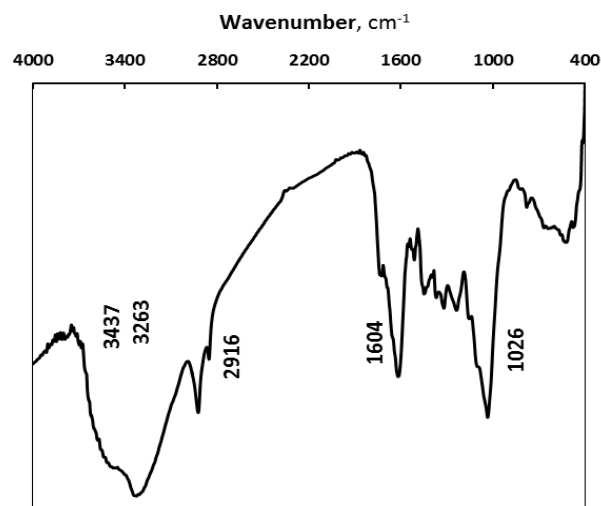


Figure 8. FT-IR of spectra of *C. siliqua* bark after biosorption of metals

4. Conclusions

Biosorption by *C. siliqua* bark is a safe, ecofriendly and effective method for the removal of Ni(II), Zn(II), Cu(II), Cd(II) ions from aqueous solutions. Biosorption process parameters like pH, initial metal ions concentration, biosorbent dose, contact time and temperature were studied. The kinetic results provided the best correlation of the experimental data of biosorption of metal ions onto *C. siliqua* bark by pseudo second-order equation. The biosorption isotherms could well be fitted by the Langmuir model. It can be concluded that since the *C. siliqua* bark is an easily, locally available, low-cost adsorbent and has a considerable high biosorption capacity, it may be treated as an alternative adsorbent for treatment of aqueous solutions containing Ni(II), Zn(II), Cu(II) and Cd(II) ions.

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