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ORIGINAL ARTICLE

Response Surface Modeling and Optimization of Effective Parameters for Zn(II) Removal From Aqueous Solution Using *Gracilaria Corticata*

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KEYWORDS

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ABSTRACT: Biosorption of Zn(II) from aqueous solution by biomass marine alga, namely *Gracilaria corticata* was investigated in this paper. Four independent variables, including initial zinc concentration (50-150 mg L^{-1}), initial solution pH (3-7), contact time (10-50 min), and biomass amount (1-2 g/100mL) were studied in the biosorption process. Optimization of the process conditions for maximizing Zn(II) removal from aqueous solutions by *Gracilaria corticata* was carried out using Box-Behnken design, including response surface methodology (RSM) based on 27 different experimental data. The optimal operating conditions for 95.0% removal of Zn(II) were as follows: initial zinc concentration of 100 mg L^{-1}, initial solution pH of 5, contact time of 30.5 min, and biomass amount of 2 g/100 mL. In addition, the equilibrium isotherms were described by investigation of Langmuir and Freundlich isotherms. The Freundlich adsorption isotherm model well matched the experimental data (R^2 = 0.981). The kinetic data fitted pseudo-second order model with a correlation coefficient of 0.9953. *Gracilaria corticata* was found to be well applicable for zinc removal based on the experimental results.

INTRODUCTION

One of the most important and dangerous environmental pollutions is caused by heavy metals in industrial wastewater [1]. Trace concentrations of zinc are important for the physiological functions of living tissues and regulation of many biochemical processes. Zinc discharged into natural waters, sewages, or industrial wastewaters can have severe toxic effects on humans and aquatic ecosystems. Therefore, the removal of zinc from industrial wastewaters prior to discharging into the environment is essential [2, 3].

Methods such as complexation [4], ion exchange [5], membrane filtration [6,7] and chemical chelating [8] have different drawbacks, including low selectivity, high energy consumption, production of a lot of toxic waste as a result of using different reagents, incomplete metal removal, and high investment and running costs [9]. Given its low cost and good performance, biosorption, which utilizes the ability of various biological compounds to bind and isolate heavy metals from aqueous solutions, is a considerable alternative process [10].

In order to identify highly efficient biosorbents for metal removal, different types of biomass such as bacteria, fungi, and algae have been extensively studied in the last decade. Selected seaweed species have shown to have significant sorption capacities for a wide range of heavy metal ions [11, 12]. The global production of algae is a few million tons per year. Almost 94% of edible seaweed

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is obtained by maritime culture; it is a widely available biomass source [13]. Seaweeds are found throughout the world's oceans and come in three basic colors: brown, red, and green. One of the red species extensively found in Queshm Island and Bostaneh harbor, Iran, is *Gracilaria corticata.*

The biomass of *Gracilaria corticota* could be used as an effective biosorbent for removal of heavy metals such as Cu, Ni, As, and Hg from contaminated water [14-17].

In this paper, the removal of zinc from aqueous solutions using *Gracilaria corticata* was carried out to evaluate the biosorption potentials. The effects of four operating parameters, namely initial zinc concentration, pH, contact time, and adsorbent amount were studied. Most conventional methods of studying a process consist of keeping some factors constant while evaluating the effect of other variable factors on the process. This often lacks the ability of efficiently showing the interactions among parameters. In addition, a large number of experiments have to be performed, which is a time consuming process. A very useful tool for this purpose is experimental design because it provides statistical models, which help understand the interactions among optimized parameters [18].

These methods include mathematical models for chemical processes design and results analysis. Response surface methodology (RSM) is one of the suitable methods used in many fields [19]. RSM is a collection of statistically useful techniques for the analysis of independent factors effects on the response and can be used to evaluate the relative significance of several factors, affecting the process. The main objective of RSM is determination of optimal operational conditions for system [20]. Box-Behnken is one of RSM designs requiring fewer runs. Box-Behnken design is a type of response surface method that provides detailed information about the solution space and allows researchers to better understand forces affecting model output [21].

The main objective of this work was the evaluation of *Gracilaria corticata* potential for zinc biosorption. The effects of four independent variables, including initial zinc concentration, initial solution pH, contact time, and the used biomass amount were investigated. Box-Behnken experimental design under RSM was used in determination of optimal conditions for Zn(II) elimination in wastewater. Biosorption capacities were investigated using Langmuir and Freundlich isotherms.

MATERIALS AND METHODS

Biomass preparation

Zn(II) was removed from aqueous solutions using *Gracilaria corticata* from Queshm Island and Bostaneh harbor, Iran. The fresh alga sample was first washed with seawater, and then, was washed with tap water to remove the sand particles and salts. The cleaned alga was sun dried for 4 days, chopped to 5-10 mm particles in size, and used in the biosorption experiments.

Instrumentation and software

An Agilent Technology-735 instrument was used to record the zinc concentration by inductively coupled plasma optical emission spectrometry (ICP-OES). A Metrohm pH meter, model 780, equipped with a combined glass calomel electrode was used to record pH values. A Labtech shaking, model LsI-3016A (Korea), mechanical shaker was used to shake solutions. The experiments were designed and the results were analized in MINITAB (Version 16). All programs were run on a PC with Windows XP operation system.

Solutions preparation

All solutions were prepared with double distilled, deionized water. The zinc stock solution was prepared at a concentration of 1000 mg L^{-1} from $ZnSO_4.7H_2O$. All other solutions were prepared by successive dilutions of the stock solution using double distilled water. The pHs of solutions were adjusted using 0.1 M HCl or NaOH. Universal buffer solution was prepared using 0.04 M acetic, boric, or phosphoric acid solutions. All the reagents and materials used in this work, purchased from Merck Chemical Co., were of analytical reagent grade. The adsorption experiments were carried out at ambient temperature.

Biosorption studies

In each run, a total volume of 100 mL sample solution containing known concentrations of zinc at different pH values was poured into a 250 mL- conical flask. A known weight of marine alga was then added to the flask and the mixture was shaken using a mechanical shaker at constant speed (180 rpm) in predetermined time intervals. The adsorbate was decanted and filtered from the adsorbent. The zinc concentration in the filtrates was then analyzed.

Equation 1 was used to calculate the removal percentage of Zn(II):

$$Removal\% = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

where C_i (mg L^{-1}) and C_e (mg L^{-1}) are initial and equilibrium zinc concentrations, respectively. Equation 2 was used to calculate the amount of zinc adsorbed per adsorbent unit mass at equilibrium time(q_e):

$$q_e = \frac{V(C_i - C_e)}{m} \qquad (2)$$

where q_e (mg g^{-1}) is zinc quantity adsorbed by biosorbent, C_i and C_e are initial and equilibrium concentrations of zinc solution, respectively, m is biosorbent weight (g), and V is Zn(II) solution volume.

RESULTS AND DISCUSSION

Preliminary optimization

Zn(II) adsorption by *Gracilaria corticata* method was optimized under various conditions. Important factors were optimized using univariate procedure in this method. The optimal experimental conditions, affecting adsorption efficiency, including initial zinc concentration, pH, contact time, and biomass amount, were established and the effects of operational parameters were optimized by Box-Behnken design.

Experimental results showed that the percentage of zinc removal by biosorption using *G. corticata* at different pH levels (3 to 7) has a bell shape in which the maximum removal was obtained at pH level of 5. In order to examine the effect of biomass amount, the process was repeated using 1.5 g of algae. According to the results, it is clearly concluded that the percentage of zinc removal linearly and moderately relates to the amount of *G. corticata* used, such that the percentage of removal increases fairly as the amount of *G. corticata* increases.

Similarly, to evaluate the effect of initial zinc concentration on the removal percentage, the biosorbtion processes were carried out with different initial concentrations of 50 to 150 mg L^{-1}. According to the results, the removal percentage has a downward exponential curvature pattern, indicating that it decreases as the initial concentration increases. Moreover, different experiments were carried out to study the effect of 10-50-min contact time on the removal percentage of the process. The results clearly indicate that the removal percentage linearly increases with contact time. However, the removal percentage reaches its maximum after about 20 min and becomes roughly constant afterwards.

Experimental design

RSM is a statistical method to determine operational conditions from experimental design using quantitative data. RSM is a collection of statistical and mathematical techniques used for modeling and evaluating the effect of independent factors on metal removal. The standard RSM design, called Box-Behnken design [22], was used to investigate factors, affecting zinc removal. Box-Behnken design was used for four independent variables, including initial zinc concentration (X_1), solution pH (X_2), contact time (X_3), and biomass amount (X_4) determined by 1, 0, and -1 at three minimum, average and maximum levels.

The number of experiments (N) was calculated using: $N = 2k(k-1) + C_0$, where k is the number of factors and C_0 is the number of repetitions of central points [23]. Zn(II) initial concentration, solution pH, contact time, and alga amount were selected as input variables, and removal percentage ($R\%$) was considered as system response in the design of experiment. A total of 27 experiments, including three repetitions of central points were applied in this study to investigate the effects of four main independent variables on zinc removal efficiency.

Table 1 gives the experimental range and levels of four independent variables for zinc removal by biomass. Table 2 shows the empirical conditions and results obtained by zinc ion removal using *G. corticata*.

Table 1. Variables in Box-Behnken design

Factors	Symbol	Low Level (-1)	High Level (+1)
Initial zinc concentration (mg L^{-1})	X_1	50	150
pH	X_2	3	7
Contact time (min)	X_3	10	50
Adsorbent amount (g)	X_4	1	2

Table 2. Matrix in Box-Behnken design and response for each experiment

Run No.	Actual level of factors				Response
	X_1	X_2	X_3	X_4	(Removal %)
1	50	3	30	1.5	69.0
2	150	3	30	1.5	66.7
3	50	7	30	1.5	77.4
4	150	7	30	1.5	69.4
5	100	5	10	1.0	37.0
6	100	5	50	1.0	65.8
7	100	5	10	2.0	42.2
8	100	5	50	2.0	87.3
9	50	5	30	1.0	65.6
10	150	5	30	1.0	60.6
11	50	5	30	2.0	81.4
12	150	5	30	2.0	75.4
13	100	3	10	1.5	34.3
14	100	7	10	1.5	40.4
15	100	3	50	1.5	77.6
16	100	7	50	1.5	79.0
17	50	5	10	1.5	44.9
18	150	5	10	1.5	36.9
19	50	5	50	1.5	84.8
20	150	5	50	1.5	75.7
21	100	3	30	1.0	61.8
22	100	7	30	1.0	62.0
23	100	3	30	2.0	73.7
24	100	7	30	2.0	78.5
25	100	5	30	1.5	73.8
26	100	5	30	1.5	75.0
27	100	5	30	1.5	75.1

Equation 3, a second order equation, illustrates the optimal conditions prediction based on the relationship between system responses (Y) and independent variables, referred to as factor (X_i):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 \quad (3)$$

where β_0 is a constant value, β_1, β_2, β_3 and β_4 are linear coefficients, β_{12}, β_{13}, β_{14}, β_{23}, β_{24} and β_{34} are cross product coefficients, and β_{11}, β_{22}, β_{33} and β_{44} are quadratic coefficients. It is assumed that the independent variants are controllable and give a result with less error.

Results of BBD experiments

The data regression and graphical analyses were carried out using MATLAB software. The optimal quantities were obtained by solving regression equation. The optimal values and combined effect between factors within the specified range were predicted and described using the model equation (Equation 4).

$$Y = -40.4143 + 0.096X_1 + 9.2509X_2 + 2.5673X_3 + 31.9889X_4 - 0.0143X_1X_2 - 0.0003X_1X_3 - 0.0103X_1X_4 - 0.0291X_2X_3 + 1.141X_2X_4 + 0.409X_3X_4 - 0.0003X_1^2 - 0.7684X_2^2 - 0.0338X_3^2 - 11.5548X_4^2 \quad (4)$$

$\frac{\partial Y}{\partial X_1}$, $\frac{\partial Y}{\partial X_2}$, $\frac{\partial Y}{\partial X_3}$, and $\frac{\partial Y}{\partial X_4}$ were equalized to zero in order to compute the optimal parameter values. In addition, X_1, X_2, X_3, and X_4 were obtained corresponding to maximum Y, based on simultaneous solution. The optimal parameter values are as follows:

$X_1 = 100$, $X_2 = 5$, $X_3 = 30.5$ and $X_4 = 2$.

Analysis of variance (ANOVA) was performed to evaluate the significance of regression model and its terms, as well as the effect of factors and their interactions (Table 3) [24, 25]. The significance of each term in the model was investigated based on *p*-value. The *p*-values below 0.05 are considered statistically significant. It was concluded that the solution pH (X_2), contact time (X_3), adsorbent dosage (X_4) and their quadratic were the main factors, and X_1X_2 and X_3X_4, the cross product factors, were significant according to the ANOVA results.

R^2 coefficients were estimated in order to further validate the model. Normally, a regression model with $R^2 > 0.90$ is considered to have a very high correlation [26]. The high R^2 value (0.9964) suggested an excellent correlation between empirical and predicted values, and 99.64% variability of the response could be explained by the model and only about 0.36% of the total variation cannot be explained by this model. Additionally, the adjusted R^2 should be in a reasonable agreement with R^2. The adjusted R^2 value (0.9922) was found to be very close to R^2.

The lack of fit test measures the failure of the model to represent experimental data in the experimental domain at points which are not included in regression analysis [27]. The *p*-value of lack of fit (0.203) indicates that the model applied for fitting Y is significant and represents the relationship between response and independent variables. Therefore, this model can be used to obtain the biosorption of metal ion by the adsorbent. The *p*-value, which determines the significance of coefficients, is presented in Table 3.

The significance of each coefficient was determined by *p*-values listed in Table 4. As shown, X_1, X_2, and X_3 of the linear and their square coefficients were significant at 5% probability level for the biosorption efficiency.

Table 3. Analysis of variance (ANOVA) of the second-order polynomial equation

Variables	DF[a]	SS[b]	MS[c]	F-values	*p*-value
Model	14	6518.36	465.597	236.43	0.000
X_1	1	3.09	3.086	1.57	0.234
X_2	1	39.88	39.882	20.25	0.001
X_3	1	400.45	400.453	203.35	0.000
X_4	1	25.69	25.689	13.05	0.004
X_1^2	1	3.51	3.505	1.78	0.207
X_2^2	1	50.39	50.386	25.59	0.000
X_3^2	1	976.83	976.830	496.03	0.000
X_4^2	1	44.50	44.505	22.60	0.000
X_1X_2	1	8.13	8.130	4.13	0.065
X_1X_3	1	0.32	0.317	0.16	0.695
X_1X_4	1	0.26	0.265	0.13	0. 720
X_2X_3	1	5.41	5.408	2.75	0. 123
X_2X_4	1	5.21	5.208	2.64	0.130
X_3X_4	1	67.01	67.011	34.03	0.000
Residual	12	23.63	1.969		

Table 3. Continued

Lack-of-Fit	10	22.58	2.258	4.32	0.203
Pure Error	2	1.05	0.523		
Total	26	6541			

R^2 = 99.64; Predicted R^2 = 97.98; Adjusted R^2 = 99.22
[a] DF: degree of freedom
[b] SS: sum of squares
[c] MS: mean square

Table 4. Analysis of variance (ANOVA) for Box-Behnken

Source	Coefficients	T-values	*p*-value
β_0	-40.4143	-3.188	0.008
β_1	0.0960	1.252	0.234
β_2	9.2509	4.500	0.001
β_3	2.5673	14.260	0.000
β_4	31.9889	3.612	0.004
β_{11}	-0.0003	-1.334	0.207
β_{22}	-0.7684	-5.058	0.000
β_{33}	-0.0338	-22.272	0.000
β_{44}	-11.5548	-4.754	0.000
β_{12}	-0.0143	-2.032	0.065
β_{13}	-0.0003	-0.401	0.695
β_{14}	-0.0103	-0.367	0.720
β_{23}	-0.0291	-1.657	0.123
β_{24}	1.1410	1.626	0.130
β_{34}	0.4093	5.833	0.000

Interaction effects of biosorption variables

The effect of different variables on response factor (R%) is visualized by three dimensional (3-D) response surface plots. The relationship between these parameters and Y is shown by surface plots. Four independent variables, including initial zinc concentration, solution pH, contact time, and adsorbent amount had significant effect on zinc removal.

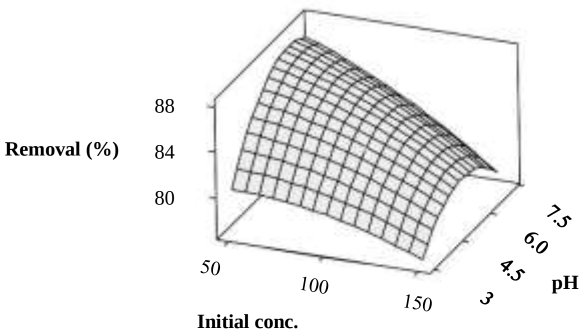
The 3-D response surface plot used to represent the combined effect of initial concentration and pH on removal is shown in figure 1a. The two parameters of contact time (30min) and adsorbent amount (2g) were kept constant. According to the figure, the initial pH has a significant effect on zinc biosorption. The pH scale ranges from 3 to 7. The adsorption rate increased as pH increased. Maximum adsorption was observed at pH of 5. The adsorption rate decreased at pH’s more than 5. H^+ ions are attached to the sorption sites and more Zn^{2+} ions are left unabsorbed under acidic conditions due to the competence of H^+ ions and Zn^{2+} for these sites. At higher pH’s, the – COO^- ligand on the adsorbent increases the negative charge density. As a result, the electrostatic attraction of metal ions with positive charge increases at the ligand surface and the adsorption rate increases. OH^- concentration increases as pH value increases and the adsorption rate decreases due to the formation of metal hydroxide deposit. According to the figure, the maximum adsorption has occurred at the lowest initial metal concentration and pH of 5.

Figure 1b shows the effect of pH and adsorbent amount at constant initial concentration (100 mg L^{-1}) and contact time (30 min). The maximum zinc removal (88%) occurred using 2 g of the adsorbent at pH of 5. The removal percentage was directly proportional to the adsorbent amount. Metal removal efficiency obviously increased as the adsorbent amount increased. In other words, the increased adsorbent amount created more binding sites and increased the removal of zinc ions. No remarkable changes were observed in the removal rate due to the effect of the density of adsorbent and the number of available binding sites on using higher adsorbent amounts.

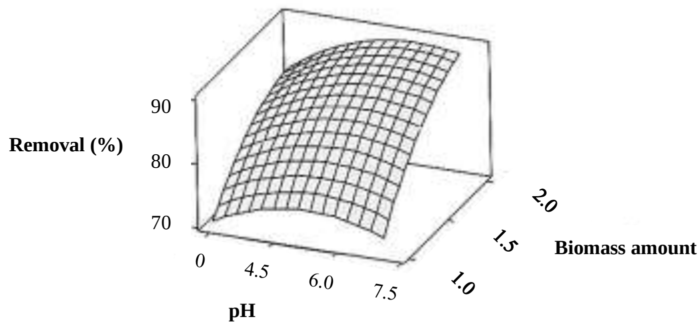
Figure 1c shows the interactive effect of initial zinc concentration and contact time on adsorption rate at constant pH (5) and adsorbent amount (2g). The removal rate increased as the contact time increased. The maximum removal occurred at a contact time of 30 min, after which the zinc removal became roughly constant. The maximum removal (91%) was observed at pH of 5 using 2 g of adsorbent**.**

Figure 1d shows the combined effect of the initial solution concentration and adsorbent amount on the metal ion removal at constant pH (5) and contact time (30min). The zinc uptake increased by increasing the adsorbent amount and decreased by increasing the initial zinc concentration. The adsorbent surface was saturated at high initial concentrations, which led to the decreased zinc removal. At low concentrations, there were more effective binding sites for heavy metal ions adsorption. However, the high concentration indicated that the number of cations was greater than that of the binding sites. Thus, the adsorption rate was dependent on the initial concentration and decreased with an increase in the concentration. The maximum removal (90%) occurred with the lowest initial solution concentration and highest adsorbent amount.

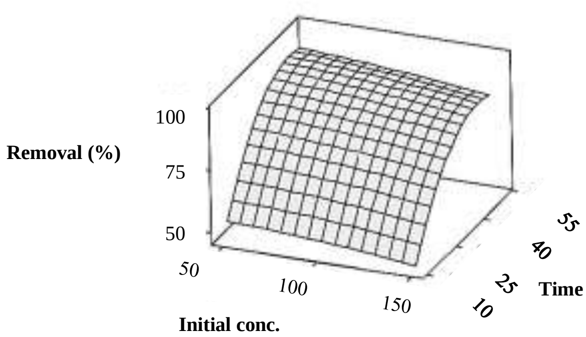
The metal ion removal increased as contact time and adsorbent amount increased (figure 1e). The maximum adsorption (96%) occurred at constant pH (5) and initial solution concentration ($100 mgL^{-1}$). The response surface plot, Figure 1f, which explores the combined effect of pH and contact time, shows that maximum zinc uptake (86%) occurred at a contact time of 30 min and pH of 5.



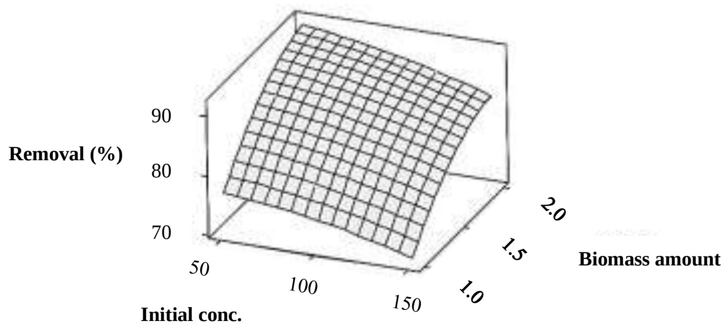
(a)



(b)



(c)



(d)

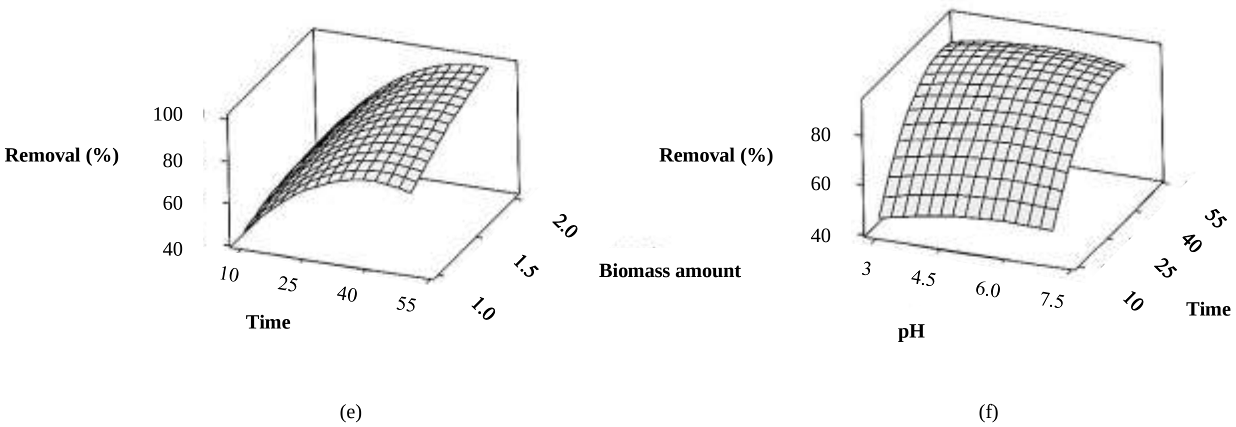


Figure 1. Response surface plots for the effect of variables: (a) X_1 and X_2, (b) X_2 and X_4, (c) X_1 and X_3, (d) X_1 and X_4, (e) X_3 and X_4, and (f) X_2 and X_3 on zinc adsorption

Adsorption Isotherms

The modeling of metal ions' adsorption isotherms was carried out using Langmuir [28] and Freundlich [29] isotherm models in this research.

Langmuir adsorption isotherm is a rule for physical adsorption by non-living biomass used for monolayer adsorption on the adsorbent surface with a restricted number of sites with equal affinity. The adsorption isotherm can be modeled using equation (5):

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad (5)$$

where q_e is the amount of metal adsorbed per minute, C_e is metal equilibrium concentration, Q_m is adsorbent maximum uptake capacity, and K_L is equilibrium adsorption constants calculated from the slope and intercept of Langmuir plot.

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m}\frac{1}{C_e} \qquad (6)$$

Freundlich adsorption isotherm was applied for heterogeneous surfaces and multilayer sorption. Freundlich adsorption isotherm is shown by the following equation:

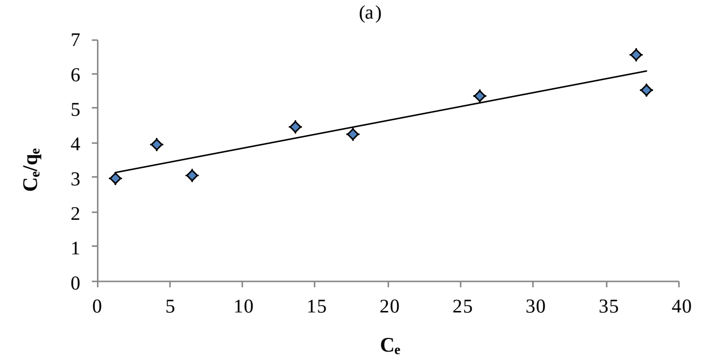
$$q_e = K_f C_e^{1/n} \qquad (7)$$

where q_e and C_e have the same definitions as in Langmuir equation, and K_f and n are Freundlich model constants representing the sorption capacity and intensity calculated from the slope and intercept of the linear plot of lnC_e vs. lnq_e.

Table 5 shows the adsorption isotherm constants. Figure 2 shows the Langmuir and Freundlich isotherms for zinc removal drawn for present data. The adsorption isotherm plots are best fitted in both isotherm models since they are linear. However, given the higher correlation coefficient of Freundlich model (0.9810) compared to Langmuir isotherm (0.8697), the adsorption process is fitted more in the former. This suggests the heterogeneous surface characteristics of the present biosorbent with several possible functional groups responsible for sorption of the zinc ions.

Table 5. Isotherm constants for Zn(II)

Biosorbent mass	**Isoterm model**					
	Langmuir constant			Freundlich constant		
	R^2	Q_m (mg/g)	K_L (L/mg)	R^2	K_f(mg/g)	n (g/L)
2 g	0.870	0.327	37.87	0.981	0.383	1.26



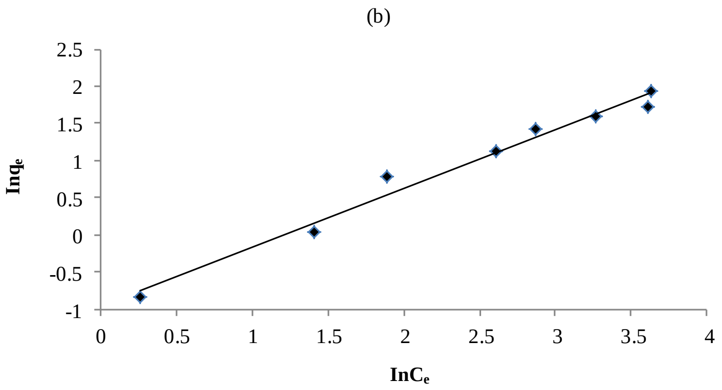


Figure 2. The Langmuir (a) and Freundlich (b) isotherm for biosorption of Zn(II)

Biosorption kinetics

Biosorption kinetics is one of the most important parameters that significantly depict the biosorbent features [30]. In order to investigate the sorption mechanism and describe the kinetic biosorption data, two adsorption kinetic models were used. The first order model is shown by equations (8) and (9):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (8)$$

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \qquad (9)$$

where q_e and q_t are the amounts of adsorbed ion at equilibrium at time t, respectively, and k_1 is the adsorption rate constant (obtained by plotting log $(q_e - q_t)$ vs. $'t'$.

The second order model is shown by equations (10) and (11):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (10)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (11)$$

where k_2 is adsorption constant. The plot of t/q_t vs. $'t'$ should be drawn to calculate the equation coefficients. This plot gives a straight line with a slope of $1/q_e$ and an intercept of $1/k_2 q_e^2$, which are used to calculate the model constants [31].

Table 6 shows the equation and rate constant of the first and pseudo-second order adsorption kinetics of Lagergren for zinc removal using alga. According to the obtained results, the adsorption of metal ion on *Gracilaria corticata* fitted the second order kinetic model due to the higher value of R^2 .

Comparison of this work with other similar works

Table 7 shows the comparison results of some of this method parameters for zinc removal with similar reported methods.

Table 6. Equations and Rate constants

Order	Equation	Rate constant	R^2
Lagergren first order	$\log(q_e - q_t) = 8.0386 + 0.007t$	0.0161 min^{-1}	0.8825
Pseudo second order	$t/q_t = 0.054 + 0.0102t$	18.58 g/(mg-min)	0.9953

Table 7. Various adsorbent with similar reports for zinc removal

Adsorbent	Objective of the study	pH	Isotherm	Kinetic	Initial conc. (mgL^{-1})	Removal (%)	References
jatropha cuecas	To study the biosorption process of Zn(II) from aqueous solution	4	Langmuir	second-order	10-50	69.4-70.5	[32]
Nonliving biomass	To evaluate the effects of nonliving biomass on biosorption of Lead (II) and Zinc (II) ions	5.5	Langmuir	-	100	87.0	[33]
lemon peel and banana peel	To study the influence of natural biosorbent on removal of zinc from wastewater	4 4	-	second-order	50	87.5 90.5	[34]
Crustaceous shell	To study the effects of chitin extraction from crustaceous shell on zinc removal from aqueous solution	7	Freundlich	second-order	50	90.7	[35]
Leaves of Araucaria cookii	To evaluate the effect of leaves of Araucaria cookie on zinc removal from wastewater	5.8	Freundlich	-	200	97.9	[36]
biomass marine alga	To evaluate zinc removal from wastewater by using seaweed	5	Freundlich	second-order	100	95.0	Present work

CONCLUSIONS

The objective of this work was to find out the optimal process conditions for Zn(II) removal from aqueous solutions using biomass of *Gracilaria corticata*. The effects of initial zinc concentration, initial solution pH, contact time, and biomass amount, as independent variables, on the zinc removal efficiency were evaluated by RSM using Box-Behnken design. The results indicate that *G. corticata* can be considered as an efficient biosorbent for Zn(II) removal from industrial wastewater. The optimal conditions for maximum zinc removal (95%) were obtained, including initial zinc concentration of 100 mg L^{-1}, initial solution pH of 5, contact time of 30 min, and biomass amount of 2g/100 mL. Freundlich model can be used for modeling of adsorption isotherms based on the adsorption isotherm studies. According to the kinetic studies, the zinc removal was better described by pseudo-second order model. *Gracilaria corticata* biomass was an efficient biosorbent for zinc removal from industrial wastewaters based on the obtained experimental results.

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Conflict of interests

The authors declare no conflict of interest.

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