

Biosorption Studies of Cr(VI) Ions from Electroplating Wastewater by Walnut Shell Powder

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Abstract Biosorption of Cr(VI) ions from aqueous solutions and electroplating wastewater by walnut shell powder has been investigated in a batch biosorption process. The biosorption of Cr(VI) ions was found to be dependent pH, initial chromium ion concentrations, biosorbent dose, contact time and temperature. The experimental equilibrium biosorption data were analyzed by Langmuir, Freundlich, and Temkin isotherm models. The Langmuir model gave a better fit than the Freundlich and Temkin models. The maximum biosorption capacity calculated from the Langmuir isotherm was 138.89 mg/g at optimum conditions. The kinetic studies indicated that the biosorption process of the chromium ions followed well pseudo-second-order model. The negative values of ΔG° (-3.51 kJ/mol) and positive value of ΔH° (12.95 kJ/mol) revealed that the biosorption process was spontaneous and endothermic. Biosorption process was successfully applied to the treatment of an electroplating wastewater sample, where the concentration of chromium (VI) ions, organic materials and COD were effectively reduced. According to the sorption capacity, walnut shell powder considered as an effective, low cost, and environmentally friendly biosorbent for the removal of Cr(VI) ions from aqueous solution and electroplating wastewater.

Keywords Biosorption, Electroplating Wastewater, Walnut Shell Powder, Cr(VI) Ions

1. Introduction

The major sources of Cr(VI) release into the environment by waste streams are electroplating, leather tanning, paint dyes and textiles industries. Chromium in the aquatic environment has been classified in group A of human carcinogens by United States Environmental Protection Agency (USEPA). Therefore, USEPA has limited the industrial charge of Cr(VI) to surface water up to < 0.05 mg/L. The most commonly methods used for the removal of Cr(VI) from aqueous solutions and industrial effluents are chemical reduction, electrochemical precipitation, chemical precipitation, chemical oxidation-reduction, ion exchange, reverse osmosis, electro dialysis, evaporation and adsorption. These methods have significant disadvantages, including high energy requirements, incomplete metal removal, generation toxic sludge needs treatment and expensive equipments. Biosorption of toxic heavy metals by biomaterials has been suggested as a potential alternative to the conventional methods for recovery of toxic heavy metals from wastewater[1-2]. Many biomaterials such

as micro-algae[3], fungi[4], fungal biomass[5-7], walnut hull [8], almond green hull[9], *Helianthus annuus* stem waste [10], banana skin, green tea waste, oak leaf, walnut shell, peanut shell and rice husk[11], *Ocimum americanum* L. seed pods[12], chemically modified coir pith[13], groundnut shell[14], activated carbon from tamarind wood activated with zinc chloride[15], olive stone[16], grape waste[17], hazelnut[18], walnut, hazelnut and almond shell [19], pistachio hull waste[20], agriculture wastes, carbons [21], rice husk-based active carbon[22], fruit shell of gulmohar[23], coconut husk[24], husk of bengal gram[25], eucalyptus bark[26], agricultural waste biomass[27], pine needles[28], sugar cane bagasse[29], leaf mould[30] and waste pomace of olive factory[31].

2. Materials and Methods

2.1. Adsorbent

Walnut fruit was collected from a local fruit field in the north part of Iraq and the brown hard shell of the walnut fruit was thoroughly rinsed with distilled water to remove dust and soluble materials. Then it was allowed to dry at room temperature. The dried walnut shell was crushed and grounded to a fine powder in a grinding mill (Retsch RM 100) and sieved to get size fraction < 44 μm , and then dried in an

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oven at 60°C for 24 h. The dried biosorbent was stored in a desiccator and used for the batch experiments.

2.2. Materials

Analytical grade of $K_2Cr_2O_7$, HCl and NaOH were purchased from Fluka AG. A stock solutions of 1000 mg/L of Cr(VI) ions were prepared by dissolving KCr_2O_7 in 1000 mL of distilled deionized water. Desired test solutions of Cr(VI) ions were prepared using appropriate subsequent dilutions of the stock solution. The range of concentrations of Cr(VI) ions prepared from standard solution varies between 10 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. Electroplating Wastewater

The chromium rinse water samples were collected from an electroplating factory, Jordan. The electroplating wastewater collected was analyzed for different physico-chemical properties, Table 1, viz. total dissolved solids, hydrogen ion concentration, COD, conductivity, sulphate, chlorides, phosphate, chromium and zinc (II). The concentration of each of the component was determined by standard analysis methods for water and wastewater.

2.4. Analysis

The concentrations of Cr(VI) 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, The chemical oxygen demand (COD) of electroplating wastewater was analyzed by a COD reactor (Thermo reakter TR 420, Merck), Conductivity was measured by a WTW conductometer (inoLab Cond. Level 1). FT-IR (IR Prestige-21, Shimadzu) was used to identify the different chemical functional groups present in the walnut shell powder and also used to determine the functional groups which are responsible for the chromium binding with walnut shell powder. The analysis was carried out using KBr and the spectral range varying from 4000 to 400 cm^{-1} .

Table 1. Characterization of Cr(VI) electroplating wastewater

pH	4.42
Cr (IV)	34.68
Zinc (II)	4.53
Chlorides (mg/L)	0.54
Sulfates (mg/L)	1.02
Phosphate (mg/L)	0.75
Conductivity (mS/cm)	3.52
COD (mg/L)	468

2.5. Batch Biosorption Experiments

Batch biosorption experiments were conducted by mixing

biosorbent with Cr(VI) ion 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 Cr(VI) 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:

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

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 Cr(VI) ions was calculated from the following equation:

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

3. Results and Discussion

3.1. FTIR Spectral Analysis

The FT-IR spectra of walnut shell powder (before and after sorption of chromium) were used to determine the vibrational frequency changes in the functional groups in the adsorbent. The FT-IR spectra of the adsorbent display a number of absorption bands indicating the complex nature of studied adsorbent. In native walnut shell powder, the broad absorption band at 3430 cm^{-1} is indicative of the existence of bonded hydroxyl group. The absorption peak around 2905, 1744 and 1053 cm^{-1} is assigned to -CH, C=O and C-O stretching, respectively. The peak observed at 1623 cm^{-1} corresponds to C=C stretching that may be attributed to the lignin aromatic group (Fig. 1). The additional peak at 604 cm^{-1} can be assigned to bending modes of aromatic compounds. The -OH absorption band was observed to shift to 3427 cm^{-1} when walnut shell powder is loaded with Cr(IV). The -CH stretching band also shifted to 2928 cm^{-1} . It seems that these functional groups participate in metal binding. The changes in FT-IR spectra confirm the complexation of Cr(VI) with functional group present in the adsorbent.

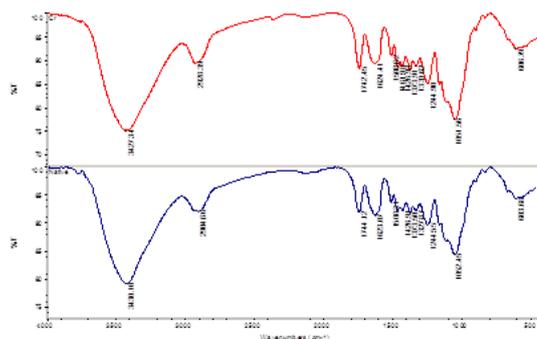


Figure 1. FT-IR spectra of native walnut shell and loaded-Cr(VI) sample

3.2. Effect of pH

The effect of pH on the biosorption of Cr(VI) ions onto

walnut shell powder was studied at pH 1.0–6.0. The maximum biosorption was observed at pH 2.0 for Cr(VI) ions. Therefore, the remaining all biosorption experiments were carried out at this pH values. pH is a vital parameter affecting the biosorption process. It was observed that the biosorption efficiency of Cr(VI) decreased as the pH increased. The maximum uptake capacity of the walnut shell powder was 138.89 mg/g for an initial Cr(VI) concentration of 40 mg/L at pH of 2.0 and 30°C. The increased binding of Cr(VI) at low pH can be explained by two factors. First, biosorption of Cr(VI) at pH 2.0 suggests that the negatively charged chromium species (chromate/dichromate in the medium) bind through electrostatic attraction to positively charged functional groups on the surface of biosorbent. As the pH increased, the overall surface charge on the cells became negative and biosorption decreased. In alkali conditions, carboxylate group exists in deprotonated form and has net negative charge. As a result, the surface charge of the biosorbents become negative and biosorption of Cr(VI) decreases. Secondly, the solution chemistry of Cr(VI) ions can affect the biosorption process. Previous studies[9, 18] showed that chromium exhibits different types of pH dependent equilibria in solutions. Sorbate and chromium form stable complexes such as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , CrO_4^- and HCr_2O_7^- , the fraction of any particular species is dependent on chromium concentration and pH. In low chromium concentration, the main fraction is HCrO_4^- with pH below 5.0, whereas the CrO_4^- increases with increase of pH value and becomes the main form with pH above 6.0.

3.3. Effect of Initial Metal Concentration

Chromium (VI) ions biosorption was studied in batch experiments (pH 2.0) using different initial Cr(VI) concentrations of 10, 20, 40, 60, 100 mg/L. The equilibrium uptake of the biosorbent was 11.44, 12.98, 16.26, 17.42 and 18.65 mg/g at initial concentration 10, 20, 40, 80 and 100 mg/L chromium ions, respectively. It is evident that the amount of chromium adsorbed onto the biosorbent increases gradually with an increasing concentrations of Cr(VI). The increase of adsorption yield with the increase in chromium ion concentration is probably due to higher interaction between the metal ions and metal sequestering sites of biosorbent.

3.4. 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 Cr(VI) was investigated. The biosorption of Cr(VI) 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.

3.5. 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 concentration. The biosorption efficiency for Cr(VI) ions as a function of biosorbent dosage was investigated. The percentage of the Cr(VI) biosorption steeply increases with the biosorbent loading up to 0.5 g/0.1 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 94.82% for Cr(VI) was attained at biosorbent dosage, 0.5 g/0.1 L. Therefore, the optimum biosorbent dosage was taken as 0.5 g/0.1 L for further experiments.

3.6. Effect of Temperature

The effect of temperature was studied using initial Cr(IV) concentration 40 mg/L at pH 2.0. The results showed that, the rate of Cr(IV) biosorption increased with an increased in temperature from 20°C to 40°C. At the temperature range (25 – 35°C) the absorption capacity is nearly constant, then further increase in temperature result in slight decrease in Cr(IV) biosorption.

3.7. Biosorption Isotherms

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of Cr(VI) ions onto walnut shell powder was modelled using three adsorption isotherms:

3.7.1. Langmuir Isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites[32]. 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 2. These values for walnut shell 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:

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

where K_L is the Langmuir constant and C_o is the initial

concentration of Cr(VI) 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 was found to be 0.204-0.719 for concentration of 10–100 mg/L of Cr(VI). They are in the range of 0-1 which indicates the favorable biosorption.

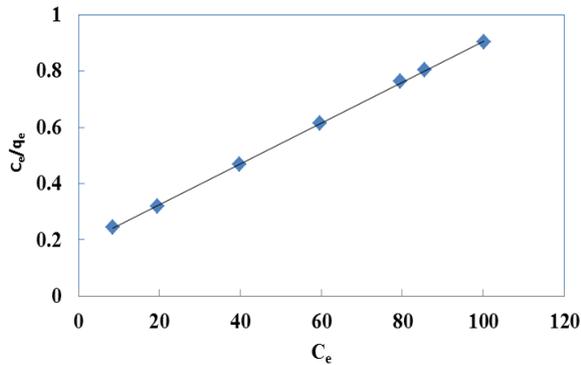


Figure 2. Langmuir isotherm for Cr(VI) ions onto walnut shell powder

3.7.2. Freundlich Isotherm

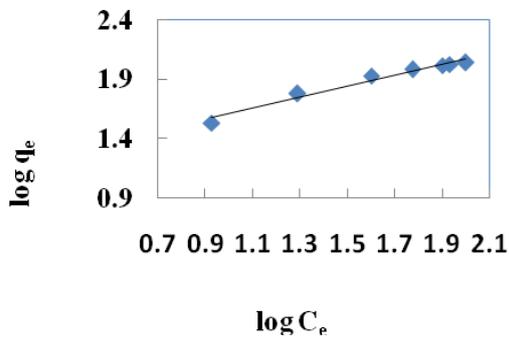


Figure 3. Freundlich isotherm for Cr(VI) ions onto walnut shell powder

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[33]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

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 $\ln C_e$, Fig. 3 on the basis of the linear of Freundlich equation (5). 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 2.163 for walnut shell powder, Table 2. Since n lie between 1 and 10, this indicate the physical biosorption of Cr(VI) onto walnut shell powder. The values of regression coefficients R^2 are regarded as a measure of goodness of fit of the experimental data to the isotherm models.

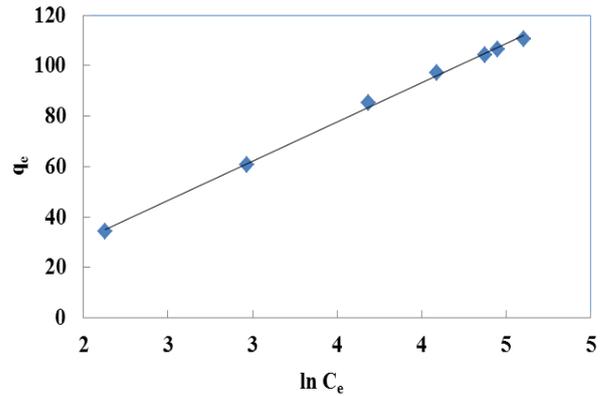


Figure 4. Temkin isotherm for Cr(VI) ions onto walnut shell powder

3.7.3. Temkin Isotherm

Temkin isotherm equation[34] 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:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \tag{6}$$

A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants b_T and A_T from the slope and the intercept, Fig. 4. 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 2.

Table 2. Isotherm constants and correlation coefficient for Cr(VI) ions onto walnut shell powder at 30 °C

Langmuir		
q_{max} (mg/g)	K_L (L/mg)	R^2
138.89	0.039	0.999
Freundlich		
K_F (mg/g)	N	R^2
14.09	2.16	0.969
Temkin		
b_T	A_T (L/mg)	R^2
81.03	0.37	0.998

3.8. 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 Cr (VI) uptake onto walnut shell powder.

3.8.1. Pseudo First-order Kinetics

The pseudo-first order equation of Lagergren[35] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

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 (7) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (8)$$

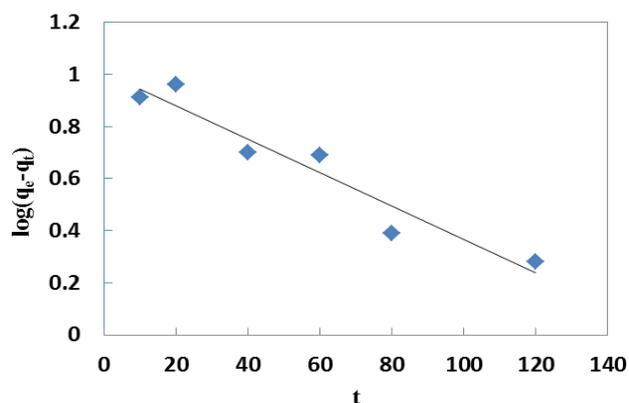


Figure 5. Pseudo-first order kinetics for Cr(VI) onto walnut shell powder

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 (8) 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), Fig. 5. The calculated values and their corresponding linear regression correlation coefficient values are listed in Table 3. R^2 was found to be 0.926, which shows that this model cannot be applied to predict the adsorption kinetic model.

3.8.2. Pseudo-second Order Kinetics

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

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg/g) and K_2 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 (9) becomes:

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad (10)$$

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 (10) should give a linear relationship, from which q_e and k can be determined from the slope and intercept of the plot, Fig. 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 3. 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.

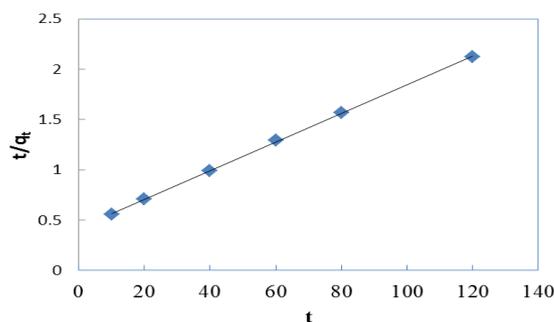


Figure 6. Pseudo-second order kinetics for Cr(VI) ions onto walnut shell powder

Table 3. Kinetics models of Cr(VI)

Pseudo-first order		
k_1	q_e (mg/g)	R^2
0.014	10.186	0.926
Pseudo-second order		
k_2	q_e (mg/g)	R^2
2E-04	71.429	0.999

3.9. Thermodynamic Parameters

In order to describe thermodynamic behaviour of the biosorption of Cr(VI) ions onto walnut shell powder, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from following equations[36-38]:

$$\Delta G^\circ = -RT \ln K_D \tag{11}$$

where R is the universal gas constant (8.314 J/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:

$$K_D = \frac{C_a}{C_e} \tag{12}$$

where, C_a is mg of adsorbate adsorbed per litre 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 (37,38):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

Equations (12) and (13) can be written as:

$$-RT \ln K_D = \Delta H^\circ - T\Delta S^\circ \tag{14}$$

or

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{15}$$

According to eq. 15, 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 Cr(VI) onto walnut shell powder are reported in Table 4. 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 an increase in adsorption with rise in temperature. This could be possibly because of activation of more sites on the surface of walnut shell 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 Cr(VI) biosorption onto walnut shell powder was in the range of (-3.51 to -4.63) kJ mol⁻¹ and so the biosorption was predominantly physical biosorption. A positive value of ΔS° as 56.18 J/ mol K showed increased randomness at solid solution interface during the adsorption of Cr(VI) ions onto walnut shell powder.

Table 4. Thermodynamic parameters for Cr(VI) ions onto walnut shell powder at different temperatures and pH = 2.0

T (K)	K_D (L/mg)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
293	4.22	-3.51	12.95	56.18
303	5.01	-4.06		
313	5.93	-4.63		

3.10. Treatment of Electroplating Wastewater

The application of Cr(VI) ions biosorption onto walnut shell powder on electroplating wastewater, collected from an electroplating unit of chromium. The main characteristic of the effluent samples before and after the biosorption process are listed in Table 5.

Table 5. Characterization of electroplating wastewater samples

Biosorption	Cr(VI) (mg/L)	pH	Conductivity (mS/cm)	COD (mg/L)
Before biosorption	34.68	4.4	3.52	486
After biosorption	<1	5.8	1.88	80

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 absorption of Cr(VI) ions by walnut shell powder 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 walnut shell powder. The initial COD concentration of 486 mg/L decreased to less than 80 mg/L showing a removal efficiency of about 83%.

3.11. Comparison of Walnut Shell Powder with Other Biosorbents

Table 6. Maximum biosorption capacity q_{max} (mg/g) of Cr(VI) by various adsorbents

Biosorbent	q_{max} (mg/g)	Reference (give reference number instead of name of the authors below)
Gulmohar fruit shell	12.28	[23]
Eucalyptus bark	45	[26]
Hazelnut shell	17.7	[18]
Walnut hull	98.12	[8]
Coconut husk	29	[24]
Almond shell	3.4	[19]
Walnut shell	8.01	[19]
Ground nut shell	5.88	[19]
Hazelnut shell	8.28	[19]
Rice straw	3.15	[22]
Maize com cob	0.82	[27]
Oak pine	0.47	[11]
Almond green hull	2.04	[9]
Coir pith	165	[13]
Bengal gram husk	2.81	[25]
Pine needles	21.5	[28]
Sugar cane bagasse	13.4	[30]
Leaf mould	27.6	[30]
Waste pomace of olive	13.9	[31]
Walnut shell powder	138.89	This work

A comparative of the maximum biosorption capacity (q_{max}) of walnut shell powder with those of some other biosorbents reported in literature is given in Table 6. 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 Cr(VI) biosorption capacity of the walnut shell powder.

4. Conclusions

In this work, we have studied the biosorption of Cr(VI) ions by walnut shell powder under various conditions. The pH has much effect on the biosorption of Cr(VI) ions from aqueous solutions and electroplating wastewater. The kinetic results provided the best correlation of the experimental data of biosorption of Cr(VI) ions onto walnut shell powder by pseudo second-order equation. The biosorption isotherms could well be fitted by the Langmuir model. The negative values of ΔG° and positive value of ΔH° revealed that the biosorption process was spontaneous and endothermic. Biosorption process was successfully applied to the treatment of an electroplating wastewater sample, where the concentration of chromium (VI) ions, organic materials and COD were effectively reduced. According to the sorption capacity, walnut shell powder considered as an effective, low cost, and environmentally friendly biosorbent for the removal of Cr(VI) ions from aqueous solution and electroplating wastewater.

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