

Kinetic and Thermodynamics of Biosorption Ni(II) Ions From Electroplating Wastewater onto *Sophora japonica* Seeds Powder

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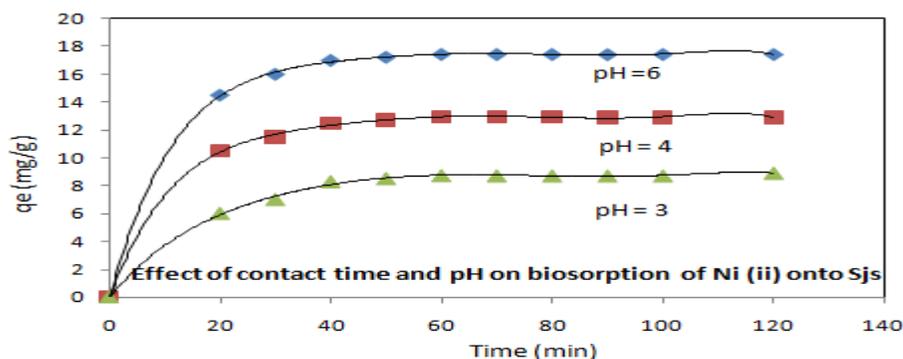
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- **Novelty and Highlights:**

- 1 –An efficient, ecofriendly and new biosorbent *Sophora japonica* seeds
- 2 –*Sophora japonica* seeds was successfully used for the removal of Ni(II) ions
- 3 – An alternative adsorbent for the treatment of wastewater containing metal ions.

- **Graphical Abstract:**



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Abstract: The removal of Ni(II) ions from aqueous solutions and electroplating wastewater onto *Sophora japonica* seeds powder has been studied by using batch adsorption technique. The biosorption studies were determined as a function of pH, contact time, initial metal ion concentration, biosorbent dosage and temperature. The kinetic study showed that the biosorption of the Ni(II) ions followed pseudo-second-order kinetic model. Experimental data obtained were analyzed with Langmuir and Freundlich, isotherm models and in each case the Langmuir model appears to have better regression coefficients. Thermodynamic parameters: ΔG° , ΔH° and ΔS° were calculated indicating that the biosorption of Ni(II) ions onto *Sophora japonica* seeds powder was a spontaneous and endothermic process. The biosorption process was successfully applied to the treatment of an electroplating wastewater sample, where the concentration of nickel and COD were effectively reduced. The results of the study showed that *Sophora japonica* seeds powder (SjsP) can be efficiently used as a low-cost and ecofriendly alternative for the removal of Ni(II) ions from aqueous solutions and electroplating wastewater.

Introduction

Metal ion contamination of drinking water and wastewater, with metal ions is a serious and ongoing problem. Heavy metals are toxic at high concentrations and are high frequency pollutants seen in municipalities and specific industries. Since contaminated wastewater can easily find its way into both surface water and ground water, this problem should be of great concern to anyone who obtains his drinking water from these sources. Nickel is well known as a heavy metal pollutant present in effluents of electroplating industries, alloy manufacturing, mining, and refining industries. According to WHO, the permissible limit of nickel in drinking water is 0.5 mg/L. Different methods of treating effluent containing Ni(II) have been developed over years which include chemical precipitation, chemical oxidation or reduction, electrochemical treatment, ion exchange, reverse osmosis, filtration, evaporation recovery and ion exchange [1-3]. However, most of these techniques have some disadvantages such as complicated treatment process and high cost. Another major disadvantage is the production of toxic chemical sludge. 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. In recent years, the searches for low-cost agricultural by-products have

been widely studied for metal ions removal from water and wastewater. These include maize cob [4], *Azadirachta indica* bark [5], *Ashoka* leaf powder [6], rice straw [7], rice husk [8], *Eucalyptus* bark, mango bark and pine apple fruit peel [9], *Moringa oleifera* bark [10], *Certonia siliqua* bark [11], *Citrus reticulata* (fruit peel orange) [12], Barley straw [13], *Thespesia populneabark* [14], Cashew nut shell [15], and (*Eriobotrya japonica*) loquat bark [16].

This paper presents the study of biosorption characteristics of *Sophora japonica* seeds (Sjs) powder for removal of Ni(II) ions from aqueous solutions and electroplating wastewater in batch process. Biosorption efficiency of Sjs powder for Ni(II) ions was shown as a function of pH solution, contact time, initial metal ion concentration, biosorbent dose and temperature. Experimental data were analyzed by Langmuir and Freundlich isotherms. Kinetic and thermodynamic of the biosorption process were also investigated.

Experimental

Preparation of the biosorbent

Sophora japonica seeds (Sjs) were collected from the trees planted at the campus of Royal Scientific Society, Jordan (RSS) and the seeds were thoroughly rinsed with distilled water to remove dust and left to dry at room temperature. The dried seeds were crushed and grounded to a fine powder in a grinding mill (Retsch RM 100) and sieved to get size fraction < 44 μm . The Sjs powder was dried in an oven at

60°C for 24 h and stored in a desiccator to prevent water adsorption before its use for the batch experiments.

Chemicals and equipment

All reagents used were of AR grade. Deionized distilled water was used throughout the experimental studies. Stock solutions (1000 mg/L) were prepared by dissolving $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Desired test solutions of metal ions were prepared using appropriate subsequent dilutions of the stock solution. The range of concentrations of metal ions prepared from standard solution varies between 5 and 100 mg/L. ACS reagent grade HCl and NaOH (E. Merck) were used to adjust the solution pH. The concentrations of Ni(II) ions in the solutions before and after equilibrium were determined by AAS6300 atomic absorption spectrometer (Shimadzu). 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) was used to identify the different chemical functional groups present in the *Sophora japonica* seeds powder. FT-IR analyses also used to determine the functional groups which are responsible for the metal binding with Sjs powder. The analysis was carried out using KBr and the spectral range varying from 4000 to 400 cm^{-1} . The chemical oxygen demand (COD) of electroplating wastewater was analyzed by a COD reactor (Thermoreakter TR 420, Merck). Conductivity was measured by a WTW conductometer (inoLab Cond. Level 1).

Batch Biosorption Study

Batch biosorption experiments were conducted by mixing biosorbent with Ni(II) ions solutions 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 metal ions 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:

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

Results and Discussion

Effect of pH: The pH has been identified as one of the most important parameter that is effective on metal sorption. It is directly related with competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface. The effect of pH on the biosorption of Ni(II) ions onto Sjs powder was studied at pH 1.0–8.0, **Fig.1**. The maximum biosorption was observed at pH 5.0–6.0 for Ni(II) ions. Therefore, all the remaining biosorption experiments were carried out at this pH value. The biosorption mechanisms on the SjsP surface reflect the nature of the physicochemical interaction of the solution. At highly acidic pH ($\text{pH} < 3.0$), the overall surface charge on the active sites became positive and metal cations and protons compete for binding sites on SjsP, which results in lower uptake of metal. The biosorbent surface was more negatively charged as the pH solution increased from 5.0 to 6.0. The functional groups of the Sjs were more deprotonated and thus available for the metal ions. Decrease in biosorption yield at higher pH ($\text{pH} > 6$) is not only related to the formation of soluble hydroxylated complexes of the metal ions, but also to the ionized nature of the SjsP surface of the biosorbent under the studied pH. Previous studies also reported that the maximum biosorption efficiency of Ni(II) ions on biomass was observed at pH 6.0.

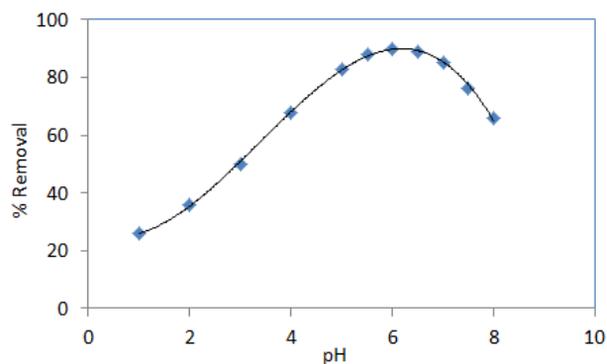


Fig.1. Effect of pH on the percent removal of Ni(II) ions by Sjs

Effect of biosorbent dose: The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration. The biosorption efficiency for Ni(II) ions as a function of biosorbent dosage was investigated. The percentage of the metal biosorption steeply increases with the biosorbent loading up to 0.5 g/0.1L. 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 95.57% for Ni(II) was attained at biosorbent dosage, 0.5 g/0.1L. Therefore, the optimum biosorbent dosage was taken as 0.5 g/0.1L for further experiments. This can be explained by when the biosorbent ratio is small, the active sites for binding metal ions on the surface of Sjs is less, so the biosorption efficiency is low. As the biosorbent dose increased, more active sites to bind metal ions, thus it results an increase in the biosorption efficiency until saturation.

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 Ni(II) ions by Sjs was investigated. The biosorption of Ni(II) ions increased considerably until the contact time reached 60 min at 30°C. Further increase in contact time did not enhance the biosorption, so, the optimum contact time was selected as 60 min for further experiments.

Biosorption isotherms: An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of Ni(II) ions onto Sjs was modeled using four adsorption isotherms:

Langmuir isotherm: The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites [17]. 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:

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

where K_L is the Langmuir constant related to the energy of adsorption and q_{max} is the maximum adsorption 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 **Fig. 2**. Values of q_{max} , K_L and regression coefficient R^2 are listed in **Table 1**. These values for Sjs 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 [12].

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

where K_L is the Langmuir constant and C_o is the initial concentration of Ni(II) ions. The value of separation parameter R_L provides important information about the nature of adsorption. 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 for Ni(II) ions biosorption by Sjs was found to be 0.04-0.89 for concentration of 5–100 mg/L of metal ions. They are in the range of 0-1 which indicates the favorable biosorption.

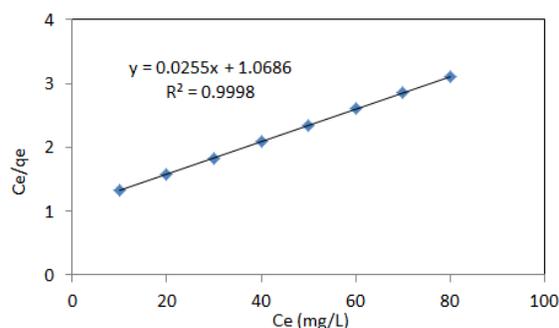


Fig. 2. Langmuir isotherm for biosorption of Ni(II) ions onto Sjs

Freundlich isotherm: 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 the 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 [18]:

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

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 $\ln C_e$. 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 1.714 for Ni(II). **Table 1.** Since n lies between 1 and 10, this indicates the physical biosorption of Ni(II) onto Sjs. The values of regression coefficients R^2 are regarded as a measure of goodness of fit of the experimental data to the isotherm models.

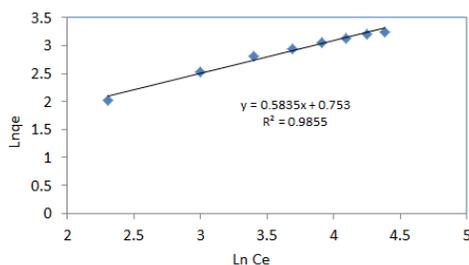


Fig. 3. Freundlich isotherm for biosorption of Ni(II) onto Sjs

Table 1. Langmuir and Freundlich isotherm model parameters for biosorption Ni(II) onto Sjs

Langmuir	q_{\max} (mg/g)	K_L	R^2
	39.22	0.024	0.9998
Freundlich	n	K_F	R^2
	1.714	2.123	0.9855

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 Ni(II) uptake onto Sjs.

Pseudo first-order kinetics: The pseudo-first order equation of Lagergren[19] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (6)$$

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 (6) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (7)$$

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 (7) 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 60 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). The calculated values and their corresponding linear regression correlation coefficient values are listed in **Table 2.** R^2 was found to be 0.8924, which shows that, this model cannot be applied to predict the adsorption kinetic model.

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

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (8)$$

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 (8) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (9)$$

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 equation (9) should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot, **Fig. 4**. 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.

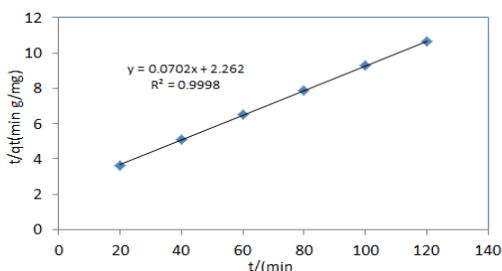


Fig 4. Pseudo-second order kinetics for Ni(II) ions onto Sjs

Table 2. Values of rate constants of biosorption for Ni(II) ions onto Sjs

Pseudo-first order	k_1 (min^{-1})	q_e (mgg^{-1})	R^2
	0.0051	5.32	0.8924
Pseudo-second order	k_2 ($\text{mg g}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	R^2
	0.002	14.25	0.9998

Thermodynamic parameters: In order to describe thermodynamic behaviour of the biosorption of Ni(II) ions onto Sjs, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from following equations.

$$\Delta G^\circ = -RT \ln K_D \quad (10)$$

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:

$$K_D = \frac{C_a}{C_e} \quad (11)$$

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:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

Equations (11) and (12) can be written as:

$$-RT \ln K_D = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

or

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (14)$$

According to equation 14, 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 Ni(II) ions onto Sjs 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, ΔG° increase as the temperature increased, indicating more driving force and hence resulting in higher biosorption process. This could be possibly because of activation of more sites on the surface of Sjs 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. In 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.

Table 3. Thermodynamic parameters for the biosorption of Ni(II) ions onto Sjs at different temperatures

T/K	K_D	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
293	2.29	-2.02	26.32	96.63
303	3.22	-2.95		
313	4.58	-3.96		

The ΔG° for Ni(II) biosorption onto Sjs was in the range of (-2.02 to -3.96) kJ/ mol and so the biosorption was predominantly physical biosorption. A positive value of ΔS° as 96.63 J/ mol K showed increased randomness at solid solution interface during the adsorption of Ni(II) ions onto *Sphora japonica* seeds powder.

Treatment of electroplating wastewater: *Sphora japonica* seeds (SjsP) as an adsorbent was used for removal of Ni(II) ions from electroplating wastewater by batch process. Electroplating wastewater collected from one of the nickel electroplating industries in Jordan and analyzed by standard methods for examination of water and wastewater [20]. The main characteristic of the electroplating wastewater samples before and after the biosorption process are listed in **Table 4**.

It was observed that the relatively high COD content of the electroplating wastewater indicates the presence of organic materials added to electroplating baths such as brighteners and wetting agents. The adsorption of Ni(II) ions by Sjs from electroplating wastewater was found to be slower than that of aqueous solutions. This may be attributed to the presence of organic materials, which compete for biosorption onto SJs. The initial COD concentration of 286 mg/L decreased to less than 68 mg/L showing a removal efficiency of about 75%.

Table 4. Analysis of electroplating wastewater before and after biosorption by Sjs.

Parameter	Before	After
pH	3.1	6.7
COD (mg/L)	286	68
Ni(II) (mg/L)	14.88	0.66
Conductivity (ms/cm)	4.2	2.5
Ni(II) % Removal	95.57	

FT-IR spectral analysis: An untreated *Sophora japonica* seeds powder sample and treated with 20 mg/L Ni(II) ions solution were analyzed by FT-IR. The Sjs displays a number of absorption peaks, reflecting its complex nature, **Fig. 6**. The band at 3371 cm^{-1} could be ascribed to the stretching absorption band of amino (-NH) and hydroxyl (-OH) groups. This band shifted to 3437 cm^{-1} in nickel loaded-Sjs indicating participation of these functionalities in metal binding. The bands at 2924 cm^{-1} and 2850 cm^{-1} could be assigned to -CH stretching vibrations of -CH₂ and -CH₃ functional groups. The adsorption bands at 1743 cm^{-1} in native SJs spectra was assigned to the carboxyl group

stretching vibration, which shifted to 1747 cm^{-1} in metal-loaded Sjs. Peaks at 1573 cm^{-1} and 1388 cm^{-1} are indicative of the N-H stretching of the primary and secondary amides, and the presence of amide (III) or sulfamide band, respectively [10]. The strong bands at 1037 cm^{-1} and 1053 cm^{-1} can be assigned to the C-O stretching vibrations of alcohols. Additional peak at 524 cm^{-1} can be assigned to bending modes of aromatic compounds was shifted to 594 cm^{-1} confirms the participation of this group in Ni(II) bindings. FT-IR study of *Sophora japonica* seeds powder indicates that the carboxyl (-C=O), hydroxyl (-OH) and amine (-NH) groups are mainly involved for binding Ni(II) ions onto Sjs.

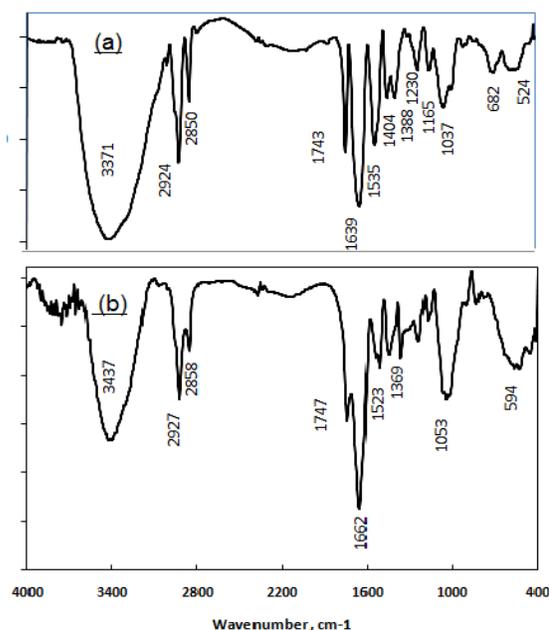


Fig. 6. FT-IR spectra of : (a) Sjs; Ni-loaded Sjs

Comparison of *Sophora japonica* seeds powder with other biosorbents: A comparative of the maximum biosorption capacity, q_{max} of *Sophora japonica* seeds with those of some other biosorbents reported in literature is given in **Table 5**. Differences in q_{max} are due to the nature and properties of each biosorbent such as surface area and the main functional groups in the structure of the biosorbent. A comparison with other adsorbents indicated a high Ni(II) biosorption capacity of the *Sophora japonica* seeds powder.

Table 5. Maximum absorption capacity (mg/g) of Ni(II) ions by different biosorbents in literature.

Biosorbent	q _{max} (mg/g)	Ref.
<i>Moringa oleifera</i> bark	30.38	10
Barley shell	35.6	13
cashew nut shell	18.87	15
coconut shell	3.68	21
potato peel	13.09	22
Rice husk	8.86	23
Loquat bark	27.55	16
<i>S.japonica</i> seeds	39.22	This work

Conclusions

The experimental investigation concluded that *Sophora japonica* seeds powder could be used as potential biosorbent for removal of Ni(II) ions from aqueous solutions and electroplating wastewater. The batch biosorption parameters: pH of solution, biosorbent dose, contact time, initial metal concentration and temperature were found to be effective on the biosorption process. The kinetic studies revealed that the biosorption process followed the pseudo-second order kinetic model. Thermodynamic parameters ΔG° , ΔH° and ΔS° showed the endothermic and spontaneous nature of the biosorption of Ni(II) onto *Sophora japonica* seeds. Langmuir model showed the best fit for the experimental data. The maximum biosorption capacity of Ni(II) onto *Sophora japonica* seeds at pH 6.0 and 30 °C is 39.22 mg/g. Compared to various biosorbents reported in the literature, the *Sophora japonica* seeds powder showed good promise for its use in wastewater treatment.

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