

Research Article

New Sustainable Biosorbent Based on Recycled Deoiled Carob Seeds: Optimization of Heavy Metals Remediation

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In this study, an efficient biosorbent was developed from deoiled carob seeds, a agroindustrial waste. The biosorption efficiency was evaluated for cadmium and cobalt ions removal from aqueous solution under various parameters such as treating agent, solution pH, biosorbent dosage, contact time, initial metal ions concentration, and temperature. The effect of some major inorganic ions including Na⁺, K⁺, Ca²⁺, Mg²⁺, and Al³⁺ on the biosorption was also established. Based on this preliminary study, four independent variables including solution pH, biosorbents dosage, initial metal concentration, and treating agent were chosen for the optimization of the process using full-factorial experimental design. It was found that chemical pretreatment of the raw deoiled carob seeds with NaOH strongly enhances its biosorption potential. Thus, the optimal conditions for high biosorption of cadmium(II) and cobalt(II) were achieved at pH of 6, biosorbent dosage of 1 g/L, and initial metal concentration of 50 mg/L. The biosorbents were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), Boehm titration, and the point of zero charge (pH_{PZC}).

1. Introduction

Heavy metal pollution imposes ecological and public health problems according to hazardous and irrecoverable effects of metal ions on the environment and aquatic ecosystems [1]. Besides, the toxic and harmful effects to organisms living in water, heavy metals also accumulate throughout the food chain and may affect human beings [2]. In this way, the removal and recovery of heavy metals from aqueous effluents before being disposed in the environment is required [3].

Various methods have been used to remove heavy metal ions such as chemical precipitation [4], membrane filtration [5], ion exchange [6], solvent extraction [7], flotation [8],

and electrochemical treatment [9]. Among all these mentioned methods, sorption is an effective and eco-friendly method for the removal of heavy metal ions from wastewaters due to its simple design, easy operation handling, and availability of different sorbents with large efficacy to remove a wide range of heavy metals [10–12]. Activated carbons are widely used as adsorbents in wastewater treatment because of their high surface areas and active functional groups, but their high cost inhibits sometimes their use [13]. Therefore, there is a need to develop other biosorbents from alternative low-cost raw materials for the same role as activated carbon. Recently, low-cost precursors have become the focus of researchers for example, chitosans [14], bark of *Pinus elliottii* [15], *Jatropha curcas* [16],

sugarcane bagasse [17], *Eichornia crassipes* [18], coconut [19], agricultural peels [20–22], sunflower stalks [23], raw carob shells and chemically treated carob shells [24], *Diploptaxis harra*, and *Glebionis coronaria* L [25].

The aim of this study is to assess the applicability of chemically treated deoiled carob seeds for the removal of cadmium(II) and cobalt(II) ions from aqueous solution. Biosorption studies were carried out under various parameters such as solution pH, biosorbents dosage, contact time, initial metal ions concentration, and temperature. The biosorption kinetic data were tested by pseudo-first-order and pseudo-second-order kinetic models. The equilibrium data were analyzed using Langmuir and Freundlich models. This paper also discussed the combined effect of the most influencing parameters, which are solution pH, biosorbent dosage, concentration of the solution, and the treating agent. Full-factorial experimental design with two levels (2^4) and surface response methodology were used to acquire the optimal parameters for high removal of Cd(II) and Co(II) ions.

2. Experimental

2.1. Materials. All the chemicals used in the preparation and the biosorption studies were of analytical grade. Cd ($(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), NaCl (99.5%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98\%$), HCl (37%), Na_2CO_3 , and NaHCO_3 were obtained from Sigma-Aldrich (Germany). Mg ($(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (97%) was provided from SDS (France), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and HNO_3 (65%) from Scharlau (Spain), and NaOH (98%) was provided from Merck (Germany).

2.2. Preparation of the Biosorbents. The deoiled residue was obtained as a by-product from the hydrodistillation process of carob seeds from the region of Khenifra in Morocco. The biomass was repeatedly washed with demineralized water and then oven dried at about 120°C for 24 h min in order to remove excess moisture. The dried biomass was then grounded using mortar and pestle and sieved to get a size fraction lower than $160\ \mu\text{m}$, referred as Raw-seeds. For the chemical treatment, 10 g of the Raw-seeds was treated with 100 mL of 1 M solution of HCl or NaOH for 2 h. The biosorbents were then filtered and washed with distilled water until neutral pH. The pretreated biosorbents were then dried in an oven at 120°C for 24 h and stored in glass bottles under following names HCl-seeds and NaOH-seeds for further use.

2.3. Characterisation. FTIR transmittance spectra of the biosorbents were recorded in the region of $4000\text{--}400\ \text{cm}^{-1}$ using a Scottech-SP-1 spectrophotometer. Basic and oxygenated acidic surface groups were assessed by Boehm titrations [26]. About 0.1 g of each sample was mixed with 50 mL of 0.01 M aqueous reactant solution (NaOH, Na_2CO_3 , NaHCO_3 , or HCl). The mixtures were stirred at 500 rpm for 24 h at room temperature. Then, the suspensions were filtered by a $0.45\ \mu\text{m}$ membrane filter. To determine the oxygenated groups content, back titrations of the filtrate (10 mL) were achieved with standard 0.01 M-HCl solution.

Basic groups contents were also determined by back titration of the filtrate with 0.01 M-NaOH solution. The morphological characteristics were analyzed by scanning electron microscopy (SEM). Small amount of each sample was finely powdered and mounted directly onto aluminum sample holder using the two-sided adhesive carbon model. Energy dispersive X-ray (EDX) was also performed to determine the elemental composition of the raw carob seeds and the both treated samples. The point of zero charge (pH_{PZC}) was determined by the pH drift method according to the method proposed by Noh and Schwarz [27]. The pH of NaCl aqueous solution (50 mL at 0.01 mol/L) was adjusted to successive initial values in the range from 2.0 to 12.0 by addition of HNO_3 (0.1 N) and/or NaOH (0.1 N). Furthermore, 0.05 g of each biosorbent was added in 50 mL of solution and stirred for 6 h. The final pH was measured and plotted against the initial pH. The pH_{PZC} was determined at the value for which $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$.

2.4. Batch Biosorption Procedure. Stock solutions were prepared by dissolving desired weight of each metal ion in distilled water, and necessary concentrations were obtained by dilution. Biosorption experiments were investigated in a series of beakers containing 100 mL of the metal ion solution at desired concentration and desired weight of the biosorbent. The mixtures were stirred for 2 h at 500 rpm using a magnetic stirrer. The influence of pH was performed by varying the pH from 2.0 to 7.0 at an initial metal concentration of 100 mg/L. The pH of the solutions was adjusted with either 0.1 M of HCl or 0.1 M of NaOH and using a SensION + PH31 pH meter. The biosorbent dosage was varied from 0.5 to 5 g/L. The contact time was varied between 5 and 210 min at room temperature with initial pH solution. Biosorption equilibrium was established for different metal ion concentration between 20 and 200 mg/L. The effect of temperature was tested from 10 to 50°C using a thermostatically controlled incubator. The effect of some major inorganic ions including Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Al^{3+} on the biosorption was studied for each heavy metal at a constant initial metal concentration of 100 mg/L. The concentration of each ion was varied from 10 to 100 mg/L.

After each biosorption experiment completed, the solid phase was separated from the liquid phase by centrifugation at 3000 rpm for 10 min. Metal ions concentration was determined using a PerkinElmer atomic absorption spectrophotometer (Analyst 200).

The biosorption capacity and biosorption removal efficiency were calculated using the following equations:

$$q_{t,e} = \frac{(C_0 - C_{t,e})}{R}, \quad (1)$$

$$\% \text{ removal} = \frac{(C_0 - C)}{C_0} * 100, \quad (2)$$

where $q_{t,e}$ (mg/g) is the biosorbed quantity at any time or at equilibrium, C_0 (mg/L) is the initial metal ion concentration, $C_{t,e}$ (mg/L) is the metal ion concentration at a time t or at

equilibrium, and R (g/L) is the mass adsorbents per liter of solution.

Kinetic and equilibrium parameters were estimated with the aid of the nonlinear regression method using Origin 6.0 software.

2.5. Design of Experiment for the Optimization of Cd(II) and Co(II) Biosorption. The methodology of experimental design was used for modeling and optimization of the biosorption processes of Cd(II) and Co(II) ions from aqueous solutions. The four most influencing factors are solution pH (A), biosorbents dosage (B), initial metals concentration (C), and treating agent (D). The values of variable levels are presented in Table 1. The experiments were made according to a full-factorial design at two levels (2^4), with 16 experiments.

In addition, a first-order polynomial model was also used for modeling sorption of Cd(II) or Co(II) ions. The general equation of the first-order polynomial model is presented in

$$Y = b_0 + b_1A + b_2B + b_3C + b_4D + b_{12}AB + b_{13}AC + b_{14}AD + b_{23}BC + b_{24}BD + b_{123}ABC + b_{124}ABD + b_{134}ACD + b_{234}BCD + b_{1234}ABCD, \quad (3)$$

where Y (mg/g) is the responses of interest (adsorption capacity of Cd(II) (Y_1) and adsorption capacity of Co(II) (Y_2)).

The results were analyzed using the Trial software Design Expert 10.0.0.

3. Results and Discussion

3.1. Characterization

3.1.1. FT-IR Analysis of the Biosorbents. The infrared spectra of Raw-seeds, NaOH-seeds, and HCl-seeds are illustrated in Figure 1. The figure shows broad absorption band for Raw-seeds at 3200–3600 cm^{-1} due to the stretching of the N–H bond of amino groups and indicative of bonded hydroxyl group [11], and this band was separated into more resolute three bands after the chemical pretreatments with NaOH and HCl. Two bands at around 3200–3400 cm^{-1} indicate the presence of carboxylic acid and amino groups, and the other one near 3500 cm^{-1} is related to the OH stretching vibration mode in alcohol and phenol groups. The band at 2930 cm^{-1} corresponds to the symmetrical and asymmetrical–CH–vibrations in lipids. The peaks located at 1620 cm^{-1} are characteristics of C=O stretching for aldehydes and ketones, which can be conjugated or nonconjugated to aromatic rings [28]. The–C–O, C–C, and–C–OH stretching vibrations can be attributed to peaks in the region of 1180–1048 cm^{-1} . The spectra showed bands located at 630 cm^{-1} , assigned to OH– ions.

3.1.2. Boehm Titration of the Biosorbents. The oxygen functional groups are very important characteristics of the biosorbents because they determine the surface properties

TABLE 1: Process factors and their levels.

Factors	Levels	
	Low (–)	High (+)
A. pH	4	6
B. Biosorbent dose (g/l)	1	3
C. Initial concentration (mg/l)	50	100
D. Treating agent	HCl	NaOH

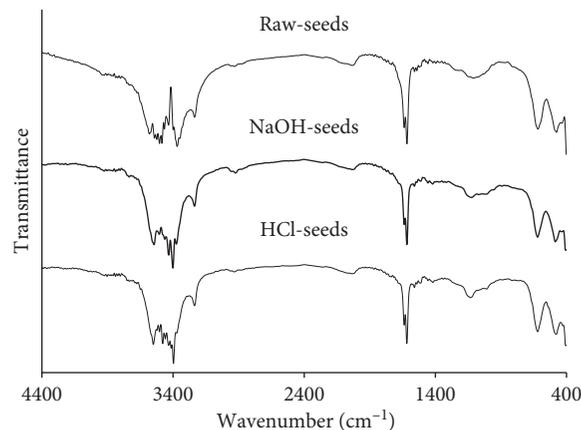


FIGURE 1: FT-IR spectra of Raw-seeds, HCl-seeds, and NaOH-seeds biosorbents.

and hence their quality as biosorbents. These functional groups are mainly divided as acidic or basic, which affect the surface charge and consequently the biosorption capability of the biosorbents. The Boehm's titration method provides qualitative and quantitative information regarding the total amount of basic groups and the amounts of acidic functional groups such as carboxylic, lactonic, and phenolic. From Table 2, it can be seen that Raw-seeds, HCl-seeds, and NaOH-seeds' surface constituted mainly of acidic groups, which are due to phenolic, lactonic, and carboxylic groups and a less quantity of basic groups. So, the surface of these biosorbents is acidic. The biosorbents having greater surface acid groups have higher cation exchange properties. According to the experimental data, the HCl-seeds had an important amount of acidic groups than Raw-seeds followed by NaOH-seeds. The use of chemical reagents acid in the treatment process produces an increase in the amount of acid groups present in the biosorbent surface. It was observed that the concentration of lactonic and phenolic groups in HCl-seeds is higher than those of carboxylic groups.

3.1.3. Morphology of the Biosorbents. The surface texture and morphology of biosorbents were analyzed by SEM in order to compare the morphology of raw and chemically treated carob seeds. The SEM images of these biosorbents are depicted in Figure 2. As it is clearly shown, there is a significant difference among the tree samples. In fact, no obvious pores can be seen for Raw-seeds. Then, for the HCl-seeds, the surface morphology does not have well-defined pores. However, the NaOH-seeds' surface indicates some

TABLE 2: Chemical groups on the surface of the biosorbents.

Biosorbent	Carboxylic groups (meq/g)	Lactonic groups (meq/g)	Phenolic groups (meq/g)	Total acid groups (meq/g)	Total basic groups (meq/g)
Raw-seeds	0.4070	0.4880	0.4900	1.3850	0.3750
HCl-seeds	0.3810	0.5150	0.5240	1.4200	0.3650
NaOH-seeds	0.4090	0.4830	0.4990	1.3910	0.3870

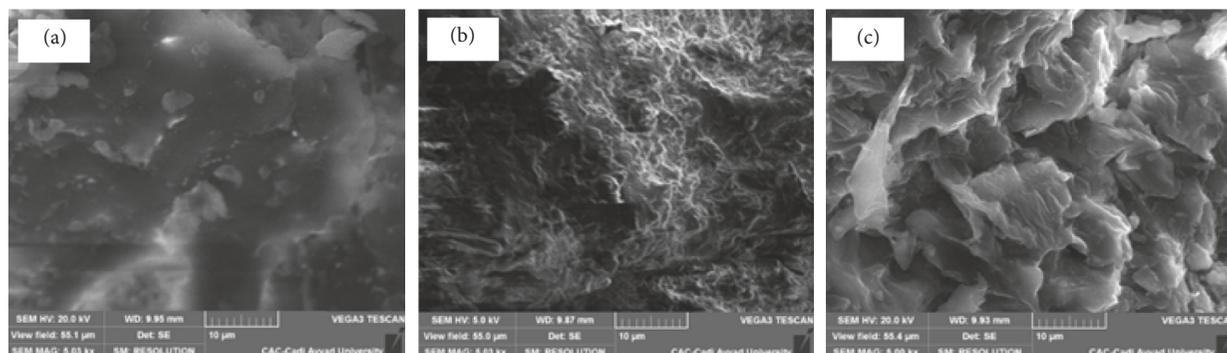


FIGURE 2: SEM images of (a) Raw-seeds, (b) HCl-seeds, and (c) NaOH-seeds.

irregular cavities and a changing in the external texture as a result of the reaction between the raw material and the treating agent. These different characteristics allow NaOH-seeds to contribute a high adsorption performance of heavy metals. These results suggest that the NaOH is an effective agent for creating well-developed pores on the surface of the raw material, which is already shown for the alkaline-treated carob shells [24].

3.1.4. EDX Analysis. EDX is an analytical technique to identify the element presence on the material surface based on its characteristic X-ray energy. This technique is normally coupled with SEM analysis to gain more complete result. The elemental compositions of Raw-seeds, NaOH-seeds, and HCl-seeds are tabulated in Table 3. In addition, the elemental compositions are presented under peaks in Figure 3. The major components of the raw carob seeds were set up to be carbon (56.13 weight%) and oxygen (35.31 weight%). However, these Raw-seeds also contain a small percentage of phosphorus, sulfur, chlorine, potassium, and calcium. After the HCl treatment, a small reduction in the percentage of carbon (54.71 weight%) and a significant rise in the quantity of oxygen (45.10 weight%) was seen. An extinction of potassium and calcium was noticed. However, for NaOH-seeds, it can be also seen that the percentage of carbon decreases (48.32 weight%), and the oxygen content increased to acquired 40.35 weight%. A change in the elemental composition was noticed after the NaOH treatment which mainly falls within an appearance of new elements, including sodium, magnesium, and aluminum and a disappearance of other elements such as phosphorus, sulfur, and chlorine. As a result, it might be concluded that the alkaline treatment increases the percentage of oxygen in HCl-seeds followed by NaOH-seeds and reduced the amount of carbon for both biosorbents as the same order.

3.1.5. pH of Zero Charge. The pH_{PZC} is an important characteristic for the biosorbent as it indicates its acidity-basicity and the net surface charge of the biosorbent in solution. The pH_{PZC} was 5.9, 2.3, and 6.9, respectively, for Raw-seeds, HCl-seeds, and NaOH-seeds. We can see that the Raw-seeds have an acidic surface. After the treatment by HCl, we found an increase in the acidity of the biomaterial at 2.3. But, after NaOH treatment, an increase in the pH_{PZC} appears. The low pH_{PZC} is in agreement with the predominance of surface acid groups. This result indicates that, for pH lower than 5.9, 2.3, and 6.9, the surfaces of the Raw-seeds, HCl-seeds, and NaOH-seeds are positively charged. Then at these pH, the biosorption of the studied metals was inhibited, due to the electronic repulsion between metal ions and positively charged functional groups. Inversely, for pH superior of 5.9, 2.3, and 6.9, the number of negatively charged sites on the Raw-seeds, HCl-seeds, and NaOH-seeds' surface increases, and metal biosorption becomes more important.

3.2. Biosorption Performance

3.2.1. Effect of Solution pH on the Biosorption. The pH of the solution has a significant impact on the uptake of heavy metals, since it indicates the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate [29]. The pH of the solution controls the electrostatic interactions between the sorbent and the sorbate [30]. However, the dependence of heavy metal biosorption on pH was different for each metal. Figure 4 shows the effect of pH on biosorption of Cd(II) and Co(II) onto Raw-seeds, HCl-seeds, and NaOH-seeds. It can be seen that the metal biosorption increases with increasing solution pH, and it is strongly dependent on pH solution. It is known generally that the percent removal of the heavy

TABLE 3: Elemental composition of Raw-seeds, HCl-seeds, and NaOH-seeds.

Element	Raw-seeds		HCl-seeds		NaOH-seeds	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C	56.13	65.81	54.71	61.72	48.32	58.11
O	35.31	31.09	45.10	38.19	40.35	36.43
Na	—	—	—	—	4.13	2.59
Mg	—	—	—	—	0.90	0.53
Al	—	—	—	—	0.34	0.18
P	0.23	0.11	0.10	0.05	—	—
S	0.23	0.10	0.07	0.03	—	—
Cl	0.21	0.08	0.02	0.01	—	—
K	4.94	1.78	—	—	0.17	0.17
Ca	2.95	1.04	—	—	1.98	1.98

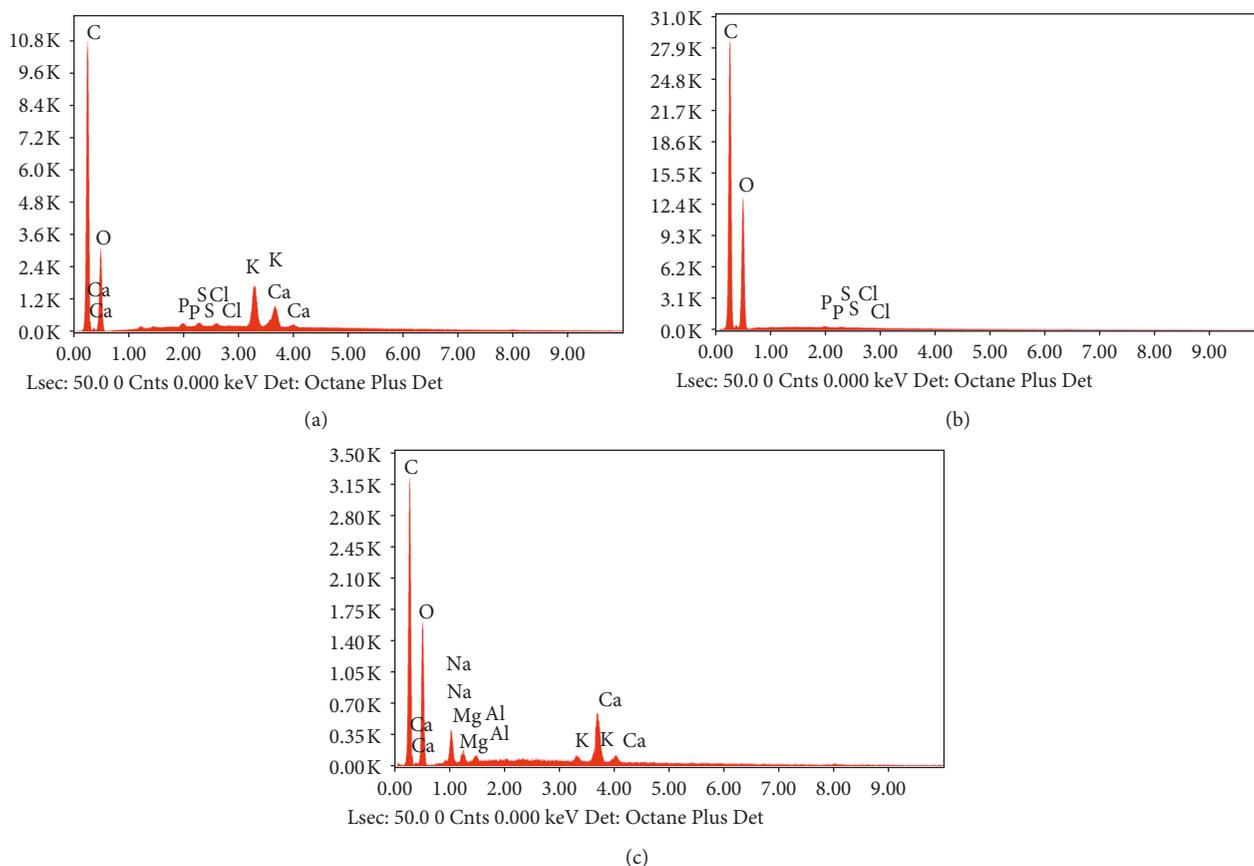


FIGURE 3: EDX analysis of (a) Raw-seeds, (b) HCl-seeds, and (c) NaOH-seeds.

metal ions increases with pH. At low pH, the cations compete with the H^+ ions in the solution for the sorption sites and therefore biosorption declines. In contrast, as pH increased, the competition between proton and metal cation decreases which means that there are more negative groups available for the binding of metal ions which results a greater metal uptake. On the other hand, at higher pH, metal cations start to form hydroxide complexes or precipitate as their hydroxides, which decrease the biosorption of metal ions [31, 32]. The pH_{PZC} values indicate that the biosorbent acquires a positive charge below a pH of 5.9, 2.3, and 6.9, respectively, for Raw-seeds, HCl-seeds,

and NaOH-seeds. Above these values, the biosorbents' surface becomes negatively charged [33]. Therefore, the ionic sorbent-sorbate interaction becomes progressively significant for pH higher than 5.9, 2.3, and 6.9. As shown in the figure, the sorption capacities for Cd(II) and Co(II) by NaOH-seeds are greater than those biosorbed by Raw-seeds and HCl-seeds. This may be related to the properties of biosorbent and metal sorbate.

3.2.2. Effect of Biosorbents Dosage. The biosorbent dosage is an important parameter because this parameter determines

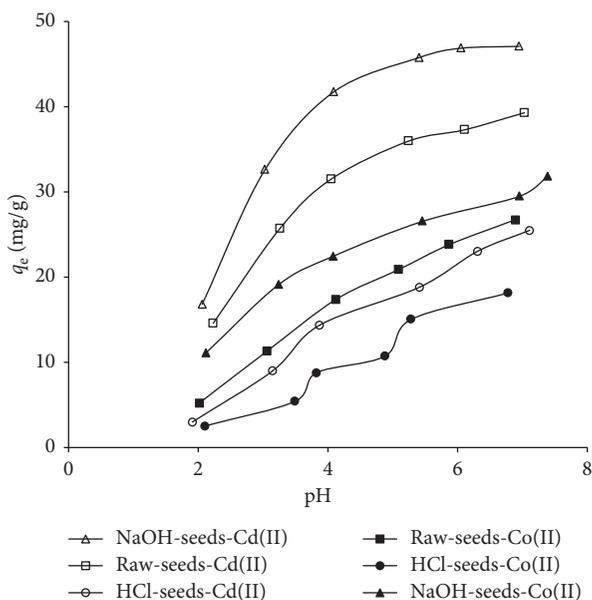


FIGURE 4: Effect of pH on the biosorption of Cd(II) and Co(II) onto the biosorbents: $C_0 = 100$ mg/L, contact time = 120 min, $R = 2$ g/L, and $T = 25^\circ\text{C}$.

the capacity of biosorbent for a given Cd(II) and Co(II) concentration and also determines sorbent-sorbate equilibrium of the system. Figure 5 represents the Cd(II) and Co(II) removal efficiencies for the study biosorbents. This figure indicates that the percentage removal of Cd(II) and Co(II) increased with increasing biosorbent dose due to the increase in the total available surface area and the number of active sites for biosorption of the biosorbent particles [32]. The percentage removal of Cd(II) increased from 20.70 to 76.06%, from 10.60 to 23.65%, and from 32.20 to 99.91% when the biosorbents dosage was increased from 0.5 to 5 g/L, respectively, for Raw-seeds, HCl-seeds, and NaOH-seeds. For Co(II), the biosorption yield increased from 12.73 to 36.94%, from 3.34 to 13.50%, and from 17.02 to 55.69% when the biosorbents dosage was increased from 0.5 to 5 g/L, respectively, for Raw-carob, HCl-carob, and NaOH-carob. Therefore, the biosorption yield was almost the same when the biosorbent dosage was higher than 3 g/L. This trend could be explained as a consequence of a partial aggregation of biosorbent at higher sorbent dosage, which results in the decrease in effective surface area for the [34] biosorption [35].

3.2.3. Biosorption Kinetics. The effect of contact time on the biosorption of Cd(II) and Co(II) metal ions is reported in Figure 6. The evolution of the biosorbed amount of metal ions with the contact time indicates that the equilibrium was relatively fast and was totally reached in about 45 min for the biosorption of Cd(II) by both the biosorbents and was 60 min in the case of Co(II). This equilibrium time is very short in comparison with other literature results [36–38], which is one of the advantages of our biosorbents. In Figure 4, two kinetic regions can be observed: the first one is characterized by a high biosorption rate, which is due to the

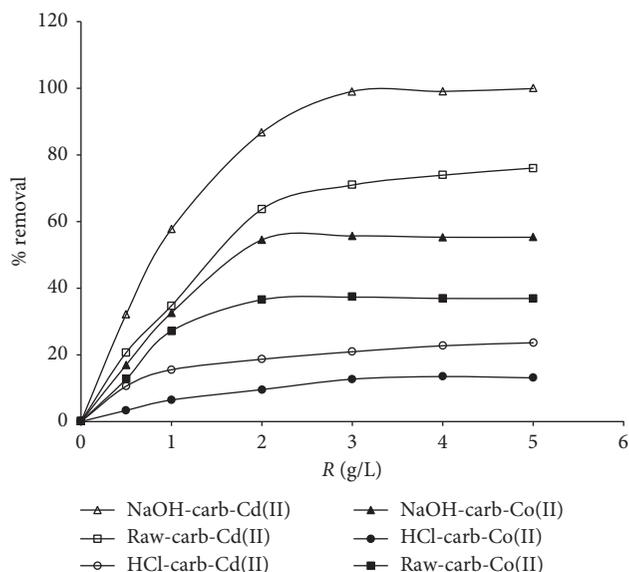


FIGURE 5: Effect of biosorbents dosage on the removal of Cd(II) and Co(II) by the biosorbents: $C_0 = 100$ mg/L, contact time = 120 min, initial pH, and temperature = 25°C .

fact that initially the number of sites of available biosorbent is higher and the driving force for mass transfer is greater. Metal ions easily access first the biosorption sites. As time progresses, the number of free sites of Raw-seeds, HCl-seeds, and NaOH-seeds decreases and the nonbiosorbed cations in solution are assembled on the surface, thus limiting the biosorption capacity.

In order to determine the biosorption efficiency of Cd(II) and Co(II) on three biosorbents, two kinetic models are used; the pseudo-first-order and the pseudo-second-order kinetic models. Kinetic data were analyzed on the basis of the regression coefficient (r^2) and the amount of metal biosorbed per unit weight of the biosorbent.

The Lagergren first-order rate expression based on solid capacity is generally expressed as follows [39]:

$$q = q_e(1 - e^{-k_1 t}), \quad (4)$$

where q_e and q (both in mg/g) are, respectively, the amounts of metal biosorbed at equilibrium and at any time t (min) and k_1 (1/min) is the rate constant of biosorption.

The pseudo-second-order equation is expressed as [40]

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}, \quad (5)$$

where k (g/mg min) is the pseudo-second order rate constant.

The obtained data and the correlation coefficients, r^2 , are listed in Table 4. The results show that the calculated equilibrium values using pseudo-first-order model kinetic were very close to the experimental ones (q_{exp}) than the others calculated from the pseudo-second-order model and also showed the best fit to the experimental data with the highest correlation coefficients ($r^2 = 0.999$) for the both metal ions. From these results, it was concluded that

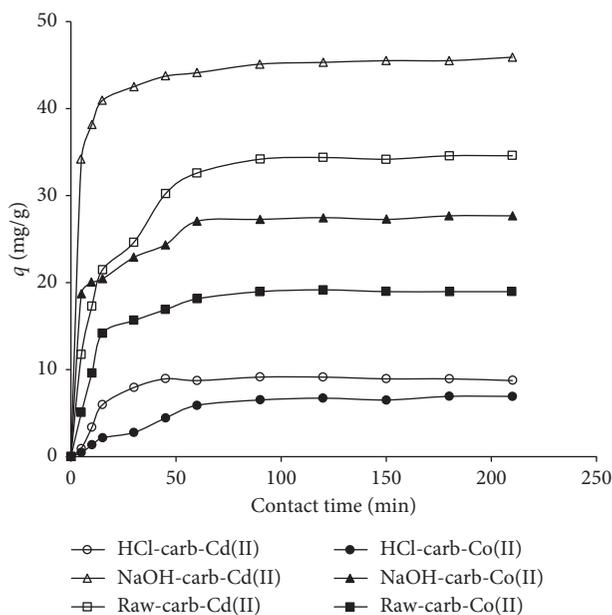


FIGURE 6: Kinetics of Cd(II) and Co(II) biosorption by the biosorbents: $C_0 = 100$ mg/L, $R = 2$ g/L, initial pH, and temperature = 25°C.

TABLE 4: Pseudo-first-order and pseudo-second-order kinetic parameters for the biosorption of Co(II) and Cd(II).

Metal	Biosorbent	q_e (mg/g)	Pseudo-first-order			Pseudo-second-order		
			q_e (mg/g)	k_1 (1/min)	r^2	q_e (mg/g)	k_2 (g/mg·min)	r^2
Cd(II)	Raw-seeds	34.578	34.159	0.071	0.996	37.230	0.002	0.992
	HCl-seeds	8.942	9.076	0.043	0.991	10.380	0.005	0.972
	NaOH-seeds	45.905	45.863	0.296	0.992	42.649	0.009	0.994
Co(II)	Raw-seeds	18.963	18.964	0.064	0.998	20.697	0.004	0.993
	HCl-seeds	6.929	7.090	0.022	0.984	8.907	0.002	0.973
	NaOH-seeds	27.676	27.605	0.051	0.999	28.741	0.005	0.997

the biosorption of Cd(II) and Co(II) onto Raw-seeds, HCl-seeds, and NaOH-seeds could be better described by the pseudo-first-order model. This may be due to rapidity transfer speed of Cd and Co molecules to the surface of the biosorbent and the availability of active sites.

3.2.4. Biosorption Isotherms. The biosorption isotherms describe how the sorbate molecules are distributed between the liquid phase and solid phase when the system reaches the equilibrium. The analysis of isotherm data by fitting them to different models is important to find a sustainable model that can be used [41]. The biosorption isotherms are illustrated in Figure 7. It is obvious that the amount of metal biosorbed increases as its equilibrium concentration increased. This trend may be due to the high driving force for mass transfer at a high initial heavy metal concentration. In addition, if the heavy metal concentration in solution is higher, the active sites of biosorbent are surrounded by much more ions, and the biosorption phenomenon occurs more efficiently. Thus, biosorption amount increases with

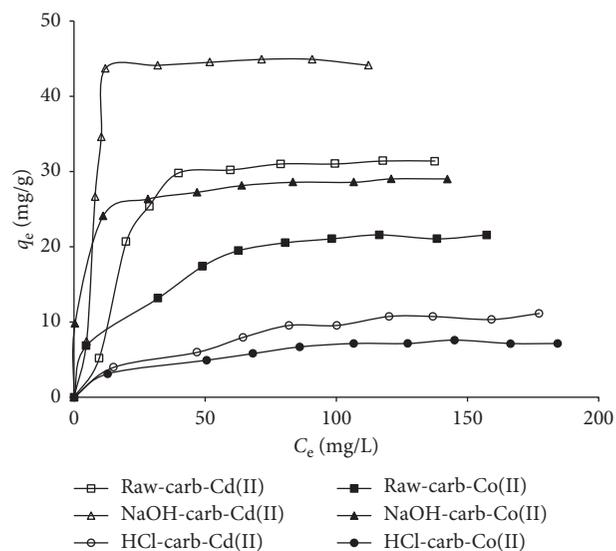


FIGURE 7: Adsorption isotherms of Cd(II) and Co(II) biosorption by the biosorbents: $R = 2$ g/L, initial pH, contact time = 120 min, and temperature = 25°C.

the increase of initial ion concentration [42]. The isotherms' form was type L for Raw-seeds, HCl-seeds, and NaOH-seeds according to Giles classification [43].

Several biosorption isotherms can be used to correlate the biosorption equilibrium in heavy metals biosorption on several biosorbents. Some well-known isotherms are Langmuir and Freundlich models.

(1) *Langmuir Model*. Langmuir isotherm assumes two main points in the biosorption process. First, the biosorption happens at specific homogeneous biosorption sites in the biosorbent. Second, the monolayer biosorption and maximum biosorption occurs when biosorbed molecules form a saturated layer on the surface of adsorbent. All biosorption sites involved are energetically identical, and the intermolecular force decreases as the distance from the biosorption surface increases [44].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}, \quad (6)$$

where q_m (mg/g) is the maximum monolayer biosorption capacity, K_L (L/mg) is the Langmuir equilibrium constant related to the biosorption affinity, and C_e is the equilibrium concentration.

(2) *Freundlich Model*. Freundlich isotherm is an empirical equation assuming that the biosorption process takes place on heterogeneous surfaces, and biosorption capacity is related to the concentration of biosorbed metal ions at equilibrium. Freundlich isotherm is suitable in treating metal ions' biosorption at higher concentrations. However, this isotherm is not suitable for low concentration range.

Freundlich isotherm model is represented by the following equation [45]:

$$q_e = K_F C_e^{1/n}, \quad (7)$$

where K_F ($\text{mg}^{1-1/n}/\text{g}/\text{L}^n$) is the Freundlich constant and n is the heterogeneity factor. The K_F value is related to the biosorption capacity, while $1/n$ value is related to the biosorption intensity.

(3) *Analysis of Adsorption Isotherms*. The calculated isotherm parameters for each model and correlation coefficients analyzed by nonlinear regression method are presented in Table 5. This table shows that the Langmuir model indicates higher values of correlation coefficients ($r^2 > 0.993$) in the biosorption of Co(II) than Cd(III) biosorption onto the three biosorbents. For these reasons, it can be approved that Langmuir equilibrium isotherm describes the metal biosorption process using the studied biosorbents well. This process is occurred by the formation of metal ion monolayer onto the biosorbent surface with finite number of identical sites, which are homogeneously distributed over the biosorbent surface [46]. The q_{max} values were 34.85, 14.08, and 49.11 mg/g for Cd(II) and 24.74, 7.65, and 28.18 mg/g in the case of Co(II) respectively, for Raw-seeds, HCl-seeds, and NaOH-seeds. We can also conclude that NaOH-seeds' biosorption capacity is superior than that of

Raw-seeds and HCl-seeds. On the other hand, the biosorption of Cd(II) on the three biosorbents is greater in comparison to that of the Co(II) biosorption. This may be due to the nature of the interaction between each sorbate and biosorbent. However, the Freundlich model provides two parameters: k_f and n . k_f is related to the biosorption capacity and biosorption intensity of the metal ions on the different biosorbents and represents the quantity of metal ions biosorbed onto biosorbent at equilibrium concentration. n represents the strength of metal ions' biosorption on the biosorbent. n value from 1 to 10 indicates relatively strong biosorption. The obtained n values in the studied biosorbents were more than 1, which indicates relatively a strong biosorption of the metal ions on the biosorbents [47].

Table 6 presents a comparison of the maximum adsorption capacity of Raw-seeds, HCl-seeds, and NaOH-seeds with various adsorbents reported in the literature for the adsorptive removal of Cd(II) and Co(II). Though there were variations in some experimental conditions, the table shows that the biosorption capacity of Raw-seeds, HCl-seeds, and NaOH-seeds for the both heavy metals is most higher compared to other adsorbents used in previous studies. This can be explained by the nature of functional groups present in the surface of Raw-seeds, HCl-seeds, and NaOH-seeds.

3.2.5. *Effect of Temperature*. The variation of sorption efficiencies of Cd(II) and Co(II) on Raw-seeds, HCl-seeds, and NaOH-seeds as function of solution temperature is shown in Figure 8. It was observed that the temperature does not have significant influence on the biosorption capacity in the studied range. The variation in temperature had two major effects on the sorption process. An increase in the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles as a result of reduced viscosity of the solution [61]. In addition, several authors have shown that further increases in the temperature may lead to a decrease in the metal removal percentage. This may be attributed to an increase in the relative desorption of the metal from the solid phase to the liquid phase, deactivation of the biosorbent surface, destruction of the active sites on the biosorbent surface owing to bond disruption [62], or weakness of the sorbent active site binding forces and the sorbate species and also between the adjacent molecules of the sorbed phase [63].

3.2.6. *Effect of Inorganic Ions*. Industrial effluents often contain more than one metal ion. Consequently, biosorption becomes competitive, in which several metal ions compete for a limited number of binding sites [64]. Figure 9 shows the effect of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Al^{3+} ions on the biosorption of Cd(II) and Co(II). From this figure, we can conclude that the monovalent cations K^+ and Na^+ have less influence on the biosorption. On the other hand, divalent and trivalent ions inhibit the biosorption on the both biosorbents. The degree of inhibition by the inorganic ions followed the sequence: $\text{K}^+ < \text{Na}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Al}^{3+}$ for the both metals. The monovalent cations Na^+ and K^+ are

TABLE 5: Model isotherm constants for the biosorption of Cd(II) and Co(II) biosorption onto Raw-seeds, HCl-seeds, and NaOH-seeds.

Isotherms	Parameters	Raw-seeds		HCl-seeds		NaOH-seeds	
		Cd(II)	Co(II)	Cd(II)	Co(II)	Cd(II)	Co(II)
Langmuir	q_m (mg/g)	34.85	24.74	14.08	7.65	49.11	28.18
	K_L (L/mg)	0.082	0.054	0.021	0.086	0.150	1.100
	r^2	0.996	0.997	0.992	0.999	0.999	0.993
Freundlich	N	5.176	5.890	3.352	12.082	4.564	6.091
	K_F (mg ^{1-1/n} /g/Ln)	12.61	9.47	2.40	13.97	17.53	4.68
	r^2	0.988	0.994	0.988	0.999	0.991	0.973

TABLE 6: Comparison of biosorption capacity (q_m) of Raw-seeds, HCl-seeds, and NaOH-seeds for Cd(II) and Co(II) with different other biosorbents.

Adsorbent	q_m (mg/g) Cd(II)	q_m (mg/g) Co(II)	References
Pine bark	28.00	—	[48]
Peat	22.50	—	[49]
Hazelnut shells	5.42	—	[50]
Waste tea leaves	31.48	—	[51]
Aquatic plant <i>Najas graminea</i>	28.00	20.6	[52]
Black carrot residues	—	5.35	[53]
Coir pith	—	12.82	[54]
<i>J. rubens</i> (red algae)	30.50	32.6	[55]
Saw dust	26.73	—	[56]
Neem bark	25.57	—	[57]
Mangosteen shell	3.15	0.34	[11]
Areca catechu	10.66	—	[58]
	—	27.15	[59]
Rose waste biomass	—	20.63	[60]
	31.35	17.41	[24]
<i>Sargassum wightii</i>	14.90	10.46	[24]
Raw-carob	49.63	30.04	[24]
HCl-carob			
NaOH-carob			
Raw-seeds	31.35	17.41	Present study
HCl-seeds	14.90	10.46	Present study
NaOH-seeds	49.63	30.04	Present study

bound by ionic attraction and therefore do not compete directly with the binding of heavy metals by the biosorbents. However, divalent and trivalent ions prevent the biosorption on the both biosorbents. The decreasing of Al^{3+} with high concentrations may be attributed to favorable electrostatic effects due to the increased number of positively charged surface binding sites arising from Al^{3+} . However, the effect of ionic strength is explained as the result of competition of ions with the heavy metals for electrostatic binding to the surface of Raw-seeds, HCl-seeds, and NaOH-seeds. Because, the functional groups are negatively charged, they will electrostatically attract any cation, be it inorganic or heavy metal ions of interest [65].

3.3. Optimization of Biosorption Conditions

3.3.1. Experimental Design. Table 7 shows the adsorption conditions and experimental results for the two responses of cadmium and cobalt removal. As can be seen, there was a considerable variation in the removal efficiency of cadmium and cobalt at different values of the already selected

factors. Consequently, the maximum sorption capacities of cadmium and cobalt were 85.73 and 51.90 mg/g, respectively. These greater capacities were obtained for the initial concentration of 50 mg/l, pH = 6, biosorbent dose of 1 g/l with carob seeds treated by NaOH agent. The regression analysis was performed to adjust the response functions with the experimental data. The values of regression coefficient estimated are presented in Table 8. From the table, the biosorbent dose and initial concentration present a negative effect on cadmium and cobalt ions removal, while the pH and treating agent have a positive effect on elimination of two heavy metals. The analysis of the interaction effects shows a significant interaction between biosorbent dose and treating agent for cadmium removal ($b_{24} = -6.09$) with a negative impact and a significant interaction between biosorbent dose and initial concentration for cobalt removal with a positive effect ($b_{23} = 2.58$).

3.3.2. Analysis of Variance (ANOVA). Analysis of variance (ANOVA) was carried out to justify the adequacy of the models. After discarding the insignificant terms, the

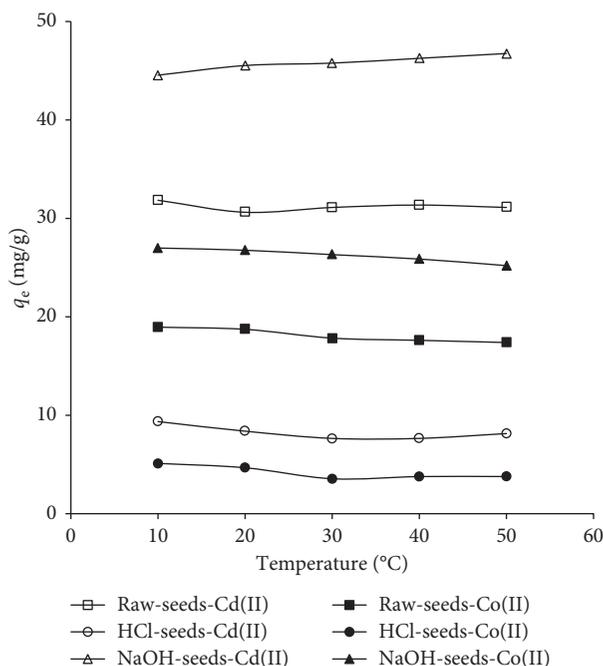


FIGURE 8: Effect of temperature on Cd(II) and Co(II) biosorption by the biosorbents: $R = 2 \text{ g/L}$, initial pH, contact time = 120 min, and $C_0 = 100 \text{ mg/L}$.

ANOVA data for the coded quadratic models for the two responses at a confidence level of 95% are reported in both Tables 9 and 10. The quality of the model developed was evaluated based on correlation coefficient, R^2 , and standard deviation. Data given in Tables 9 and 10 demonstrate that the two models were significant at p values < 0.05 . The closer the R^2 to unity and the smaller the standard deviation, the more accurate the response could be predicted by the model. The regression equations, in terms of their coded factors, are expressed by the following second-order polynomial equations:

$$Y1 = 38.93 + 5.23A - 12.86B - 4.42C + 11.89D - 2.41AB - 1.57AD + 1.95BC - 6.09BD + 1.66BCD, \quad (8)$$

$$Y2 = 23.24 + 2.15A - 4.93B - 6.32C + 7.83D - 0.95AB + 2.58BC - 2.48BD. \quad (9)$$

According to these equations, it is revealed that the pH and treating agent have a positive effect on cadmium ions removal. Moreover, the removal of the cadmium decreased if biosorbents dosage and initial metals concentration increases. Additionally, the interactions pH (A)–biosorbents dosage (B), pH (A)–treating agent (D), biosorbents dosage (B)–initial concentration (C), biosorbents dosage (B)–treating agent (D), and biosorbents dosage (B)–initial concentration (C)–treating agent (D) also had a significant effect on cadmium sorption. The interactions AB, AD, and BD presented a negative effect on cadmium ions removal. Then, the interactions BC and BCD presented a positive

effect on cadmium removal. When this interaction is in the high level, the removal of cadmium increased. It is the same in the case of cobalt. Furthermore, the interactions pH de la solution (A)–biosorbents dosage (B), biosorbents dosage (B)–initial metals concentration (C), and biosorbents dosage (B)–treating agent (D) also had a significant effect on cobalt sorption. In fact, the interaction BC had a positive effect on cobalt sorption proving an increase in this response. On the other hand, the interaction AB and BD present a negative effect for cobalt sorption.

3.3.3. Response Surface Analysis. The three-dimensional (3D) response surface of the tested factors is presented for identifying the type of interaction between the studied factors. For biosorption of cadmium, there are significant interactions between pH and biosorbent dose and another one between biosorbent dose and initial concentration. Figure 10 presents response surfaces plots for these significant interactions. This figure indicates that the sorption of cadmium increased with increasing of pH and decreasing of biosorbent dose with a fixed initial concentration at 50 mg/l with NaOH treating carob (Figure 10(a)). Furthermore, the sorption of Cd(II) increased with decreasing of biosorbent dose and initial concentration (Figure 10(b)). A maximal sorption cadmium response is observed at pH=6 and initial concentration of 50 mg/l at a biosorbent dose of 1 g/l with NaOH treating carob.

Figure 11 presents the significant interaction between pH and biosorbent dose and another one between biosorbent dose and initial concentration, for the sorption of cobalt. Figure 11(a) shows that the biosorption of Co(II) increased with increasing of pH and decreasing of biosorbent dose with a fixed initial concentration at 50 mg/l

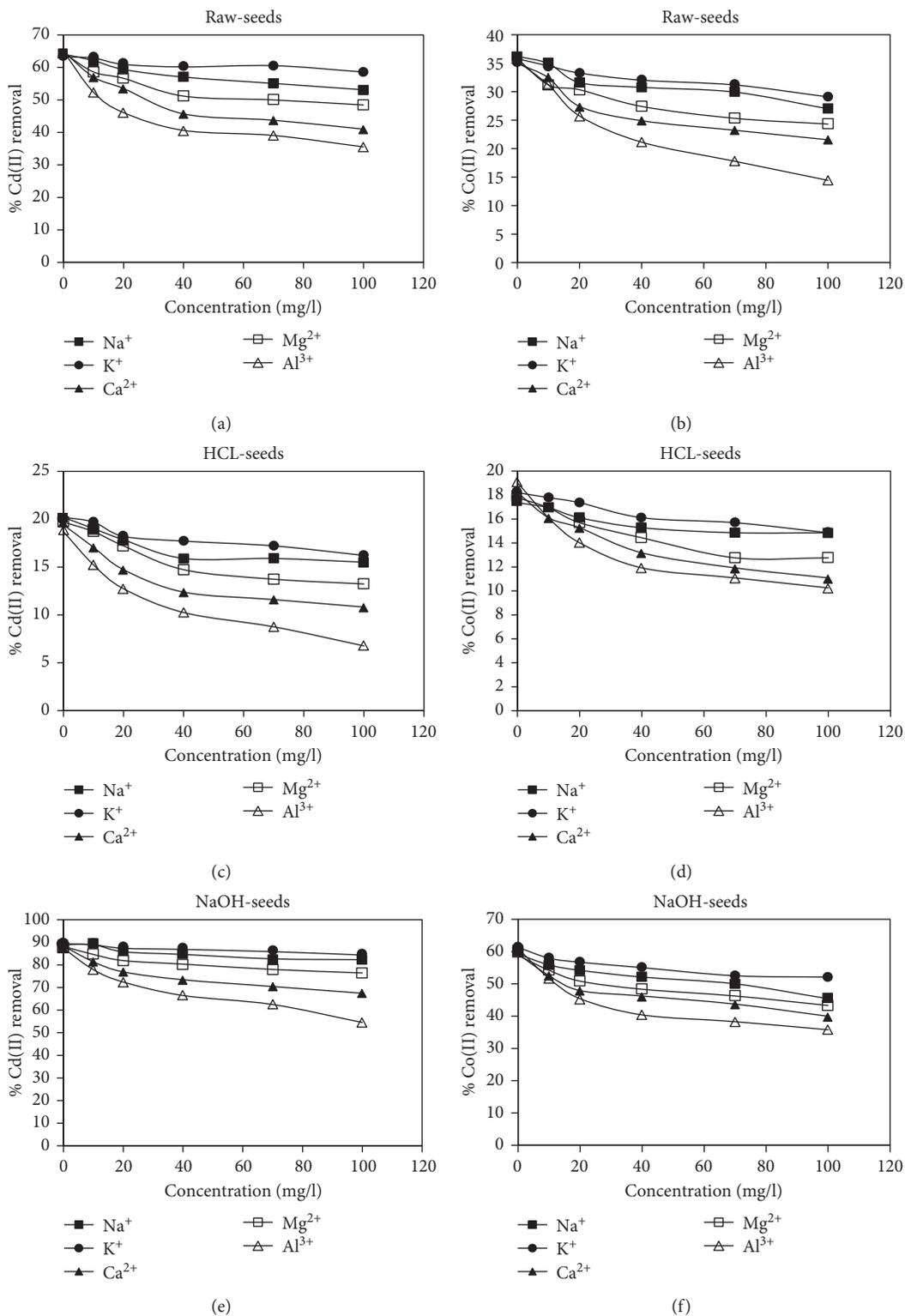


FIGURE 9: Effect of Na⁺, K⁺, Ca²⁺, Mg²⁺, and Al³⁺ concentration on the inhibition of the biosorption of Cd(II) and Co(II) onto biosorbents.

with NaOH treating carob. Moreover, when the initial concentration and the biosorbent dose decrease, the sorption of cobalt increases at pH = 6 with NaOH treating carob (Figure 11(b)). So, the best cobalt biosorption was obtained with pH = 6, biosorbent dose of 1 g/l, concentration of 50 mg/l, and NaOH treating carob.

3.3.5. Optimization. The two responses were optimized simultaneously by using the desirability function approach. The response variable was 1.00. Hence, “R²” is in consistent enough with the “R²_{Adj.}.” Thus, R² = 0.9979, R² = 0.9955 and R²_{Adj.} = 0.9947, R²_{Adj.} = 0.9916 for Cd(II) and Co(II) sorption responses. The model F-value of the

TABLE 7: Factorial experimental design matrix coded, real values, and experimental results of the responses.

Run	Coded values				Actual values				Responses	
	A	B	C	D	A	B	C	D	Cd(II)	Co(II)
1	-1	-1	-1	-1	4	1	50	HCl	30.59	24.22
2	+1	-1	-1	-1	6	1	50	HCl	46.21	29.30
3	-1	+1	-1	-1	4	3	50	HCl	19.23	14.48
4	+1	+1	-1	-1	6	3	50	HCl	29.34	18.05
5	-1	-1	+1	-1	4	1	100	HCl	19.56	5.58
6	+1	-1	+1	-1	6	1	100	HCl	38.86	12.36
7	-1	+1	+1	-1	4	3	100	HCl	11.57	8.64
8	+1	+1	+1	-1	6	3	100	HCl	20.92	10.71
9	-1	-1	-1	+1	4	1	50	NaOH	70.11	42.86
10	+1	-1	-1	+1	6	1	50	NaOH	85.73	51.90
11	-1	+1	-1	+1	4	3	50	NaOH	32.10	26.53
12	+1	+1	-1	+1	6	3	50	NaOH	33.48	29.17
13	-1	-1	+1	+1	4	1	100	NaOH	56.32	27.61
14	+1	-1	+1	+1	6	1	100	NaOH	66.89	31.56
15	-1	+1	+1	+1	4	3	100	NaOH	30.11	18.81
16	+1	+1	+1	+1	6	3	100	NaOH	31.80	20.13

TABLE 8: Values of model coefficients of the two responses.

Main coefficients	Y1	Y2
b_0	38.93	23.24
b_1	5.23	2.15
b_2	-12.86	-4.93
b_3	-4.42	-6.32
b_4	11.89	7.82
b_{12}	-2.41	-0.95
b_{13}	-0.11	-0.39
b_{14}	-1.57	-0.03
b_{23}	1.95	2.58
b_{24}	-6.09	-2.48
b_{34}	-0.11	-0.22
b_{123}	0.06	0.03
b_{124}	-0.49	-0.18
b_{134}	-0.49	-0.41
b_{234}	1.66	-0.22
b_{1234}	0.61	0.43

TABLE 9: Analysis of variance for sorption of cadmium ions.

Source	Sum of squares	df	Mean square	F value	p value; prob > F	
Model	6488.97	9	720.99	313.12	<0.0001	Significant
A	437.22	1	437.22	189.88	<0.0001	
B	2645.07	1	2645.07	1148.73	<0.0001	
C	313.043	1	313.04	135.95	<0.0001	
D	2262.37	1	2262.37	982.524	<0.0001	
AB	93.14	1	93.14	40.445	0.0007	
AD	39.45	1	39.45	17.13	0.0061	
BC	61.03	1	61.03	26.51	0.0021	
BD	593.24	1	593.24	257.64	<0.0001	
BCD	44.40	1	44.40	19.28	0.0046	
Residual	13.81	6	2.30			
Cor. total	6502.796	15				

$$R^2 = 0.9979; R_{adj}^2 = 0.9947.$$

both responses is greater, in order of 313.12 and 255.37 for Cd(II) and Co(II) sorption, respectively. Further, these results explain that the models are suitable. Then, it was found that there was good agreement between experimentally and model predicted response factor which confirms the adequacy and the significance of the proposed model. The optimal conditions for high sorption of cadmium(II) and cobalt(II) were achieved at pH = 6, biosorbent dose of 1 g/l, and initial concentration = 50 mg/l with carob seeds treated by NaOH. The greater sorption capacities were 85.73 mg/g for Cd(II) and 51.90 mg/g for Co(II).

4. Conclusion

During this study, raw carob seeds and chemically treated carob seeds were used as low-cost natural biosorbents for the removal of Cd(II) and Co(II) from aqueous solutions.

The biosorption productivity was tested by using different biosorption conditions. According to these studies, it was found that the biosorption yield increases with the increase of biosorbent dosage with an optimum at 0.1 g/L. The optimum sorption was obtained at basic pH medium. The sorption process was very rapid, since the equilibrium time was obtained at 90 min for Cd(II) and 60 min for Co(II). Biosorption kinetics data were properly fitted with the pseudo-first-order kinetic model. The equilibrium biosorption was increased with an increase in the initial ions concentration in solution. The biosorption isotherm could be well fitted by the Langmuir equation. The temperature does not have much influence on the biosorption performance. Other tests show that the presence of inorganic ions had specific effects on Cd(II) and Co(II) biosorption onto biosorbents, with the inhibition effect observing the following sequence: $K^+ < Na^+ < Mg^{2+} < Ca^{2+} < Al^{3+}$. From these studies, it can be also seen that chemical pretreatment the raw carob shell with NaOH strongly enhances its

TABLE 10: Analysis of variance for sorption of cobalt ions.

Source	Sum of squares	df	Mean square	F value	p value; prob > F	
Model	2302.19	7	328.88	255.37	<0.0001	Significant
A	74.23	1	74.23	57.64	<0.0001	
B	388.97	1	388.97	302.03	<0.0001	
C	639.204	1	639.20	496.33	<0.0001	
D	980.24	1	980.24	761.14	<0.0001	
AB	14.54	1	14.54	11.29	0.0099	
BC	106.31	1	106.31	82.55	<0.0001	
BD	98.69	1	98.69	76.63	<0.0001	
Residual	10.30	8	1.29			
Cor. total	2312.50	15				

$R^2 = 0.9955$; $R^2_{adj} = 0.9916$.

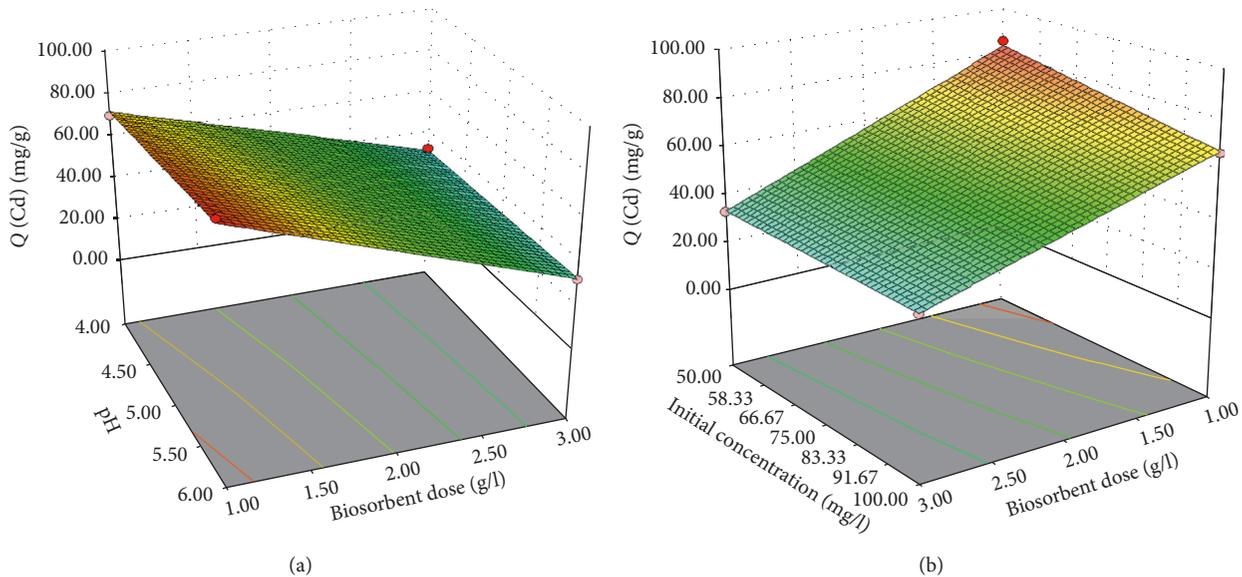


FIGURE 10: Surface response plots for the cadmium ions removal.

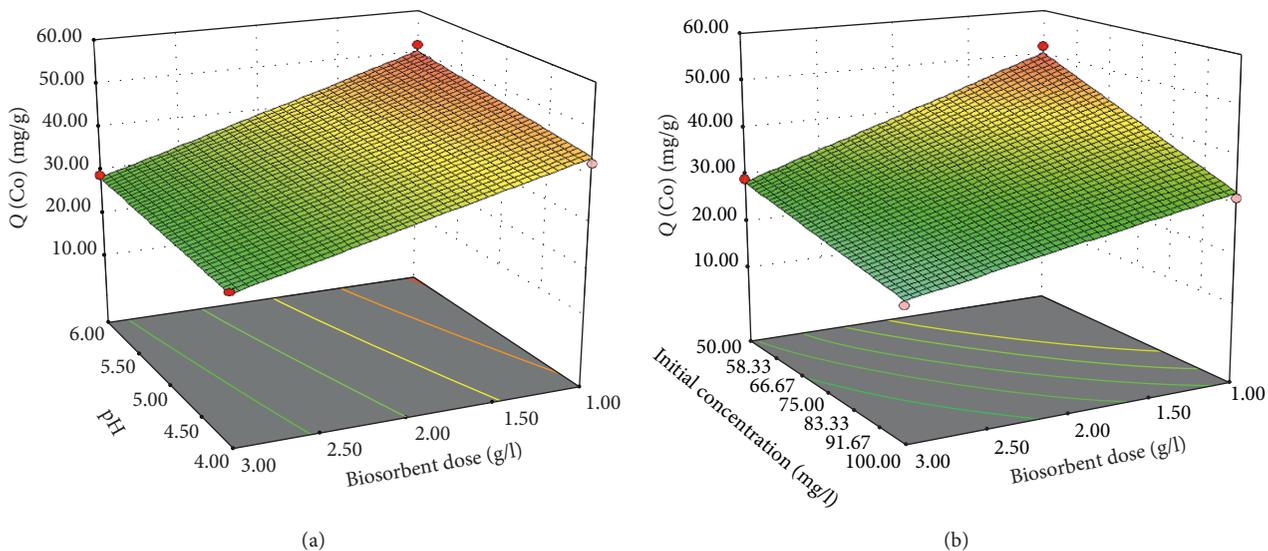


FIGURE 11: Surface response plot for the cobalt ions removal.

biosorption potential for the cadmium(II) and cobalt(II) ions. Full-factorial experimental design was used to determine the optimum conditions of different variables which affect the removal of Cd(II) and Co(II) ions. In order to achieve approximately the greater values of biosorption capacities of treated carob shell for Cd(II) and Co(II) ions, the optimum values of different process parameters were found to be 85.73 mg/g for Cd(II) and 51.90 mg/g for Co(II). These higher sorption efficiencies are obtained at pH=6, biosorbent dose of 1 g/l, and initial concentration = 50 mg/l with carob shell treated by NaOH.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Supplementary Materials

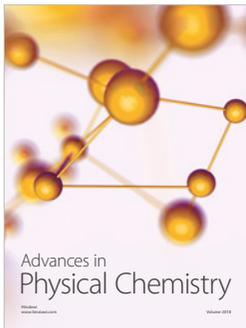
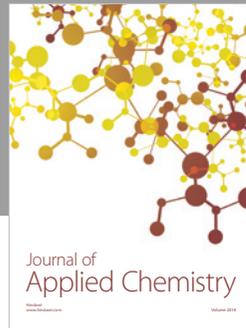
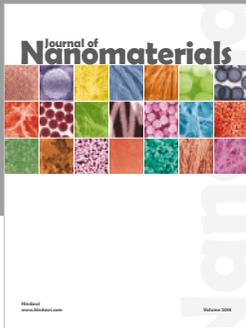
In summary, efficient biosorbents were developed from deoiled carob seeds. The biosorption efficiency was evaluated for cadmium and cobalt ions removal from aqueous solution under various parameters. Based on this preliminary study, four independent variables including solution pH, biosorbents dosage, initial metal concentration, and treating agent were chosen for the optimization of the process using full-factorial experimental design. It was found that chemical pretreatment of the raw deoiled carob seeds with NaOH strongly enhances its biosorption potential. The optimal conditions for high biosorption of cadmium(II) and cobalt (II) were achieved at pH of 6, biosorbent dosage of 1 g/L, and initial metal concentration of 50 mg/L. (*Supplementary Materials*)

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