



Biosorption of Zinc by Red Marine Macroalga *Hypnea musciformis*: Optimization, Isotherm, Kinetic and Thermodynamic Studies

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Abstract: Box-Behnken Design (BBD) was employed to optimize the operating conditions of independent variables pH (4.5-6.5), biosorbent dosage (0.5-1.5 g/L), and agitation speed (50-150rpm) for the removal of Zinc (II) ions from the aqueous solutions using novel marine red biomass *Hypnea musciformis* as efficient, eco friendly and low cost adsorbent. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models were employed to describe the equilibrium isotherm. The maximum uptake capacity of Zinc derived from Langmuir model was 125mg/g at pH 6, sorbent dosage 1.45 g/L and agitation speed 148 rpm. The experimental data was used to predict the theoretical response (the adsorption percentage of Zinc) by a quadratic polynomial regression model in three-level-three-factor BBD under Response surface methodology (RSM) using Design Expert software. Thermodynamic studies indicate that the sorption of Zinc metal ions was feasible, spontaneous and endothermic. Kinetic study of Zinc biosorption process was best described by pseudo second order model of chemical sorption. FTIR (Fourier transform infrared spectrometer) analysis indicates that functional groups such as hydroxyl, carboxylic, C=O and C-O groups were responsible for the binding of Zinc heavy metal on to the red biomass.

Keywords: *Hypneamusciformis*; Zinc; biosorption; RSM; Kinetics; Isotherm

I. Introduction

Zinc is one of the toxic heavy metals being sourced from culprits like mining, melting, electroplating, batteries, galvanizing, pigments, alloy processing and coating for prevention of corrosion. Despite the fact that zinc is an essential micronutrient for humans in cell growth, metabolic activities and immune system, it is still toxic as promulgated by the World Health Organization (WHO) by setting the maximum permissible concentration of zinc in potable water as 5 PPM in consonance with the US Environmental Protection Agency (EPA) which has accentuated that the same shouldn't exceed 5 mg/l [1]. When taken in by humans beyond threshold, it might cause nausea, neurological signs such as seizure and ataxia, vomiting, depression, gastrointestinal distress and increased thirst. Its abnormal concentration could be fatal leading to renal failure and prostate cancer. Hence it becomes environmental prerequisite that the industrial effluents carrying heavy metals should undergo an uncompromising tough task of rigorous treatment at the coal field so as to ensure the permissible range before its confluence with the domestic streams. Several such conventional methods of technological treatments as Chemical Precipitation, Complexation, Ion Exchange, Flocculation, Coagulation, Membrane Filtration, and Electro Chemical Process have been employed for the purpose of obliteration of harmful heavy metals from the effluents [2, 3]. However, these techniques have proved to be practically unviable or infeasible as they suffer high operational costs, more time consumption, complexity in process, maintenance cost, and involvement of more human resources and above all they are ineffective particularly when the concentration is below 100 mg/L. Hence alternative cost effective and environment-friendly technologies are being explored on the attainment of feasibility in all respects.

Biosorption is a proven alternative to traditional methods for the removal of heavy metals from aqueous solution as it can accumulate heavy metals even in low concentrations [4, 5]. Taking into account of high uptake capacity, abundance and readiness in availability, eco-friendly, economical feasibility, possible reuse, easy handling, no nutrient requirement, less sludge formation and high metal selectivity [6], biosorption method becomes most viable and economically feasible. Various types of biomass in non-living state have been investigated for their heavy metal sequestering capacities. Microorganisms like bacteria, fungi, algae and agro based sources were

utilized as bio sorbents for heavy metal recovery [7-10]. On a comparative study, it has been established that various species of green, red and brown seaweed or marine algal biomasses are used as biosorbent materials 15.3% more than any other kinds of biomass [11,12]. The presence of polysaccharides and proteins on the algal cell wall include functional groups such as carboxyl, hydroxyl, phosphate, sulphate, carbonyl or amino have high binding capacity with heavy metals.[13]. The rigorous and intensive research on the mechanisms of biosorption has been strengthened due to the employability of seaweed biomass to alienate heavy metals from industrial effluents by many researchers [14-16].

The recent years have witnessed several researchers have potentially experimented on metal biosorption involving various red, green and brown marine weeds. It has been ascertained that of all the biomasses put into study, marine algae are researchers-centric owing to its abundance at any time availability, its uptake capacity of heavy metals at an economic cost. Since no researchers have so far attempted biosorption of zinc on red biomass, *Hypnea musciformis* as sorbent with the employment of Response surface methodology (RSM), we have blaze trailed on this marine macro algae as a sorbent for the removal of zinc from aqueous solution. The operating variables were optimized using RSM and at the optimized conditions, equilibrium isotherm, uptake kinetics and thermodynamic studies were carried out for the sorption process. The functional groups responsible for Zinc sorption were identified by FTIR analysis.

II. Materials and Methods

A. Preparation of Sorbent

The fresh Red algal biomass, *Hypnea musciformis*, was collected from the coasts of Mandapam, Ramanathapuram district, Tamilnadu, India. It was washed thoroughly with distilled water to remove sand, salts and other impurities adhered. Then the biomass was sun dried and further dried in oven at 50°C for 48 h to remove the moisture. The dried biomass was then ground using domestic mixer. The particle size of the ground biomass was determined using Zetasizer (6.12), Nano series, Malvern instruments Ltd, UK. The mean particle diameter of the ground biomass was found to be 1503 nm.

B. Preparation of Metal Ion Solution

The stock solution of zinc (II) of 1000 ppm concentration was prepared by dissolving 4.4 grams of analytical grade Zinc sulphate heptahydrate in 1 litre of distilled water.

C. Characterization of Sorbent

Scanning Electron Microscopy (SEM)

The surface morphology of green biomass was assessed by scanning electron microscope (JSM-5610 LV, JEOL, USA), with voltage of 10 KV and at high vacuum mode.

Fourier transform infrared (FTIR) spectroscopy

FTIR was used to determine the presence of functional groups on the sorbent surface for both raw and Zinc loaded biomass. FTIR analyses were conducted by KBr pellets method using FTIR spectrophotometer (Thermo scientific- Nicolet iS5 FTIR, USA) in the wave number region of 4000 – 400 cm⁻¹.

BET

The surface area, average pore diameter and pore volume were determined by Brunauer Emmett and Teller method using Micrometrics ASAP 2020 and the observed values are: 0.8576 m²/g, 269.24 Å and 0.0057 cm³/g respectively. Nitrogen was used as adsorptive agent for the biomass sample of 0.8146 g.

D. Experimental design

Box- behnken design (BBD) under Response surface methodology (RSM) was followed for optimising the biosorption of zinc by red biomass *Hypnea musciformis*. RSM is a collection of statistical and mathematical techniques which can be used to evaluate the relationship between a set of controlled experimental factors and the designed response. Batch experiments were conducted base on BBD, to study the effects of 3 variables including pH, sorbent dosage (g / L) and agitation speed (rpm) on percentage removal of zinc. The coded values of the process parameters were determined by the following equation.

$$x_i = \frac{(X_i - X_0)}{\Delta X} \quad (1)$$

Where X_i is the coded value of the i^{th} independent variables.

X_i is the uncoded value of the i^{th} independent variables and

X_0 is the uncoded value of the i^{th} independent variables at center point

X is the step change value in X_i

The range and levels of independent variables were given in Table 1 and the BBD experimental design is in Table 2. Regression analysis was performed to estimate the response function as a second order polynomial. A second order polynomial model fitted to the experimental data was developed and could be described by the following equation:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} X_{ij} \quad (2)$$

Where Y is the predicted response.

$\beta_i, \beta_{ii}, \beta_{ij}$ are coefficients estimated from regression and represent the linear, quadratic and interaction effect respectively; β_0 is the intercept term; $X_i, X_j, \dots, X_k$ are the input variable in coded form.

Table 1 Experimental range and levels of operating variables for removal of Zinc using *Hypnea musciformis*

Variables	Code	Levels		
		-1	0	+1
pH	A	4.5	5.5	6.5
Sorbent dosage, g/L	B	0.5	1.0	1.5
Agitation speed, rpm	C	50	100	150

The range of variables was decided on the basis of literature reports for heavy metals biosorption by red biomass. A statistical program package (design expert 7.1.5) was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equation was validated by ANOVA analysis. Response surface plots were drawn to determine the individual and interactive effects of test variables on percentage removal of Zinc.

E. Batch sorption experimental procedure

Based on Box Behnken design (BBD), experiments were carried out in 250 ml Erlenmeyer flasks containing 100 ml of 100 ppm Zinc solution. The solution was agitated in incubated orbital shaker (Labline instruments, India) for a period of 60 min and 30°C in order to study the effects of pH, sorbent dosage and agitation speed on the sorption of Zinc onto red biomass. After 60 minutes of agitation, the biosorbent was separated from the aqueous experimental sample solution using filter paper (whatman No.41). The presence of zinc concentration in the aqueous solution was analyzed by using ICP-AES (Perkin Elmer, Germany). The percentage of zinc removal was taken as a response (Y) of the experimental design and calculated as

$$\text{Zinc removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

Where C_0 (mg L⁻¹) is the initial concentration of zinc and C_e (mg L⁻¹) is the final or equilibrium concentration of zinc. The amount of adsorbed zinc per unit mass of adsorbent (q_e , mg g⁻¹) was determined according to equation (4)

$$q_e \text{ (mg/g)} = \frac{(C_0 - C_e)V}{m} \quad (4)$$

Where V is the volume of solution in liter and m is the biosorbent in gram.

Table 2 BBD based experimental design and its response for Zinc sorption on to *Hypnea musciformis*

Run order	A	B	C	Percentage Zinc Sorption	
	pH	SD	Speed	Experimental	Predicted
1	0	0	0	72.25	72.22
2	-1	1	0	41.69	45.87
3	0	0	0	72.25	72.22
4	1	-1	0	59.61	55.43
5	1	1	0	81.02	80.89
6	-1	0	1	41.42	41.40
7	-1	-1	0	17.38	17.51
8	0	-1	1	68.07	67.96
9	0	1	1	91.54	87.38
10	1	0	1	71.25	75.54
11	-1	0	-1	28.8	24.51
12	0	1	-1	80.21	80.32
13	1	0	-1	63.28	63.30
14	0	0	0	72.15	72.22
15	0	-1	-1	41.74	45.90

III. Results and Discussion

F. Fitting model

Box-behnken design was carried out for studying the effects of 3 independent variables and the results obtained from the BBD experiments, along with the theoretically predicted responses were shown in Table 2. The quadratic

regression model was used to explain the mathematical relationship between the independent variables and the dependent responses for Zinc removal in terms of coded factor is:

$$Y = +72.22 + 18.23 * A + 13.46 * B + 7.28 * C - 0.73 * A * B - 1.16 * A * C - 3.75 * B * C - 20.75 * A^2 - 1.55 * B^2 - 0.28 * C^2 \quad (5)$$

Where, Y is the percentage removal of Zinc and A, B and C are coded values of pH, sorbent dosage (g/L) and agitation speed (rpm), respectively.

The ANOVA results for Zinc removal were shown in Table 3. The Model F-value of 32.30 implies the model is significant. There is only a 0.07% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, A^2 are significant model terms. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Our ratio of 18.541 indicates an adequate signal. This implies that the linear effects of pH, sorbent dosage and agitation speed were most significant factors. Square effect of pH also played a significant role.

Table 3 ANOVA for Zinc removal using red algal biomass *Hypnea musciformis*

Source	Sum of squares	df	Mean square	F-value	P value
Model	6192.22	9	688.02	32.3	0.0007
A-pH	2659.76	1	2659.76	124.86	0.0001
B-Sorbent dosage	1448.83	1	1448.83	68.01	0.0004
C-Agitation speed	424.13	1	424.13	19.91	0.0066
AB	2.1	1	2.1	0.099	0.7661
AC	5.41	1	5.41	0.25	0.6358
BC	56.25	1	56.25	2.64	0.1651
A^2	1589.32	1	1589.32	74.61	0.0003
B^2	8.81	1	8.81	0.41	0.5485
C^2	0.29	1	0.29	0.014	0.9111
Residual	106.51	5	21.3		
Lack of Fit	106.5	3	35.5	10650.5	< 0.0001
Pure Error	6.67E-03	2	3.33E-03		
Cor Total	6298.73	14			

Std. Dev – 4.62; R-squared – 0.9831; Mean – 60.18; Adj R-squared – 0.9527; C.V. % – 7.67
Pred R-squared – 0.7295; PRESS – 1704.09; Adeq Precision – 18.541

G. Effects of variables on Zinc removal efficiency

The interactive effects of operating variables on zinc removal efficiency are illustrated in three dimensional response surface plots (Fig. 1(a) to 1(c)). The interactive effect of pH and sorbent dosage on the zinc removal efficiency was studied in the pH range of 4.5 to 6.5 and the results are shown in the figure 1(a). From the plot, it was observed that the sorption efficiency increases with the increase in pH from 4.5 to 6. This is due to the fact that, as the number of negatively charged sites increased due to deprotonation of the hydrogen ions from the functional group present on the sorbent. At pH 6, a maximum zinc removal efficiency of 94.57 % was achieved. However at solution pH less than 4.5 (highly acidic), the removal efficiency of zinc was found to be less than 35%. This is because of the competition between hydronium ions (H_3O^+) and zinc ions to the few negatively charged binding sites of the biomass. Further increase in pH beyond 6, the sorption efficiency of zinc decreases due to the precipitation of zinc as hydroxide or in the form of $Zn(OH)_2$. Therefore, the pH is pegged at 6 for further experimental studies. It can be inferred from the results that the solution pH was one of the most important factor which influences metal sorption and also the surface properties of the biomass. Similar observations were reported for red biomass [17].

The effect of sorbent dosage on the zinc removal efficiency was studied in the range of 0.5 to 1.5 g/L. The results are shown in Fig 1(b). From the plot, maximum removal efficiency was observed at 1.45 g/L. The sorption of metal efficiency increases with increase in sorbent from 0.5 to 1.45 g/L and decreases with further increase in sorbent dosage. Therefore, the optimum dosage of biosorbent is 1.45 g/L for further experimental studies. Partial aggregation of the biomass which minimizes the effective surface area could be the reason for the decrease in zinc removal efficiency at higher biomass dosage [18]. The effect of agitation speed was studied by changing the agitation speed in the range of 50 to 150 rpm. The results obtained are shown in Fig 1c. From the plot, it was inferred that maximum sorption of zinc occurred at 148 rpm. The sorbent accumulates at the bottom of the flask instead of spreading in the sample solution, at low agitation speed. As a result, the lower layer wraps up the active sites of the sorbent within that and hence they are not exposed to the phenomenon of zinc ion removal while the upper layer active sites of sorbent adsorb the zinc ion. At higher agitation speed, zinc removal efficiency decreases, may be due to the desorption tendency of sorbent [19].

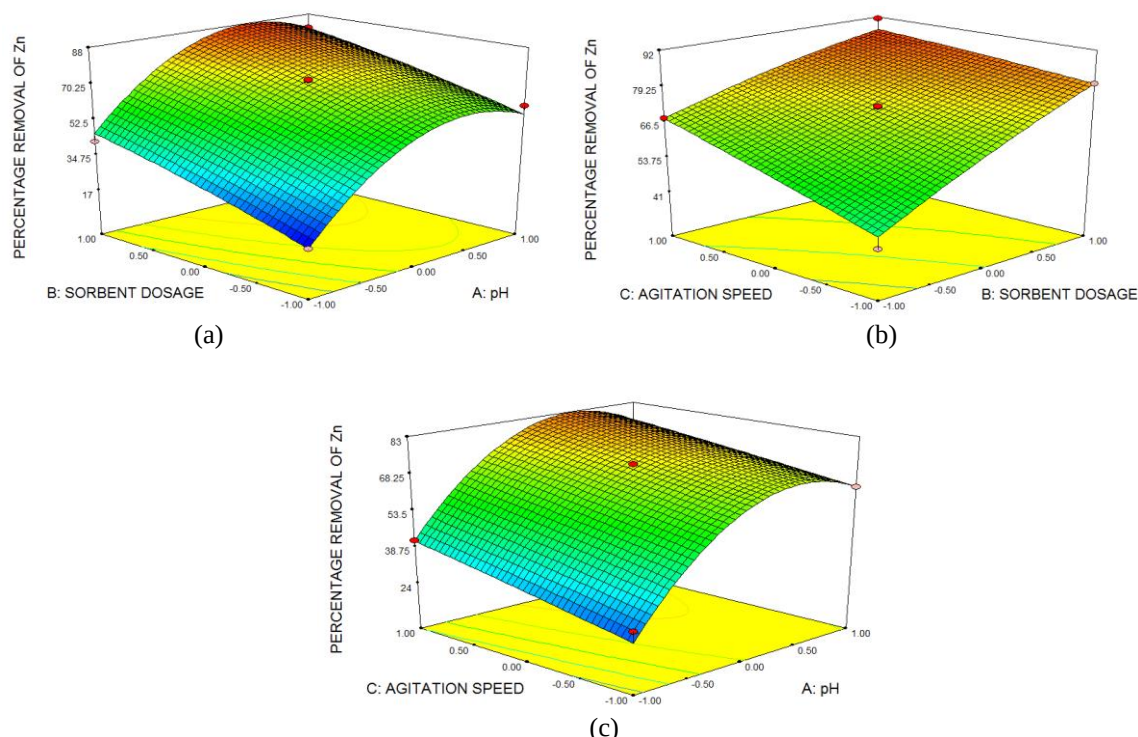


Figure 1. 3-D Response surface plot of Zinc sorption onto red biomass *Hypneamusciformis*; (a) the interactive effects of pH and sorbent dosage ; (b) the interactive effects of sorbent dosage and agitation speed ; (c) the interactive effects of agitation speed and pH

H. Sorption isotherm study

The sorption capacity of a sorbent can be described by equilibrium sorption isotherm, which is characterized by definite constants whose values express the surface properties and affinity of the sorbent. In this study, four sorption isotherm models namely Langmuir, Freundlich, Dubinin – Radushkevich and Temkin were selected to evaluate the batch experimental data.

Langmuir isotherm

The Langmuir isotherm assumes that sorption occurs at specific homogenous sites on the sorbent and is used successfully in many monolayer sorption processes. The linear form of Langmuir isotherm [20] is expressed by

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

Where q_e is the equilibrium concentration of the metal on the sorbent (mg/g), $q_{\max}$ is the monolayer sorption capacity (mg/g), C_e is the equilibrium concentration of the metal in the solution (mg/L) and k_L is the Langmuir sorption constant (L/mg) related to the free energy of sorption. The plots of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ were drawn as shown in Fig.2 (a) for six different initial metal concentration at constant temperature and depicts the linear form of Langmuir isotherm over the whole concentration range studied. In general, good sorbents have high $q_{\max}$ and a high correlation co-efficient (R^2). The values of $q_{\max}$, R^2 , and b are tabulated in Table 4. Table 5 represents the comparison of sorption capacity ($q_{\max}$, mg/g) of various red algae for Zinc [21-29]. The high correlation co-efficient ($R^2 = 0.983$) indicates that the sorption of the zinc metal on to the red biomass *Hypnea musciformis*, best suits the Langmuir model.

Freundlich isotherm

The freundlich isotherm is an empirical equation used to describe the adsorption on heterogenous surfaces [30].The linear form of Freundlich isotherm is represented by the equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

where K_f is the Freundlich isotherm indicating adsorption capacity and $\frac{1}{n}$ is the sorption intensity. The values of K_f and $\frac{1}{n}$ were calculated from the intercept and slope of the plot between $\log q_e$ versus $\log C_e$ shown in Fig. 2(b). The values of K_f , $\frac{1}{n}$ and the correlation coefficient (R^2) are given in Table 5. Generally, $\frac{1}{n}$ values between 0 and 1 indicate good sorption at studied conditions [31]. In this study, $\frac{1}{n} = 0.192$ indicates that the sorption of zinc onto

red biomass was favorable. However, compared to the R^2 values, as shown in Table 4, the Langmuir isotherm equation fits the experimental values better than the Freundlich isotherm equation.

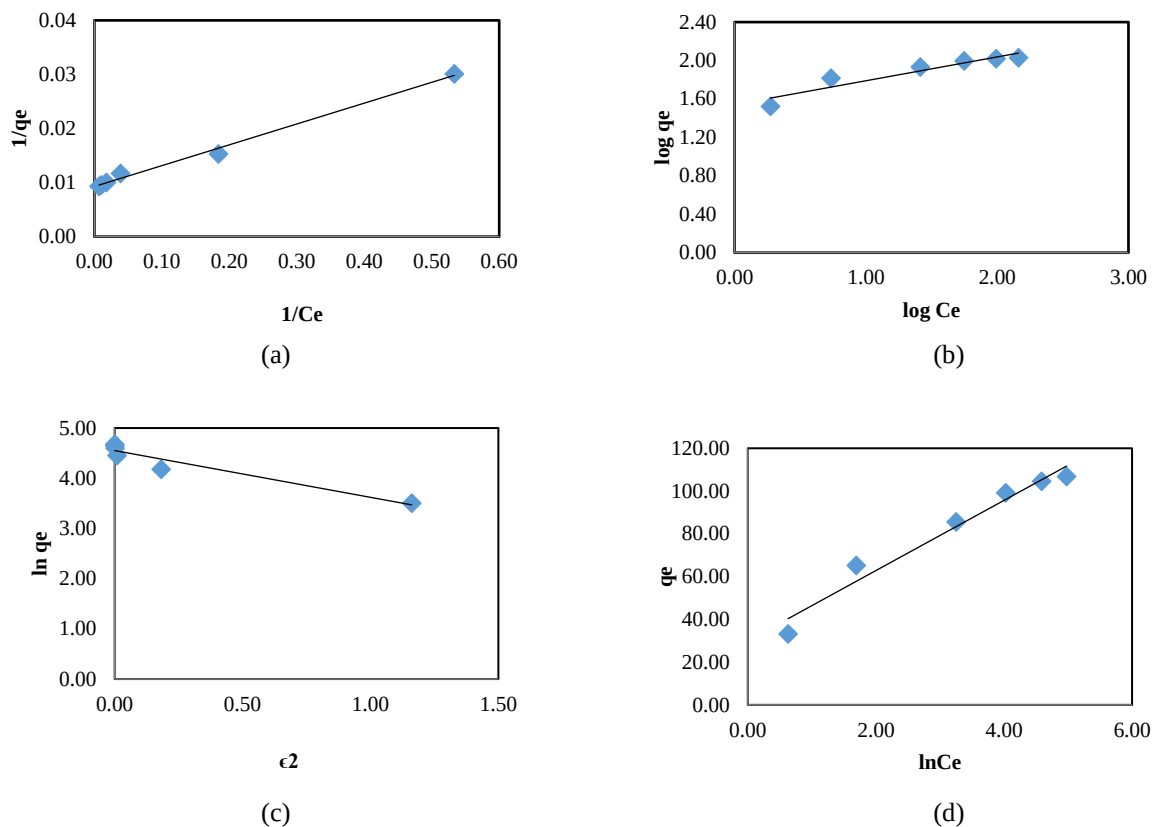


Fig.2. (a) Langmuir (b) Freundlich (c) Dubinin- Radushkevich and (d) Temkin isotherms for Zinc sorption

Dubinin- Radushkevich (D-R) isotherm

D-R isotherm was applied to determine the nature of sorption processes as physical or chemical using the experimental data. The linear form of the D-R isotherm equation [32] is:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (8)$$

Where, q_e is the amount of metal ions adsorbed on per unit weight of biomass (mg/g), q_m is the maximum sorption capacity (mg/g), β is the activity co-efficient related to mean sorption energy (mol^2/kJ^2) and ϵ is the Polanyi potential described as

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (9)$$

Where, R is the universal gas constant 8.314×10^{-3} in kJ/mol K , T is the temperature in Kelvin and C_e is the equilibrium concentration of the zinc in solution (mg/L). The mean free energy of sorption per molecule of sorbate required to transfer one mole of ion from the infinity in the solution to the surface of biomass and can be determined by the equation:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (10)$$

Dubinin- Radushkevich (D-R) isotherm constant β , and q_m were evaluated from the slope and intercept of plot $\ln q_e$ versus ϵ^2 , as shown in Fig. 2(c) and the results are presented in Table (4).

The energy values obtained ($E = 0.705 \text{ kJ/mol}$) have $E < 8 \text{ kJ/mol}$, which indicates that the adsorption is a physical process, since a chemical adsorption process has an $E > 8 \text{ kJ/mol}$. However, the sorption capacity was lower than the Langmuir model which was shown in the Table (4).

Temkin isotherm

The Temkin isotherm equation assumes that the heat of absorption of all the molecules in layer decreases linearly with coverage due to adsorbent- adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy [33]. The Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} \ln (K_T C_e) \quad (11)$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (12)$$

Equation(9) can be arranged linearly as

$$q_e = B \ln K_T + B \ln C_e \quad (13)$$

Where, T is the temperature in Kelvin, R is the Universal gas constant in kJ/mol K, K_T is the equilibrium binding constant in L/mg, b is the variation of sorption energy in J/mol.

$B = \frac{RT}{b}$, is the Temkin constant related to the heat of sorption. Fig. 2(d) shows the plot of q_e versus $\ln C_e$ the isotherm constants were found and shown in Table 4. The correlation factors show that the Langmuir model approximation to the experimental values was better than the Temkin model. Consequently, among the four isotherm modes used, the Langmuir model offers the best correlation factor. Similar observation was made of the Langmuir isotherm model on red macro alga *Ceramium virgatum* [34].

Table 4 Various Isotherm model parameters for Zinc sorption on to red alga *Hypnea musciformis*

Isotherm model	Parameters	Zn(II) sorption at 303.15 K
Langmuir	q_m (mg/g)	125
	K_L (L/mg)	0.2
	R^2	0.983
Freundlich	K_f (L/mg)	34.75
	$1/n$	0.248
	R^2	0.891
Dubinin- Redushkevich	q_m (mg/g)	94.73
	β (mol ² /kJ ²)	0.931
	E (kJ/mol)	0.733
	R^2	0.922
Temkin	B	16.41
	K_T (L/mg)	6.215
	R^2	0.964

Table 5 Comparison of adsorption capacities of various red algae for the removal of Zinc

Biosorbent	pH	Temperature C	Time (min)	Speed rpm	C_o range (mg/L)	Biomass Dosage (g/L)	Max uptake (mg/g)	Reference
<i>Porphyridium purpureum</i>	6	20	120	25			2.01	21
<i>Gracillariasp.</i>	5.5	22 ± 1 °C	60	200	6.5 – 137.3	-	26.15	22
<i>Palmariapalmata</i>	6.5	30	-	275	0-60	1	28.49	23
<i>Asparagopsis armata</i>	6	-	120	-	10,25,50,	0.5 - 2	21.6	24
<i>Chondrus crispus</i>					100&150		45.7	
<i>Chondrus crispus</i>	6	RT	120	-	10,25,50,	0.5,1 & 2	42.5	25
					100&150			
<i>Gelidium</i>	5.3	20	60	100	10 to 300		13	26
<i>Gymnogongrosturulosus</i>	5.5	RT			25 to 500		44.46	27
<i>Gracilariaverrucosa</i>	5	20	60	100	10 to 400	0.1 - 20	96.1	28
<i>Gracilariacorticata</i>	6	30	60	160	15 to 250	15 - 25	18.51	29

I. Effect of temperature and thermodynamic study

The effect of temperature on the sorption of zinc ions was studied in the temperature range of 298.15 K to 313.15 K. An increase in temperature from 298.15K to 313.15 K increases the uptake capacity from 62.56 to 67.67 mg/g of Zinc by red biomass. This effect is due to the rate of sorbate diffusion across the external boundary layer and in the internal pores of the sorbent particles because, liquid viscosity decreases as the temperature increases. Thermodynamic behavior of the sorption of zinc onto green biomass was calculated from following equation:

$$\Delta G^\circ = -RT \ln k \quad (14)$$

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ \quad (15)$$

Where, R is the universal gas constant (8.314 x 10⁻³ kJ/mol K), T is the temperature in Kelvin and k is the equilibrium constant, calculated as the surface and solution metal distribution ratio ($k = q_e/C_e$) [35], ΔG° is the Gibbs free energy (kJ/mol), ΔH° is the enthalpy change (kJ/mol) and ΔS° is the entropy change (kJ/mol K).

The thermodynamic feasibility and the nature of the sorption process can be described from the equation (15). The intercept and slope of the plot ΔG° versus T, gives the values of ΔH° and ΔS° respectively, for the adsorption process of zinc using red biomass *Hypnea musciformis*, as shown in Fig. 3. The calculated thermodynamic parameters are presented in Table 6. The positive values of ΔH° suggest the endothermic nature of the sorption [36] and the positive values of ΔS° show the increasing randomness at the solid-solution interface during the sorption process [37]. The negative values of ΔG° indicate the spontaneous nature of the sorption process and the higher negative value reflects a more energetically favorable adsorption [38].

Table 6 Thermodynamic parameters for the sorption of Zinc onto red alga *Hypnea musciformis*

Metal ion	Temp (K)	ΔG° (kJ/mol)	ΔS (kJ/mol K)	ΔH (kJ/mol)
Zn(II)	298.15	-21.851	0.36	85.61
	303.15	-23.676		
	308.15	-25.304		
	313.15	-27.314		

J. Sorption kinetics

The sorption kinetics behavior of zinc ions onto red biomass was analyzed to examine the mechanism of the sorption process and to test the experimental data, by adopting three kinetic models: pseudo first order, pseudo second order and intra-particle diffusion. It was observed that 43% of zinc was removed aqueous solutions within 10 minutes of contact time. The rate of Zn uptake increased with increase in contact time upto 60 minutes and further there is no significant sorption. Kinetic data are often used for the scale-up of biosorption system.

Pseudo first order model

The linear form of pseudo first order model [39] as described by Lagergren is expressed as

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (16)$$

Where K_1 is the rate constant of the first order equation (min^{-1}), q_t and q_e are the amount of the zinc ions sorbed at given time and equilibrium (mg/g) respectively and t is the time in minutes. The values of K_1 and q_e were calculated from the slope and intercept, respectively of the plot $\log(q_e - q_t)$ versus t (Figure Not given). The values of q_e , K_1 , and the correlation coefficient (R^2) are given in Table 7.

Pseudo second order model

Linear form of pseudo second order can be expressed as [40] ;

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (17)$$

Where K_2 is the rate constant of second order equation (g/mg min), q_t and q_e are the amount of the zinc ions sorbed at given time and equilibrium (mg/g) respectively and t is the time in min. The values of K_2 and q_e were calculated from the slope and intercept, respectively of the plot $\frac{t}{q_t}$ versus t . The values of q_e , K_2 , and the correlation

coefficient (R^2) are given in Table 7. When compared with the correlation coefficients, R^2 from the Table 7, it is observed that pseudo second order model fits with the experimental data better than the pseudo first order.

Intra particle diffusion model

Intra particle diffusion model, described by Weber and Morris [41], is tested for the diffusion mechanism and it is given by:

$$q_t = K_{id} t^{0.5} + C \quad (18)$$

Where K_{id} is the intra particle diffusion rate constant in $\text{mg g}^{-1} \text{min}^{-0.5}$ and C is the intercept which gives intra particle accumulation in the boundary layer. The values of K_{id} and $t^{0.5}$ can be calculated from the plot q_t versus $t^{0.5}$ and the values are reported in Table 7. Results clearly suggest that intra particle diffusion was not only the sole rate controlling factor. However, based on the results from the table pseudo second order model has higher correlation coefficient value indicating that the sorption of zinc on the red biomass follows pseudo second order kinetic model, suggesting chemisorption mechanism. Higher values of R^2 show a better fitness of the sorption data [42].

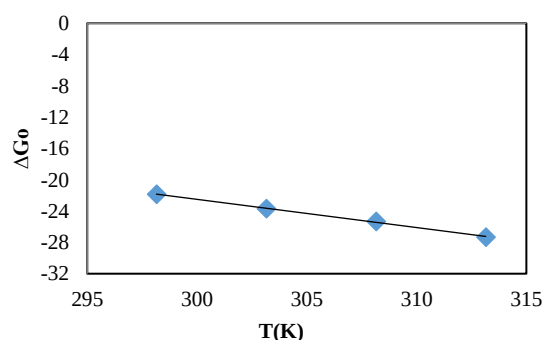


Fig 3. Effect of thermodynamic parameters for sorption of Zinc on to red biomass: pH - 6; biomass dosage - 1.45g/L; agitation speed - 148 rpm ; initial concentration - 100 mg/L

Table 7 Kinetic parameters of Zinc sorption onto red biomass *Hypnea musciformis*

Kinetic model	Parameters	Zn(II) sorption at temperature 303.15 k
Pseudo first order	$K_1(\text{min}^{-1})$	0.062
	R^2	0.964
Pseudo second order	$K_2((\text{g}/\text{mg})\text{min})$	0.0004
	R^2	0.989
Intra particle diffusion	$q_e, \text{cal} (\text{mg}/\text{g})$	90.91
	$K_{id}((\text{mg}/\text{g})\text{min}^{-0.5})$	3.892
	R^2	0.986

K. Scanning electron microscope analysis

The morphological changes of red biomass surface before and after Zinc loading was analyzed by the electron microscopic images. Red biomass surface cells before Zinc loading were rough and rigid as shown in Fig.5 (a). After Zinc loading the surface becomes smooth and swollen, this can be observed from the Fig. 5 (b). This confirms the sorption of Zinc onto the surface of the sorbent.

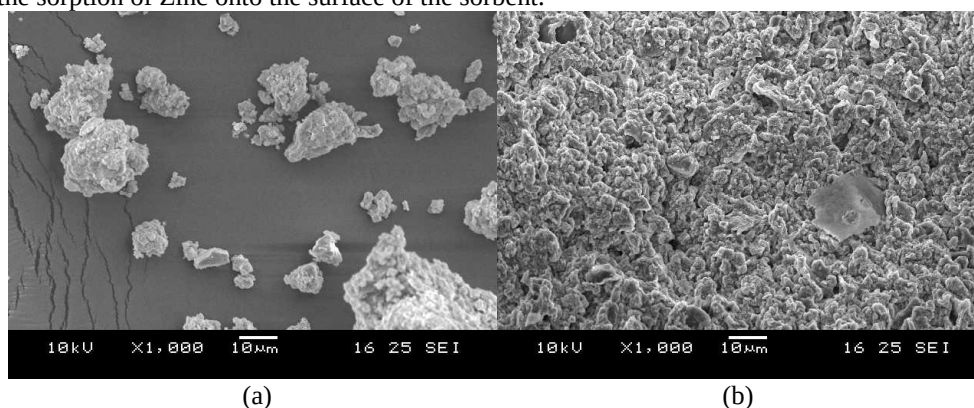


Figure 5. SEM images of Zinc on red alga *Hypnea musciformis*: (a) before sorption and (b) after sorption

L. Fourier transform infrared spectrometer (FTIR)

FT-IR spectrum identifies the functional group present in the uptake of Zinc onto red biomass. Fig 6 (a&b) shows the FTIR spectra of fresh and Zinc loaded red biomass in the range of 4000-400 cm^{-1} . The broad and strong band shift from 3424.05 to 3446.93 cm^{-1} corresponds to bonded hydroxyl (O-H) group [43]. The peak shift from 2920.20 and 2922.23 cm^{-1} can be assigned to C-H stretching of aliphatic group [44]. Band shift from 1647.33 to 1639.84 cm^{-1} can be ascribed to C=O stretching of carboxyl group [45]. A slight change in the wave number from 1384.17 to 1382.55 cm^{-1} can be attributed to O-H bending of the phenolic & carboxylic group [46]. Peak change from 1073.22 to 1030.05 can be assigned to C-O stretching of carboxylic group [47]. The infrared spectral wavelengths of each sorption peak and the corresponding functional groups were shown in Table 8. Therefore, observations from the FTIR analysis clearly shown that the important functional groups such as hydroxyl, carboxylic, C=O and C-O groups were responsible for the binding of Zinc heavy metal on to the red biomass.

V. Conclusions

In an attempt to explain the effect of main operating parameters such as pH, adsorbent dose and agitation speed and their interactions on the phenomenon of removal of Zinc, the present study of RSM, based on the three-factor-three-level BBD was put into use as a tool for the experimental design. The outcome of RSM indicated that the Zinc removal efficiency was significantly affected by all the variables. The chosen Red biomass is found to be highly potential and most suitable for an efficient removal of Zinc from solution. According to the ANOVA results, the model presents a high R^2 value (0.9831) for Zinc removal efficiency. At optimum pH (6), agitation speed (145 rpm), and biomass dosage (1.45g /L) the maximum uptake capacity was 125mg/g. From the kinetics study, it was found that the sorption follows pseudo second order model. Sorption of Zn was analyzed using Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm models and found that the Langmuir model represent a better fit based on the correlation coefficient. SEM confirmed the presence of Zn ions on the biomass surface. Temperature affects the sorption process and the thermodynamic parameters show the spontaneous character of the sorption reaction.

Table 8 FTIR spectral characteristic of red biomass *Hypnea musciformis*

Wavelength range (cm)	Red biomass		Assignment
	Before	After	
3500-3200	3424.05	3446.93	bonded -OH group
2900-2800	2920.2	2922.23	C-H stretching
1680-1630	1647.33	1639.84	C=O stretching
1400-1300	1384.17	1382.55	bending -OH group
1200-800	1073.22	1030.05	C-O stretching

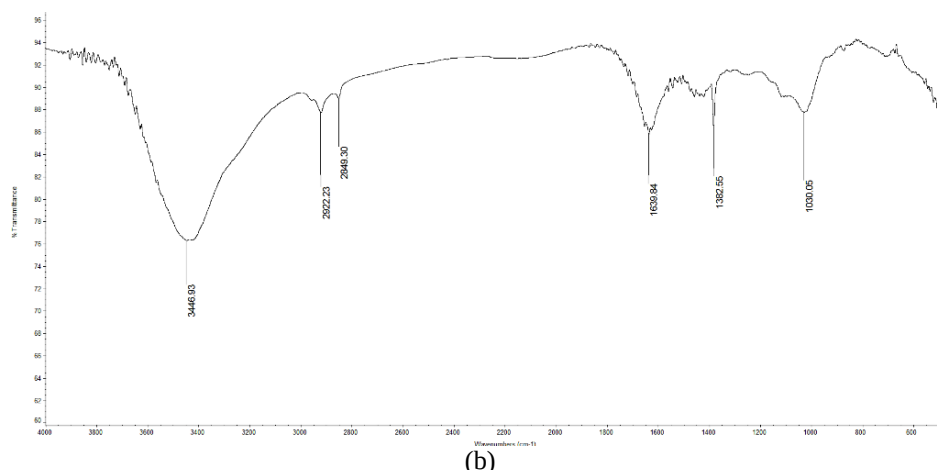
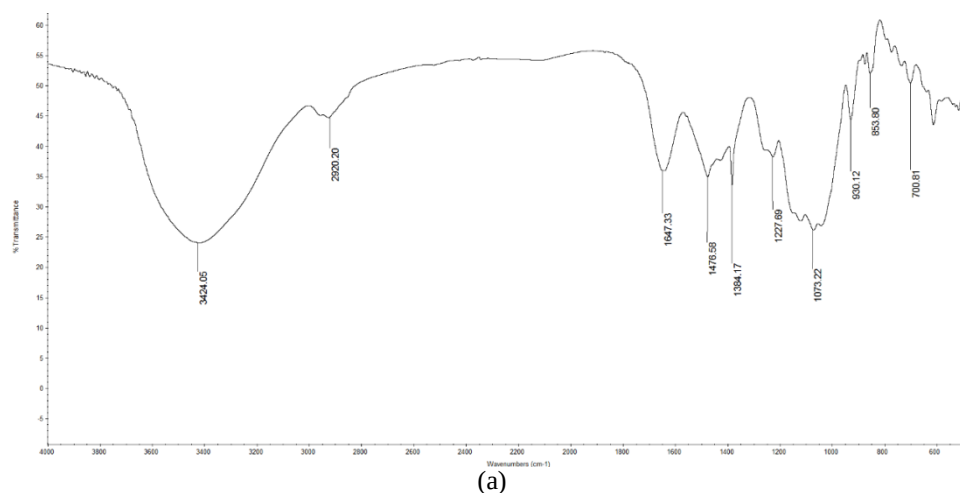


Figure 6. FTIR images for Zinc on *Hypnea musciformis* (a) before sorption and (b) after sorption

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