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RESEARCH ARTICLE

USE OF CENTRAL COMPOSITE DESIGN IN OPTIMIZING ZINC REMOVAL BY AN ECOFRIENDLY BIOSORBENT PITHOPHORA CLEVEANA WITTROCK: APPLICATION OF ISOTHERMS

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ABSTRACT

The ultimate aim of research worldwide is to make the environment a pollution free environment with clean as well as safe air and water. Our subject is too closely related to the on the ongoing research, i.e., removal of toxic constituents from the aqueous solutions for dependable and clean water for several uses. Pithophora Cleveana Wittrock was used as an biosorbent for the removal of zinc metal ions from aqueous solutions. Batch experiments were taken out over an agitation time of 0.5-30 min, using 0.1 g of Pithophora Cleveana Wittrock, 30 mL of 20 mg/L of individual metal concentration at pH 5, temperature 303 K and 180 rpm shaking speed. The removal percentage of zinc at the end of 20 min of contact time was then measured. The Central Composite Design (CCD) software was used to design the experiments and determine the optimum conditions. The equilibrium isotherm models Langmuir, Freundlich, Temkin, Redlich-Peterson and Dubinin–Radushkevich (D–R) were employed to analyze the fitness of the equilibrium data. Langmuir isotherm for Zinc with an average higher correlation coefficient of 0.996, followed by D–R, Freundlich, Temkin, and Redlich-Peterson with a correlation coefficient of 0.9484, 0.925, 0.903 and 0.2177 respectively. Confirmatory experiments conducted at the suggested optimized conditions showed experimental findings within 5% of the projected values. From the CCD, the suggested optimum values for metal ion concentration, pH, biosorbent dosage and Zinc removal efficiency were 37.6 mg/L, 5.09, 0.3 g and 78.97%, respectively.

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INTRODUCTION

In the developing country like India, an alarming increase in the population is one of the reasons for rapid industrialization. This lays a guide for the release of modern wastes, particularly water loaded with toxic metals. These wastewaters are generally not treated prior to discharge into the water bodies and the heavy metals which are of low biodegradability create genuine ecological issues. The release of these heavy metals beyond specific limits causes a hazardous effect on living organisms. Hence, the adoption of any technology is important to remove heavy metals from water bodies (Han *et al*., 2007). Among all pollutants, zinc attracted our attention, as it is commonly found in the effluents of a large number of industries. This metal is an essential element for different life processes and is also a micronutrient if present in little amounts. On the other hand, a ceaseless exposure to zinc is adverse for human wellbeing (Bhattacharya *et al*., 2006; Mishra and Patel 2009). Numerous strategies have been proposed for evacuating overwhelming metals and among them chemical precipitation, membrane filtration, ion exchange and adsorption are the most generally utilized processes. The feasibility of such processes is sometimes limited due to technical and economic factors (Karthikeyan *et al*., 2007; Benguella and Benaissa 2002). It is surely understood that adsorption procedure has got a significant consideration because of its high limit in the removal of heavy metals. With a view, to make stronger the effectivity of the adsorption approaches, it is critical to enhance more cost-effective and easily available adsorbents with excessive adsorption capacities. The promising approach for heavy metal elimination from aqueous solutions is biosorption. Biosorption describes metal elimination by passive binding in living and dead biomass from water bodies in a mechanism that isn't managed with the aid of metabolic steps. The metal linkage is founded on the chemical properties of the cellular envelope without requiring biologic endeavor (Volesky 2001;

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Palmieri 2001; Valdman 2001). Recently, biosorption, making use of algae as a biosorbent has risen to be a capable substitute for the predominant routine physico-synthetic methodologies for zinc removal. A considerable amount of biomass, like green growth, fungi, bacteria, yeast, moss were researched with the expectation of finding additional proficient or prudential biosorbent. Amongst them, green growth has ended up being money related and ecofriendly materials, as they're inexhaustibly accessible, have recovery and metallic recuperation probability, lesser amount of compound and/or natural slime to be arranged off, exorbitant effectiveness in weaken effluents and have enormous floor subject to volume proportion. It presents a profitable solution for industrial wastewater management. Also, algae possesses high metal holding capacities, when you find out some functional groups like amino, hydroxyl, carboxyl and sulfate on the extraneous of the cell walls of polysaccharides, proteins or lipids, which can act as retention sites for metals. The non-achievable structure has been proposed as ability sorbents in perspective that these are basically lifeless materials, which need no sustenance to maintain the biomass. In malice of the fact that there are encounters of biosorption of zinc metal particles by method for marine on a par with contemporary water algae demonstrating different eliminating efficiencies, most extreme bioorption limits (q_e) and binding constants, however, there aren't any reports on the removal of zinc from aqueous solutions utilizing Pithophora Cleveana Wittrock. The main objective of this work is to investigate the capability of Pithophora Cleveana Wittrock which has branches emerging below the septum of the main filament as a biosorbent to remove zinc particles from aqueous environment. The components considered for the study are pH, contact time, dosage, temperature, the size of the biosorbent and metal ion concentration. Experiments were carried out by utilizing Langmuir, Freundlich, Redlich-Peterson, Temkin, Dubinin–Radushkevich biosorption models were connected to portray the equilibrium isotherms and to decide the isotherm constants. The disadvantages in traditional enhancement strategies are wiped out by streamlining each one of the parameters by Central Composite Design (CCD) (Box and Wilson 1951) using Response Surface Methodology (RSM).

MATERIALS AND METHODS

Biosorbent collection and treatment

The Pithophora Cleveana Wittrock used in the present survey were gathered from the river Nagavali, Palakonda, Andhra Pradesh, INDIA. The gathered algae were washed with deionized water several times to get rid of unwanted material. The washing procedure was kept till the wash water contains no malicious dirt. The washed algae were then totally dried in sunlight for 10 days. The dried leaves were then cut into little slices and powdered using domestic mixer. In the present study the powdered materials in the range of 75-212 μm average particle size were then immediately used as biosorbents without any pre-treatment.

Preparation of metal solution

A stock solution of zinc concentration 1000 mg/L was prepared by dissolving required amount of zinc sulfate in 1000 ml of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared metal solutions varied between 20 to 100 mg/L and they were prepared by diluting the zinc stock solution, which were obtained by dissolving in deionized water.

Reagents utilized

Metal ion solutions were prepared by diluting stock metal ion solutions, which were obtained by dissolving weighed quantity of zinc sulfate of analytical reagent grade obtained from MERCK (India) in double distilled water.

Batch biosorption experiments conducted

Biosorption studies were carried out at 25°C with an initial concentration range from 20 to 100 mg/L, biosorbent dosage range from 0.1 to 0.5g and size of the biosorbent ranges from 75-212 μm. Equilibrium was attained by shaking the flasks for 3 hours at 180 RPM in an orbital shaker. A known volume of the solution was removed and filtered for zinc analysis. Known amounts of biomass were contacted with each metal solution. The effects of following parameters such as pH, dosage, initial metal ion concentration and contact time were studied. Bioorption experiments were carried out in duplicate.

Metal *Analysis*

The final concentration of metal ions was analyzed by Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) at a wavelength of 213.9 nm, slit width 0.2 nm and lamp current 5.0 mA for zinc.

Calculation of biosorption capacity

In order to assess the amount of zinc ions held per unit mass of Pithophora Cleveana Wittrock, the biosorption capacity was computed using the following equation:

$$q_e = \frac{V(C_i - C_f)}{1000\,w} \quad \text{……. (1)}$$

where V is the volume of the solution in mL and w is the mass of the biosorbent in g. Preliminary trails had demonstrated that metal biosorption losses to the flask walls and to the filter paper were negligible. All the trails were rehashed five times and the average values have been recorded. Additionally, blank trails were run to gaurantee that no biosorption was taking place on the walls of the apparatus used.

RESULTS AND DISCUSSION

The effect of contact time

Fig.1 show the explained biosorption time of zinc by Pithophora Cleveana Wittrock from solutions containing 20-100 mg/L of zinc ions separately. As seen in the figure, the biosorption equilibrium was established in 20 min for zinc metal.

Table 1. Equilibrium constants for Zinc onto Pithophora cleveana Wittrock

Langmuir Isotherm			
$Q_{\max}(mg/g)$	$b(L/mg)$	R^2	--
11.890	0.1288	0.996	--
Freundlich Isotherm			
$K_f\,(mg/g)$	$n\,(g/L)$	R^2	--
1.431	2.785	0.925	--
Redlich-Peterson Isotherm			
$A\ (L/g)$	$B\ (L/mg)$	g	R^2
3.975	13.765	0.81	0.2177
Temkin Isotherm			
$A_T\ (L/mg)$	b_T	R^2	--
0.1894	121.99	0.903	--
D–R Isotherm			
$K_d\ (\mathrm{Mol}^2 kJ^{-2})$	$Q_0\ mg/g$	R^2	$E\ kJ/mol$
0.00988	9.86	0.9484	7.11

Table 2. K_R values at 303 K relating to the initial metal ion concentrations at pH 5.0

C_o (mg/L)	20	40	60	80	100
K_R Zinc	0.279596	0.33431	0.11455	0.143396	0.072031

Table 3. Process variables and their level

Factors	Name	Units	Low actual	High actual	Low coded	Middle coded	High coded
X_1	pH		3	7	-1	0	1
X_2	Initial concentration	mg/L	20	100	-1	0	1
X_3	Biosorbent dosage	g	0.1	0.5	-1	0	1

Table 4. Experimental design in terms of coded factors

S.No.	pH	Concentration, mg/L	Dosage, g	% Adsorption
1	-1.00000	-1.00000	-1.00000	63.49
2	-1.00000	-1.00000	1.00000	67.18
3	-1.00000	1.00000	-1.00000	45.92
4	-1.00000	1.00000	1.00000	48.12
5	1.00000	-1.00000	-1.00000	66.74
6	1.00000	-1.00000	1.00000	68.4
7	1.00000	1.00000	-1.00000	46.34
8	1.00000	1.00000	1.00000	47.28
9	-1.68179	0.00000	0.00000	54.77
10	1.68179	0.00000	0.00000	56.24
11	0.00000	-1.68179	0.00000	75.12
12	0.00000	1.68179	0.00000	44.26
13	0.00000	0.00000	-1.68179	54.74
14	0.00000	0.00000	1.68179	57.94
15	0.00000	0.00000	0.00000	74.86
16	0.00000	0.00000	0.00000	74.1

Table 5. ANOVA for the biosorption of Zinc

Source	SS	DF	Mean Square	*F* Value	*p*-value Prob > F
X_1	3.115	1	3.115	7.278	0.035677
X_2	401.031	1	401.031	937.078	0.000000
X_3	1238.428	1	1238.428	2893.798	0.000000
X_1^2	240.940	1	240.940	562.997	0.000000
X_2^2	14.090	1	14.090	32.924	0.001218
X_3^2	365.850	1	365.850	854.871	0.000000
$X_1 X_2$	2.989	1	2.989	6.984	0.038397
$X_1 X_3$	1.353	1	1.353	3.162	0.125712
$X_2 X_3$	0.611	1	0.611	1.427	0.277396
Error	2.568	6	0.428		
Total	1823.748	15		R^2=0.99859; R^2 (Adj) = 0.99648	

DF:degree of freedom; SS: sum of squares; F: factor F; *P*: probability.

Table 6. Estimated regression coefficients and corresponding *t* and *p* values for the biosorptionof Zinc

Term	Coefficient	SE Coefficient	*t*-value	*p*-value
Constant	-104.455	6.18725	-16.8823	0.000003
X_1	48.229	1.64858	29.2549	0.000000
X_1^2	-4.569	0.14926	-30.6117	0.000000
X_2	0.816	0.06602	12.3648	0.000017
X_2^2	-0.009	0.00038	-23.7276	0.000000
X_3	290.389	13.05687	22.2403	0.000001
X_3^2	-436.402	14.92576	-29.2382	0.000000
$X_1 X_2$	-0.021	0.00810	-2.6428	0.038397
$X_1 X_3$	-2.856	1.60618	-1.7781	0.125712
$X_2 X_3$	-0.097	0.08098	-1.1944	0.277396

Table 7. The experimental values vs predicted values for biosorption of Zinc

S.No.	Experimental values of biosorption	Predicted values of biosorption
1	63.49	63.19
2	67.18	66.60
3	45.92	45.92
4	48.12	48.22
5	66.74	66.19
6	68.4	67.95
7	46.34	46.47
8	47.28	47.13
9	54.77	55.01
10	56.24	56.62
11	75.12	76.01
12	44.26	43.98
13	54.74	54.94
14	57.94	58.36
15	74.86	74.42
16	74.1	74.42

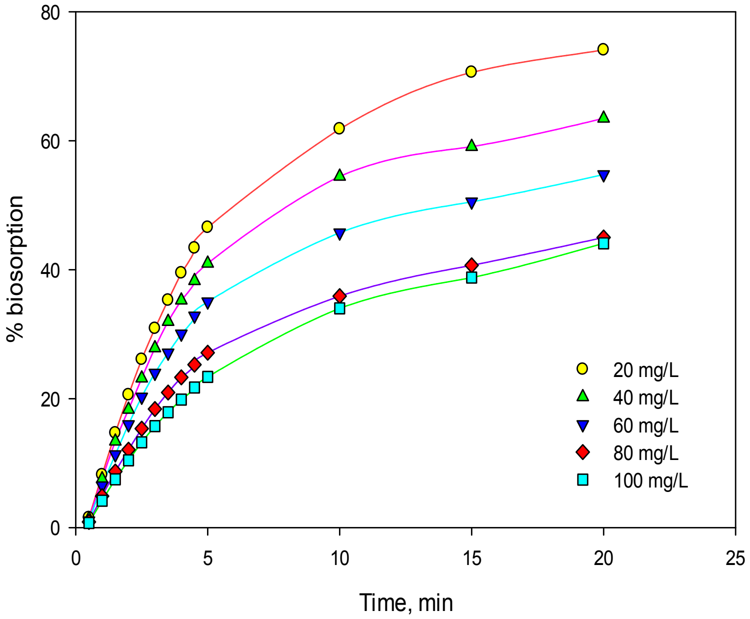

Fig.1. Effect of contact time on biosorption of Zinc by Pithophora cleveana Wittrock of 0.1 g/30 mL of biosorbent concentration

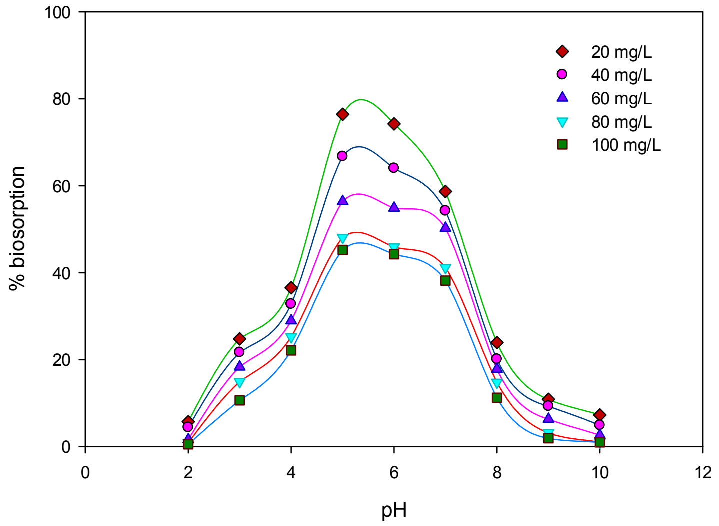

Fig.2. Effect of pH on biosorption of Zinc by Pithophora cleveana Wittrock of 0.1 g/30 mL of biosorbent concentration.

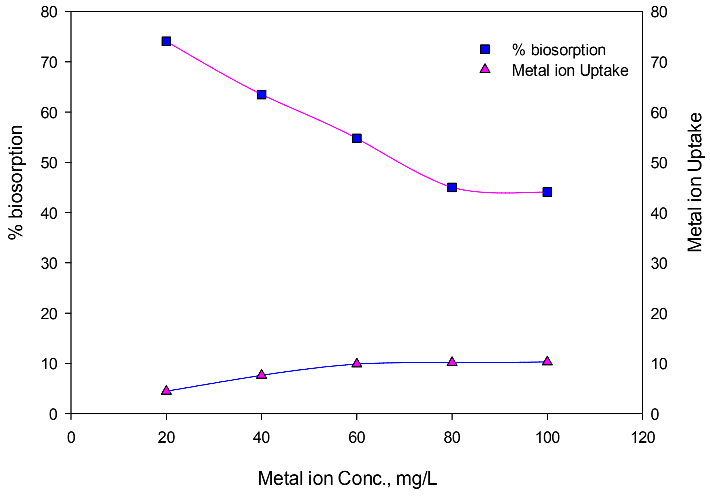

Fig.3. Effect of metal ion concentration on the biosorption capacity of Zinc by Pithophora cleveana Wittrock of 0.1 g/30 mL of biosorbent concentration.

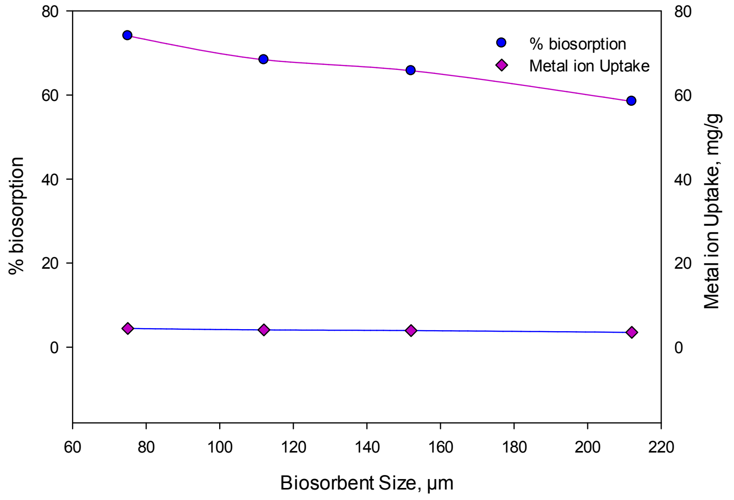

Fig.4. Effect of biosorbent particle size on biosorption of Zinc for 20 mg/L of metal and 0.1 g/30 mL of biosorbent concentration.

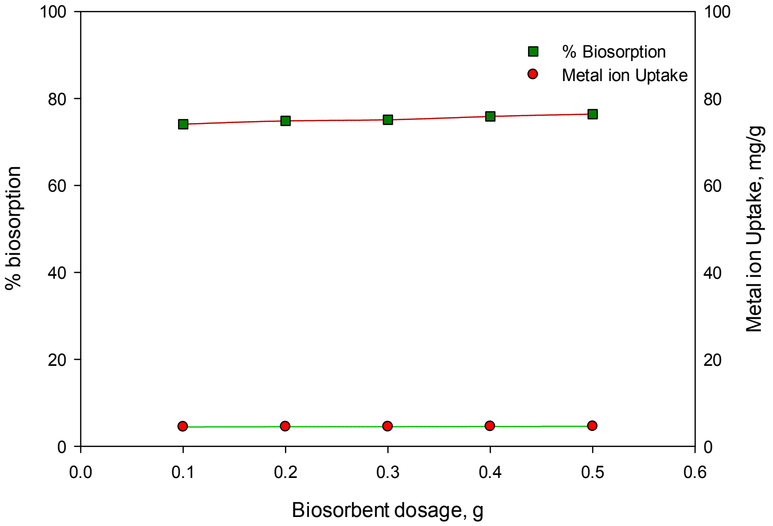

Fig.5. Effect of biosorbent dosage on biosorption of Zinc for 20 mg/L of metal ion concentration.

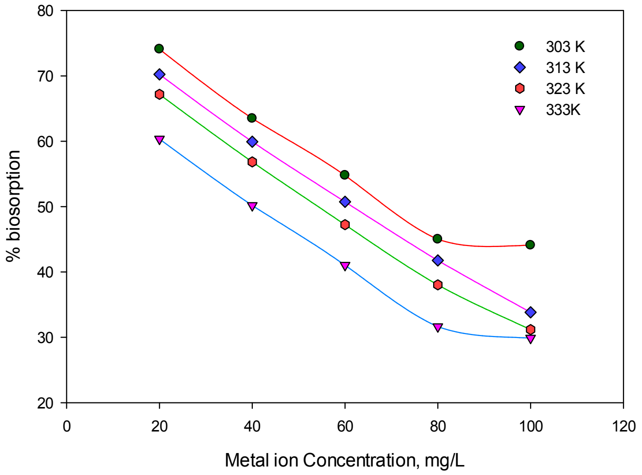

Fig.6. Effect of temperature on biosorption of Zinc by Pithophora cleveana Wittrock of 0.1 g/30 mL of biosorbent concentration.

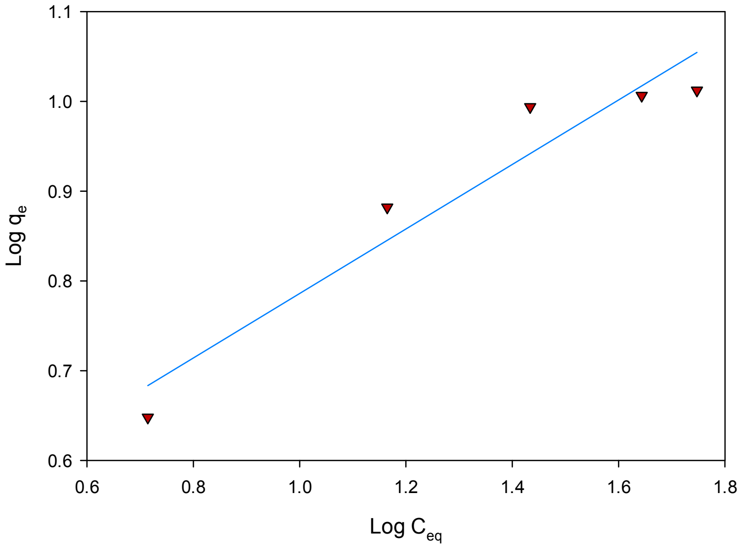

Fig.7. Freundlich adsorption isotherm at 0.1 g/30 mL of biosorbent concentration.

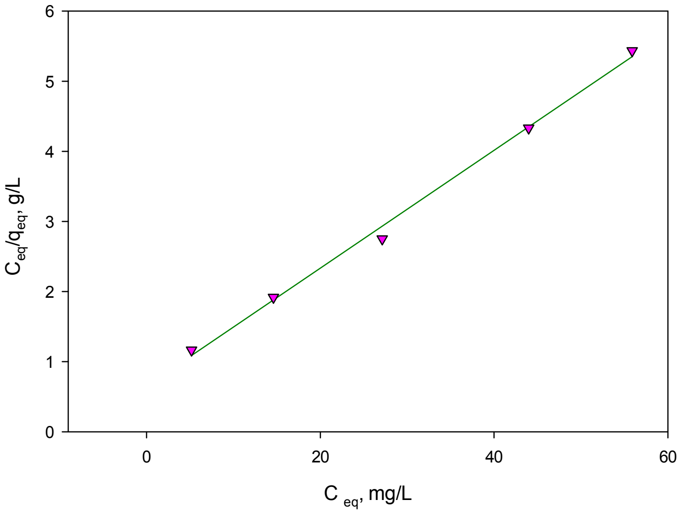

Fig.8. Langmuir adsorption isotherm at 0.1 g/30 mL of biosorbent concentration.

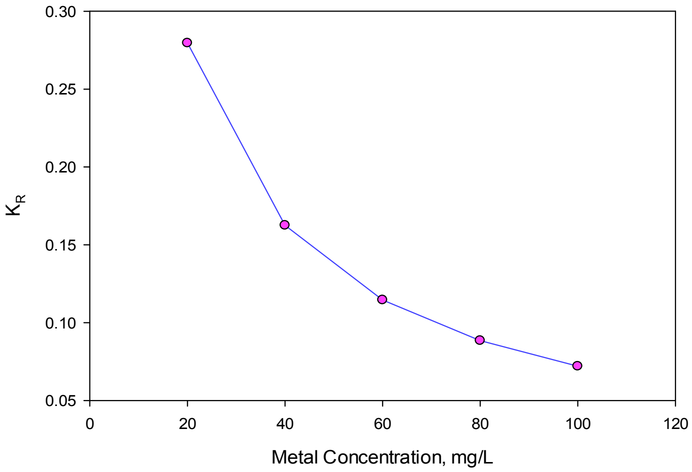

Fig.9. Values of the separation factor, K_R for the biosorption of Zinc using Pithophora cleveana Wittrock.

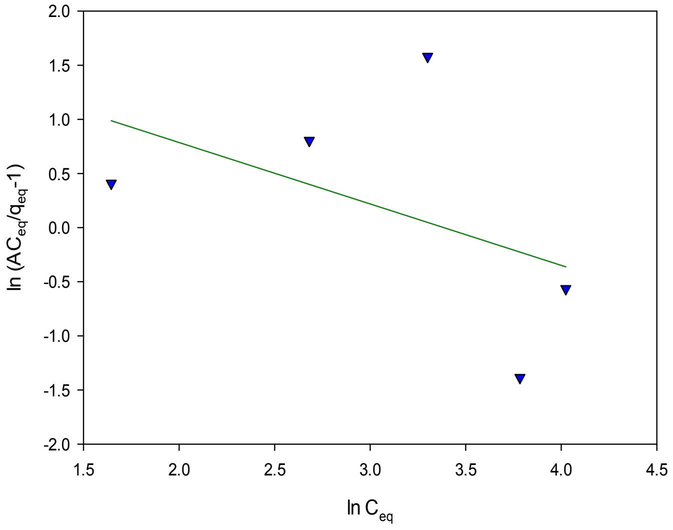

Fig.10. Redlich-Peterson adsorption isotherm at 0.1 g/30 mL of biosorbent concentration.

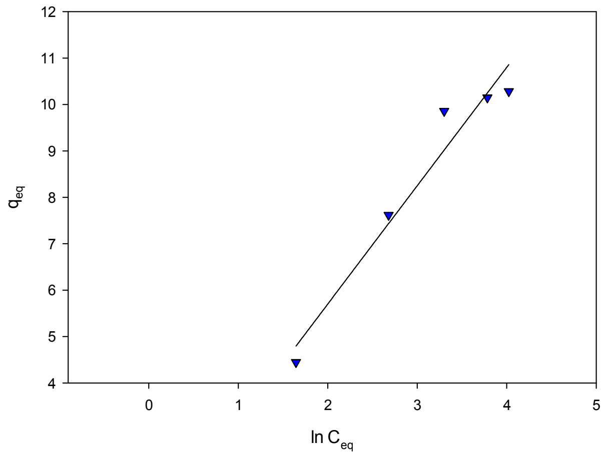

Fig.11. Temkin adsorption isotherm at 0.1 g/30 mL of biosorbent concentration.

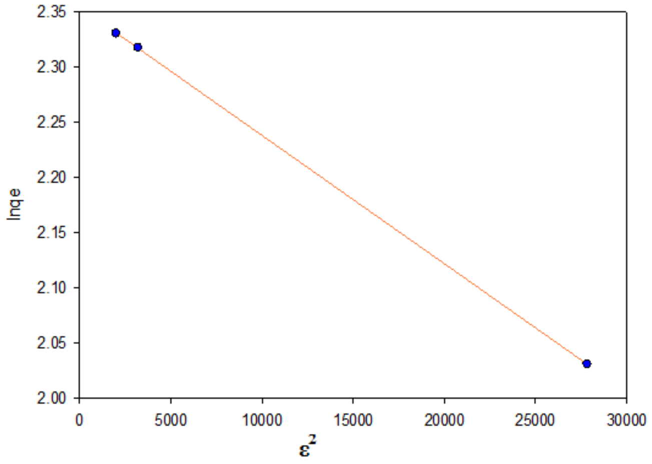

Fig.12. Dubinin-Radushkevich (D-R) adsorption isotherms at 0.1 g/30 mL of biosorbent concentration

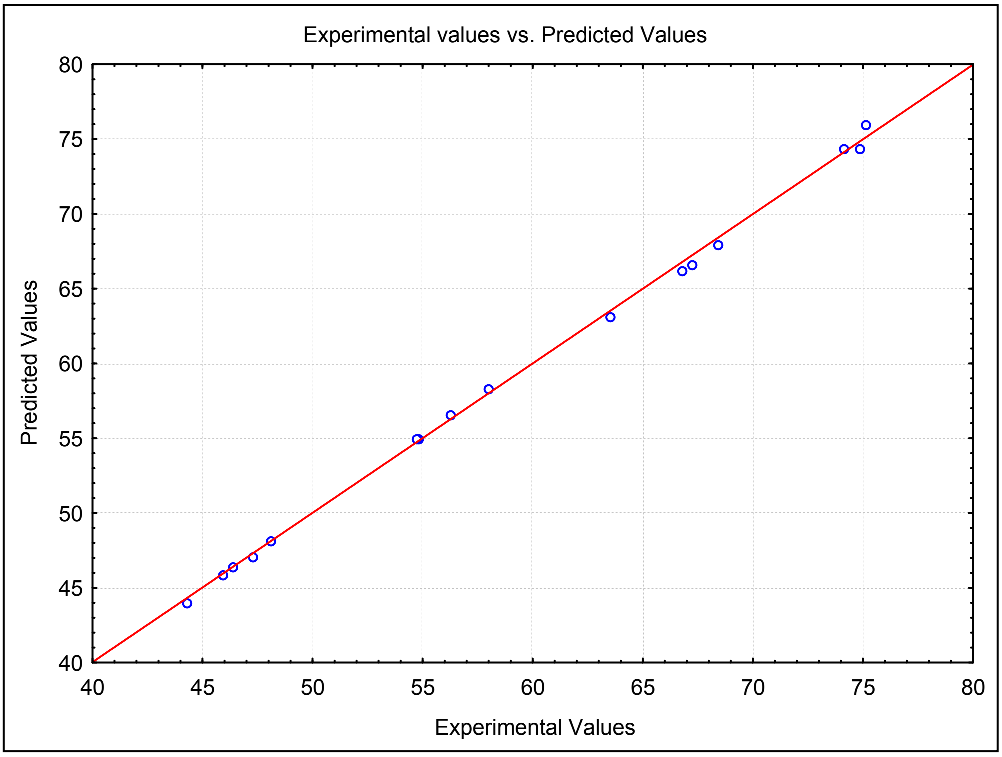

Fig.13. Correlation plot of experimental valuesvs Predicted values for biosorption of Zinc

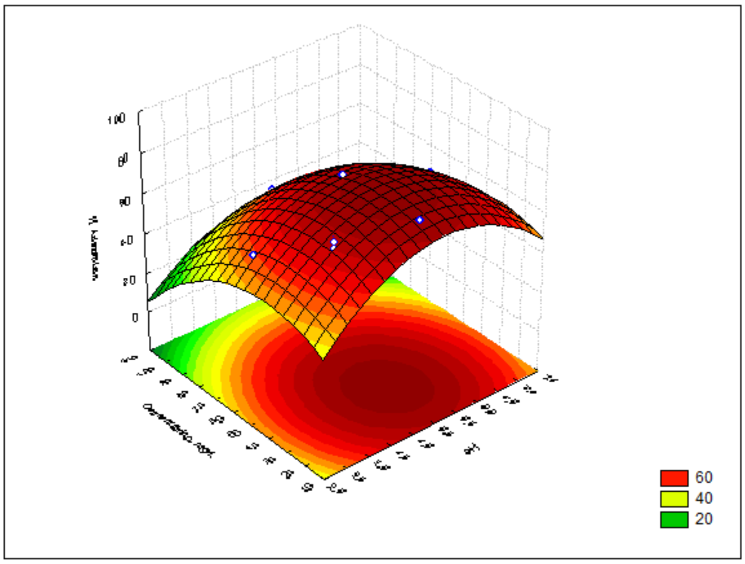

Fig.14. Response surface plot of pH vs concentration for the biosorption of Zinc

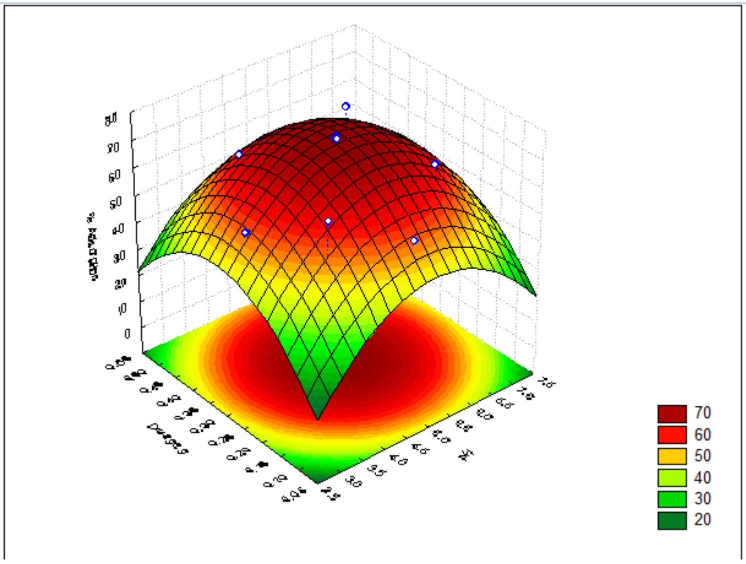

Fig.15. Response surface plot of pH vs dosage for the biosorption of Zinc

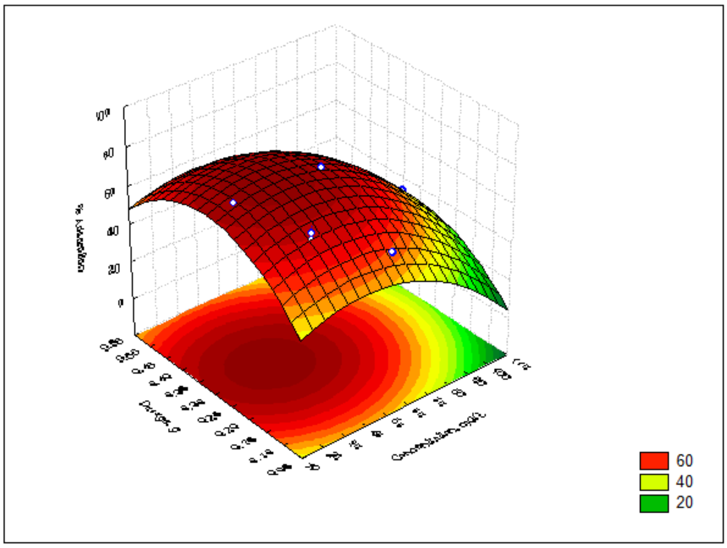

Fig.16. Response surface plot of concentration vs dosage for the biosorption of Zinc

This suggested that the biosorption process is quite fast. Such rapid biosorption process has been correlated with the characteristics of the biomass, and its physico-chemical interactions with the metal ion. The effect of contact time on percentage biosorption of zinc onto Pithophora Cleveana Wittrock was studied over an agitation time of 0.5-30 min, using 0.1 g of Pithophora Cleveana Wittrock, 30 mL of 20 mg/L of metal concentration at pH 5, temperature 303 K and 180 RPM shaking speed. The results depicted in Fig.1 indicate that the percentage biosorption increases from 1.53 to 74.1% for zinc upto contact time of 20 min with 20 mg/L of concentration.

Effect of pH

The pH of the solution affects the surface charge of the biosorbents as well as the degree of ionization and speciation of different pollutants. Change in pH affects the biosorptive process through dissociation of functional groups on the biosorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of biosorption process. The solution pH has been reported to be the most important variable governing the biosorption of metal ions by biosorbents. Accordingly, for obtaining the optimum pH for metal ion biosorption by Pithophora Cleveana Wittrock, the removal of zinc from the aqueous solution was studied at different pH values (Fig.2).

It was observed that the biosorption was very little at the initial pH 2 (5.72% for 20 mg/L of metal solution). The low metal biosorption at pH below 3 may be explained on the basis of active sites being protonated, resulting in a competition between H^+ and M^{2+} for occupancy of the binding sites. A sharp increase in the biosorption occurred in the pH range 3-4 (36.52% at pH value 4 from a solution of concentration of 20 mg/L).

Further increase in biosorption was significant as the optimum biosorption of the zinc metal was reached at a pH value of 5 (76.43%). The pH dependence of metal uptake is due to solubility of metals and the ionization state of various functional groups (carboxylate, phosphate and amino groups) on fungal cell walls. Zinc showed a trend of declining sorption when the pH was increased from 5 to 10. This may be attributed to the lower polarity of zinc ions at higher pH values. Above the pH value of 5, insoluble metal hydroxides start to precipitate and the precipitate was separated before analysis of the samples, and so the biosorption rate was decreased.

Effect of metal ion concentration

Experiments were undertaken to study the effect of initial zinc concentration on the zinc removal from the solution. The results obtained are shown in Fig.3.

From the data it is observed that the zinc metal uptake increases and percentage biosorption of the metals decreases with an increase in the initial metal ion concentration. This increase (4.45 to 13.23 mg/g) is the result of increase in the driving forces i.e. concentration gradient. However, the percentage biosorption of zinc ions on Pithophora Cleveana Wittrock decreased from 74.1 to 44.1%). Though an increase in metal uptake was observed, the decrease in percentage biosorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage biosorption at higher concentration levels shows a decreasing trend, whereas the equilibrium uptake of zinc displays an opposite trend. At lower concentrations, most of the zinc ions present in solution could interact with the binding sites and thus the percentage biosorption was higher than those at higher initial zinc ion concentrations. At higher concentrations, the lower biosorption yield is due to the saturation of biosorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

The effect of biosorbent size

The effect of different biosorbent particle sizes (75-212 µm) on the percentage removal of zinc on Pithophora Cleveana Wittrock was investigated and showed in Fig.4. It reveals that the biosorption of zinc on Pithophora Cleveana Wittrock decreases from (74.81 to 58.5%) with the increase in particle size from 75 to 212 µm with 20 mg/L of zinc concentration in solution. It is well known that decreasing the average particle size of the biosorbent increases the surface area, which in turn increases the biosorption capacity.

Effect of biosorbent dosage

The effect of biosorbent dosage on zinc uptake and zinc percentage removal is shown in Fig.5. This figure shows that the percentage biosorption and zinc uptake increased marginally with the increase in biosorbent dosage. The increase in biosorbent dosage from 0.1 to 0.5 g. resulted in an increase from 74.1 to 76.42% for biosorption of zinc at 20 mg/L. This is because of the availability of more binding sites for complexation of zinc ions. The increase in metal uptake by increasing biosorbent dosage is attributed to many reasons, such as availability of solute, electrostatic interactions, interference between binding sites, and reduced mixing at high biomass densities. Thus, the biosorption sites remain unsaturated during the sorption process due to a lower biosorptive capacity utilization of the sorbent, which decreases the biosorption efficiency. Some of these reasons contributed also in limiting the maximum percentage removal, thus 100% removal was not attained. This suggests that a more economical design for the removal of heavy metal ions can be carried out using small batches of sorbent rather than in a single batch.

Effect of Temperature

The rate of biosorption is a function of initial metal ion concentration as well as its temperature. The percent biosorption of zinc onto Pithophora Cleveana Wittrock is shown in Fig.6 as a function of the initial metal ion concentration at 303, 313, 323 and 333 K. The percentage biosorption of zinc ions on Pithophora Cleveana Wittrock decreased from 74.1 to 60.35% as the temperature increased from 303 to 333 K at 20 mg/L. The percentage biosorption at higher temperature levels shows a decreasing trend because at lower temperatures, all zinc ions present in solution could interact with the binding sites and thus the percentage biosorption was higher than those at higher temperatures. This happens because of more interaction of the ions in solution due to convection. At higher temperatures, lower biosorption yield is due to the mobilization of ions in solution because of highly energized ions. As a result, the purification yield can be increased by reducing the temperature. The decrease of the percentage biosorption at increased temperature indicated that the biosorption of zinc ions to Pithophora Cleveana Wittrock is exothermic in nature.

Studies on biosorption isotherms

Freundlich Isotherm

This empirical model can be applied to nonideal sorption on heterogeneous surfaces as well as multilayer sorption. The Freundlich expression is an empirical equation based on biosorption onto a heterogeneous surface. The Freundlich equation is represented as,

$$q_{eq} = K_f C_{eq}^n \quad \text{.......... (2)}$$

where K_f and n are Freundlich constants characteristic of the system. K_f and n are indicators of biosorption capacity and biosorption intensity, respectively. Eq. (2) can be linearized in logarithmic form and Freundlich constants can be determined. The logarithmic plot of sorbed and equilibrium concentration gives a straight line with a coefficient of determination close to unity (0.925 for zinc). The value of 1/n (0.359 for zinc g/L) and K_f (1.431 for zinc mg/g) are derived from the slope and intercept of the straight line for zinc which is shown in Fig.7. and tabulated in Table 1.

The magnitude of K_f and *1/n* shows easy separation of zinc ions from aqueous solutions with high biosorptive capacity of Pithophora Cleveana Wittrock, especially at 303±1 K and pH = 5.0.

Langmuir Isotherm

The Langmuir model is probably the best known and most widely applied sorption isotherm. It has produced good agreement with a wide variety of experimental data. The Langmuir equation has been used extensively for dilute solutions in the following form,

$$q_{eq} = \frac{Q_{\max} b C_{eq}}{1 + bC_{eq}} \quad \text{........ (3)}$$

where $Q_{\max}$ is the maximum amount of the metal ion per unit weight of biosorbent to form a complete monolayer on the surface bound at high C_{eq} (mg/g), and b is a constant related to the affinity of the binding sites (L/mg). $Q_{\max}$ represents a practical limiting biosorption capacity when the surface is fully covered with metal ions and assists in the comparison of biosorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. $Q_{\max}$ and b can be determined from the linear plot of C_{eq}/q_{eq} Vs C_{eq}. In Fig.8 C_e/q_e is plotted against C_{eq} yielding a straight line with R^2 (0.996) indicating that sorption data fit well into the Langmuir model. The value of Qmax (11.890 mg/g for zinc) was calculated from the slope of the linear plot, whereas the value of b (0.1288 L/mg for zinc) was derived from the intercept for zinc ions. From the value of b, a dimensionless parameter, K_R was estimated using the following equation

$$K_R = \frac{1}{1 + bC_i} \quad \text{.......... (4)}$$

The values of K_R for zinc at different concentrations are shown in Fig.9. The K_R values indicated that biosorption is higher at lower concentrations of zinc than higher concentrations. However, the Pithophora Cleveana Wittrock would be an effective biosorbent for removing zinc from solution. K_R values are shown in Table-2.

Redlich-Peterson Isotherm

Redlich and Peterson incorporated the features of the Langmuir and Freundlich isotherms into a single equation and presented a general isotherm equation. It can be portrayed as

$$q_{eq} = \frac{AC_{eq}}{1 + BC_{eq}^g} \quad \text{......... (5)}$$

where A (L/g) and B (L/mg) are the Redlich-Peterson isotherm constants and g is the Redlich Peterson isotherm exponent, which is in between 0 and 1. The linearized form of the equation is given by:

$$\ln\left(\frac{AC_{eq}}{q_{eq}} - 1\right) = g \ln\left(C_{eq}\right) + \ln(B) \quad \text{..........(6)}$$

Redlich-Peterson isotherm equation contains three obscure parameters A, B and g. where upon, a minimization technique is embraced to boost the coefficient of determination, between the theoretical information for q_{eq} anticipated from the linearized type of Redlich-Peterson isotherm equation and the experimental trials.

Fig.10 shows the plot between $\ln\left(\frac{AC_{eq}}{q_{eq}} - 1\right)$ versus *ln* (C_{eq}). The calculated Redlich-Peterson constants and their corresponding linear regression coefficient of determination is shown in Table-1.

Temkin Isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is more linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has generally been applied in the following form:

$$q_{eq} = \frac{RT}{b_T}\ln\left(A_T C_{eq}\right) \qquad \ldots\ldots\ (7)$$

where A_T (L/mg) and b_T are Temkin isotherm constants.

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on biosorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions (Aksu 2002). The biosorption data were analyzed according to the linear form of the Temkin isotherm and the linear plots are shown in Fig.11. Examination of the data shows that the Temkin isotherm provides a close fit to the zinc biosorption data. The linear isotherm constants and coefficients of determination are presented in Table-1.

D–R Isotherm

Dubinin–Radushkevich isotherm is generally used to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Dabrowski, 2001). The D–R equation is given by the accompanying relationship:

$$q_e = q_o e^{-K_d \varepsilon^2} \qquad \ldots\ldots\ (8)$$

where q_e is the measure of the metal ions adsorbed at the equilibrium conditions, K_d identified with the mean free vitality of sorption, q_o is the infusion capacity obtained from the theoretical data, and ε is the Polanyi potential. The values of q_m and K_d can be obtained by plotting $\ln q_e$ versus ε^2 (Dubinin 1960).

The Dubinin–Radushkevich (D–R) constant can be applied to identify the mean energy of biosorption by the following equation

$$E = \frac{1}{\sqrt{2K_d}} \qquad \ldots\ldots\ (9)$$

As the root mean square measures the deviation of experimental and calculated values, it was utilized to decide how well models speak to the experimental data. The mean free energy change of biosorption (E) can be figured using eq. (9). The magnitude of E can be utilized for assessing the sort of biosorption. The biosorption behavior can be depicted as the physical biosorption when the mean biosorption energy (E) is somewhere around 1.0 and 8.0 kJ/mol. However, the chemical biosorption is more than 8.0 kJ/mol of the mean biosorption energy (Mahramanlioglu *et al*., 2002). 'E' of zinc is represented in Table-1. The calculated E value is 7.11 kJ/mol for zinc and found to be in the range of a typical free energy attributed to physical biosorption and chemical interactions. Comparative perceptions were accounted in different studies (Singh and Pant 2004, Seki and Yurdakoc 2005, Foo and Hameed 2010). Temperature dependence is one of the remarkable feature of the Dubinin-Radushkevich (D–R) isotherm model which shows that when the biosorption data at different temperatures are plotted as a function of the logarithm of the amount biosorbed ($\ln q_e$) vs ε^2 the square of potential energy (Fig.12), all suitable data will lie on the same curve, named as the characteristic curve (Kaewsarn and Yu 2001).

All the four equilibrium models were fitted to the equilibrium data. Table-1 represents the calculated isotherm constants. Based on the linear regression correlation coefficient R^2 the best fit equilibrium model is determined. From the table it was evident that the sorption data very well represented by Langmuir isotherm for zinc with an average higher correlation coefficient of 0.996, followed by D–R, Freundlich, Temkin, and Redlich-Peterson with a correlation coefficient of 0.9484, 0.925, 0.903 and 0.81 respectively. The strong electrostatic force of attraction is indicated by the higher biosorption capacity Q_{max} (>>1) (Kamsonlian and Shukla 2013).

Experimental design using the CCD Model

The typical experimental procedure, one factor at a time technique, can rarely be used to set up relationships among the entire experimental input factors and the output responses. Although the traditional technique can be applied to find the predominant factors, it is a time consuming system. Moreover, in view that the outcomes are valid handiest only under fixed experimental conditions so the prediction for different conditions is uncertain. To resolve this hindrance, design of experiment (DOE) offers higher substitute to study the outcomes of variables and their responses with less number of experiments.

Utilizing DOE based on response surface methodology (RSM), the total mix proportions can be achieved with minimal number of experiments without the necessity for finding out all viable combination tests. Further the input phases of the different variables for a unique level of response will also be decided. RSM is a group of statistical procedure for designing experiments, constructing units, evaluating the results of factors and searching for the most appropriate conditions of the factors. RSM additionally quantifies relationships among one or more measured responses and the vital input reasons. The RSM includes various designs, with their own properties and traits. Critical composite design (CCD), field-Behnken design and three-degree factorial design is probably the trendiest designs practically used by the researchers. The CCD was used to interpret the results of the variables towards their responses and subsequently within the optimization studies. It is held by adding two experimental points along each coordinate axis at opposite sides of the origin and at a length equal to the semi - diagonal of the hyper cube of the factorial design. The new acute values (low and high) for each parameter are summed in this model (Kumar *et al*., 2008). In this study four parameters: pH of the solution, initial zinc concentration in the solution (C_o), biosorbent dosage (w) are considered and thus k=3 and α= 2 which is calculated from the following equation

$$\alpha = \left[2^k\right]^{\frac{1}{4}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots..(9)$$

The optimization of zinc uptake was carried out by three chosen independent factors. The ranges and levels of variables investigated in the research are given in Table-3. Therefore, CCD with four factors is applied using STATISTICA 6.0 with the bounds of initial pH = 3–7, w = 0.1–0.5 g, C0 = 20–100 mg/L as shown in Table-3. Total sixteen experiments are required to calculate the coefficients of second-order polynomial equation which were fitted with experimental data. The total number of experimental points (N) in a CCD is calculated from the following equation:

$$N = 2k + 2k + X_o \qquad \text{……………………(10)}$$

X_o is the number of central points. Thus, total number of experimental runs, N= 16 (k=3; X_o = 1 and α= 2 from eq.10. The experimental data from CCD was fitted with a second-order polynomial model and the following regression equation was obtained for the biosorption of zinc:

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x^2{}_i + \sum\sum_{i<j}^{k} \beta_{ij} x_i x_j + \in \qquad \text{…………..(11)}$$

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. To test the statistical significance of each model term in the equation and the goodness of fit of the regression model, Analysis of variance (ANOVA) is utilized.

Development and Statistical analysis

In this work, RSM is used to seek out the most efficient values of the method parameters which incorporate pH, metallic ion concentration and biosorption dosage as shown in Table-3. CCD is applied to obtain a correlation between the biosorption of the wastewater and the process variables investigated. The quadratic model suggested by the software is selected. Experiments are decided to obtain a quadratic model consisting of 16 trials consisting of 1 replicate at the center point. The design of this experiment is given in Table-4, along with the experimental values and predicted values. The maximum biosorption is >99 %. Regression analysis is performed to fit the response function of zinc biosorption. The coded values of variables in eq. 13 represent % zinc biosorption (Y) as a function of pH ($X1$), concentration ($X2$), dosage ($X3$). The data acquired was fitted to a second-order polynomial equation. Regression analyses, ANOVA and response surfaces were executed using the Design Expert Software (Version 8.0.7.1) subsequently. The experimental data with multiple regression analysis was obtained from the following regression equation for the biosorption of zinc:

$$\% \text{ biosorption} = -104.455+48.229X_1+0.816X_2+290.389X_3-4.569X_1^2-0.009X_2^2 -436.402X_3^2-0.021X_1 X_2-2.856X_1 X_3-0.097X_2 X_3 \qquad \text{………………..(10)}$$

Where X_1, X_2 and X_3 are the code values for the independent variables, $X_1 X_2$, $X_1 X_3$, $X_2 X_3$, X_1^2, $X_2^2$and X_3^2 are the significant model terms for the biosorption of zinc.

Analysis of variance

The criticalness of the second–order polynomial equation is assessed by the F-test of ANOVA as represented in Table-5. Probability>F value indicates the competence of any model. The model has prob>F values less than 0.0001 means that the experimental data obtained can be experimentally explained with 99% accuracy by the model generated by RSM (Myers and Montgomery 2002) whereas a low p-value (<0.05) indicates that the model is considered to be statistically valid (Kaewsarn and Yu 2001). The F-value of 2893.798 and p-value of <0.0001 represent that the model is statistically significant. The interrelationship of the free variables and response can be elucidated by the regression model as shown in Table-6. The model is most appropriate by determination of correlation R^2, 99.8% (0.998) value which is close to 1 (Garg 2008). In this model X_1, X_2 and X_3 represents the pH, Concentration, Dosage respectively. Table-7 gives a relationship between the experimental values and predicted values by setting up the legitimacy of the model furthermore shows that they are in nearby concurrence with each other. The actual and the predicted percentage biosorption of zinc are shown in Fig.13.

Interaction effects of biosorption variables

The % biosorption of zinc with the definite set of free variables is pictured through three-dimensional perspective of response surface plots (Figs.14-16). All the response surface plots report that at low and high levels of variables, the % biosorption by the biosorbent is maximal; however, there exists a section where neither an extending nor a decreasing pattern in the % biosorption is taken note. This special case affirms that there is a vicinity of perfect condition for the biosorption variables to support the % biosorption. The pH assumes an imperative in % biosorption as is apparent from the plots (Figs.14-16). A comparatively strong association was seen between pH with C_o, pH and w which is reflected by the corresponding P values *0.038397, 0.125712* and *0.277396* respectively as deduced from the curvature of the contour. The 'C_o' of the biosorption has appreciable amounts of interaction effect with pH (P = *0.038397*) from Fig.15.

Optimization by response surface modeling:

The metal ion concentration 37.6 mg/L, pH 5.09, biosorbent dosage 0.3 g was determined as the optimum biosorption conditions in batch studies for the biosorbent Pithophora Cleveana Wittrock. The model support has been portrayed as ideal levels of the process variables, foreseen by the model to perform the greatest % biosorption of 78.97.

Conclusion

The Pithophora cleveana Wittrock was assessed to be one of the conceivable biosorbent for the expulsion of zinc from wastewaters. The zinc biosorption was impacted by pH, contact time, initial metal ion concentration, biosorbent dosage and biosorbent size and temperature. The most extreme biosorption 74.10% was observed at pH 5.0 and contact time of 20 minutes. Zinc biosorption fits best in equilibrium data by Langmuir and DRK isotherms with R^2 value of 0.996. CCD in RSM was used to locate the optimal conditions for the maximum percentage removal of zinc. The perfect conditions were at pH 5.09, metal ion concentration 37.6 mg/L, biosorbent dosage 0.3g and correlation coefficient of 0.998 with an biosorption of 78.97%.

Henceforth, this model can be adequately used to focus on the importance the individual, combined and immediate effects of distinctive test variables of biosorption.

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