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Biosorption of cobalt (II) by Intact and Chemically Modified Brown Algae: Optimization Using Response Surface Methodology and Equilibrium, Dynamics and Thermodynamics Studies

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Abstract
By using response surface methodology, Batch shaking biosorption of cobalt (II) experiments were conducted in order to examine the combined effects of operating parameters. The results indicate that magnesium nitrate performed as an effective biosorbent surface modifier, which increases the rate of adsorption capacity. At optimal conditions (initial pH 7.0, temperature 45◦C, biosorbent concentration 0.1 g/100ml, and initial cobalt concentration 300mg/l for Mg-treated biomass) the biosorption capacity of the algae for cobalt was found to be 80.55 mg/g. The Langmuir and Freundlich isotherms were applied to the equilibrium data. The results are best fitted by the Freundlich model. Evaluation of the experimental data in terms of biosorption dynamics showed that the biosorption of cobalt (II) onto algal biomass followed the pseudo-second-order dynamics well. Using the thermodynamic equilibrium coefficients obtained at different temperatures, the thermodynamic parameters (ΔG◦, ΔH◦ and ΔS◦) were also evaluated.

Keywords: *Biosorption, Response Surface Methodology, Pretreated Algae, Cobalt, Sargassum sp.*

1. Introduction

Cobalt containing compounds discharged through different industrial activities constitute one of the major causes of water pollution. Heavy metals pose a significant threat to the environment and public health because of their toxicity, accumulation in the food chainand persistence in nature [1,2]. So it is necessary to remove cobalt at the time of release of effluent. There are some conventional methods for treatment of liquid effluent for removal of heavy metals such as ion exchange, chemical precipitation, reverse osmosis, and co-precipitation which are designed to remove radionuclides and metal ions from the effluents [3]. These conventional techniques can reduce metal ions, but they do not appear to be highly effective due to the limitations in the pH range as well as the high material and operational costs [4]. Therefore, there is growing interest in using low-cost, easily available materials for the adsorption of metal ions. A low-cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste material from another

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industry. Biosorbent materials derived from suitable biomass can be used for the effective removal and recovery of heavy metal ions from industrial solutions. Many algae, yeasts, bacteria and other fungi are known to be capable of concentrating metal species from dilute aqueous solutions and accumulating them within their cell structure [5]. Among biosorbent materials algae have proved to be both economic and eco-friendly as they are abundantly available, have regeneration and metal recovery potentiality, lesser volume of chemical and/or biological sludge, high efficiency in dilute effluents, and a high surface area to volume ratio [6]. The cell walls of brown algae generally contain components such as cellulose and alginicacid which contain several functional groups (amino, carboxyl, sulphate and hydroxyl) that could play an important role in the biosorption process [7]. The binding strength of alkaline earth metals to alginic acid was found to decrease in the order Ba(II) >Sr (II) > Ca (II) > Mg (II) [8,9]. Haug interpreted the preferential binding of heavier ions to stereochemical effects, since larger ions might better fit a binding site with two distant functional groups [10]. Also, the preferential binding of larger ions can be attributed to stereochemical effects such as the coordination of the oxygen atoms surrounding the metal ion [11]. According to the trends, cobalt ion is preferable to replace magnesium instead of calcium ion because Mg(II) has less binding strength. So for pretreatment of biomass, Mg(II) was used as a surface modifier instead of other ions such as Ca(II).

The aim of this study was to conduct a central composite design (CCD) analysis to find the significant factors that influenced the removal of cobalt from aqueous solution by marine brown algae *Sargassum sp.* and understand their impact on the process. The effect of some operating variables such aschemical modification of the biomass, temperature, pH, adsorbent dose and initial concentration of Co^{2+} on biosorption was studied using CCD, which gives a mathematical model that shows the influence of each variable and their interactions. In addition, the equilibrium, dynamic and thermodynamic parameters were calculated

In the statistical design, the factors involved in an experiment are simultaneously changed. The most important advantages are that not only the effects of individual parameters but also their relative importance in a given process are evaluated and the interaction of two or more variables can also be derived. This is not possible in a classical one factor at a time experiment [2].

2. Mathematical description

The amount of metal uptake by algae was calculated from the differences between the metal quantity added to the biomass and the metal content of the supernatant using the following equation:

$$q = \frac{V(C_0 - C)}{M_{ads}} \quad (1)$$

where q is the amount of metal ions adsorbed on the biosorbent at any time, t, in mg/g, V is the volume of metal containing solution in contact with the biosorbent in ml, C_0 is the initial concentration of metal in mg/l, C is the metal concentration in the solution at any

time t (min) in mg/l, and M_{ads} is the amount of added biosorbent on dry basis in g[12].

2-1. Dynamic parameters of biosorption

It is known that the biosorption process is time-dependent; so in this study the pseudo-first-order and pseudo-second-order dynamic models have been discussed to identify the rate and kinetics of sorption of cobalt on *Sargassum sp*. adsorbent.

Pseudo-first-order Lagergren model considers that the rate of occupation of biosorption sites is proportional to the number of unoccupied sites. The linear form of the model is:

$$log(q_{eq} - q_t) = log\ q_{eq} - \frac{k_1 t}{2.303} \quad (2)$$

where q_{eq} and q_t (mg g^{-1}) are amount of cobalt adsorbed at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) shows the equilibrium rate constant of pseudo-first-order adsorption. k_1 and q_{eq} can be determined from the linear plot of log ($q_{eq} - q_t$) versus t.

The adsorption dynamics may also be described by pseudo-second-order model. Pseudo-second-order model considers that the rate of occupation of biosorption sites is proportional to the square of the number of unoccupied sites and after being integrated and rearranged:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (3)$$

Where q_{eq} and q_t (mg g^{-1}) are amount of cobalt adsorbed at equilibrium and at time t (min), respectively, and k_2 (g mg^{-1} min^{-1}) is the equilibrium rate constant of pseudo-first-order adsorption. k_2 and q_{eq} can be determined from the linear plot of t/q_t versus t. This model is more likely to predict dynamic behavior of biosorption with chemical sorption being the rate-controlling step. Due to the presence of greater number of metal ions in industrial wastewater, the sorption equilibrium was reached much faster due to faster occupancy of sorption sites by metal ions [2,13].

2-2. Equilibrium parameters of biosorption

The biosorption isotherms are characterized by definite parameters whose values express the surface properties and affinity of biosorbent for different heavy metal ions [14]. Several isotherm equations have been used for the equilibrium modeling of biosorption systems. In this study, the Langmuir and Freundlich adsorption models were tested to determine the relationship between adsorbed cobalt ions on the algal cell (q_{eq}) and unadsorbed cobalt ions in solution (C_{eq}). The most widely used isotherm equation for modeling equilibrium is the Langmuir equation, based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules [5]. The linear form of Langmuir isotherm is given by the following equation:

$$\frac{1}{q_{eq}} = \frac{1}{b q_m C_{eq}} + \frac{1}{q_m} \quad (4)$$

where q_{eq} (mg/g) is the amount adsorbed at

the equilibrium, C_{eq} (mg/l) the equilibrium concentration, q_m (mg/g) is the Langmuir constant representing the maximum monolayer adsorption capacity and b(l/mg) is the Langmuir constant related to energy of adsorption and the affinity of the binding sites [1,15]. The equilibrium parameters (q_m and b) are determined from the linear plot of $1/q_{eq}$ versus $1/C_{eq}$.

The adsorption data was also analyzed by Freundlich model. The Freundlich expression is used for heterogeneous surface energy term. The Freundlich isotherm equation is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases [5]. Freundlich equation is commonly presented as shown below:

$$q_{eq} = kC_{eq}^{\frac{1}{n}} \tag{5}$$

The logarithmic form of Freundlich model is given by the following equation:

$$\log q_{eq} = \log k + \frac{1}{n}\log C_{eq} \tag{6}$$

where k and n are constants related to the adsorption capacity and intensity of the adsorbent characteristics of the system, respectively. The fractional values of biosorbent surface indicate a favorable biosorption of metal ions onto biomass [16]. The plots of log q_{eq} versus C_{eq} determine values of 1/n and k.

2-3. Thermodynamic parameters of biosorption

The determination of thermodynamics parameters has great importance in evaluating spontaneity and heat change for the biosorption reactions. The Gibbs free energy change of the adsorption process (ΔG°) is related to the standard thermodynamic equilibrium constant (K_{eq}°) of the biosorption system by the classic equation[17,18]:

$$\Delta G^o = -RT\ln K_{eq}^o \tag{7}$$

Where T is the absolute temperature (kelvin) and R is the universal gas constant which is 8.314 (j/mol k).

The apparent equilibrium constant (K'_e) of the adsorption is defined as [17, 19]:

$$K_e^{'} = \frac{C_{ad,eq}}{C_{eq}} \tag{8}$$

Where $C_{ad,eq}$ is the amount of adsorbed metal ion on the biosorbent per volume of the solution at equilibrium and C_{eq} is the equilibrium concentration of the metal ion in the solution. The Gibbs free energy change (ΔG°) reflects the feasibility and spontaneous nature of the process. At a given temperature, the higher the negative value of ΔG°, the more energetically favorable adsorption process.

In order to determine the nature of the biosorption process regarding heat of adsorption and also affinity of biosorbent to metal ion, enthalpy changes (ΔH°), and entropy changes (ΔS°) should also be estimated. These parameters can be estimated by the van't Hoff equation [17, 19]:

$$\ln K_{eq}^{o} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{9}$$

Where ΔH° and ΔS° can be obtained from the slope and intercept of a van't Hoff plot of ln K° vs 1/T.

3. Materials and methods

3-1. Preparation of biosorbents

Samples of marine algae *Sargassum sp.* were collected from Persian Gulf on the coast of Qeshm, Iran. Algal samples were washed with tap water and distilled water to remove sand and excess sodium and potassium ions. After drying overnight at a maximum temperature of 55°C to avoid degradation of the binding sites [14], the samples were grounded to an average particle size of 0.7 mm. The biomasses were subsequently loaded with Mg^{2+} in a solution of 0.1 M $Mg(NO_3)_2.6H_2O$ (biomass concentration of 10 g/l) for 24 h under slow stirring. Then pretreated biomass was washed several times with deionized water until a stable wash solution pH was reached and excess magnesium ions were removed from the biomasses. The Mg-pretreated biomasses were then dried overnight in an oven at 55ºC and subsequently natural algae and Mg-pretreated algae were used for biosorption experiments.

3-2. Preparation of synthetic metal solution

A stock solution of cobalt, with 1000 ppm concentration was prepared using analytical grade ($Co(NO_3)_2.6H_2O$). This solution was diluted depending upon requirements. All solutions were prepared in deionized water. The initial pH of cobalt solutions was adjusted with diluted or concentrated HNO_3 and NaOH solutions before mixing with the biosorbent. All chemicals used wereof analytical grade (Sigma Aldrich, Germany).

3-3. Characterization test

3-3-1. Energy dispersive X-ray spectroscopy (EDX)

To determine the chemical composition of biosorbent before and after treatment by 0.1 M $Mg(NO_3)_2.6H_2O$ and also after Co^{2+} sorption, a system of analysis for energy dispersive X-ray spectroscopy (EDX, RONTECH, Germany) was used.

3-3-2. Analysis of cobalt concentration

Dissolved cobalt concentrations in solution were assessed by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Optima, 7300DV, USA). The ICP analyses were conducted at wavelength of 228.616 nm.

3-4. Batch adsorption experiments

In order to determine the contact time required for the sorption equilibrium experiments, the sorption dynamics experiments were conducted on natural and Mg-pretreated algae first. 0.1 gram of biomass was added to a series of 250 ml Erlenmeyer flasks containing 100 ml of 100 mg Co/l $Co(NO_3)_2.6H_2O$ solution. The flasks were agitated at 150 rpm and 25ºC for 24 h in a shaker. Samples were withdrawn at predetermined time intervals (2, 5, 15, 30, 45, 60, 90, 120, 150, 180 and 1440 min). After appropriate dilution, the samples were analyzed by the ICP-AES for metal concentrations. According to the preliminary sorption dynamic tests, the equilibrium was reached after 90 min of contact. Batch adsorption experiments were conducted to study the effect of magnesium ion as a surface modifier of biomass, temperature, pH, initial cobalt concentration, and the dosage of biomass. Each experiment was carried out in 250 ml Erlenmeyer flasks containing 100mL $Co(NO_3)_2.6H_2O$ solution with known initial cobalt concentration which was mixed with different amount of biomass. To adjust the temperature,

Gallenkamp shaker was used, enabling us to set the temperature of the solution. The flasks were shaken at 150 rpm for a period contact time of 90min. The pH of initial solution was adjusted to the desired values with diluted or concentrated HNO_3 and NaOH solutions before mixing with the biosorbent. Cobalt solution was filtrated through Whatman filter paper. Filtered samples were analyzed for residual cobalt ion concentration.

3-5. Experimental design

In this study, the effects of operating parameters were optimized using response surface methodology (RSM). RSM is essentially a particular set of mathematical and statistical methods for designing experiments, building models, evaluating the effects of variables, estimating interaction between variables and searching optimum conditions of variables to predict targeted responses [15, 16].The application of statistical experimental design techniques in sorption processes could result in improved product yields, reduced process variability, aswell as reduced development time and overall costs [20].

In this study, central composite design (CCD) was used for the RSM in the experimental design which is well suited for fitting a quadratic surface and usually works well for the process optimization [15, 16].The CCD consisted of 2^k factorial runs with 2k axial runs and r center runs. The center points were used to evaluate the experimental error and the reproducibility of the data. The independent variables were coded to the (−1,1) interval where the low and high levels were coded as −1 and +1, respectively. The axial points were located at (±α, 0, 0), (0,±α, 0) and (0, 0, ±α) where α is the distance of the axial point from center and makes the design rotatable[5]. In the study, α was fixed at 2.0.

Therefore, central composite design with four numeric factors (initial cobalt (II) concentration: 50–300 mg/l, biosorbent concentration: 0.1–0.5 g/100ml, initial pH: 2.5–7.0 and temperature: 15–45 °C) and one categorical factor at 2 levels (natural *Sargassum sp* and Mg- pretreated *Sargassum sp.* algae) was applied using Design-Expert version 7 (Stat-Ease Inc., Minneapolis, USA) as shown in Table 1. Performance of the process was evaluated by analyzing the response of biosorbent for cobalt (II) ions. The responses were biosorption capacity of natural and modified algae, y_1 and y_2 respectively.

In the optimization process, the responses can be simply related to chosen factors by linear or quadratic models. Aquadratic model, which also includes the linear model, is given as:

$$y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} b_{ij} x_i x_j \qquad (10)$$

where b_0, b_i, b_{ii}, b_{ij} are a constant, a linear coefficient, a square coefficient and an interaction coefficient, respectively [15, 21, 22].

In this work a central composite design was used to estimate the effect of five independent factors (temperature, x_1; initial concentration of cobalt (II), x_2; biosorbent dosage, x_3; initial pH, x_4; natural brown algae and Mg- pretreated brown algae, x_5) on the biosorption capacities (y_1, y_2) as the responses were processed for Eq. (10) including analysis of variance (ANOVA) to obtain the interaction between the process

variables and the responses. The quality of the fit of polynomial model was expressed by the coefficient of determination R^2 and R^2_{adj}. The statistical significance was checked with adequate precision ratio and F-test [5]. The second-order polynomial models were represented as response, whilst keeping third variable constant.

4. Results and discussion

4-1. Statistical analysis

In order to determine the significant terms 56 runs were statistically analyzed with CCD design. The p-values were used as a tool to check the significance of every coefficient. The smaller the magnitude of p, the more significant the corresponding coefficient is. Values of p less than 0.05 indicate model terms are significant. In this case all five factors, AB (T, C_0), BC (C_0, M_{ads}), BD (C_0, pH) and BE (C_0, Type of biosorbent) interaction terms are highly significant terms ($p < 0.05$). By eliminating the insignificant model terms automatically, the resulting ANOVA for the reduced quadratic model is summarized in Table 2. The final responses for the biosorption capacity of untreated and treated biomasses for cobalt (II) ions were obtained in Eqs. (11) and (12), respectively.

$$\begin{aligned} y_1 &= 27.01193 - 0.039876\,x_1 + 0.21785\,x_2 \\ &- 109.62840\,x_3 + 2.06483\,x_4 + 9.15733\,E \\ &- 004\,x_1x_2 - 0.13322\,x_2x_3 + 0.010372\,x_2x_4 \\ &- 3.85354\,E - 004\,x_2^2 + 98.69344\,x_3^2 \\ &- 0.35106\,x_4^2 \end{aligned} \quad (11)$$

$$\begin{aligned} y_2 &= 26.75589 - 0.039876\,x_1 + 0.24190\,x_2 \\ &- 109.62840\,x_3 + 2.06483\,x_4 + 9.15733\,E \\ &- 004\,x_1x_2 - 0.13322\,x_2x_3 + 0.010372\,x_2x_4 \\ &- 3.85354\,E - 004\,x_2^2 + 98.69344\,x_3^2 - 0.35106\,x_4^2 \end{aligned} \quad (12)$$

Table 1. The experimental range and levels of the control factors in the CCD.

Variable	Low axial (-α)	Low factorial (-1)	Center	High factorial (+1)	High axial (+α)
x_1(A): Temperature (°C)	15	23	30	38	45
x_2(B): Initial cobalt (II) concentration (mg/l)	50	113	175	238	300
x_3(C): Biomass dose (g/100ml)	0.1	0.2	0.3	0.4	0.5
x_4(D): pH	2.5	3.6	4.8	5.9	7
	Level 1		Level 2		
x_5(E): Type of biosorbent	Natural *Sargassum sp.*		Mg- pretreated *Sargassum sp.*		

* α= 2

Table 2. ANOVA for the response surface reduced quadratic model for cobalt biosorption .

Source	Sum of squares	df	Mean square	F value	p-value
Model	6424.25	12	535.35	386.89	< 0.0001
A-T	39.13	1	39.13	28.28	< 0.0001
B-C_0	3255.71	1	3255.71	2352.86	< 0.0001
C-Mads	2609.04	1	2609.04	1885.52	< 0.0001
D-pH	18.03	1	18.03	13.03	0.0008
E-E	218.63	1	218.63	158.00	< 0.0001
AB	5.90	1	5.90	4.26	0.0451
BC	22.18	1	22.18	16.03	0.0002
BD	17.02	1	17.02	12.30	0.0011
BE	27.10	1	27.10	19.59	< 0.0001
B^2	116.01	1	116.01	83.84	< 0.0001
C^2	49.87	1	49.87	36.04	< 0.0001
D^2	10.11	1	10.11	7.30	0.0098
Residual	59.50	43	1.38		
Lack of Fit	52.89	37	1.43	1.30	0.4017
Pure Error	6.61	6	1.10		
Cor Total	6483.75	55			

Non-significant value lack of fit shows the validity of the quadratic model for biosorption by *Sargassum sp.* biomass. The obtained values for the correlation between the actual and predicted response (R^2) and coefficient adjusted R^2 are 0.9908 and 0.9883, respectively. These values, which are closer to 1.0 are in reasonable agreement for cobalt (II), indicating the better fitness of the reduced quadratic model in the experimental data. Adequate precision measures the signal to noise ratio and a ratio greater than 4 is desirable. The ratio of 77.361 indicates an adequate signal. This model can be used to navigate the design space.The CV value was found to be 3.13 for biosorption capacity. Since CV is a measure expressing standard deviation as a percentage of the mean, the smaller values of CV give better reproducibility. In general, a CV higher than 10 indicates that variation in the mean value is high and does not satisfactorily develop an adequate response model [16]. Data in Table 3 confirmed these results.

Table 3. Statistical results of the ANOVA for reduced quadratic model.

R^2	0.9908
Adjusted R^2	0.9883
C.V %	3.13
Adequate Precision	77.361

The predicted values calculated from the statistical model versus the actual response values obtained by the experiment were shown in Fig. 1. It approves the suitability of the model since all the points are located around the diagonal line. The normal probability and studentized residuals plot is shown in Fig. 2 for the biosorption capacity of *Sargassum Sp.* for cobalt (II) ions. In Fig. 2, residuals show how well the model satisfies the assumptions of the analysis of variance (ANOVA) where the studentized residuals measure the number of standard deviations separating the actual and predicted values. Fig. 2 shows that no response transformation needed nor was there an apparent problem with normality.

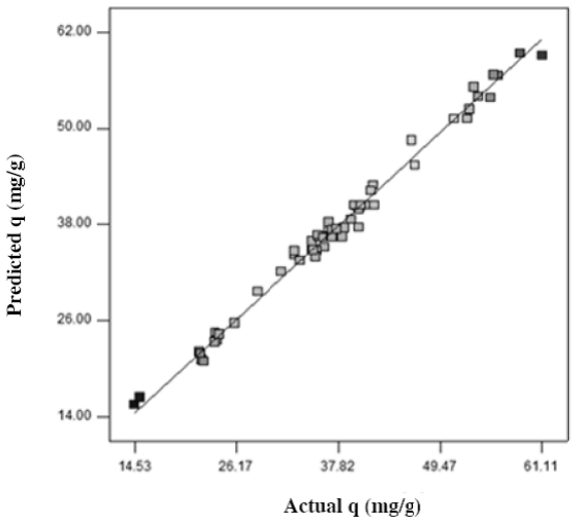


Figure 1. Scatter graph of the predicted response values versus the actual response values for the biosorption capacity of biomass for cobalt.

4-2. Statistical optimization

The aim of the process was to maximize biosorption capacity of biosorbent for cobalt (II) ions and find optimized conditions. The optimum values for temperature, initial cobalt (II) concentration, biosorbent dosage and pH were estimated to be 45°C, 300 mg/l, 0.1 g/100ml, and 7.0, respectively. According to the optimum conditions, the best biosorbent which had the maximum metal uptake (80.5 mg/g) was $Mg(NO_3)_2.6H_2O$-treated biomass (Mg-treated biomass).The results for optimized parameters by Design-Expert software are presented in Table 4.

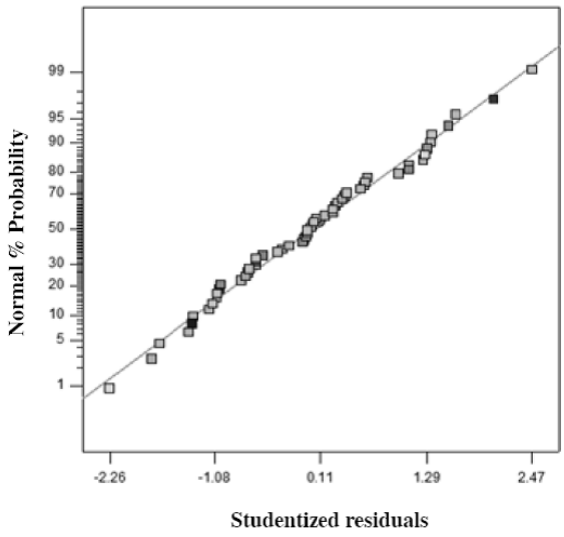


Figure 2. Normal plot of studentized residuals verses normal % probability for bearing the experiment for cobalt ions.

Table 4. Optimum values of the process parameters for maximum biosorption capacity.

Parameters	T(°C)	C_0 (mg/l)	M_{ads}(g)	pH	Type of biosorbent
Value	45	300	0.1	7	Mg-treated biomass

The software calculated the expected responses and associated confidence intervals based on the prediction equations (Eqs. (11) and (12)). The 95% confidence interval (C.I.) is the range in which the process average was expected to fall 95% of the time, while the 95% prediction interval (P.I.) is the range in which it was expected that any individual value would fall 95% of the time[23]. As shown in Table 5, the P.I. is larger (a wider spread) than the C.I. since more scatter in individual values is expected than in averages. In this Table, SE mean refers to the standard deviation associated with the prediction of an average value at the selected component-levels, while the standard deviation associated with SEpred. indicates the prediction of an individual observation at the selected factor levels.

4-3. Effect of pretreatment on biosorption capacity and sorption mechanism

The chemically modified biosorbents increase the stability of the biosorbent material and enhance the biosorbent properties[24]. The interactive effect of initial cobalt (II) concentration and type of biomass on the cobalt uptake of biomass holding other variables at their central values is shown in Fig. 3. The capacities of treated *Sargassum sp.* and untreated *Sargassum sp.* for cobalt ion at different concentration noted that the treatment of $Mg(NO_3)_2$ had enhanced the adsorption capacity. At the sorption of cobalt, the adsorption capacity for untreated *Sargassum sp.* and treated *sargassum sp.* increased from 15.43 to 45.49 mg/g and 16.37 to 52.45 mg/g with the increase of the initial concentration in 50–300 mg/l, respectively. According to the Table 2, the interaction between initial cobalt (II) concentration and type of biomass (BE) was highly significant ($p<0.0001$). EDX spectra taken in spot profile mode showed the enhancement of magnesium peaks on EDX spectra of biomass after treatment compared with biosorbent before Mg-treatment (Fig. 4a, b) and also confirmed the presence of cobalt (Fig.4c), suggesting bonding of metal cations onto algae surface by interactions with negatively charged functional groups. Additionally, for the samples after biosorption, we observed that the peaks of Mg on EDX spectra of biosorbent after metal sorption were omitted (Fig. 4c).The amount of magnesium and cobalt of the untreated *Sargassum sp*., Mg-treated biomass and cobalt-loaded biomass was determined using anEDX spectrometer, given in Table 6. Our data suggest that Co^{2+} ions have replaced Mg^{2+} ions from biosorbent surface and ion exchange mechanism participates in cobalt biosorption. The same conclusions were also postulated by others [25-28]. But, due to the complexity of biomaterials, maybe other mechanisms such as coordination and chelation of metals, adsorption and surface complexation of cations with exposed functional groups on the biomass act simultaneously, to varying degrees, depending on the biosorbent and the solution chemistry[8, 29-31].

Table 5. Point prediction of the responses at the optimal conditions.

Response	Prediction	SE Mean	95%C.I. low	95% C.I. high	SE pred.	95% P.I.low	95% P.I. high
q (mg/g)	80.2094	1.94	76.29	84.13	2.27	75.63	84.79

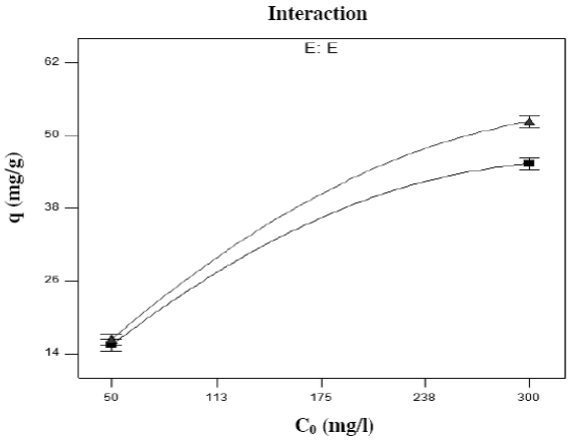


Figure 3. Interaction plot showing effect of initial cobalt (II) concentration and type of biomass on the cobalt uptake of biomass holding other variables at their central values.

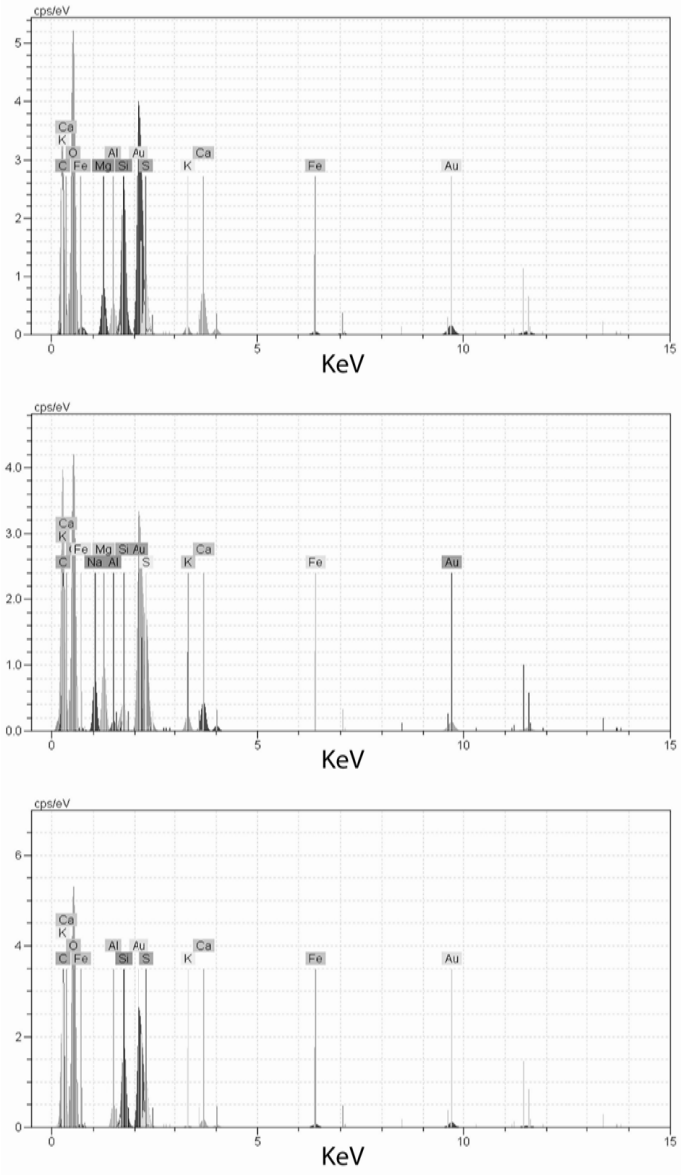


Figure 4. EDX analysis of *Sargassum sp*. before (a) and after (b) Mg treatment, and after (c) cobalt (II) sorption. Au peak comes from sample coating.

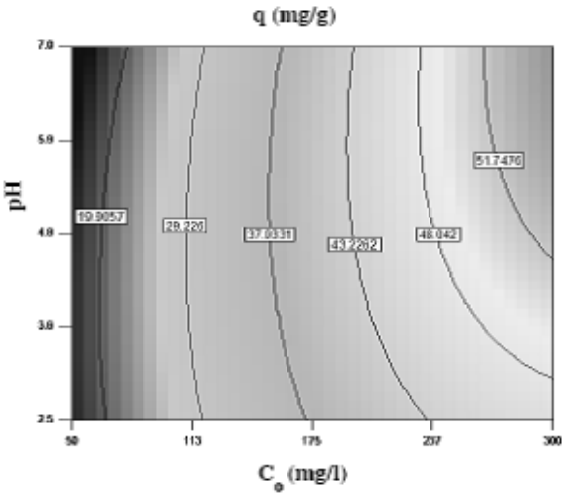
Table 6. The amount of magnesium and cobalt of the biomass.

Type of biomass	Element [wt. %]	
	Magnesium	Cobalt
Untreated *Sargassum sp.*	1.91	0.0
Mg-treated *Sargassum sp.*	4.19	0.0
cobalt-loaded *Sargassum sp.*	0.0	11.04

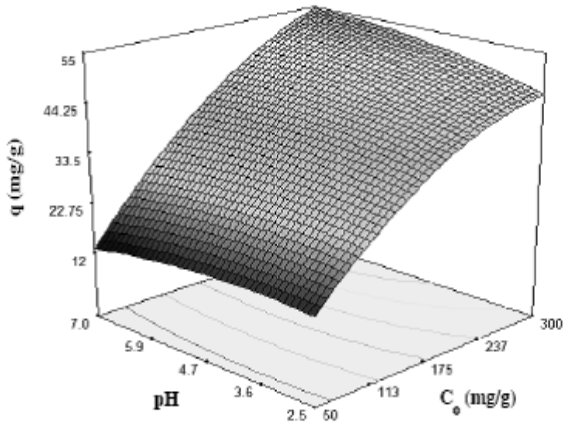
4-4. Effect of operating parameters on biosorption

As shown in Table 2, the results indicated that all linear and quadratic parameters and mutual interaction between temperature and initial cobalt (II) concentration (AB), initial cobalt (II) concentration and biomass dosage (BC) and initial cobalt (II) concentration and pH (BD) were significant ($p<0.0001$, $p< 0.05$). The response surface plots (three–dimensional graphs and contour plots) presented in Figs. 5-7 were generated by varying two factors while keeping the others constant in center values.

Adsorption solution pH influences both cell surface metal binding sites and metal chemistry in water [14]. Cobalt predominantly exists as Co^{2+}cation within a broad pH range from 2.5 to 7.0. The concentration of Co^{2+} starts to decrease at pH 7.5. The precipitation of cobalt (formation of $Co(OH)_2$ form) started at pH 7.5. Therefore, the pH range studied was between 2.5 and 7.0, pH values above 7 were not studied because cobalt removal by hydroxide formation begins to interfere with cobalt removal by biosorption and it will be difficult to distinguish between cobalt biosorption and precipitation. Fig. 5 shows the effects of initial cobalt (II) concentration and pH (BD)



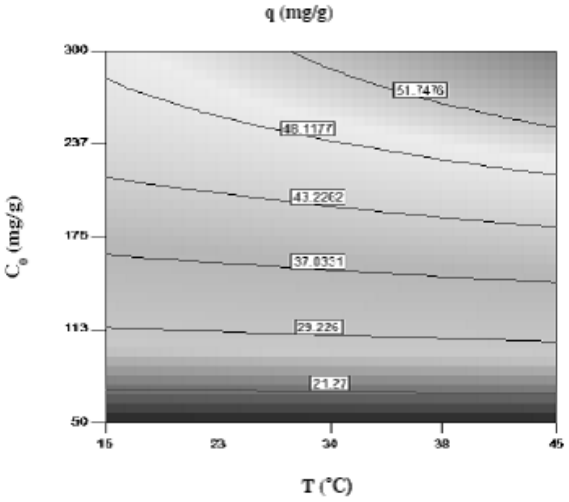
(a)



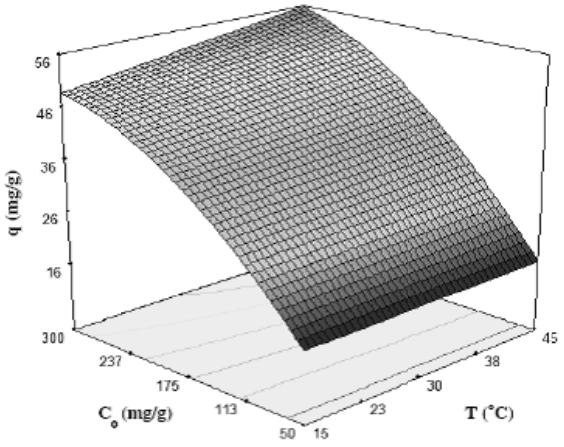
(b)

Figure 5. Three-dimentional plots showing effects of initial cobalt (II) concentration and pH (BD) on the biosorption capacity for Mg-treated biomass holding other variables at their central values.

on the biosorption capacity for Mg-treated biomass. Cobalt uptake significantly increases with metal concentration but a smaller increase with pH is observed. According to Fig. 5, the biosorption capacity at pH 7.0 and pH 2.5 was 54.73 and 46.44 mg/g, respectively, and the Co^{2+} concentration was 300 mg/l while the other parameters are in the center values (T= 30°C and M_{ads}= 0.3). The data show the biosorption uptake did not vary significantly with initial pH, indicating that the biosorbent

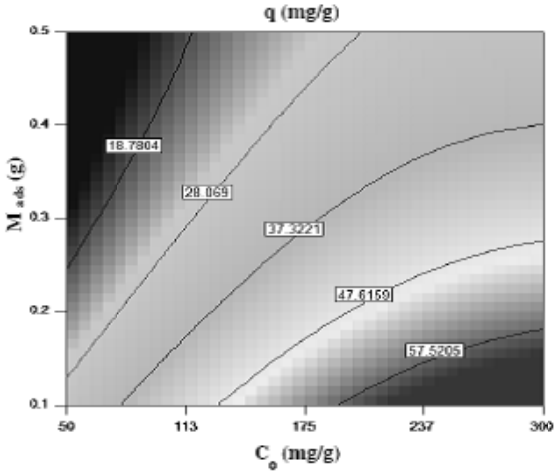


(a)

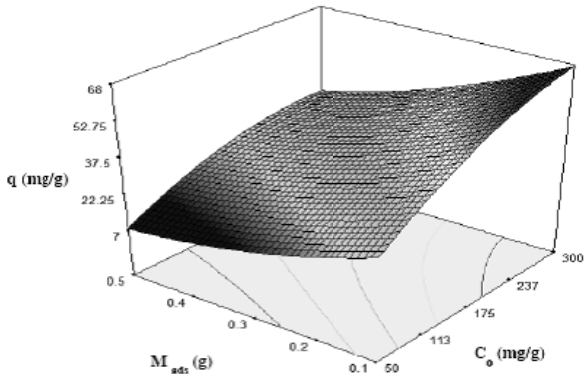


(b)

Figure 6. Three-dimensional plots showing effects of temperature and initial cobalt (II) concentration (AB) on the cobalt uptake of Mg-treated biomass holding other variables at their central values.



(a)



(b)

Figure 7. Three-dimensional plots showing effects of initial cobalt (II) concentration and biomass dosage (BC) holding the temperature at 30°C and pH 4.8.

can be used with comparable effectiveness in the pH range 2.5 to 7.0. The biosorption-capacity decreases with decreasing pH, which is explained by the greater affinity of the proton by the binding sites at the algal particles surface when compared with the metal ion. Conversely, at higher pH where cobalt concentration is much greater than H^+ concentration, the metal uptake increases. Similar results have been obtained by other authors [5, 29] who found an optimal pH range of 4–7 [5, 25, 29, 30]. At this pH range some functional groups in the algae surface, e.g. carboxyl and sulfate, become negatively charged, increasing the electrostatic interactions with the metal cation [5].

The biosorption is highly dependent on the amount of metal initially present in solution, increasing with the initial concentration. For example, the biosorption capacity changes about +41.79 mg/g by increasing initial Co^{2+} concentration from 50 to 300 mg/l at pH 7. Higher concentration of cobalt ions in the solution causes the active sites of *Sargassum sp.* to be surrounded by more cobalt ions, and biosorption would be carried out more sufficiently. Similar results are also reported

by researchers for a variety of adsorbate-adsorbent systems [3, 32]. An increase of metal uptake by increasing initial metal ion concentration is a result of the increase in the driving force of the concentration gradient, rather than increase in the initial metal ion concentration[33]. The initial concentration provides an important driving force to overcome all mass transfer resistance of cobalt between the aqueous and solid phases.

The effect of temperature on the cobalt uptakeof Mg-treated biomass holding other variables at their central values is shown in Fig. 6. The biosorption capacity of treated *Sargassum sp.* increased with the increase in biosorption temperature and initial cobalt (II) concentration.The maximum biosorption capacity occurred at 45°C. However, temperature variation between 15 and 45°C slightly increases the metal uptake capacity from 38.63 to 42.24 mg/g, respectively. The uptake capacity was calculated at pH 4.8, 175 mg/l initial cobalt (II) concentration and 0.3 g biomass dosage. These results indicate the negligible interaction effect of these two parameters on biosorption capacity which confirmed the result of ANOVA as shown in Table 2 (p value = 0.0451).The increment of sorption capacity with increasing temperature suggests an endothermic nature of the sorption of cobalt by this dried biomass. Several studies have indicated the same effect of temperature [13, 34-36]. Higher temperature causes rupture that enhances the number of available active sites, surface activity, kinetic energy of the solute, and affinity of sites for metal ions which lead to an increase in the probability of the collision between active surface binding sites and metal ions and a decrease in the thickness of the boundary layer surrounding the biosorbent [13, 35-37]. However, the temperature higher than 55ºC caused a change in the texture of the biomass and thus reduced its sorption capacity [14, 38]. In addition, the decrease of biosorption efficiency with the increase of temperature is due, most probably, to the desorption tendency of heavy metals from biosorbent surface. [39] Therefore, it depends on the type of metal and adsorbent. That is the reason for having different behavior of heavy metal uptake with temperature [38].

The effects of biomass dosage(BC) can be inferred from the response plot (Fig. 7), holding the temperature at 30°C and pH at 4.8. The biosorption capacity was decreased from 59.13 to 29.64 mg/g for the Co^{2+} ions with increasing the biosorbent dosage from 0.1 to 0.5 g, respectively.The uptake capacity was calculated at pH 4.8 and initial metal ion concentration 175mg/l. At higher biosorbent dose the uptake capacity is low, perhaps due to the unsaturation of biosorption sites through the biosorption reaction and due to the particle interaction, such as aggregation, resulted from high biosorbent concentration [40]. Such aggregation would lead to decrease in total surfacearea of the biosorbent and an increase in diffusional path length[41].

4-5. Confirmatory experiments

For validation of the statistical model, two experiments were performed under optimal conditions. Table 7 presents the experimental results under the optimal condition compared with the simulated values from the proposed model (Eq. (12)). The experimental responses for biosorption capacity were 81.11 and 79.98 mg/g which indicate that the experimental values are very close to the predicted values and hence, the model is successful in predicting the responses.

Table 7. Optimum condition verification and additional experiments.

Run	T(°C)	C_0 (mg/l)	M_{ads}(g)	pH	Type of biosorbent	Response (maximized Co^{2+} uptake)	
						q_{pre} (mg/g)	q_{exp} (mg/g)
1	45	300	0.1	7	Mg-treated biomass	80.21	79.98
2	45	300	0.1	7	Mg-treated biomass	80.21	81.11

4-6. Determination of dynamic constants at optimized condition

In order to obtain the biosorption kinetics constants of cobalt ions on Mg-treated biomass, two kinetics models were studied at optimized conditions determined by Design-Expert software (T=45°C, C_0=300 ppm, pH 7 and M_{ads}= 0.1 g). According to the results, the theoretical $q_{e(cal)}$ values calculated from the pseudo-first-order model did not give reasonable values with regard to the experimental uptake ones, $q_{e(exp)}$. Further, the correlation coefficient (R^2=0.7224) is less than 0.99, suggesting that the present adsorption system does not follow pseudo-first-order process. Similar results are also reported by other researchers[1, 17, 42, 43].

The plots between t/q_t and t for the pseudo-second-order model are shown in Fig. 8. As can be seen from Table 8, the theoretical $q_{e(cal)}$ values agree well with the experimental uptake values, $q_{e\ (exp)}$. Further, the correlation coefficient (R^2) for the pseudo-second-order kinetic model was 0.999, suggesting that the present adsorption system can be described more favorably by pseudo-second-order process.

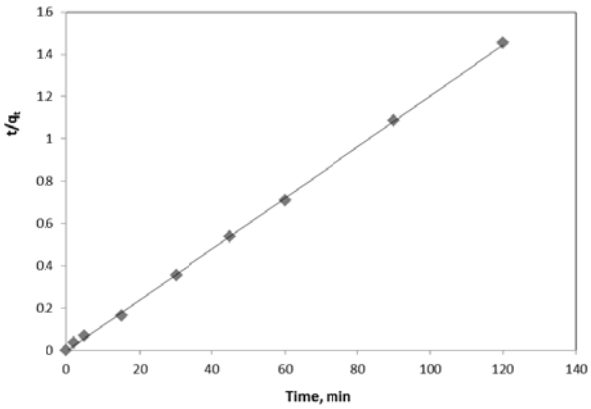


Figure 8. The linearized pseudo-order biosorptiondynamics of cobalt.

Table 8. Biosorption kinetics constants of cobalt ions on Mg-treated biomass for pseudo-second-order model at optimized conditions (T=45 °C, C0=300 ppm, pH 7 and M_{ads}= 0.1 g).

$q_{e\ (exp)}$ (mg/g)	k_2 (g/mg min)	$q_{e\ (cal)}$	R^2
82.789	0.058564	82.645	0.999

4-7. Isotherm at optimized condition

The biosorption isotherm for the sorption on cobalt on Mg-treated biomass was obtained at different temperature and constant optimized conditions determined by Design-Expert software (pH 7 and M_{ads}= 0.1). The results of the adsorption isotherms for the cobalt ions at different temperatures are presented in Table 9. The good correlation coefficients values (R^2) showed that Freundlich model is more suitable than Langmuir for adsorption equilibrium of cobalt. The better fit of equilibrium data to the Freundlich equation refers the multilayer sorption of the cobalt ions on the biosorbent [41]. However, some studies have been

Table 9. Adsorption isotherm parameters for Co (II) biosorption on Mg-treated *Sargassum sp.*

T (ºC)	Langmuir constants			Freundlich constants		
	q_m (mg/g)	b (l/mg)	R^2	k	n	R^2
15	76.33588	0.024472	0.9709	7.485141	2.398657	0.9987
23	78.74016	0.023523	0.9719	7.247697	2.336449	0.9988
30	80.64516	0.02274	0.9728	7.048553	2.285192	0.9988
38	83.33333	0.021779	0.9738	6.83282	2.230152	0.9989
45	85.47009	0.021051	0.9748	6.652732	2.184837	0.999

described better with the Langmuir isotherm [27, 29, 39]. Some authors explain that Langmuir isotherm corresponds to a dominant ion exchange mechanism while the Freundlich isotherm shows adsorption-complexation reactions taking place in the adsorption process [44]. The result in Table 9 shows that n values related to Freundlich isotherm are greater than unity representing favorable biosorption conditions and formation of relatively stronger bonds between adsorbent and adsorbate [3, 5].

4-8. Determination of thermodynamic constants of biosorption

The calculated thermodynamic parameter Gibbs free energy change, ΔG°, for the biosorption of cobalt by *Sargassum sp*. algae was calculated using Eq. 7 and 9 (Table 10). According to Eq. 9, the enthalpy change, ΔH°, and the entropy change, ΔS°, were calculated from the plot of ln K versus 1/T (R^2=0.999) to give the values 535.76 J/mol and 3.24 J/molK, respectively (Fig. 9). The negative value of ΔG° indicates the feasibility of the process and indicates the spontaneous nature of the adsorption. The ΔG° value is more negative with increasing temperature, which suggests that higher temperature makes the adsorption easier. In general, it is of note that up to −20 kJ/mol is consistent with electrostatic interaction between charged molecules and surface indicative of physisorption while more negative than −40 kJ/mol involves chemisorption and values between −20 and −40 kJ/mol indicate that both physisorption and chemisorption were responsible for adsorption[17].

For the adsorption of cobalt ions on to the *Sargassum sp*. biomass, the order of magnitude of the ΔG° value indicates a physical mechanism. However, the pseudo-second-order kinetics shows chemisorption mechanism for this system. Therefore, the nature of the adsorption process cannot be clearly specified thermodynamically, and it might only be considered as chemisorption in nature enhanced by physical effects.

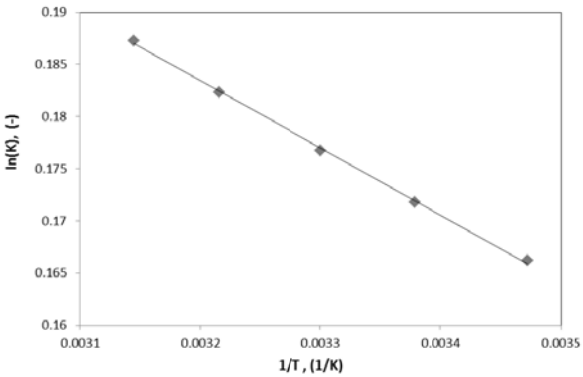


Figure 9. Thermodynamic relationship between the Gibbs free energy and temperature.

In our study, the positive value of ΔH° confirms the endothermic adsorption nature of the process. The positive value of ΔS° indicates the affinity of the adsorbent for cobalt and also confirms the increased randomness at the solid-solution interface during biosorption [2, 17]. Value of the ΔG°, ΔH° and ΔS° from the present study was compared with other metal adsorption reported in previous studies and are compiled in Table 11.

Table 10. Thermodynamic parameters and corresponding correlation coefficient for Co (II) biosorption on Mg-treated *Sargassum sp.*

Temperature (°C)	Thermodynamic parameters and corresponding R^2 value			
	ΔG° (J/mol)	**ΔH° (J/mol)**	**ΔS° (J/mol K)**	**R^2**
15	-397.935862	535.7625	3.239966	0.999
23	-422.706613			
30	-445.18927			
38	-471.420463			
45	-495.217534			

Table 11. Comparison of thermodynamic parameters with other metals adsorption.

Heavy metal ion	Sorbent	Temperature (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	Reference
Pb^{2+}	Peanut shells	20, 30, 40	-24.25 to -25.00	-16.68	25.16	[18]
Pb^{2+}	Sargassumilicifolium	20, 25, 30	-2.6 to -3.6	0.027	0.102	[13]
Sr^{2+}	Activated carbon	20, 30, 40, 60	-12.61 to -20.44	44.77	195.847	[45]
Cr (VI)	Sargassummuticum	20, 50	-7.3 to -8.7	7.1	49.1	[36]
Pb^{2+} Ni^{2+} Cd^{2+}	Orange peel	30	-3.77, -4.22, -4.99	-	-	[46]
U	Padina sp.	10, 20, 30, 40	-6.549 to -5.914	-12.552	-21.408	[17]
Cu^{2+} Cd^{2+} Pb^{2+}	Caulerpalentillifera	20, 30, 40	-16.4 to -18.5 -13.4 to -17.2 -17.9 to -19.7	13.9 42.3 8.28	103 191 89.3	[35]
Ni^{2+}	S. muticum G. caudate	20, 30, 50	-	-29.7 -16.0	-90.3 -47.7	[47]
Co^{2+}	Lemon peel	25, 45	-37.47, -38.56	-21.20	54.61	[1]
Sr^{2+}	Activated carbon	20, 30,40,60	-36.61 to -41.75	0.036.88	125.44	[48]
Co^{2+}	*Sargassum Sp.*	15, 23, 30, 38, 45	-0.397 to -0.495	0.535	3.24	This work

5. Conclusions

In this study, central composite design (CCD) was used for the RSM in the experimental design and proved to be an efficient method for testing the effect of operating conditions and their interactions on cobalt uptake by the brown algae *Sargassum sp*. The interactive effects of five independent factors: initial pH of solution, initial concentration cobalt (II), temperature, biosorbent dosage, and biomass treatment on the biosorption capacities were estimated. A reduced quadratic model was obtained to predict the biosorption capacity. ANOVA results confirmed that there was significant agreement between the model and experimental data. The optimum biosorption conditions were determined as Mg-treated biomass, initial pH 7.0, temperature 45°C, biosorbent dosage 0.1 g/100ml and initial cobalt (II) ion concentration 300 mg/l. At optimum biosorption conditions, the biosorption capacity of Mg-treated biomass for cobalt (II) ions was found to be 80.55 mg/g. The results are best fitted by the Freundlich model. The biosorption of cobalt (II) onto algal biomass followed the pseudo-second-order dynamics well. The calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the process was feasible, spontaneous and endothermic at the temperature ranges of 15–45°C.

Acknowledgment

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Nomenclature

b	the Langmuir constant (l/mg)
b_0, b_i and b_{ij}	linear and quadratic interaction coefficients, i and j = 1-5
C	metal ion concentration at any time (mg/l)
C_0	initial metal ion concentration(mg/l)
C_{eq}	residual metal ion concentration at equilibrium (mg/l)
$C.I.$	confidence interval (-)
$C.V$	coefficient variation (-)
k	adsorption capacity (-)
n	biosorption intensity (-)
$P.I.$	prediction interval (-)
q	amount of biosorbed metal perg of biosorbentat any time (mg/g)
q_{eq}	the amount of biosorbed metal per unit weight of biosorbentat equilibrium(mg/g)
q_{exp}	experimental amount of biosorbed metal per unit weight of biosorbent at equilibrium (mg/g)
q_m	maximum capacity of biosorbent
q_{pre}	predicted amount of biosorbed metal per unit weight of biosorbent at equilibrium by software(mg/g)
R^2	correlation coefficient
R^2_{adj}	adjusted correlation coefficient
M_{ads}	amount of biosorbent (g)
t	time (min)
x_i	independent variable, i=1-5
y	response (-)
V	volume of the solution (l)
T	Solution temperature (ºC)

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