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Factors affecting of zinc biosorption by *padinaboergeseni*

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ABSTRACT

The Several isotherms and kinetics models for zinc biosorption by the *padinaboergeseni* as brown algae were investigated. The effects of operating parameters such as initial *p*H, temperature, ionic strength, initial zinc concentration, biomass concentration and contact time on the Zn biosorption were analysed. Design of the experiments was done in the response surface methodology by using Box–Behnken model in the Minitab software for cooperating parameters such as initial *p*H, temperature, ionic strength and contact time. A mathematical function for zinc uptake by *padina boergeseni* was developed.

KEYWORDS

Biosorption;
Waste water treatment;
Response surface methodology;
Padina boergeseni.

INTRODUCTION

The heavy metals are toxic and destroy into harmless end products. The elimination of heavy metals is essential for several reasons, for artificial lake in industrial, for wastewater in metropolis, for storage in agricultural, for impurity insanitary and for pollution in public disposal.

Biosorption is potentially an attractive technology for waste treatment. Biosorption is received considerable attention owing to be an efficient, clean and cheap technology for waste treatment. Different studies are carried out for using inexpensive biomass for the waste treatment of waters containing heavy metals[1-5].

The present work focused on the potential use of *padina boergeseni* as a fresh and economical biomass for removal of Zn ion from aqueous solution. The isotherms and kinetics of biosorption is investigated. Experimental parameters affecting the biosorption process such as initial pH, temperature, contact time, ionic strength and metal ionic radius in row and column of periodic table are studied.

MATERIALS AND METHODS

Preparation of biomass solution

*padina boergeseni*was collected from the Persian Gulf on Bushehr Island. For the biosorption studies, the harvested fresh cells were rinsed with tap water, washed several times with distilled water and then put in an oven at 60°C for 12 h. The *padina boergeseni*was powdered with a blender and sieved to make a homogenized biomass in order to destroy biomass aggregates and increase uptake capacity[6].

Preparation of zinc solution

A stock solution of Zn was prepared by dissolving $ZnCl_2$ in 1 L of distilled water. The zinc solutions of different concentrations (25–150 mg/L) were prepared from the stock solution with deionized

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water. The *p*H value was adjusted to desirable value with 0.1 MNaOH and 0.1 M HCl. Also for the setting of ionic strength solutions, we applied solution with 1, 10, 50 and 100 mM $NaNO_3$.

Analytical methods

The zinc solution and *padina boergeseni* were contacted together in particular time and then pass through a filter paper. Afterward, the concentration of zinc was determined by analyticjenacontrAA 300 atomic absorption spectrometer.

Zincbiosorption experimental details

The different experimental parameters such as *p*H (2.0 – 8.0), temperature (25–65 °C), contact time (10 –100 min), ionic strength (0–100 mM $NaNO_3$ solution) and metal ionic radius in row with different atomic numbers (Z=26-30) and in column for IIB of periodic table (Zn, Cd and Hg) were arranged.

The metal uptake, q_e (mg/g), milligram of metal biosorbed per gram of biomass was determined according to eqn (1)

$$q_e = \frac{(C_i - C_e)V}{1000w} \quad (1)$$

where C_i (mg/L) is the initial metal concentration, C_e (mg/L) is the metal concentrations at various time intervals, V (mL) is the volume of the solution and w (g) is the mass of sorbent.

RESULTS AND DISCUSSION

Effect of initial pH

The effect of the initial *p*H on zinc biosorption by the *padinaboergeseni* was plotted in Figure 1. The results indicate that very low and very high pH values, leading to a reduction in the amount absorbed and the maximum biosorption capacities were obtained at *p*H 6.0 for Zn.

In low pH, carboxylate group in alginic acid and sulphonate group in fucoidan as the active sites on the biomass are protonated and less available. In high pH, carboxylate group in alginic acid and sulphonate in fucoidan as the active sites on the biomass are deprotonated and further available and so the absorption increases. Also we must consider the competition of hydronium ion with zinc ion for absortion on the biomass especially in low pH.[7]

Effects of temperature

The variation of the biosorbed Zn with contact time was studied for different temperatures as shown in Figure (2).

The biosorption yield decreased for zinc ion by increasing temperature from 25 to 55°C. This result indicated the exothermic nature of Zn biosorption onto *Padina boergeseni* algae. A decrease in the biosorption of zinc by increasing temperature may be due to the damage of active binding sites in the biomass[8] or increasing tendency to desorb Zn from the interface to the solution[9].

Effects of contact time for different initial Zinc concentrations

The effects of contact times on the biosorption

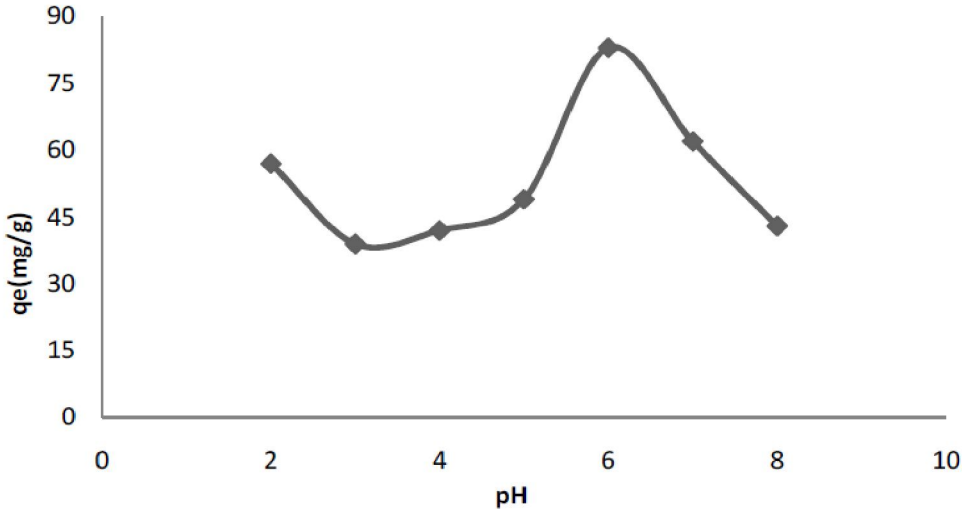

Figure 1 : Effect of *p*H on Zinc biosorption

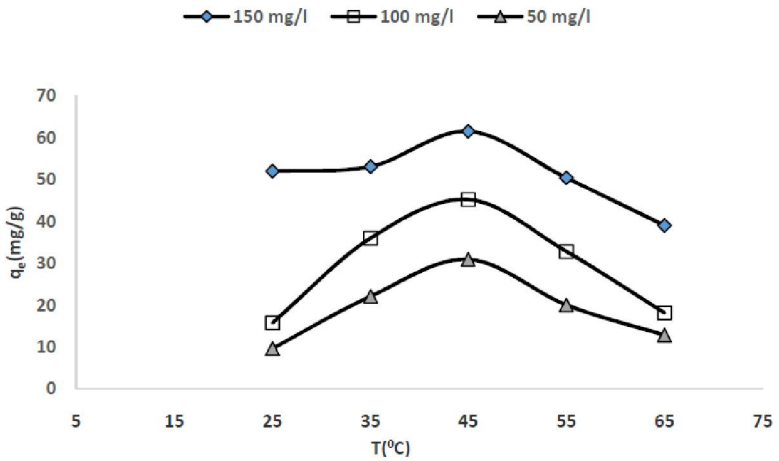

Figure 2 : Effect of contact time and temperature (metal concentration = 150 mg/L; biomass dosage = 0.2 g/L; *p*H =6)

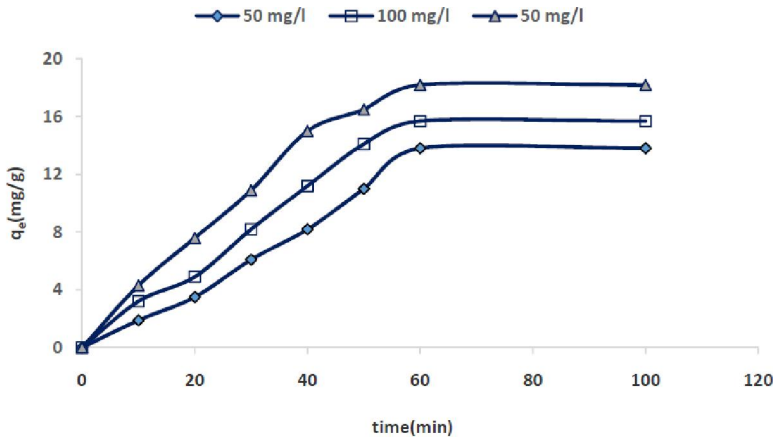

Figure 3 : Effect of contact time and concentration (temperature = 25°C; biomass dosage = 0.2 g/L; *p*H=6)

of zinc were measured for three different initial zinc concentrations 50, 100and 150 mg/L. As shown in Figure 3, the metal uptake increases with rise in contact time up until60 minute for three different initial zinc concentrations and then it is unvarying. These trends can be related to the saturation of the active site on the biomass. The optimum contact time was selected as 60 minute for further experiments.

Ionic strength effect

100 mg of biomass was exposed to 50 mL of the metal solution as blank (0mM), low (1 mM), medium (10 mM), high (50mM) and very high (100 mM) of $NaNO_3$ salt, for adjustment the ionic strength. Also, the pH value was controlled by using 0.1 M HCl and 0.1 M NaOH. Flasks were shaken for 1h at 25°C and 200rpm. The samples were then filtered under vacuum and analyzed by analyticjenacontrAA 300 atomic absorption spectrometer.

Ionic strength lead to the three effects for uptake of heavy metal such as zinc: 1) The more ionic strength, lead to the increase in ionic concentrations that cause to competition with our heavy metal cation 2) In the high concentration of ionic strength, the functional groups such as sulphonate, carboxylate and hydroxyl encompassed with major cation in the solution cause reducing our heavy metal uptake in the biomass, i.e. *padina boergeseni* 3) The higher ionic strength, lead to the diminish activity of all ion in solution among our heavy metal.

Nitrate was chosen as the anion because of its low tendency for complex formation with most metals[10]. The effect of Na^+ is more pronounced during the uptake of weakly bound metals such as Zn^{2+} or Ni^{2+}. Strongly bound metals such as Cu^{2+} are generally less affected by solution ionic strength[11].

Isotherm studies

Isotherm models have been shown to be the suit-

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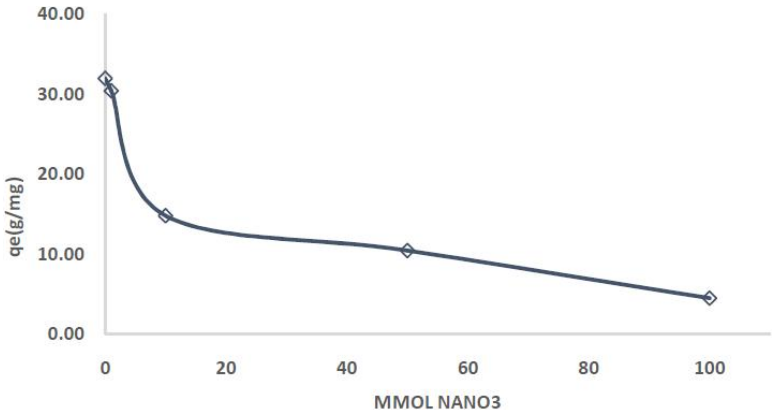

Figure 4 : Effect of Ionic Strength (temperature = 25°C; biomass dosage = 0.2 g/L; *p*H=6)

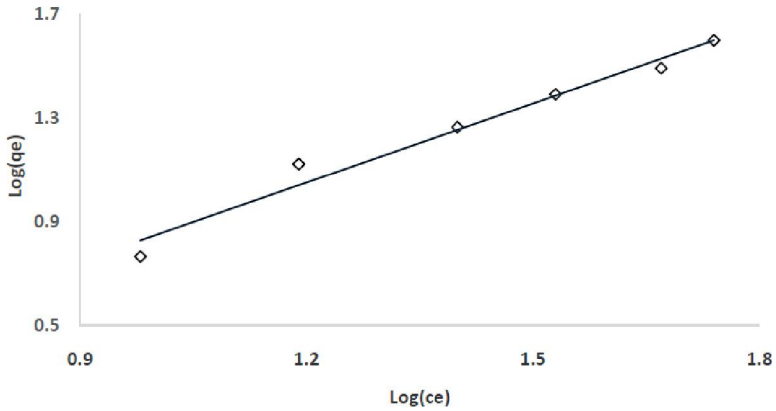

Figure 5 : Freundlich isotherm for the adsorption ofzinc on *padina boergesenibiomass* (*p*H=6, biomass dose =0.2 g/ 100 mL, initial zinc concentration =25–150 mg/L)

able method for comparing the binding activities among metals and algae[12-14].The biosorption data were fitted for Freundlich and Langmuir isotherm equations.

The Figure 4 was shown the Freundlich isotherm for zinc removal by*Padina boergeseni* algae.

The Freundlichisotherm for equilibrium biosorption was described by eqn. (2)[15]

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

Where q_e (mg/g) is the biomass capacity, C_e (mg/L) is the equilibrium lead concentration; K_F (mg/L) and n are Freundlich constants related to the sorption capacity and intensity, respectively. The linear form of Freundlicheqn (2) is given as below:

$$log\ q_e = log\ K_F + \frac{1}{n} log\ C_e \quad (3)$$

The log C_e versus log $q_e$was plotted to generate the intercept (K_F) and the slope (n).

The Langmuir isotherms equation is valid for monolayer sorption onto surface containing finite number of identical sorption sites, described as follows[16]

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (4)$$

Where q_{max} (mg/g) is the maximum sorption capacity, C_e (mg/L) is the equilibrium concentration in the solution, q_e (mg/g) is the equilibrium lead concentration in the sorbent, and b (L/mg) is the sorption affinity constant related to the binding energy of sorption.

The eqn (4) rearranged to the following linear form as eqn (5)

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}} \quad (5)$$

The $1/q_e$ versus $1/C_e$ was plotted to produce the intercept value of $1/q_{max}$ and the slope value of $1/K_L q_{max}$. The Figure 5 was shown the Langmuir isotherm for zinc removal by *padina boergeseni*

The calculated Freundlich and Langmuir values and their corresponding linear regression correlation coefficient values are shown in TABLE 1. The

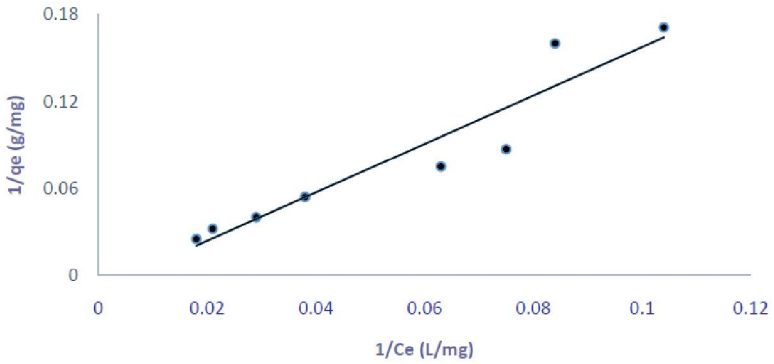

Figure 6 : Langmuir isotherm for the adsorption of zinc on *padina boergesen*ibiomass (*p*H =6, biomass dose = 0.2 g/100 mL, initial zinc concentration =25–150 mg/L)

TABLE 1 : Langmuir and Freundlich isotherms constants

Langmuir isotherms model			Freundlich isotherms model		
q_{max} (mg/g)	K_L(L/mg)	R^2	K_F (mg/g)	n	R^2
101.01	0.0059	0.9008	0.678	0.982	0.9732

linear regression correlation coefficient values, R^2 found 0.9732, which shows that multilayer and heterogenousbiosorption of the zinc ions on *padinaboergeseni*.

The kinetics of biosorption

Experimental data were tested by pseudo–first order and pseudo–second order kinetic model. The linearized pseudo–first order kinetic model takes the following form[17-19]

$$log\ (q_e - q_t) = log\ q_e - \frac{k_1 t}{2.303} \quad (6)$$

whereq_t (mg/g) and q_e (mg/g) are the amounts of metal at time t (min.) and equilibrium, respectively, and k_1 (1/min) is the first–order rate constant. The plots of log (q_e–q_t) versus t (min.) for different initial zincconcentrations at 5 °C were shown in Figure 6.

The pseudo–second order kinetic model which is given in the following form[20]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

whereq_t (mg/g) and q_e (mg/g) are the amounts of metal at time t (min.) and equilibrium, respectively, and k_2 (mg/g. min.) is the second–order rate constant. The linear plots of t/q_t versus t for different initial zincconcentrations at 25 °C were shown in Figure 7.

The correlation coefficients obtained from the pseudo-second order rate kinetic model were greater than 0.99 for all of the initial zincion concentrations *padina boergeseni* (see TABLE 2)

That exposed the Zn cations are bound to two bindingsites on the sorbent surface of *padina boergesen*ias biomass[21].

$2R\ (s) + Me^{2+}\ (aq) = R_2Me^{2+}\ (ads)$ (8)

The optimization of biosorption conditions by response surface methodology

The response surface methodology (RSM) was described experimental data by forming a mathematical relationship between the cooperating factors and biosorption based on design of the experiment (DOE). Therefore, the optimum condition for the biosorption of Zn by *padina boergesen*iwas determined by means of Box–Behnken model in the Minitab software. Four variables includininitial*p*H (A) ionic strengh (B) temperature (C) and contact time (D) of solutions on Zn uptake were investigated[22–24]. The behaviour of the system is controlled by an empirical second–order polynomial model eqn (9)

$$Y_{calc} = \beta_0 + \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \quad (9)$$

where β_0, β_i, β_j and $\beta_{ij}$are coefficients estimated from regression, Y_{calc} is the predicted response, $\beta_i X_i$, the first order effect, $\beta_{ii} X_i^2$, the second order effect, and $\beta_{ij} X_i X_j$, the interaction effect on the predictedresponse[25–27].

Four parameters (A: *p*H, B: ionic strengh C: temperature,, D: contact time) were coded at three lev-

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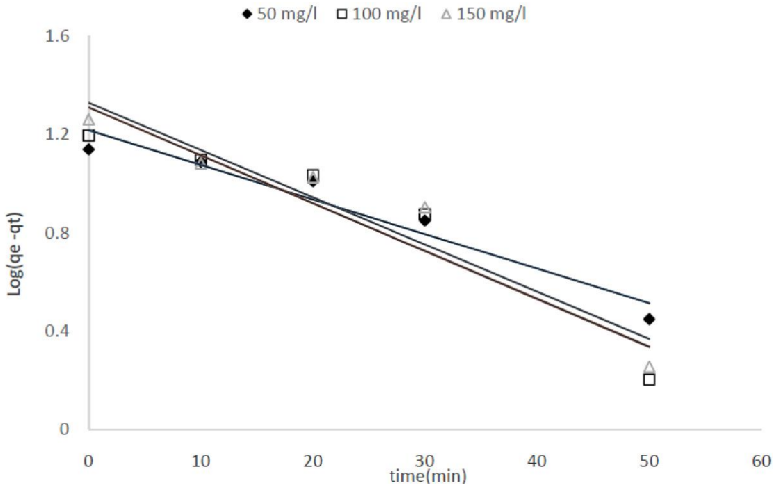

Figure 7 : Pseudo–first–order kinetic plots at different initial zinc concentrations

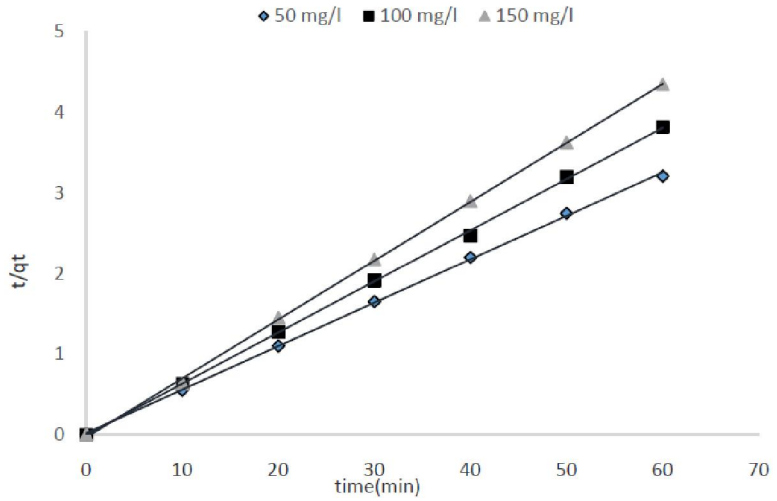

Figure 8 : Pseudo–second–order kinetic plots at different initial zincconcentrations

TABLE 2 : The pseudo-first order and pseudo-second order parameters

	pseudo-second order			pseudo-first order		
Initial concentrations (mg/L)	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2
50	18.52	0.188	0.9995	16.44	0.0324	0.9387
100	18.52	0.188	0.9995	21.23	0.0442	0.9164
150	13.68	0.073	0.9996	21.23	0.0442	0.9164

TABLE 3 : The ranges and levels of independent variables for zinc uptake

Independent variable		Range and levels		
		-1	0	1
A	initial pH	4	5	6
B	ionic strengh (mM)	1	50	100
C	Temperature (º C)	35	45	55
D	Contact time (min.)	20	40	60

els, -1, 0, +1. The series and levels of individual variables were given in TABLE 3.

The design of experimental (DOE) in Box-Behnken modelwere performed as shown in TABLE

TABLE 4 : The box-behnken model for experimental design

	A	B	C	D	Y obs	Y calc	Y opt
1	0	-1	0	1	22.64	20.30	20.30
2	0	0	-1	-1	22.04	19.71	19.71
3	0	0	1	-1	23.54	24.80	24.80
4	0	1	1	0	18.34	23.60	23.56
5	-1	0	0	1	17.98	18.53	17.88
6	1	0	1	0	23.78	25.49	24.46
7	1	0	0	-1	22.81	22.82	21.78
8	0	1	0	-1	23.23	22.41	22.41
9	0	0	1	1	15.67	20.42	20.42
10	-1	-1	0	0	15.87	20.12	20.30
11	1	0	-1	0	24.95	20.88	19.84
12	0	0	-1	1	22.79	16.28	16.28
13	1	1	0	0	21.58	18.71	18.51
14	0	-1	-1	0	20.89	20.77	20.73
15	0	0	0	0	23.10	23.20	23.20
16	1	-1	0	4	24.10	-1.46	-3.33
17	-1	0	1	0	25.46	25.11	24.46
18	1	0	0	1	22.14	21.97	20.93
19	-1	0	1	0	24.48	25.11	24.46
20	0	0	0	0	22.92	23.20	23.20
21	0	0	0	0	21.38	23.20	23.20
22	0	-1	0	-1	21.04	24.20	24.20
23	0	-1	0	1	14.78	20.30	20.30
24	0	1	0	0	22.92	22.30	22.31
25	0	1	1	0	25.30	23.60	23.56
26	-1	1	0	0	28.79	27.59	26.10
27	-1	0	0	-1	24.76	25.49	24.83

TABLE 5 : Analysis of variance (ANOVA) for response surface quadratic model

Term	Coefficient factor	*F* value	*P*-value
constant	23.2 00	40.275	0.000
A	0.1908	0.663	0.052
B	–0.895	–3.107	0.009
C	2.309	8.017	0.000
D	–1.951	–6.776	0.000
A*A	0.8483	1.964	0.073
B*B	–0.003	–0.007	0.995
C*C	–1.054	–2.440	0.031
D*D	–1.845	–4.727	0.001
A*B	–0.537	–1.077	0.302
A*C	–3.792	–7.602	0.000
A*D	1.527	3.062	0.010
B*C	0.042	0.085	0.934
B*D	–2.155	–4.320	0.001
C*D	1.917	3.844	0.002

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4for the biosorption of zinc using the*padina boergeseni*.

The results of second-order response surface model in the form of analysis of variance (ANOVA) were shown in TABLE 5.

The theoretical values were investigated for the best conditions for zinc uptake by modification of the general eqn (9). For this purpose, two statistical methods i.e. p-values and t-test were chosen for evaluations the coefficients in eqn (9).If the P value is less than 0.05 ($P< 0.05$), the corresponding coefficients were chosen. The more significant coefficient was selected according to eqn (10) by the smaller values of the p-value and the bigger values of the t-value were chosen[28].

$$Y_{calc} = 23.20 + 0.1908A - 0.8950B + 2.309C - 1.951D + 0.848A^2 - 0.0029B^2 - 1.054C^2 - 1.845D^2 - 0.837AB - 3.792AC + 1.527AD + 0.042BC - 2.155BD + 1.917CD \quad (10)$$

We can used, this mathematical function i.e. eqn (10) for prediction of lead biosorption for other conditions.

Finally, the optimum combination of parameters for the zinc uptake after contact time of 60 minute was reported as follow initial *p*H =6, temperature = 45°C, biomass concentration = 0.2 g/L, initial lead concentration = 150 mg/L.

CONCLUSION

The biosorption of zinc on was*padina boergeseni* investigated in a batch system. The Langmuir and Freundlich isotherm models were applied to the equilibrium data at different temperature. The pseudo-second-order kinetic was responsible for biosorption mechanism. The maximum response adsorption of Zinc on *padina boergeseni*, is 71.52 mg/g, that obtained for 150.0 mg/L initial metal concentration, 0.40 mg biomass, 40 °C and pH =6.

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