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ORIGINAL PAPER

Study of cobalt (II) biosorption on *Sargassum* sp. by experimental design methodology

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Abstract In this study, the biosorption of cobalt (II) ions on *Sargassum* sp., brown algae, was investigated in a batch system. The combined effects of operating parameters such as biomass treatment, initial pH, temperature, initial metal ion concentration, and biosorbent dosage on the biosorption of cobalt (II) ions on *Sargassum* sp. were analyzed using response surface methodology. The $Mg(NO_3)_2$ was used as a pretreatment agent for *Sargassum* sp. The optimum biosorption conditions were determined as Mg-treated biomass, initial pH 7.0, temperature 45 °C, biosorbent dosage 0.1 g, and initial cobalt (II) concentration 300 mg/l. At optimum biosorption conditions, the biosorption capacity of Mg-treated biomass for cobalt (II) ions was found to be 80.27 mg/g after 90-min biosorption. The Langmuir and Freundlich isotherm models were applied to the equilibrium data. The results are best fitted by the Freundlich model.

Keywords Biosorption · Cobalt · Pretreated algae · Response surface methodology · *Sargassum* sp.

Introduction

Cobalt containing compounds are widely used in many industrial applications such as mining, metallurgical, electroplating, paints, petrochemical, electronic, and nuclear power plants. Acute cobalt poisoning in humans may cause serious health problems including allergy, vomiting, neurotoxicological symptoms, damage to the heart, thyroid, and liver, whereas chronic exposure can induce partial or complete loss of smell and gastrointestinal troubles (Suhasini et al. 1999; Bhatnagar et al. 2010). It is therefore 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, coagulation, and co-precipitation (Dahiya et al. 2008). Although these conventional techniques can reduce metal ions, 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 (Ozer et al. 2008). The most popular of these technologies is activated carbon adsorption which is widely used; however, this technique is expensive. Therefore, there is a 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 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 (Ozer et al. 2008). Among biosorbent materials, algae have proved to be both economic and eco-friendly, as they are abundantly available, have regeneration and metal recovery potentiality, have high efficiency in dilute effluents, and have high surface-area-to-volume ratio (Pahlavanzadeh et al. 2010). Untreated algae generally contains light metal ions such as Ca^{2+} and Mg^{2+} which are originally bound to the acid functional groups of the alga and were acquired from

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seawater (Davis et al. 2003). The basic and important mechanism in biosorption which explains the heavy metal ions uptake is ion exchange due to the electrostatic interactions between the metal cations and anionic carboxyl groups. The carboxylic groups are generally the most abundant acidic functional groups in brown algae (Davis et al. 2003). The adsorption capacity of the algae is directly related to the presence of these sites on the alginate polymer (Kleinubing et al. 2011). Alginic acid or alginate is the common name given to a family of linear polysaccharides containing mannuronic and guluronic acid. Based on the amount of protons released, the affinity of alginic acid to metal ions follows the order Pb(II) > Cu(II) > Cd(II) > Ba(II) > Sr(II) > Ca(II) > Co(II) > Ni(II) > Mn(II) > Mg(II). The binding strength of alkaline earth metals to both polymannuroate and polyguluronate was found to decrease in the order Ba(II) > Sr(II) > Ca(II) > Mg(II) (Davis et al. 2003; Kleinubing et al. 2011). Haug (1961) interpreted the preferential binding of heavier ions to stereochemical effects, since larger ions might better fit a binding site with two distant functional groups. 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 (papageorgiou et al. 2006). According to the trends, cobalt ion prefers 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 mechanism of binding metal ions by inactivated algal biomass may depend on the species and ionic charges of the metal ions, the algal organisms, the chemical compositions of the metal ion solution, and other external environmental factors such as pH and temperature (Pahlavanzadeh et al. 2010).

Design-Expert software is a program to help optimize the process. This software provides highly efficient design of experiments for factorial designs, response surface methods (RSM), mixture design techniques, and combined designs. Response surface methodology (RSM) is a collection of mathematical and statistical procedures and one approach to evaluate the relative significance of several effective factors by estimating the shape of the response surface and selecting optimum conditions in a limited number of experiments. Second-order models are widely used in RSM to approximate the true response surface. The central composite design (CCD) is the most popular RSM and is used to build second-order models (Omidvar et al. 2014). The results are statistically analyzed by this software. In the statistical methods, the variables involved in an experiment are being 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 that the interaction of two or more variables can also be derived. This is not possible in a classical one factor at a time experiment (Demim et al. 2014). Accuracy and precision of experiments are evaluated by the ANOVA results and confirmatory experiment.

The aim of this study was to conduct a central composite design (CCD) analysis for 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—chemical modification of the biomass, temperature, pH, adsorbent dose and initial concentration of Co^{2+}-, and also their interactions on biosorption was studied using CCD, which gives a mathematical model that shows the influence of each variable and their interactions.

Materials and methods

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 of sodium and potassium ions. After drying overnight at a maximum temperature of 55 °C to avoid degradation of the binding sites (Diniz et al. 2006), 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 $Mg(NO_3)_2{\cdot}6H_2O$ (biomass concentration of 10.0 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 55 °C, and subsequently natural algae and Mg-pretreated algae were used for biosorption experiments.

Preparation of synthetic metal solution

A stock solution of cobalt, with 1,000 ppm concentration, was prepared using ($Co(NO_3)_2{\cdot}6H_2O$). 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 used chemical materials were of analytical grades (Sigma Aldrich, Germany).

Characterization test

Scanning electron microscopy

The surface morphology of the algae was visualized by a scanning electronic microscope VEGA \\ SEM (TESCAN a.s., Czech Republic). To determine the chemical composition of biosorbent before and after treatment by 0.1 M $Mg(NO_3)_2 \cdot 6H_2O$ and also after Co^{2+} sorption, a system of analysis for energy dispersive X-ray spectroscopy (EDX, RONTECH, Germany) was also used.

Fourier transform infrared spectroscopy

FTIR spectroscopy was used to detect vibration frequency changes in the brown algae *Sargassum* sp. before and after pretreatment. The spectra were recorded using FTIR (PerkinElmer Spectrum version 10.03.06, USA) spectrometer within the range of 400–4,000 cm^{-1} using KBr pellets.

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.

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 added to a series of 250-ml Erlenmeyer flasks containing 100 ml of 100 mgCo/l $Co(NO_3)_2 \cdot 6H_2O$ solution. The flasks were agitated at 150 rpm and 25 °C for 24 h in a shaker. Samples were withdrawn at predetermined time intervals (2, 5, 15, 30, 45, 60, 90, 120, 150, 180, and 1,440 min). These time intervals were selected according to the previous research which has indicated that the absorption rate for most metals is fast initially and the equilibrium time for Cobalt is <3 h (Ozdemir et al. 2005; Sun et al. 2008; Dahiya et al. 2008; Maresova et al. 2011; Bulgariu and Bulgariu 2012). 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 (II) concentration, and the dosage of biomass. Each experiment was carried out in 250-ml Erlenmeyer flasks containing 100 ml $Co(NO_3)_2 \cdot 6H_2O$ solution with known initial cobalt concentration which were mixed to different amount of biomass. The flasks were shaken at 150 rpm for a period contact time of 90 min. 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. 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 (Khani 2011).

Experimentation and optimization of biosorption

In the 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 and validating the models, evaluating the effects of variables, estimating interaction between variables, and searching optimum conditions of variables to predict targeted responses (Ozer et al. 2008; Khodadoust et al. 2014). The application of statistical experimental design techniques in sorption processes could result in improved product yields, reduced process variability, as well as reduced development time and overall costs (Annadurai et al. 2003).

In the 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 (Ozer et al. 2008). The CCD consisted of a 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 $(\pm\alpha, 0, 0)$, $(0, \pm\alpha, 0)$, and $(0, 0, \pm\alpha)$. In this study, α was fixed 2.0 which is the default setting of software for up to five factors that makes the design Rotatable; this creates a design that has the standard error of predictions equal at points equidistant from the center of the design.

Therefore, central composite design with four numeric factors (initial cobalt (II) concentration: 50–300 mg/l, biosorbent dosage: 0.1–0.5 g, initial pH: 2.5–7.0 and temperature: 15–45 °C) and one categorical factor at two levels (natural *Sargassum* sp. and Mg- pretreated *Sargassum* sp. algae) was applied using Design-Expert software 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. A quadratic model, which also includes the linear model, is given as;

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

where b_0, b_i, b_{ii}, b_{ij} are a constant, a linear coefficient, a square coefficient, and an interaction coefficient, respectively (Ozer et al. 2008; Mafi Gholami et al. 2012; Khodadoust et al. 2014).

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; and 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. (2) including analysis of variance (ANOVA) to obtain the interaction between the process variables and the responses. Analysis of variance (ANOVA) of proposed results is undertaken to identify the individual and interactive effect of all variables. The validated model can be plotted in tridimensional graph to generate a surface response corresponding to a response function that admit to determine the best operating conditions of the process (Roosta et al. 2014). The coefficients of determination, R^2 and R^2_{adj}, expressed the quality of the fit of polynomial model. The statistical significance was checked with adequate precision ratio and F test (Ozer et al. 2008). The second-order polynomial models were represented as response, while keeping constant third variable (Freitas et al. 2009).

Results and discussion

Statistical analysis

In order to determine the significant factors and the interaction between them, 56 experimental runs were statistically analyzed with CCD design. P value was used as a tool to check the significance of every coefficient. The smaller the magnitude of P, the more significant is the corresponding coefficient. P values <0.05 indicate that model parameters are significant. In our experiment, all five factors and AB (T, C_0), BC (C_0, M_{ads}), BD (C_0, pH), and BE (C_0, Type of biosorbent) interactions are highly significant ($P < 0.05$). ANOVA results after eliminating the insignificant parameters for the reduced quadratic model are summarized in Table 2. The final responses for the biosorption capacity of untreated and treated biomasses for cobalt (II) ions were obtained in Eqs. (3) and (4), respectively.

$$\begin{aligned} y_1 = {} & 27.01193 - 0.039876x_1 + 0.21785x_2 \\ & - 109.62840x_3 + 2.06483x_4 \\ & + 9.15733E - 004x_1x_2 - 0.13322x_2x_3 + 0.010372x_2x_4 \\ & - 3.85354E - 004x_2^2 + 98.69344x_3^2 - 0.35106x_4^2 \end{aligned} \tag{3}$$

$$\begin{aligned} y_2 = {} & 26.75589 - 0.039876x_1 + 0.24190x_2 \\ & - 109.62840x_3 + 2.06483x_4 \\ & + 9.15733E - 004x_1x_2 - 0.13322x_2x_3 + 0.010372x_2x_4 \\ & - 3.85354E - 004x_2^2 + 98.69344x_3^2 - 0.35106x_4^2 \end{aligned} \tag{4}$$

Nonsignificant lack of fit P value 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

Table 1 Experimental range and levels of the control factors in the CCD

Variable	C_0 (mg/g) low axial ($-\alpha$)[a]	Low factorial (-1)	Center	High factorial ($+1$)	High axial ($+\alpha$)[a]
M_{ads} (g) $x_1(A)$: Temperature (°C)	15	23	30	38	45
$x_2(B)$: Initial cobalt (II) concentration (mg/l)	50	113	175	238	300
$x_3(C)$: Biosorbent dosage (g)	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.		

[a] $\alpha = 2$

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	6,424.25	12	535.35	386.89	<0.0001
$A–T$	39.13	1	39.13	28.28	<0.0001
$B–C_0$	3,255.71	1	3,255.71	2,352.86	<0.0001
$C–M_{ads}$	2,609.04	1	2,609.04	1,885.52	<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	6,483.75	55			

values are in reasonable agreement for cobalt (II) which is closer to 1.0, indicating the better fitness of the reduced quadratic model in the experimental data. Adequate precision value is the "signal-to-noise ratio", and a ratio >4 is desirable. The ratio of 77.361 indicates an adequate signal. This model can be used to navigate the design space. The coefficient of variance (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 small values of CV give better reproducibility. In general, a CV higher than ten indicates that variation in the mean value is high and does not satisfactorily develop an adequate response model (Ozer et al. 2008).

The predicted values calculated from the statistical model versus the actual response values obtained by the experiment are shown in Fig. 1a. It approves the suitability of the model since all the points are located around the diagonal line. The normal probability and studentized residuals plot are shown in Fig. 1b for the biosorption capacity of *Sargassum* sp. for cobalt (II) ions. In Fig. 1b, 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. Figure 1b shows that neither response transformation needed nor there was apparent problem with normality.

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, and 7.0, respectively. According to the optimum conditions, the best biosorbent which had the maximum metal uptake (80 mg/g) was $Mg(NO_3)_2{\cdot}6H_2O$-treated biomass (Mg-treated biomass). The software calculated the expected responses and associated confidence intervals based on the prediction equations (Eqs. (3), (4)). 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 to fall 95 % of the time (Mafi Gholami et al. 2012). As shown in Table 3, 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.

Table 3 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)	80.21	1.94	76.29	84.13	2.27	75.63	84.79

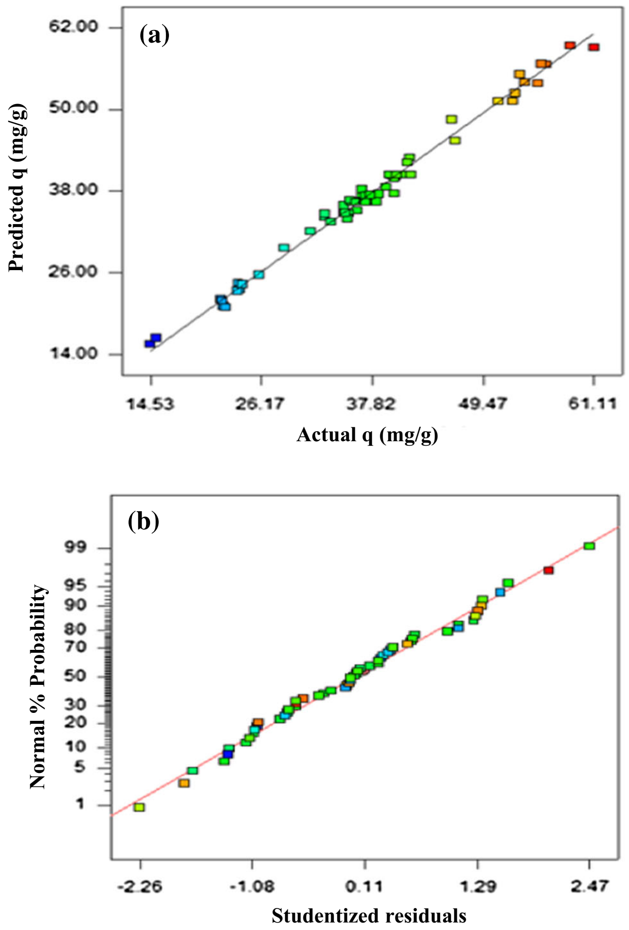


Fig. 1 **a** Scatter graph of the predicted response values versus the actual response values for the biosorption capacity of biomass for cobalt. **b** Normal plot of studentized residuals verses normal % probability for bearing the experiment for cobalt ions

Effect of pretreatment on biosorption capacity and sorption mechanism

The chemically modified biosorbent increases the stability of the biosorbent material and enhances the biosorbent properties (Khani et al. 2006). 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. 2. The capacities of treated and untreated *Sargassum* sp. for cobalt ion at different concentrations indicated that the treatment of $Mg(NO_3)_2$ had enhanced the adsorption capacity. The adsorption capacity for untreated *Sargassum* sp. and treated *Sargassum* sp. increased from 15.43 to 45.49 mg/g and 16.37–52.45 mg/g, respectively, with the increase in the initial concentration of cobalt from 50 to 300 mg/l. According to the Table 2, the interaction between initial cobalt (II) concentration and type of biomass (BE) was highly significant ($P < 0.0001$). Samples of biomasses before and after metal adsorption were observed using the SEM/EDS technique with the aim of identifying the surface microstructures and determining the chemical composition. Figure 3a shows the approximate dimensions of the natural *Sargassum* sp.; the morphology of surface of Mg-treated algae is displayed in Fig. 3b. The biomass surface after sorption of Co (II) is shown in Fig. 3c. Element mapping clearly demonstrated a uniform distribution of Co (II) onto biosorbent surface (Fig. 3d). Also EDX spectra taken in spot profile mode show the enhancement of magnesium peaks on EDX spectra of biomass after treatment comparing with biosorbent before Mg treatment (Fig. 4a, b) and also confirm 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 an EDX spectrometer, as shown in Table 4. Our findings 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 (Vijayaraghavan et al. 2005; Bishnoi et al. 2007). However, due to the complexity of biomaterials, other mechanisms such as coordination and chelation of metals, adsorption, and surface complexation of cations with exposed functional groups on the biomass might be acting simultaneously, to varying degrees, depending on the biosorbent and the solution chemistry (Suhasini et al. 1999; Sheng et al. 2004; Maresova et al. 2011).

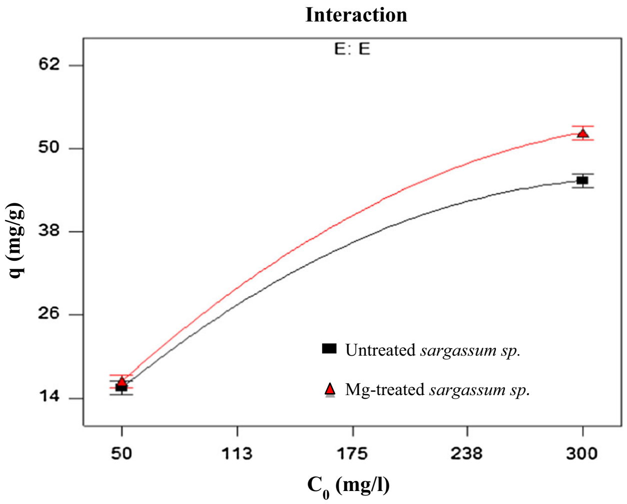


Fig. 2 Intraction plot showing effect of initial cobalt (II) concentration and type of biomass on the cobalt uptake of biomass holding other variables at their central values

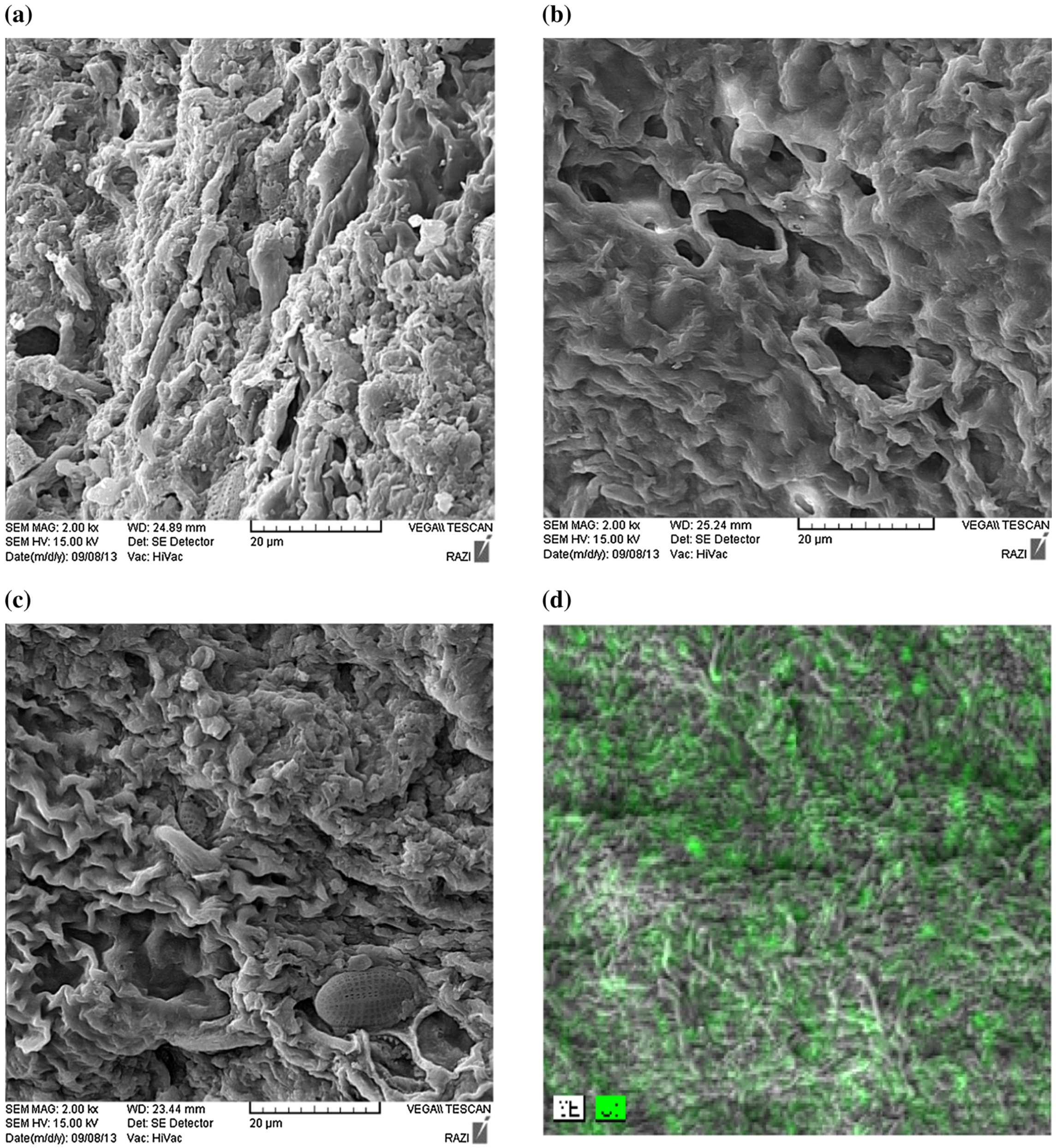


Fig. 3 SEM micrographs of biomass: **a** natural biomass; **b** Mg-treated *Sargassum* sp.; **c** Co-loaded *Sargassum* sp.; and **d** Element mapping of the surface of biomass after cobalt sorption

The FTIR spectra of the natural Mg-treated and cobalt-loaded brown marine algae *Sargassum* sp. are shown in Fig. 5a, b, and c. The FTIR spectroscopic analysis indicated broad bands at 3,418 cm^{-1}, representing carboxylic bonded −OH. For the pristine *Sargassum* sp. biosorbent, it was clear that the carboxylate ions gave rise to two bands: a strong asymmetrical stretching band at 1,645 cm^{-1} and a weaker symmetrical stretching band at 1,423 cm^{-1}. The double bands of the carboxylate ion are representative of the alginate-based polymer which is present in *Sargassum* sp. (Chen et al. 2002; Sheng et al. 2004). Both bands exhibited shifts to different extents after contact with metal solutions. The peak values suggested the chelating (bidentate) character of the metal biosorption onto carboxyl groups (Figueira et al. 1999; Sheng et al. 2004).The structure of the metal bound to carboxyl ligands on the brown algae is expected to have the following form (Figueira et al. 1999; Sheng et al. 2004):

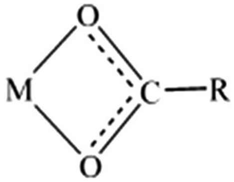
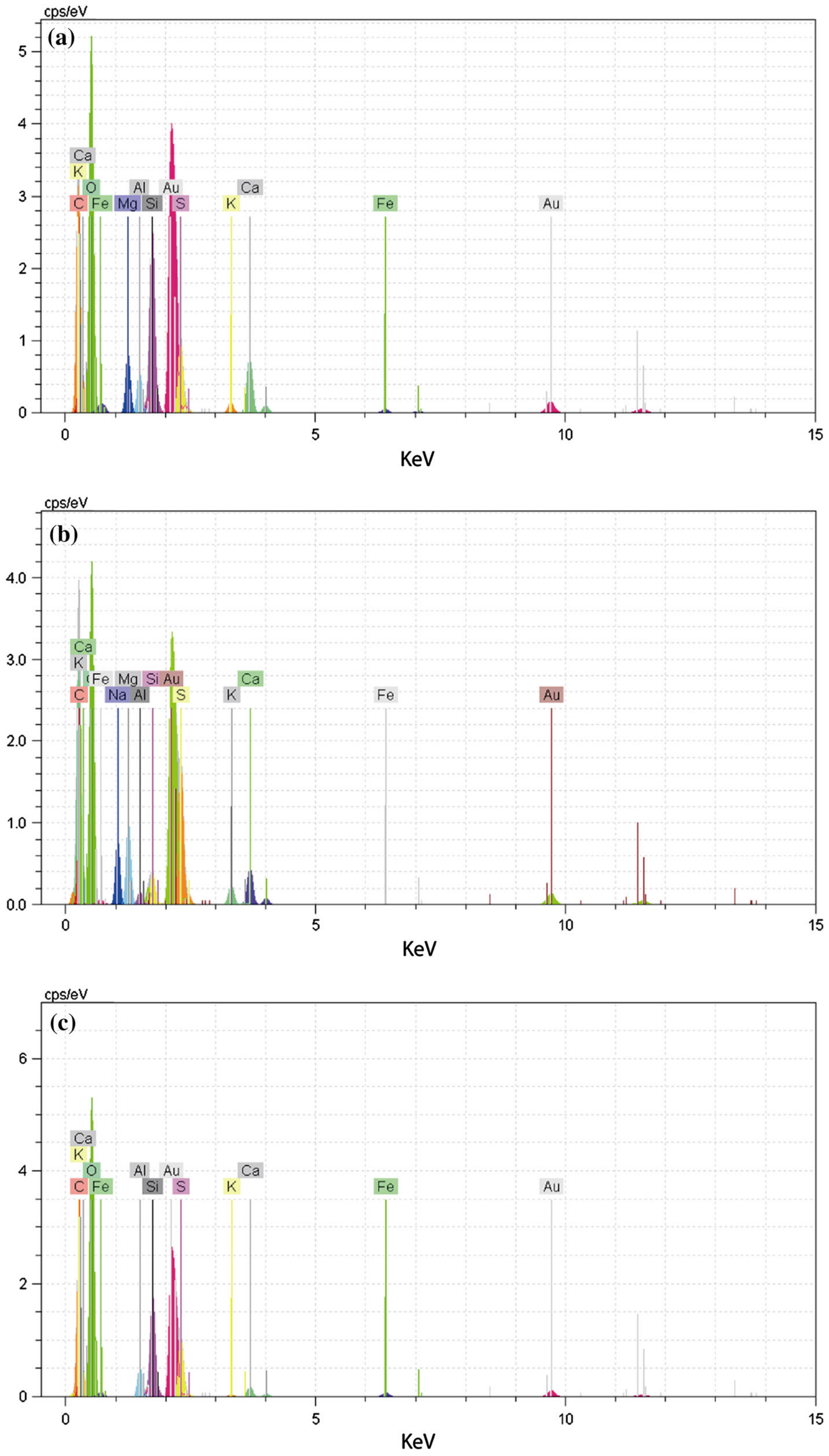


Fig. 4 EDX analysis of *Sargassum* sp. before **a** and after **b** Mg treatment and after **c** cobalt (II) sorption. Au peak comes from sample coating



It was possible to identify two absorbance peak shifts in the FTIR spectra which are characteristic of coordination compounds between carboxyl groups and the cations used. The distance between these two peaks (Δ) is related to the relative symmetry of the carboxyl group and reflects the nature of the coordination compound.

The FTIR spectra suggest the chelating character of the metal biosorption onto carboxyl groups (Figueira et al. 1999).

Table 4 Amount of magnesium and cobalt of the biomass

Type of biomass	Element (wt%)	
	Magnesium	Cobalt
Untreated *Sargassum* sp.	1.91	0.00
Mg-treated *Sargassum* sp.	4.19	0.00
Cobalt-loaded *Sargassum* sp.	0.00	11.04

Some structural characteristics of untreated *Sargassum* sp. and Mg-treated *Sargassum* sp. are presented in Table 5. The pretreatment process led to increase in density from 1.36 to 1.47 g/cm^3 and BET surface area decrease from to 13.39 to 11.64 m^2/g. The results indicated that the chemical pretreatment changes the cell wall structure of biomass.

Value of the adsorption capacity of *Sargassum* sp. adsorbent from the present study was compared with other adsorbents reported in previous studies for cobalt removal and is compiled in Table 6. It is evident from this table that

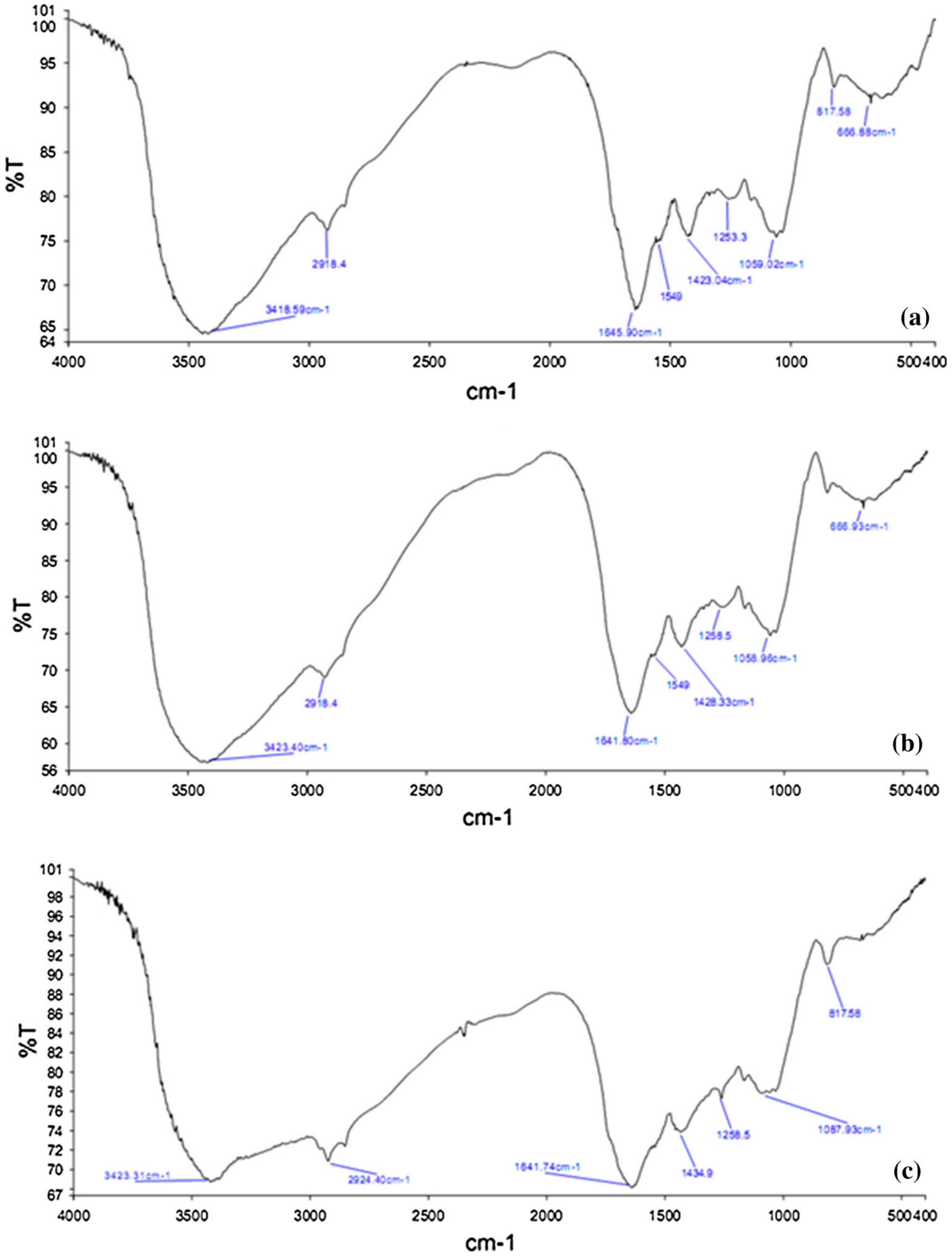


Fig. 5 FTIR spectra of the biomass: **a** natural biomass; **b** Mg-treated *Sargassum* sp.; and **c** Co-loaded *Sargassum* sp

Table 5 Structural properties of untreated and Mg-treated *Sargassum* sp

Property	Untreated *Sargassum* sp.	Mg-treated *Sargassum* sp.
Density (g/cm^3)	1.36	1.47
Pore volume (cm^3/g^1)	2.30E − 2	1.78E − 2
Pore size (nm)	6.87	6.11
Porosity (%)	3.11	2.62
BET surface area (m^2/g^1)	13.39	11.64

the adsorption capacity of Mg-treated *Sargassum* sp. for Co (II) is comparable with the other adsorbents.

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. 4, 5, 6 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 (Diniz 2006). These phenomena presumably are due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule (Ghaedi et al. 2014a). Cobalt predominantly exists as Co^{2+} cation within broad pH range from 2.5 to 7.0. The precipitation of cobalt (formation of $Co(OH)_2$ form) starts at pH 7.5, and therefore, the pH range studied was between 2.5 and 7.0. pH values above seven 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 (Suhasini et al. 1999; Dahiya et al. 2008; Li et al. 2008; Sun et al. 2008; Maresova et al. 2011). Figure 6 shows the effects of initial cobalt (II) concentration and pH (BD) on the biosorption capacity for Mg-treated biomass. Cobalt uptake significantly increases with metal concentration but a smaller rise with pH is observed. According to the Fig. 6, 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 $M_{ads} = 0.3$ g). Our findings show that the biosorption uptake did not vary significantly with initial pH, indicating that the biosorbent can be used with comparable effectiveness in the pH range 2.5–7.0. At the algal particles surface, the biosorption capacity decreases with decreasing pH, due to competition of proton with metal ions for binding to the same sorbent sites (Ghaedi et al. 2013b). Oppositely, at higher pH, where cobalt concentration is much greater than H^+ concentration, the metal uptake increases. Similar results have been obtained by other authors (Suhasini et al. 1999; Vijayaraghavan et al. 2005; Ozdemir et al. 2005; Freitas et al. 2009; Maresova et al. 2011) that found an optimal pH range of 4–7. 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 (Freitas et al. 2009).

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+}

Table 6 Comparison of adsorption capacity of various adsorbents for cobalt removal

Biosorbent type	Biosorption capacity (mg/g)	Operation condition				Reference
		pH $_{opt}$	Biomass (g/l)	C_0 (mg/l)	T (°C)	
PFB1 (fungi)	190.00	7.0	2.00	–	30	Suhasini et al. (1999)
Chryseomonas luteola TEM05 (bacteria)	45.50	6.0	1.00	150	25	Ozdemir et al. (2005)
Sargassum wightii	20.63	4.5	2.00	100	25	Vijayaraghavan et al. (2005)
Arca shell	7.82	4.0	12.50	100	25	Dahiya et al. (2008)
Aerobic granules	52.40	5.0	1.00	300	20	Sun et al. (2008)
Almond green hull	45.50	–	0.25	–	25	Ahmadpour et al. (2009)
Lemon peel	22.00	6.0	10.00	–	25	Bhatnagar et al. (2010)
Rhytidiadelphus squarrosus (moss)	7.26	6.0	2.50	–	20	Maresova et al. (2011)
Green algae	43.07	5.0	8.00	36.58	10	Bulgariu and Bulgariu (2012)
Mg-treated *Sargassum* sp.	80.55	7.0	1.00	300	45	This study

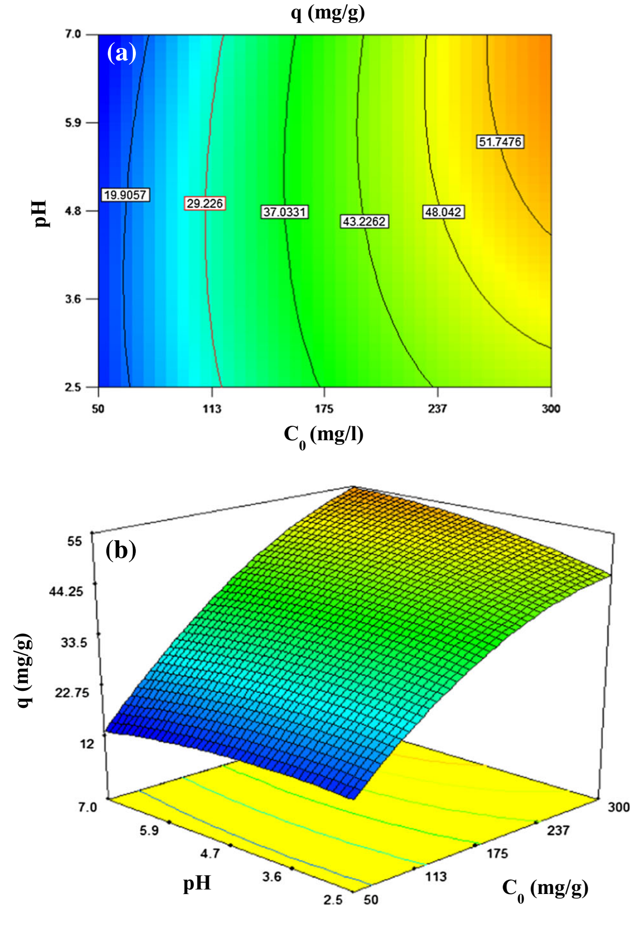


Fig. 6 Three-dimentional plots showing effects of initial cobalt (II) concentration and pH (BD) on the biosorption capacity for Mg-treated biomass holding other variables at their central values

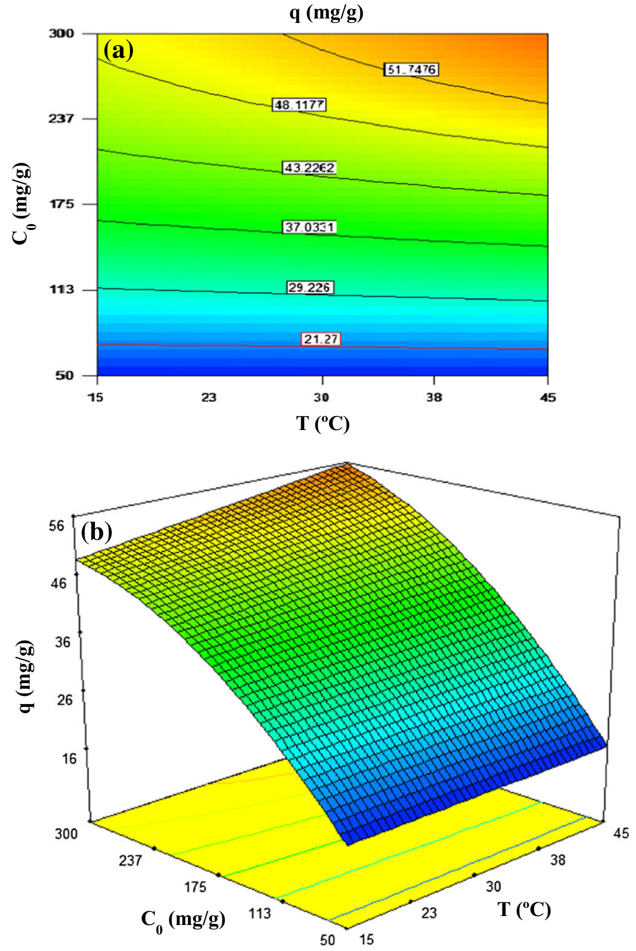


Fig. 7 Three-dimensional plots showing effects of temperature and initial cobalt (II) concentration (AB) on the cobalt uptake of Mg-treated biomass holding other variables at their central values

concentration from 50 to 300 mg/l at pH 7. At higher concentrations of cobalt ions in the solution, the active sites of *Sargassum* sp. are surrounded by more cobalt ions and biosorption is carried out more sufficiently. Similar results are also reported by researchers for a variety of adsorbate–adsorbent systems (Dahiya et al. 2008; Khani et al. 2008; Ahmadpour et al. 2009). The rise of metal uptake by increasing initial metal ion concentration is as a result of the driving force of the concentration gradient, rather than the initial metal ion concentration (Ghorbani et al. 2008). The initial concentration provides an important driving force to overcome all mass transfer resistance of cobalt between the aqueous and solid phases.

The interactive effect of temperature and initial cobalt (II) concentration (AB) on the cobalt uptake of Mg-treated biomass holding other variables at their central values is shown in Fig. 7. The biosorption capacity of treated *Sargassum* sp. increased with the rise 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 is confirmed by the result of ANOVA as shown in Table 2 (P value = 0.0451). Increased biosorption of heavy metals with increasing temperature has been ascribed to cause rupture that possibly enhances the number of active sites involved in metal sorption or the affinity of sites for metal ions, respectively (Freitas et al. 2009). However, the temperature effect seems to be contradictory, as reported by several authors: It can increase (Tsezos et al. 1981; Kuyucak et al. 1989), decrease (Khani et al. 2008; Khani 2011; Bulgariu and Bulgariu 2012; Ghaedi et al. 2013a), or keep the algae ability for metal sorption unaffected (Deng et al. 2006; Freitas et al. 2009; Ahmadpour et al. 2009).

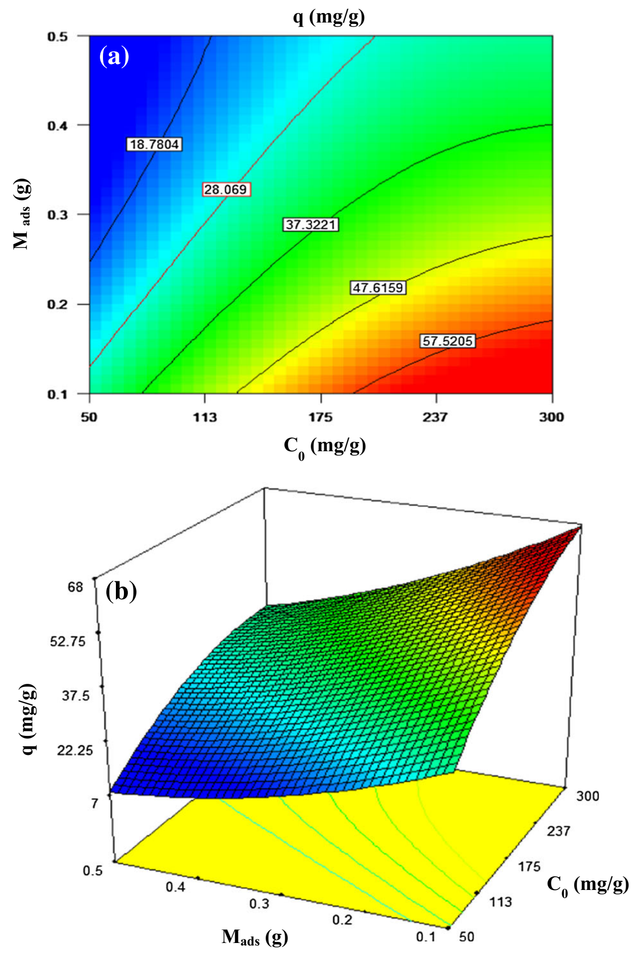


Fig. 8 Three-dimensional plots showing effects of initial cobalt (II) concentration and biomass dosage (BC) holding the temperature at 30 °C and pH 4.8

The effects of initial cobalt (II) concentration and biomass dosage (BC) can be inferred from the response plot Fig. 8, holding the temperature at 30 °C and pH at 4.8. The biosorption capacity 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, respectively. The uptake capacity was calculated at pH 4.8 and initial metal ion concentration 175 mg/l. At higher biosorbent dose the uptake capacity is low, possibly due to the unsaturation of biosorption sites and also due to the particle aggregation. Such aggregation would lead to decrease in total surface area of the biosorbent and an increase in diffusional path length (Singh et al. 2010).

Confirmatory experiments

Model validations at two experimental combinations were used for validation of the statistical model. In order to compare the experimental results under the optimum condition with the simulated values from the proposed model, experiments were performed in duplicate. Under these conditions, the experimental responses for biosorption capacity were obtained 81.11 and 79.98 mg/g. The results indicate that the experimental values are very close to the predicted values (80.21 mg/g), and hence, the model is successful in predicting the responses.

Isotherm at optimized condition

The biosorption isotherms are characterized by definite parameters, whose values express the surface properties and affinity of biosorbent for different heavy metal ions (Bulgariu and Bulgariu 2012). 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 (Ozer et al. 2008). The linear form of Langmuir isotherm is given by the following equation:

$$\frac{1}{q_{\mathrm{eq}}} = \frac{1}{bq_{\mathrm{m}}C_{\mathrm{eq}}} + \frac{1}{q_{\mathrm{m}}} \quad (5)$$

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 Lang-

Table 7 Adsorption isotherm parameters for Co (II) biosorption on Mg-treated *Sargassum*

T (°C)	Langmuir constants				Freundlich constants			
	q_m (mg/g)	b (l/mg)	R^2	χ^2	k	n	R^2	χ^2
15	76.336	0.025	0.9,728	1.471	7.485	2.399	0.9987	0.038
23	78.740	0.024	0.9719	1.545	7.248	2.337	0.9988	0.037
30	80.645	0.023	0.9728	1.638	7.049	2.285	0.9988	0.036
38	83.333	0.022	0.9728	1.680	6.833	2.230	0.9989	0.037
45	85.470	0.021	0.9748	2.142	6.653	2.185	0.9990	0.036

muir constant related to energy of adsorption and the affinity of the binding sites (Bhatnagar et al. 2010; Khani 2011). The equilibrium parameters (q_m and b) are determined from the linear plot of $1/q_{eq}$ versus $1/C_{eq}$.

The adsorption data were 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 (Ozer et al. 2008). Freundlich equation commonly presented as below.

$$q_{eq} = kC_{eq}^{\frac{1}{n}} \quad (6)$$

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

$$\log q_{eq} = \log k + \frac{1}{n} \log C_{eq} \quad (7)$$

where k and n are constants related to the adsorption capacity and intensity of the adsorbent characteristics of the system, respectively (Singh et al. 2010). The fractional values of biosorbent surface simultaneously indicate a favorable biosorption of metal ions onto biomass (Bulgariu and Bulgariu 2012). The plots of log q_{eq} versus C_{eq} determine values of $1/n$ and k.

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 five different temperatures versus initial concentrations of 50, 113, 175, 238, and 300 mg/g are presented in Table 7.

Error analysis (χ^2) was used for evaluating applicability of each model. The nonlinear Chi-square test statistic (χ^2) (the best-fit isotherm) is based on the following equation (Ghaedi et al. 2014):

$$\chi^2 = \sum \frac{\left(q_{e,exp} - q_{e,cal}\right)^2}{q_{e,cal}} \quad (8)$$

where $q_{e,exp}$ and $q_{e,cal}$ are experimental and calculated adsorption capacity value, respectively. Non-applicability of each model makes possible larger χ^2 value. In principle, the model with the higher R^2 and smaller χ^2 value represents the better fit of the model with the experimental data. The higher correlation coefficients values (R^2) and smaller χ^2 value as shown in Table 7 verifies 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 (Singh et al. 2010). However, Langmuir isotherm had a better fit in some studies (Suhasini et al. 1999; Bishnoi et al. 2007; Bulgariu and Bulgariu 2012). 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 (Khani 2011). The result in Table 7 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 (Dahiya et al. 2008; Ozer et al. 2008).

Conclusion

In the 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 for predicting 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, 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 80.27 mg/g. These findings showed the effectiveness of Mg as a surface modifier enhancing the biosorption capacity of brown alga *Sargassum* sp. for cobalt ion. Future research studying the effectiveness of this surface modifier on other metal ions is recommended.

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Glossary

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 per g of biosorbent at any time (mg/g)
q_{eq}	The amount of biosorbed metal per unit weight of biosorbent at 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: $x_1 = Tx_2 = C_0$, $x_3 = M_{ads}$, $x_4 =$ pH, $x_5 =$ type of algae
y	Response (–)
V	Volume of the solution (l)
T	Solution temperature (°C)
χ^2	Nonlinear Chi-square

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