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Biosorption of Zinc on to Gracilaria Corticata (Red Algae) Powder and Optimization using Central Composite Design

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Abstract: *This paper presents the biosorption of zinc from aqueous solutions using Gracilaria corticata (red algae) powder as a biosorbent. The equilibrium studies on biosorption of Zinc are carried out in batch process. The extent of removal depends on initial concentration of Zinc ion, pH, dosage, temperature etc. The optimum dosage is 15 g/L at the equilibrium agitation time of 60 min. The % biosorption is decreased from 94.16 % (1.559 mg/g) to 80.047 % (13.65 mg/g) with an increase in zinc initial concentration (C_0) from 25 to 250 mg/L. The extent of biosorption is maximum at pH=6. The maximum monolayer coverage capacity of Gracilaria corticata for zinc ions is 18.51 mg/g . The theoretical optimum values are evaluated using Response Surface Methodology (RSM). The quadratic model for Central Composite Design (CCD) has fitted well to the experimental data. The experimental data are well described by Freundlich, Langmuir and Redlich-Peterson isotherm models. The biosorption data follows first order kinetics with a rate constant of 2.643 g/mg-min. The biosorption is endothermic, irreversible and spontaneous.*

Keywords: *Zinc, Biosorption, Response Surface Methodology (RSM), Isotherms, Kinetics, Thermodynamics*

INTRODUCTION

Industrial effluents containing heavy metals when released in to the environment without a proper treatment could harm the human life. Zinc is among the most toxic heavy metals, affecting the environment. According to agency of toxic substance and disease registry [3], zinc finds its way into water bodies through effluents from smelters, mining, processing plants, paints and pigments and galvanizing units. The threshold limiting value of zinc in drinking water is 5 mg/L and in inland surface and marine water it is 15 mg/L. Untreated effluents from these industries have an adverse impact on the environment. If the zinc concentration in air is over 15 mg/m^3 in the work environment, metal fume fever may be caused in the workers. This is mainly attributed to ZnO fumes and dusts. Inhalation of Zn fumes cause fever, depression, malaise, cough, vomiting, salvation and head ache. The conventional methods for treatment of zinc in wastewater include: precipitation, adsorption mainly with activated carbon, ion exchange, membrane process, oxidation and reduction. These methods are expensive and often involve the use of chemicals and generate large amounts of sludge. Biosorption utilizes low cost biosorbents to sequester toxic heavy metals [9]. The advantages of biosorption over the conventional methods are low operating cost, selectivity for specific metal and short operational time. Many agricultural-based waste materials such as Modified corn cob[1], powdered waste sludge [5], palm Tree leaves [6], Powdered Fish Bones [7], Marine Green Algae [8], Maize Leaf [10], papaya wood [25], Brown Alga [16], coconut coir dust [17], tea factory waste[14], and Azadirachata indica bark [40], natural bentonite [42] were employed for the treatment of zinc containing effluents.The drawbacks in conventional optimization methods can be eliminated by optimizing all the parameters collectively by Central Composite Design (CCD) [24] using Response Surface Methodology (RSM). The purpose of this investigation is to investigate the potential of Gracilaria corticata powder to biosorb zinc ions from aqueous solutions. The four parameters - initial pH of the aqueous solution, temperature of the aqueous solution, initial zinc ion concentration and biosorbent dosage - are optimized using CCD of RSM. The equilibrium, thermodynamic and kinetic models are also applied to the experimental data.

MATERIALS AND METHODS

Preparation of biosorbent

Red algae were collected Jodugullapallem beach leaves in Visakhapatnam. Red algae were washed thoroughly with water, distilled water to remove dust and soluble impurities and dried in sunlight. The dried leaves are grinded into fine powder. The powder is sieved and the size fractions of 72, 120 and 150 µm size are used in these experiments.

Preparation of Zn (II) solution

All the chemicals used in this investigation are of AR grade and all solutions are made with distilled water. 4.4405 g of 99% $ZnSO_4.7H_2O$ is dissolved in distilled water in 1 L volumetric flask up to the mark to obtain 1000 mg/L of Zn (II) stock solution. Synthetic samples of different concentrations of zinc are prepared from this stock solution by appropriate dilutions. The pH of aqueous solution is adjusted to the desired value by addition of 0.1 N HNO_3 or 0.1N NaOH solution as per requirement.

EXPERIMENTAL PROCEDURE

10 g/L of 72 µm biosorbent is added to 50 mL of the aqueous solution (C_0 = 100 mg/L) in each of 250 mL Erlenmeyer flasks. The contents of the flasks are agitated in a shaker at a speed of 160 rpm at 30^0 C for different agitation times (1, 5, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180 min). The samples are filtered by Whattman filter paper and analyzed for zinc ion concentration in an Atomic Absorption Spectrophotometer (AAS-Perkin Elmer, A Analyst, 200 models). Air-acetylene flame is used at a wave length of 283.31 nm with a slit width of 2.7 mm and sensitivity of 8 mg/L. Zinc biosorption is calculated from the relation: % biosorption = $[(C_o–C_i) \times 100/C_o]$ where C_0 = initial concentration of zinc in the aqueous solution (mg/L) and C_i = final concentration of zinc in the aqueous solution (mg/L). From the above experimentation, the equilibrium agitation time is obtained. The experiments are repeated by varying the biosorbent size, dosage, pH of the aqueous solution, initial concentration of zinc in the aqueous solution and temperature of the aqueous solution. The experimental conditions investigated are shown in Table 1.

Table - 1: Experimental parameters investigated

S.No	Parameter	Values Investigated
1	Agitation time, t, min	1, 5, 10, 20, 30, 40, 50, 60, 90, 120, 150 & 180
2	Biosorbent size, d_p, µm	72, 120 & 150
3	Biosorbent dosage, w, g/L	5, 10, 15, 20, 25
4	Initial zinc concentration, C_0, mg/L in aqueous solution.	15, 20, 25, 50, 75, 100, 125, 150, 175 & 250
5	pH of aqueous solution	1, 2, 3, 4, 5, 6, 7, 8, 9 & 10
6	Temperature, K	283, 293, 303, 313 & 323

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RESPONSE SURFACE METHODOLOGY (RSM)

RSM is a combination of mathematical and statistical techniques used for developing, improving and optimizing the processes. RSM usually contain three steps: (i) design and experiments; (ii) response surface modeling through regression and (iii) optimization. The main objective of RSM is to determine the optimum operational conditions of the process or to determine a region that satisfies the operating specifications. Among the varieties of factorial designs available, Central Composite Design (CCD) is the more viable design. It is obtained by adding two experimental points along each coordinate axis at opposite sides of the origin and at a distance equal to the semi-diagonal of the hyper cube of the factorial design. The new extreme values (low and high) for each factor are added in this design . For a full factorial

$$\alpha = [2^k]^{1/4} \quad --- \quad (1)$$

In this investigation four factors: biosorbent dosage (w), initial Zn(II) concentration (Co),initial pH of the aqueous solution, and temperature of the aqueous solution are considered and thus k=4, Furthermore, the total number of experiments points (N) in a CCD is calculated from the following equation:

$N = 2^k + 2k + Xo$ --- (2)

Xo is the number of central points ($Xo \geq 1$)

Performance of the process is evaluated by analyzing the response of biosorbent for Zn (II) ions. The response is % biosorption of zinc (*y*). Data from CCD are subjected to a second-order multiple regression analysis to explain the behavior of the system using the least squares regression methodology for obtaining the parameter estimators of the mathematical model [27]:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x^2{}_i + \sum\sum_{i<j} \beta_{ij} x_i x_j + \in$$

where y is the response, β_0 is the constant, β_i is the slope or linear effect of the input factor x_i, β_{ii} is the quadratic effect of input factor x_i, β_{ij} is the linear by linear interaction effect between the input factor x_i and ϵ is the residual term. STATISTICA 6.0 (Stat-Ease Inc., Tulsa, OK, USA) is used for regression analysis of the data and to estimate the coefficient of regression equation. Analysis of variance (ANOVA) is utilized to test the significance of each term in the equation and the goodness of fit of the regression model. This Response Surface Model is used to predict the result by contour plots in order to study the individual and cumulative effects of the variables and the mutual interactions between the variables on the dependent variable.

RESULTS AND DISCUSSIONS

Effect of agitation time

The equilibrium agitation time is determined by agitating 50 mL of aqueous solution,(c_o=25 mg/L) with 72 µm size biosorbent dosage of 10 g/L in the interaction time intervals of 1 to180 min. The % biosorption of zinc is drawn against agitation time is shown in Fig. 1 .It is found that % biosorption of zinc is gradually increased in the first 60 min of agitation. 83.39 % (2.084 mg/g) of zinc is biosorbed in the first 1 min. The % biosorption is gradually and marginally increased up to 60 min reaching 92.57 % (2.314 mg/g). Beyond 60 min, the % biosorption is constant indicating the attainment of equilibrium conditions. The rate of biosorption is fast in the initial stages because adequate surface area of the biosorbent is available for the biosorption of zinc. As time increases, available biosorbent surface area decreases. The biosorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the biosorbent is exhausted.

Effect of biosorbent size and dosage

The percentage biosorption of zinc is drawn against biosorbent dosage at equilibrium agitation time for d_p=72 µm is shown in Fig. 2. The % biosorption of Zn (II) onto *Gracilaria corticata* biomass is increased from 85.22% (2.131 mg/g) to 93.11 % (2.328 mg/g) biomass dosage is increased from 5 to 15 g/L.

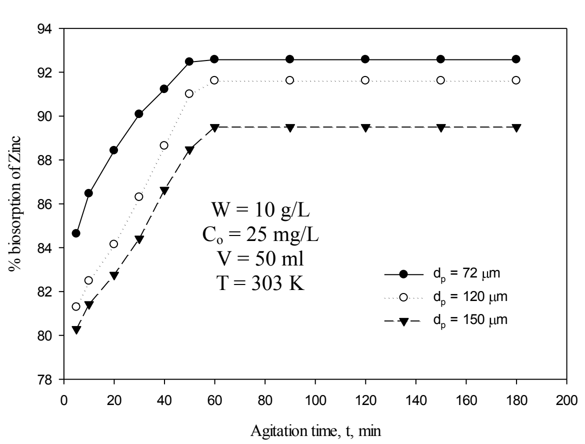


Fig – 1: Effect of Agitation time on % biosorption of Zinc

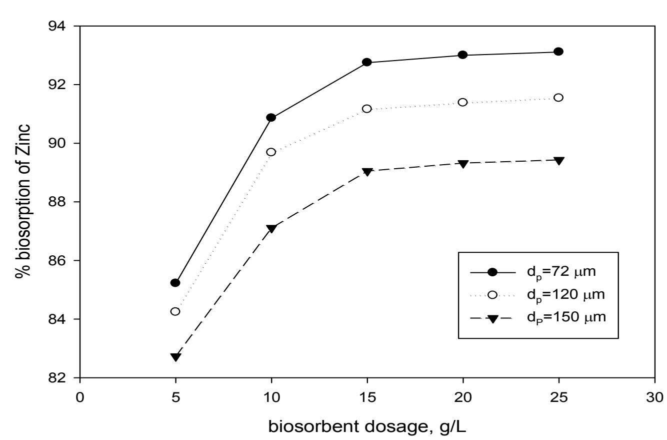


Fig – 2: Effect of Dosage and Size on % biosorption of Zinc

The observed enhancement in Zn (II) biosorption with increasing biomass dosage could be due to an increase in the number of active binding sites available for metal uptake surface area of the biosorbent . A further increase in biomass dosage over 15 g/L doesn't show a significant improvement in biosorption yield due to the saturation of the biosorbent surface with Zn (II) ions. Therefore, the optimal biomass dosage is 15 g/L. The percentage removal of zinc is increased from 89.05% (2.226 mg/g) to 92.75 % (2.382 mg/g) as the biosorbent size decreases from 150 to 72 µm for w = 15 g/L. With a decrease in biosorbent size, surface area of the biosorbent increases, there by the numbers of active sites available on the biosorbent are better exposed to the biosorbate.

Effect of initial zinc concentration

The effect of initial concentration of zinc in the aqueous solution on the percentage biosorption of zinc is shown in. Fig.3. The percentage biosorption of zinc is gradually decreased from 94.16 to 80.37 % (1.55 to 13.65 mg/g) by increasing zinc concentration from 25 to 250 mg/L at 303 k temperature. At lower concentrations of zinc, the sorption capacity of biosorbent is high. The lower % biosorption at higher concentration of zinc can be attributed to increase in the amount of biosorbate to the unchanging number of available active sites on the biosorbent.

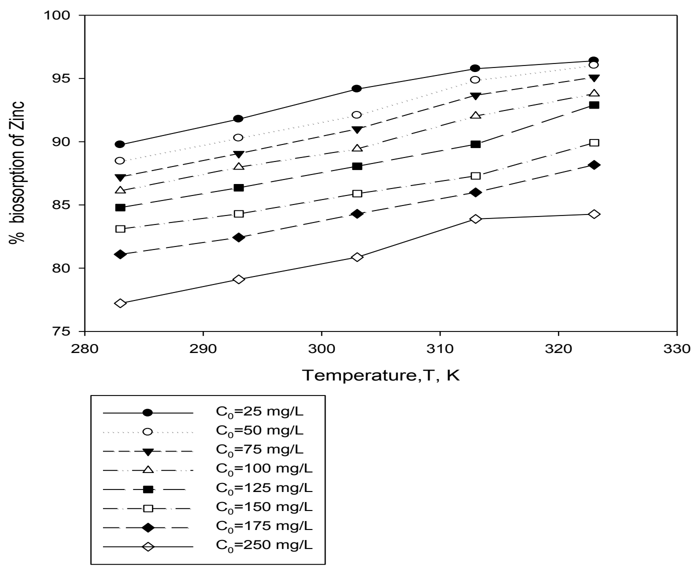


Fig – 3: Effect of initial zinc concentration on % biosorption of zinc

Effect of pH of aqueous solution

pH is an important controlling parameter in all the biosorption studies. The speciation of metal in solution is pH dependent at the same time, the state of chemically active sites is changed by variation in pH. In order to determine the optimal value, pH of the aqueous solution is varied from 1 to 10. A graph is drawn between the % biosorption of zinc and pH of aqueous solution is shown in Fig. 4. Increase in percentage biosorption of zinc is observed as pH is increased from 1 to 6 the % biosorption is decreased as pH is increased above 6. The extent of biosorption is increased from 55.05 % to 94.16 % in the pH range from 1 to 6, The % biosorption is marginally increased from 93.06 % to 93.26 %. Low pH depresses biosorption of zinc, which is due to competition of zinc ions with H^+ ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and zn^{+2} ions replace H^+ bound to the biosorbent (or forming part of the surface functional groups such as OH, SO_4., etc). The increase in removal capacity at higher pH may also be attributed to the reduction of H^+ ions which compete with zn^{+2} ions at lower pH. Above the pH of 6,zinc is hydrolyzed to $ZnOH^+$ and $Zn(OH)_2$.The predominant sorbings forms of zinc are zn^{+2} and $ZnOH^+$ that occur in the pH range of 4-6. This is the reason for higher removal of zinc in the pH range of 4-6. At pH higher than 6, precipitation of zinc occurred and removal due to biosorption is reduced.

Optimization of the biosorption conditions using RSM

In order to determine an optimum condition for biosorption of zinc ions, the parameters having greater influence over the response is to be identified. In the present study, the relationship between four independent variables and percent biosorption of zinc have fitted well with the quadratic model. The regression equation for the optimization of medium constituents: % biosorption of zinc (Y) is function of the biosorbent dosage (X_1), initial Zinc ion concentration (X_2), pH (X_3), and temperature (X_4), presents the variations in the corresponding coded values of four parameters and response based on experimental runs and predicted values proposed by CCD design. Multiple regression analysis of the experimental data yielded the following equation.

$$Y = -827.741 + 22.70\, X_1 + 3.10\, X_2 + 6.52\, X_3 + 4.505\, X_4 - 0.657 X_1^2 - 0.054\, X_2^2 - 0.827\, X_3^2 - 0.007\, X_4^2 - 0.017\, X_1X_2 - 0.073\, X_1X_3 - 0.007\, X_1X_4 - 0.007\, X_2X_3 - 0.001\, X_2X_4 + 0.018\, X_3X_4 \quad \text{---} \quad (3)$$

The coefficients of the regression model were calculated in which they contain four linear, four quadratic and six interaction terms and one block term. A positive sign of the coefficient represents a synergistic effect which means response (% biosorption of zinc) increases with the increase in effect, while a negative sign indicates an antagonistic effect which means response (% biosorption of zinc) decreases with the increase in effect. The significant of each coefficient is determined by t-values and *p*-values. The larger the magnitude of the *t*-value and smaller the *p*-value, the more significant is the corresponding coefficient term. The insignificant terms in the equation are not required to explain the biosorption. The statistical significance of the quadratic model is evaluated by the analysis of variance (ANOVA). The goodness of the fit of the model was checked by the determination coefficient (R^2). The R^2 value provides a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. The R^2 value is always between 0 and 1.The closer the R^2 value to 1, the stronger the model is and it predicts the response better. The value of the regression coefficient (R^2 = 0.9984) for eq (3) indicates that 99.83 % of the variability in the response could be explained by the model**.** In addition, the value of the adjusted determination coefficient (Adj R^2= 0.99679) is also very high to advocate for a high significance of the model. The optimal set of conditions for maximum percentage biosorption of zinc is pH = 6.44, biosorption dosage (w) = 15.03 g/L, initial zinc concentration (C_o) =23.72 mg/L and temperature = 307.8 K. The extent of biosorption of zinc calculated at these optimum conditions is 93.47 %. Table-2 , shows the comparison between the % biosorption obtained through experiments and that predicted values. The experimental values are in good agreement with predicted values which were shown in Fig. 5.

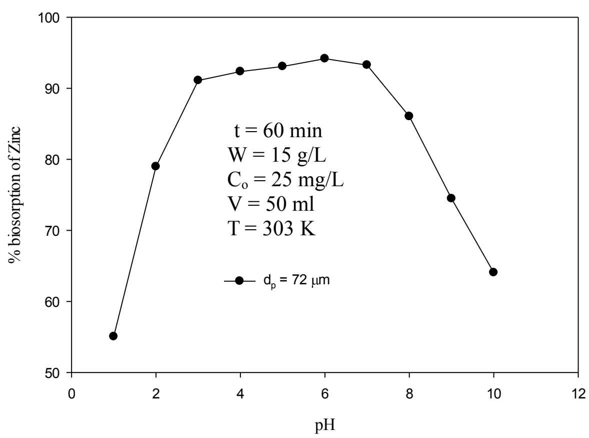


Fig – 4: Effect of pH on % biosorption of zinc

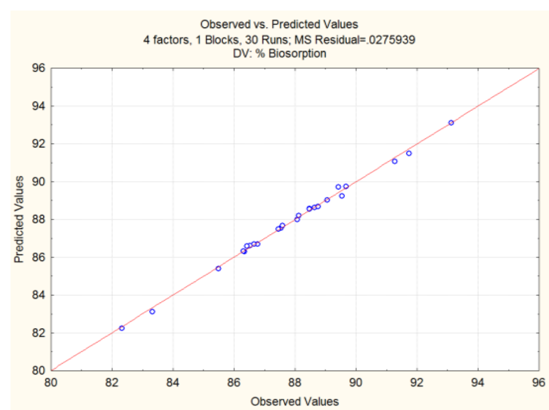


Fig. 5. Observed vs Predicted Values

Interpretation of contour plots

To investigate the interactive effect of two factors on the biosorption of zinc, contour plots are drawn using RSM. The response surface contour plots of percentage biosorption of Zinc versus the interactive effect of pH, Initial zinc concentration, biosorption dosage and temperature were shown in the Fig. 6 (a) – 6 (f). Each contour plot represents a number of combinations of two test variables with the other variable maintained at zero levels. The Maximum percentage biosorption of Zinc is indicated by the surface confined in the smallest curve (circular or elliptical) of the contour plot.

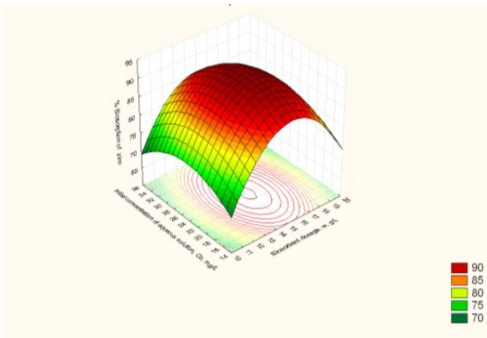


Fig - 6(a): Contour plot: Interactive effects of biosorbent Dosage (g/L) and initial concentration.

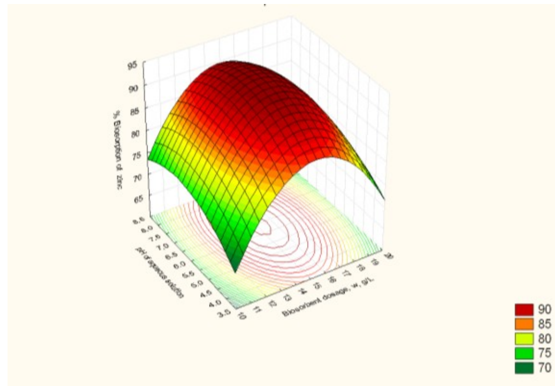


Fig - 6(b): Contour plot: Interactive effects of biosorbent dosage(g/L) and pH .

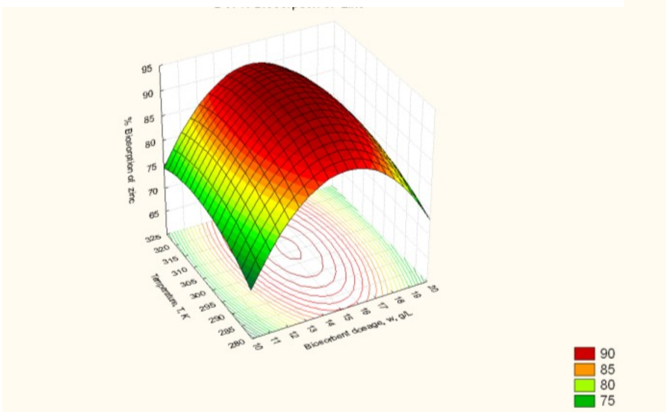


Fig- 6(c): Contour plot: Interactive effects of biosorbent dosage and Temperature (K).

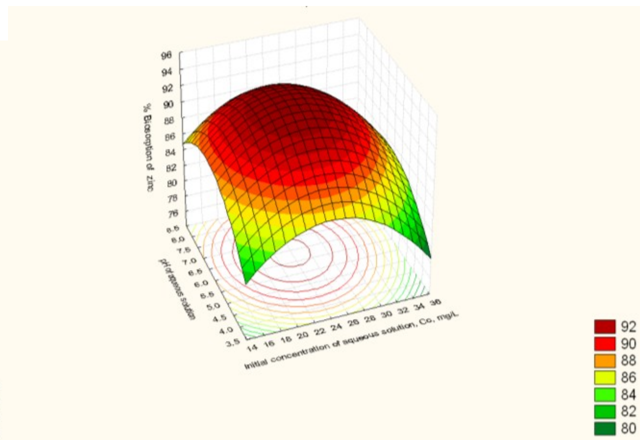


Fig - 6(d): Contour plot: Interactive effects Initial concentration (mg/L) and pH .

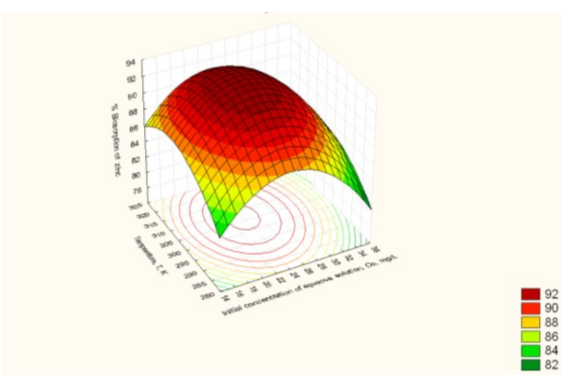


Fig - 6(e): Contour plot: Interactive effects of initial concentration and Temperature (K)

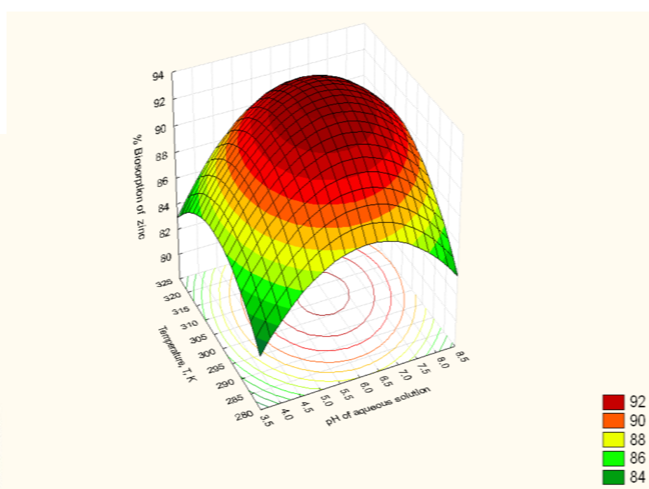


Fig - 6(f): Contour plot: Interactive effects pH and Temperature (K)

S. No	Parameters	Expt Values	RSM Values
1	Weight, w, g/L	15	15.03
2	Initial Conc, C_o, mg/L	25	23.72
3	pH	6	6.45
4	Temperature, T, K	303	307.8
5	% Biosorption of Zn	94.16	93.47

Table – 2: RSM Predicted Values

Biosorption Isotherms

Biosorption isotherms are the equilibrium relationships between the concentrations of biosorbed metal and metal in solution at a given temperature. Biosorption equilibrium is established when the concentration of sorbate in bulk solution is in dynamic balance with that on the liquid–sorbent interface. In the present investigation, Langmuir, Freundlich and Redlich-Peterson models are applied based on non-linear regression method to describe the equilibrium data. Freundlich presents an empirical equation that can be applied in case of low and intermediate concentration ranges. It is easier to handle mathematically in more complex calculations. The Freundlich isotherm is given by

$$q_e = K_f C_e^n \qquad \text{-----(4)}$$

where: K_f (mg/g) represents the biosorption capacity when metal equilibrium concentration and 'n' represents the degree of dependence of biosorption with equilibrium concentration. Taking logarithms on both sides, we get

$$\log q_e = \log K_f + n \log C_e$$

Irving Langmuir developed an isotherm named as Langmuir isotherm. It is the most widely used simple two- parameter equation. The Langmuir equation is:

$$q_e/q_m = bC_e / (1+bC_e) \qquad \text{----- (5)}$$

Where:

C_e is the concentration of the biosorbate at equilibrium
q_e is the amount biosorbed at equilibrium per unit mass of the biosorbent
q_m is the maximum amount biosorbed per unit mass of biosorbent
b is the coefficient related to affinity
Eq. (5) can be rearranged as

$$(C_e/q_e) = 1/ (bq_m) + (1/q_m) C_e \qquad \text{------ (6)}$$

Where q_m represents the maximum biosorption capacity and *b* is a Langmuir equilibrium constant related to affinity and energy of binding sites. The Redlich-Peterson model proposes a three parameter isotherm to incorporate features of both Langmuir and Freundlich equations. It is expressed as

$$q_e = \frac{AC_e}{1 + BC_e^{\,g}} \qquad \text{------ (7)}$$

where A, L/g and B, L/ mg are the Redlich-Peterson isotherm constants and 'g' is the Redlich – Peterson isotherm exponent, that lies between 0 and 1. It is found that biosorption data are well represented by Freundlich with higher correlation coefficient of 0.96 followed by Langmuir and Redlich-Peterson models with correlation coefficients of 0.93 and 0.925 respectively. The essential characteristics of Langmuir isotherm can be explained in terms of the dimensionless separation factor (R_L). R_L value of 0.8930 indicates favourable Zn(II) biosorption on to Gracilaria corticata. Freundlich ,Langmuir, and Redlich-Peterson models experimental data are drawn and shown in Fig.7- 9.

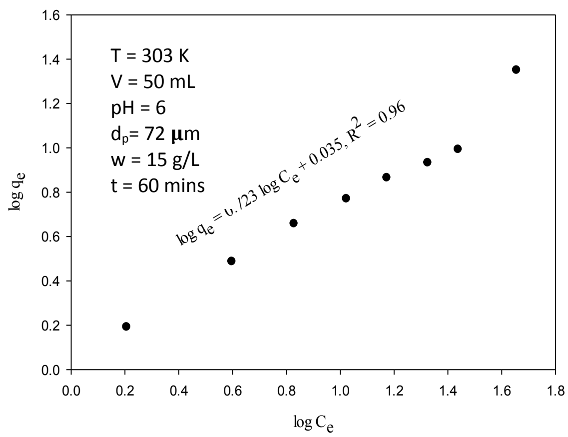


Fig – 7 : Freundlich isotherm for % biosorption of zinc

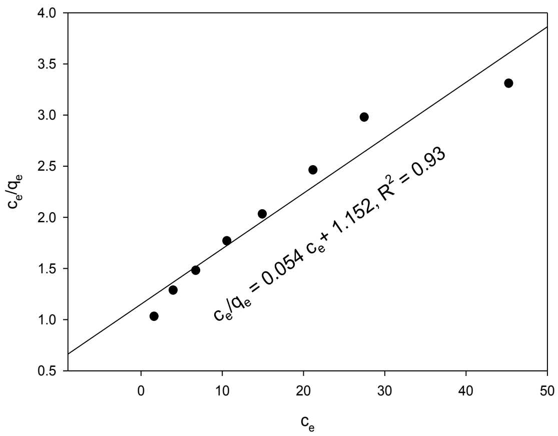


Fig – 8 : Langmuir isotherm for % biosorption of zinc

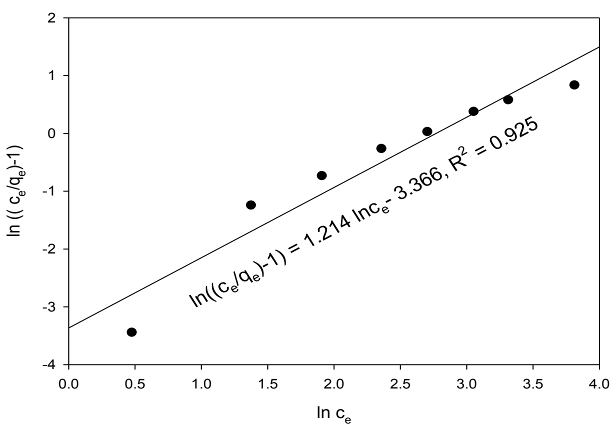


Fig – 9 : Redlich –Peterson isotherm for biosorption of zinc

The Freundlich model parameters*

k_f	n	R^2
1.035	0.723	0.96

The Langmuir model parameters*

q_m	K_L, L/mg	R^2
18.51	0.046	0.93

The Redlich-peterson model parameters*

A	B, L/mg	R^2
1.00	0.009	0.925

*parameters obtained using non-linear regression

Table – 3: Freundlich, Langmuir and Redlich – Peterson Parmeters

Biosorption kinetics

The order of biosorbate – biosorbent interactions are described by using kinetic models. Traditionally, the pseudo first order model of Lagergren finds wide application. In the case of biosorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo first order Lagergren rate equation:

$(dq_t/dt) = K_1 (q_e - q_t)$ ------ (8)

where q_t and q_e are the amounts biosorbed at t, min and equilibrium time and K_1 is the rate constant of the pseudo first order biosorption.
The above equation can be presented as

$\int (dq_t/(q_e - q_t)) = \int K_1 dt$ ------ (9)

Applying the initial condition $q_t = 0$ at t = 0, we get

$\text{Log}(q_e - q_t) = \log q_e - (K_1/2.303)t$ ------ (10)

Plot of log $(q_e - q_t)$ versus't' gives a straight line for first order kinetics, facilitating the computation of biosorption rate constant (K_1). If the experimental results do not follow the above equation, they differ in two important aspects:

1) $K_1 (q_e - q_t)$ does not represent the number of available adsorption sites and

2) log q_e is not equal to the intercept.

In such cases, pseudo second order kinetic equation:

$(dq_t/dt) = K_2 (q_e - q_t)^2$

where: 'K_2' is the second order rate constant.

The other form of the above equation is:

$(dq_t/(q_e-q_t)^2) = K_2dt$ -------- (11)

After integrating and Rearranging the terms, we get the linear form as :

$(t/q_t)=(1/K_2q_e^2)+(1/q_e)t.$ ------- (12)

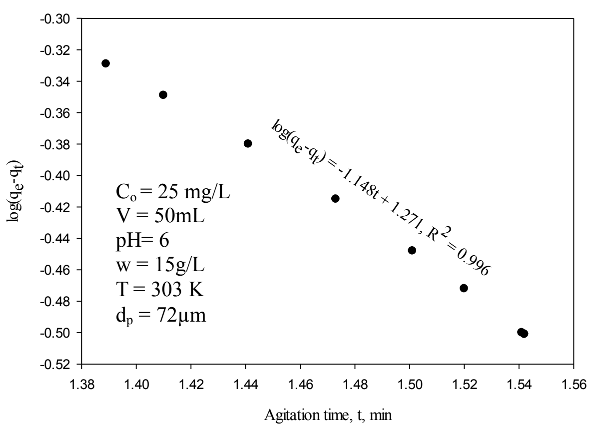
The pseudo second order model based on above equation, considers the rate -limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the biosorbate and biosorbent. If the pseudo second order kinetics is applicable, the plot of (t/q_t) vs't' gives a linear relationship that allows computation of q_e and K_2. In the present study, the kinetics is investigated with 50 mL of aqueous solution (C_0= 25 mg/L) at 303 K with different biosorbent sizes in the interaction time intervals of 1 min to 50 min. Lagergren pseudo first order plots of log (q_e-q_t) vs 't' and (t/q_t) vs 't' in the interaction time intervals of 1 to 60 min for 72 μm are drawn and shown in Fig.10 and Fig.11 respectively. The validity of pseudo first order model is conformed with a correlation coefficient of 0.99. The applicability of pseudo first order kinetics model suggested that the zinc biosorption to Gracilaria corticata is based on chemical reaction, involving the exchange of electrons between biosorbent and metal. The reaction rate constant, k and R^2 values are presented in Table-4.

d_p, μm	Equation	K_1, min^{-1}	R^2
72	$log(q_e - q_t) = -1.148t + 1.271$	2.643	0.99

Pseudo-second order kinetics

d_p, μm	Equation	K_2, g/(mg-min)	R^2
72	$t/q_t = 0.549 t + 3.40$	0.0886	0.989

Table – 4 Pseudo-first order kinetics



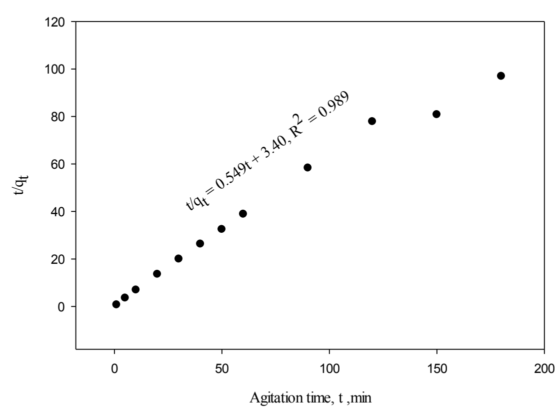


Fig – 10: First order kinetics for % biosorption of zinc **Fig – 11:** Second order kinetics for % biosorption of zinc

Biosorption thermodynamics

Biosorption is temperature dependent. In general, the temperature dependence is associated with three thermodynamic parameters namely change in enthalpy of biosorption (ΔH), change in entropy of biosorption (ΔS) and change in Gibbs free energy (ΔG).

The ΔH is related to ΔG and ΔS as

$$\Delta G = \Delta H - T\,\Delta S \quad \text{-------- (13)}$$

The van't Hoff's equation is

$$\log (q_e / C_e) = -\Delta H / (2.303\,RT) + (\Delta S / 2.303\,R) \quad \text{----- (14)}$$

Here (q_e/C_e) is the biosorption affinity.

By plotting log (q_e/C_e) as a function of (1/T), the slope [- (ΔH /2.303 R)] and intercept [ΔS/2.303 R] of the plots are determined. ΔH and ΔS values are calculated from the slope and Intercept. Enthalpy is the most commonly used thermodynamic function due to its practical significance. The negative/positive value of ΔH will indicate the exothermic/endothermic nature of biosorption and the physical/chemical in nature of sorption. It can be easily reversed by supplying the heat equal to calculated ΔH. If the value of ΔS is less than zero, it indicates that the process is highly reversible. If ΔS is more than or equal to zero, it indicates the irreversibility of process. The negative value for ΔG indicates the spontaneity of biosorption. Whereas the positive value indicates non spontaneity of sorption. Experiments are conducted to the biosorption varying the temperature from 283 to 323 K. The plots indicating the effect of temperature on biosorption of zinc for different initial concentrations are shown in Fig.12 The plots indicate that there is an increase in % biosorption of zinc with an increase in temperature. The van't Hoff's plots for the biosorption data are shown in Fig. In the present study, the enthalpy change is ΔH positive indicating that the biosorption is endothermic. The values of ΔS, ΔG and ΔH obtained in the present investigating for different initial concentrations of zinc are shown in table.5.10
The Van't Hoff plot is drawn in Fig.12. Van't Hoff plot of log(q_e/c_e) as a function of 1/T yields a straight line, from which Δ*H* and Δ*S* can be calculated from the slope and intercept, respectively The values of ΔH, ΔS and ΔG for different initial concentrations and temperatures are calculated and shown in Table-7. The negative values of ΔG at different temperatures (Table-7) indicates that zinc (II) biosorption is a spontaneous process. The biosorbent used in this study has higher affinity at higher temperatures. The change in the enthalpy (ΔH) is 23.57 J/ mol. The positive value of ΔH indicates that biosorption of zinc (II) onto Gracilaria corticata is endothermic. The positive value of ΔS (77.95 J/mol K) suggests randomness at the solid/solution interface [41].
Table 8. represents the comparison of metal uptake capacities of different biosorbents and the present work.

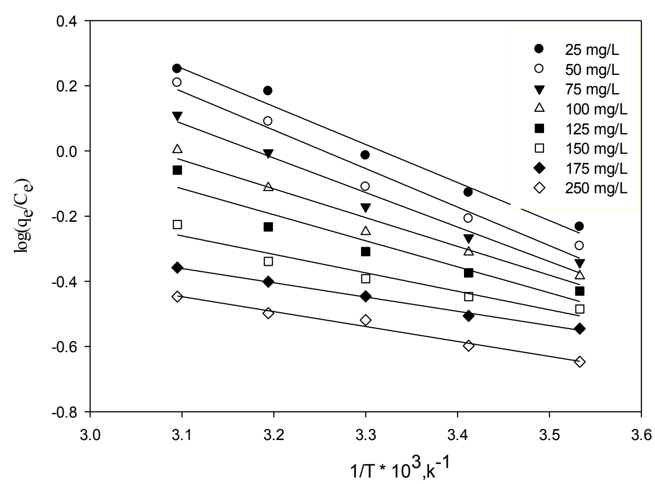


Fig – 12: Effect of Temperature on % biosorption of zinc (van't Hoff plot)

S. No	C_0, mg/L	ΔS J/(mol-K)	ΔH J/mol	- (ΔG) kJ/mol				
				283 K	293 K	303 K	313 K	323 K
1	**25**	**77.95**	**23.57**	**22.03**	**22.81**	**23.59**	**24.374**	**25.154**
2	50	77.756	23.938	21.981	22.758	23.536	24.313	25.091
3	75	68.087	21.423	19.247	19.281	20.608	21.289	21.970
4	100	54.933	17.878	15.528	16.077	16.626	17.176	17.725
5	125	48.174	16.238	13.617	14.098	14.580	15.062	15.544
6	150	30.616	11.396	8.65	8.9590	9.2652	9.5714	9.8775
7	175	20.1619	8.728	5.618	5.820	6.021	6.223	6.425
8	250	19.530	9.1138	5.517	5.713	5.908	6.1037	6.299

Table - 7: Thermodynamic parameters for biosorption of zinc for various C_0 value

Biosorbent	**Metal uptake capacity, mg/g**
Bark wastes [40]	14.7
palm tree leaves [6]	14.7
Turkish tea waste [26]	4.9
Tectona grandis [39]	16.42
E. Crasippes [27]	16.5
Pseudomonas aeruginosa [11]	16.0
Present investigation	**18.51**

Table 8. Comparison of metal uptake capacities of different biosorbents

CONCLUSIONS

- The biosorption of zinc onto Gracilaria corticata is spontaneous.
- In the range of variables studied, percentage removal of zinc is 94.16 % (1.554 mg/g), at equilibrium agitation time of 60 min, for an optimum dosage of 15 g/L, and at a pH of 6.
- With an increase in initial zinc concentration (C_o) in the aqueous solution the percentage biosorption of zinc from the aqueous solution is decreased.
- The experimental parameter values are in good agreement with RSM values.
- The biosorption of zinc is better described by Freundlich and Langmuir models. The maximum monolayer coverage capacity of Gracilaria Corticata for zinc ions is 18.51 mg/g.
- The biosorption of zinc is better described by pseudo First order kinetics
- The process is found to be endothermic, irreversible and spontaneous.

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NOMENCLATURE

C_o	Initial concentration of Zn (II) in aqueous solution, mg/L
C_t	Concentration of Zn (II) in aqueous solution after‘t’ min, mg/L
C_e	Equilibrium biosorption concentration of Zn (II), mg/L
t	Agitation time, min
t_{eq}	Equilibrium agitation time, min
T	Absolute temperature, K
w	Biosorbent dosage, g
d_p	Biosorbent size, µm
V	Volume of aqueous solution, mL
m	Amount of biosorbent taken per 1L of aqueous solution, g/L
q_e	Mass of solute biosorbed per mass of biosorbent at equilibrium, $(C_o-C_e)/m$, mg/g
q_t	Mass of solute biosorbed per mass of biosorbent at ‘t’ min, $(C_o-C_t)/m$, mg/g
q_m	Langmuir monolayer capacity, mg/g
b	Langmuir equilibrium constant
n	Freundlich constant for Zn (II) in aqueous solution, g/L
K_f	Freundlich coefficient for Zn (II) in aqueous solution, mg/g
A	Redlich-Peterson isotherm constant, L/g
B	Redlich-Peterson isotherm constant, L/mg
g	Redlich-Peterson isotherm exponent
K	Pseudo – Second order rate constant, g/mg-min
ΔG	Change in Gibbs free energy, KJ/mol
ΔS	Change in entropy, J/mol-K
ΔH	Change in enthalpy, J/mol
R_L	Dimensionless separation factor for Zn(II) in aqueous solution
R^2	Correlation coefficient
MS	Mean Squares