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Optimization of Lead Biosorption by an Ecofriendly Biosorbent *Mimusops elengi* Using Central Composite Design.

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ABSTRACT

The choice of an appropriate biosorbent for the removal of lead from the wastewater effluents was demonstrated. Batch studies were adopted to investigate the effectiveness of *Mimusops elengi* leaves for the biosorption of lead from aqueous solutions at an optimum pH 5, metal ion concentration 20 mg/L, biosorbent dosage 0.1g and temperature 303 K at an equilibrium agitation time of 180 min. Based on the experimental results, pH, metal ion concentration and biosorbent dosage were optimized using Central Composite Design (CCD). The isotherm models Langmuir, Freundlich, Temkin, Redlich-Peterson and Dubinin-Radushkevich (D-R) were applied to analyze the fitness of the equilibrium data. Langmuir isotherm with an average higher correlation coefficient of 0.984 was fitted well with the experimental data. Confirmatory experiments conducted at the suggested optimized conditions showed experimental findings within 5% of the proposed values. The sorption process was found to be mostly a physiosorption process as witnessed from the apparent energy of adsorption 7.106 kJ/mol. Overall, the outcomes evidenced that the model and experimental data were favorable on the removal of Lead and also confirms that *Mimusops elengi* could be utilized as an ecofriendly and cost-effective approach for the removal of Lead from aqueous solutions.

Keywords: Lead, biosorption, *Mimusops elengi* leaves, Central Composite Design (CCD), Equilibrium, Physiosorption

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INTRODUCTION

Universally, scientists are concerned all the more on the fast industrialization, which lays a guide for the release of modern wastes, particularly those containing substantial metals, into regular water bodies or ashore that if discharged untreated would have an inconvenient impact on the earth and human wellbeing. Overwhelming metals like chromium, copper, lead, manganese, mercury are normal toxins in soil and in accession in water. Because of their more noteworthy soundness they can't be debased and expelled from the earth.

Release of heavy metals from various industries such as mining, ore cognitive processing, smelting and alloy plating can easily cause metal pollution and has detrimental effects on human beings, animals and environmental balances. The United States Environmental Protection Agency (USEPA) issued a list of organic and inorganic pollutants which are uncovered in wastewater and constitute serious wellness hazards [1]. The most hazardous alloys listed in the report are antimony, arsenic, chromium, lead, quicksilver, etc. The presence of metal ions in natural or industrial wastewater, their potential, and sequestration has been a topic of capital importance in environmental restoration over the past two decades. Lead is among a standout amongst the most metallic elements found in the environment and a cumulative poison. It can trigger both intense and unending side effects of inebriation. Its high attraction for proteins leads to inhibition of the red blood cells and the vital transfer of oxygen. Such poisoning leads to encephalopathy in the fundamental neural systems, necrosis in kidney, and damage to the reproductive organs, anemia and many metabolic deficiency symptoms. The Environmental Protection Agency (EPA) standards for lead in wastewater and drinking water are 0.5 and 0.05 mg/L respectively [2]. Several methods were used for the treatment of wastewater includes precipitation, adsorption with activated carbon, ion exchange, membrane processes, oxidation and adsorption with activated carbon, ion exchange, membrane processes [3]. But, technical and economic factors limit sometimes the feasibility of such process [4, 5]. The promising method for heavy metal removal from wastewater is biosorption. Biosorption is a term that describes metal removal by passive binding in living and dead biomass from aqueous solutions in a mechanism that is not controlled by metabolic steps. The metal linkage is based on the chemical properties of the cellular envelope without requiring biologic activity [6, 7, 8]. The process occurs through interactions between metal species and active sites (carboxyl, amino, sulfate, etc.) present on the cell wall [9]. Recently, there has been an intensive study on the use of seeds, pods, and bark of plants which is called as biomass in removing heavy metals from wastewater. In addition, studies have been carried out to ascertain the optimum conditions necessary for efficient removal of these metals from polluted sites.

The aim of this investigation is to look into the potential of the leaves of *Mimusops elengi* to adsorb lead ions from aqueous solutions. The factors studied include pH, contact time, dosage, temperature, the size of the biosorbent and metal ion concentration. Experimental data were obtained by using Langmuir, Freundlich, Redlich-Peterson, Temkin, Dubinin-Radushkevich adsorption models to describe the equilibrium isotherms and to determine the isotherm constants. The drawbacks in conventional optimization methods are eliminated by optimizing all the parameters collectively by Central Composite Design (CCD) [10] using Response Surface Methodology (RSM).

MATERIALS AND METHODS

Preparation of *Mimusops elengi* biosorbent

The *Mimusops elengi* leaves used in the present study were collected in the garden of GMRIT, Rajam, Andhra Pradesh, INDIA. The piled up leaves were washed with deionized water several times to get rid of soil particles. The washing procedure was kept till the washwater contains no malicious dirt. The washed leaves 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 lead concentration 1000 mg/L was prepared by dissolving 1.598 g of lead nitrate 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 lead stock solution, which were obtained by dissolving in deionized water.

Chemicals utilized

Metal ion solutions were prepared by diluting stock metal ion solutions, which were obtained by dissolving weighed quantity of lead nitrate of analytical reagent grade obtained from MERCK (India) in double distilled water. The final concentration of metal ions was analyzed by atomic absorption spectrophotometer (AAS) was done by using its specific lamp for metal and at a specific wavelength.

Batch biosorption experiments

Biosorption studies were carried out at room temperature 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 . After shaking, the samples were withdrawn at suitable time intervals and then analyzed for lead concentration with AAS. The flasks were shaken for 3 hours to attain equilibrium. A known volume of the solution was removed and filtered for lead analysis. The amount of lead biosorbed was determined by the difference between the initial and the equilibrium concentrations.

METAL BIOSORPTION CAPACITY

In order to evaluate the amount of lead ions retained per unit mass of *Mimusops elengi*, the adsorption capacity was calculated using the following equation:

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

where V is the volume of the solution in mL and w is the mass of the biosorbent in g. Preliminary experiments had shown that metal biosorption losses to the flask walls and to the filter paper were negligible. All the experiments were repeated three times and the average values have been reported. Also, blank experiments were conducted to ensure that no biosorption was taking place on the walls of the apparatus used.

BIOSORPTION ISOTHERMS

Five important isotherms were applied to test the fit of data and also used for characterization of the interaction of lead with the biosorbent.

The Langmuir isotherm model is legitimate for a single layer sorption capacity onto the surface and limited number of indistinguishable sites and given by Eq. (2)

$$q_{eq} = \frac{Q_{max} b C_{eq}}{1 + b C_{eq}} \quad (2)$$

where Q_{max} is the constant representing the metal particle per unit weight of cells to form a complete single layer at high adsorption capacity C_{eq} (mg/g) and b is the direct measure identified with the partiality of the coupling destinations. Q_{max} speaks to a handy restricting adsorption limit when the surface is completely secured with metal particles and helps with the correlation of adsorption execution, especially in situations where the sorbent does not achieve its full saturation in trials. Q_{max} and b can be resolved from the linear plot of C_{eq}/q_{eq} versus C_{eq} .

The Freundlich isotherm model is developed to study the adsorption characteristics of a surface which is heterogeneous in nature and is generally related with an empirical Eq. (3)

$$q_{eq} = K_f C_{eq}^n \quad (3)$$

Where K_f and n are Freundlich constants that affect the adsorption process of a system. K_f and n are an index for adsorption capacity and intensity, respectively. The slope and intercept obtained from the linear plot between $\ln q_{eq}$ and $\ln C_{eq}$ will be used to calculate the values of K_f and n . The Freundlich isotherm is also extensively used, but the drawback is that it doesn't provide any information on the single layer adsorption capacity as in the Langmuir model.

Jossens and associates [11] altered the three parameter isotherm initially proposed by Redlich and Peterson [12] to consolidate components of both the Langmuir and Freundlich comparisons. It can be portrayed as

$$q_{eq} = \frac{AC_{eq}}{1 + BC_{eq}^g} \tag{4}$$

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:

$$\ln\left(\frac{AC_{eq}}{q_{eq}} - 1\right) = g \ln(C_{eq}) + \ln(B) \tag{5}$$

Redlich-Peterson isotherm equation contains three obscure parameters A , B and g whereupon, 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.

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:

$$q_{eq} = \frac{RT}{b_T} \ln(A_T C_{eq}) \tag{6}$$

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

Dubinín–Radushkevich isotherm is generally used to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [13]. The D–R equation is given by the accompanying relationship:

$$q_e = q_o e^{-K_d \epsilon^2} \tag{7}$$

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 [14].

The D–R constant can be applied to identify the mean energy of adsorption by the following equation

$$E = \frac{1}{\sqrt{2K_d}} \tag{8}$$

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.

RESPONSE SURFACE METHODOLOGY (RSM)

RSM is widely used tool by an association between mathematical and statistical techniques for developing, refining and optimizing the operations. RSM usually contains three steps: (i) design and experiments; (ii) response surface modeling through regression and (iii) optimization. The basic objective of RSM is to find the optimal operating conditions of the central processing unit to determine a region that meets the operating specifications. The application of statistical experimental design techniques in adsorption development can result in better product yields, closer affirmation of the output response to nominal and target requirements and shortened development time and general costs [15, 16]. Among the varieties of factorial designs available, Central Composite Design (CCD) is the more viable design. 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 [17]. For a full factorial

$$\alpha = \left[2^k\right]^{\frac{1}{4}} \tag{9}$$

In this study, three parameters: pH of the solution, initial lead concentration in the solution (C_0) and biosorbent dosage (w) were considered and thus $k=3$ and $\alpha= 2$ from eq.9. Furthermore, the total number of experimental points (N) in a CCD is calculated from the following equation:

$$N = 2k + 2k + X_0 \tag{10}$$

X_0 is the number of central points. Thus, total number of experimental runs, $N= 16$ and $X_0 = 1$ from eq.10.

Therefore, CCD with three factors is applied using STATISTICA 6.0 with the bounds of initial pH = 3–7, $w = 0.1\text{--}0.5$ g, $C_0 = 20\text{--}100$ mg/L as shown in Table-3. Pursuance of the process is evaluated by analyzing the response of biosorbent for lead ions. The response (y) is % adsorption of lead. 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 reckoners of the numerical model [18].

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i<j}^k \beta_{ij} x_i x_j + \epsilon \tag{11}$$

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. STATISTICA 6.0 is used for regression analysis of the data and to evaluate the coefficient of the 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 RSM is applied to forecast the result by contour plots in order to examine the individual and cumulative effects of the variables and the mutual interactions between the variables on the dependent variable.

RESULTS AND DISCUSSION

The effect of contact time

Figure 1. shows the effect of contact time on the biosorption of lead by *Mimusops elengi*. The optimum contact time for the biosorption of lead on *Mimusops elengi* can be observed by knowing the difference in absorbance of lead solution after adding *Mimusops elengi* biomass at different contact times. It could be observed that the biosorption of lead increased with contact time and attains equilibrium at about 180 min for *Mimusops elengi*. It shows that the biosorption of lead remained constant, implying equilibrium has been reached.

The results in the Figure 1. depicts that the percentage biosorption, increased from 13.52 to 85.67% at a contact time of 180 min with 20 mg/L metal concentration. A similar procedure was repeated for 40, 60, 80 and 100 mg/L metal concentrations of lead and the results showed the same contact time of 180 min, as optimum time and further biosorption experiments were conducted at this contact time.

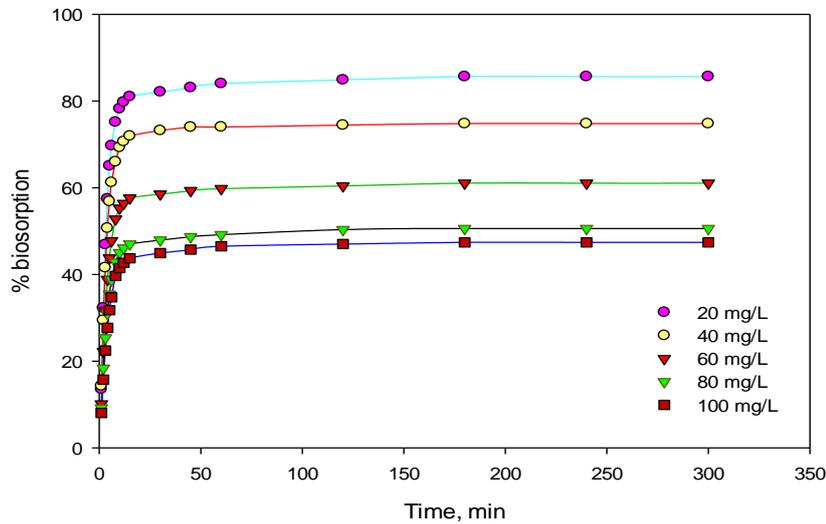


Fig.1. Effect of contact time on biosorption of Lead by *Mimusops elengi* of 0.1 g/30 mL of biosorbent concentration.

Effect of pH

It was well recognized that the pH of the medium affects the solubility of metal ions and the adsorption of the counter ions on the working groups of the biomass cell walls. Thus pH is an important process parameter on adsorption of metal ions from aqueous solutions. *Mimusops elengi* presents a high content of ionizable groups on the cell wall polysaccharides, which makes it very liable to the influence of the pH.

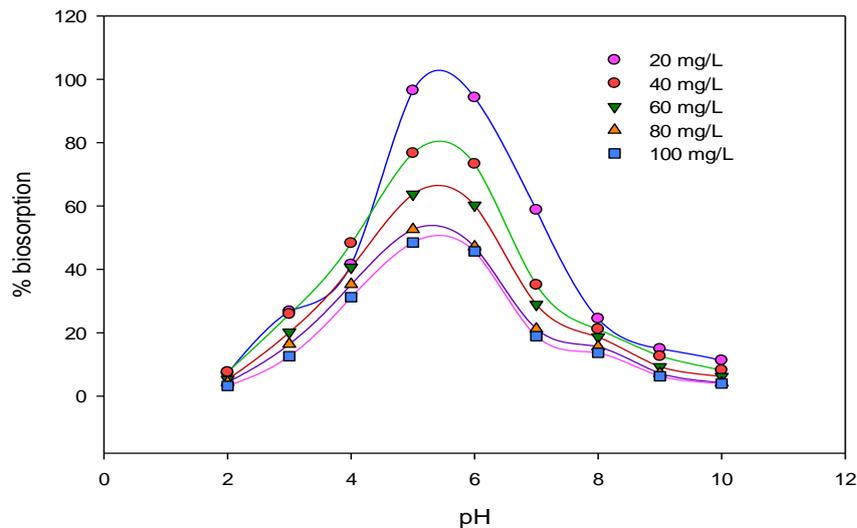


Fig.2. Effect of pH on biosorption of Lead by *Mimusops elengi* of 0.1 g/30 mL of biosorbent concentration.

It was observed from the Figure 2 that the biosorption was very little at the initial pH 2 (7.25 %) at 20 mg/L of metal ion concentration. The low metal adsorption at pH below 3 may be explained on the basis of

active sites being protonated, resulting in a competition between H⁺ and M²⁺ for occupancy of the binding sites. A sharp increase in the biosorption occurred in the pH range 3-4 (41.52% at pH 4 for a solution of concentration of 20 mg/L). The increase in metal removal as the pH increases can be explained on the basis of decrease in competition between protons and metal cations for the same functional groups and by a decrease in the positive surface charge resulting in a lower electrostatic repulsion between the surface and metal ions. Further increase in biosorption was significant as the optimum biosorption for lead reached at pH 5 (96.43 %).

Effect of metal ion concentration

The saturation period of the adsorption is entirely independent of the initial concentration. The relationship between the initial metal ion concentration of lead and percent metal ion removed from aqueous solution using *Mimusops elengi* observed was plotted in Figure 3. It could be observed that the biosorption capability of lead by *Mimusops elengi* decreased when the initial metal concentration increased up to 100 mg/L. It was noted that the metal uptake of lead increased and percentage biosorption of the metal decreased with an increase in the initial metal ion concentration. The addition of 5.14 to 14.226 mg/g for lead is an outcome of the increase in the driving forces i.e. concentration gradient. However, the percentage biosorption of lead on *Mimusops eleng* decreased from 85.67 to 47.42%. For fixed biosorbent dosage, the total available adsorption sites are limited thereby adsorbing almost the same measure of support thus resulting in a reduction in the percentage removal of the adsorbate corresponding to an increase in initial support concentration. Though an increase in metal uptake was observed, the reduction in percentage biosorption may be ascribed to lack of sufficient surface area to fit lots more metal available in the solution. The percentage biosorption at higher concentration levels shows a decreasing trend, whereas the equilibrium uptake of lead displays an opposite tendency. At lower concentrations, almost all the lead ions present in solution could interact with the binding sites and therefore the percentage biosorption was higher than those at higher initial lead ion concentrations. At higher concentrations, the lower biosorption yield is due to the saturation of adsorption sites. As a consequence, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

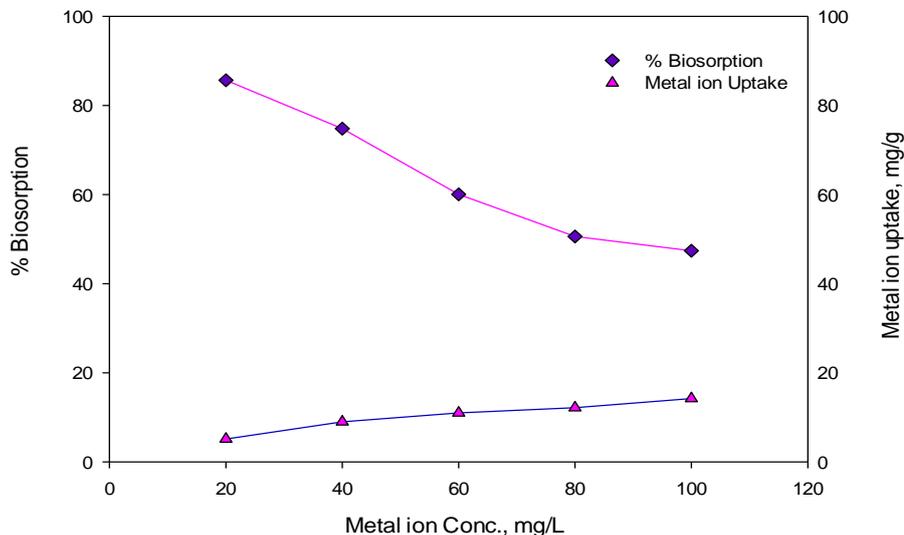


Fig.3. Effect of metal ion concentration on the biosorption capacity of Lead by *Mimusops elengi* of 0.1 g/30 mL of biosorbent concentration.

The effect of biosorbent size

The surface contact between any biosorbent and the liquid phase plays an important role in the phenomena of biosorption. The effect of particle size of *Mimusops elengi* on lead removal was studied using four particle sizes (75-212 μm). Figure 4 shows that the capacity of lead adsorption at equilibrium increased with the decrease of *Mimusops elengi* particle size indicated that lead ion biosorption occurs by a surface mechanism. It reveals that the adsorption of lead on *Mimusops elengi* decreased from 85.67 to 64.18% with

an increase in particle size from 75 to 212 μm with 20 mg/L of lead concentration in solution. A marginal decline was also observed in uptake of lead with an increase in size of the particle. Similar results were obtained for polymers and their derivatives [19, 20]

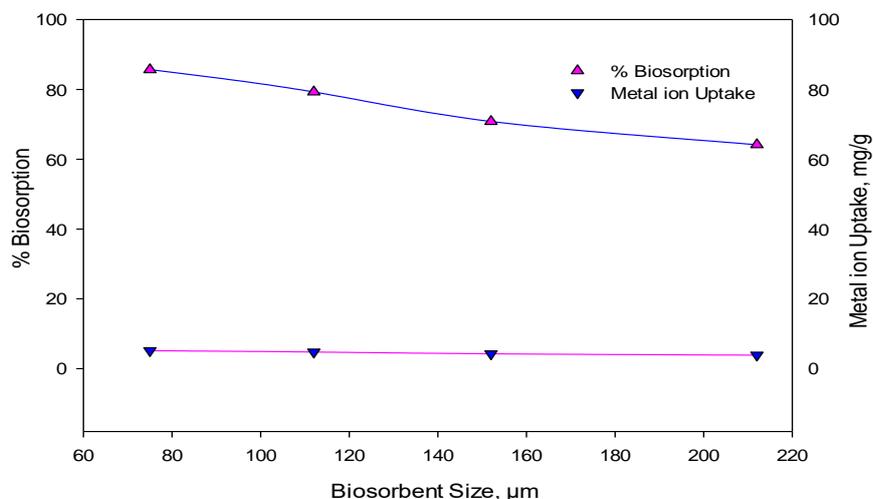


Fig.4. Effect of biosorbent particle size on biosorption of Lead for 20mg/L of metal conc. and 0.1g/30mL of biosorbent concentration.

Effect of biosorbent dosage

To determine the necessary *Mimusops elengi* quantity for a maximal removal of lead, the effect of *Mimusops elengi* mass, on removal of lead was studied. Figure 5 shows that the capacity of lead biosorption at equilibrium by *Mimusops elengi* increased with an increase in the quantity of *Mimusops elengi* (0.1 to 0.5 g). This can be explained by the fact that if the mass is more the surface of contact offered to the biosorption of lead is more and hence becomes important in the removal of more adsorbate. The amount of lead biosorbed increased with an increase in biosorbent dosage from 0.1 to 0.5 g at an initial concentration of 20 mg/L. The percentage lead removal was marginally increased from 84.93 to 85.92% for an increase in biosorbent concentration from 0.1 to 0.5 g. This shows that very small dosage of biosorbent i.e. 0.1g is sufficient to treat about 30 mL of 20 mg/L lead concentration solution effectively. This obviously proves to be advantageous over conventional adsorbents like activated charcoal, coconut shells, etc., which required more than 5g for the same removal of metals.

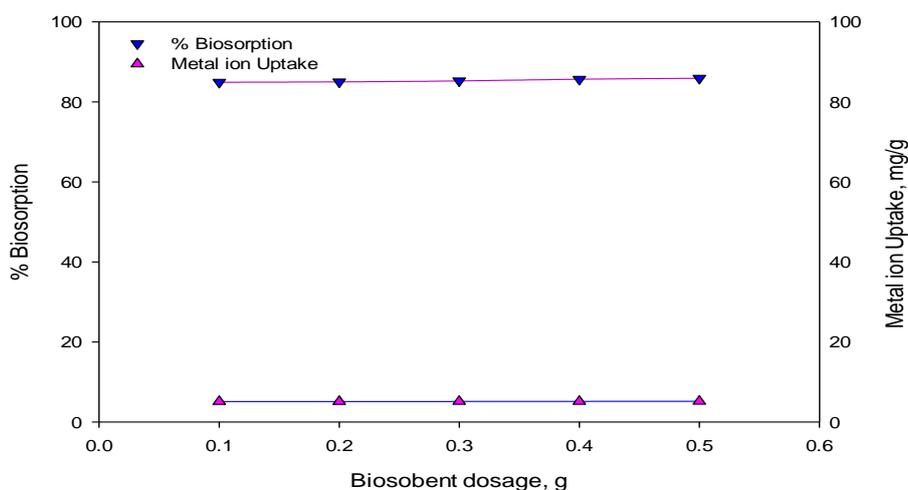


Fig.5. Effect of biosorbent dosage on biosorption of Lead for 20 mg/L of metal ion concentration.

Effect of Temperature

To study the effect of temperature of lead adsorption by *Mimusops elengi*, experiments were conducted at temperatures: 303, 313, 323 and 333 K. The results obtained are presented in Figure 6 which indicate that an increase in temperature decreased the percentage biosorption of lead ions on *Mimusops elengi* from 85.67 to 47.42%. The percentage biosorption at higher temperature levels shows a decreasing trend because at lower temperatures, all lead 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 adsorption 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. If biosorption is governed only by physical phenomena, an increase in temperature will be followed by a decrease in adsorption capacity [21]. The decrease of the percentage adsorption at increased temperature indicated that the adsorption of lead ions to *Mimusops elengi* is exothermic in nature. Similar results were also obtained by using the *Azadirachta indica* for the removal of lead [22].

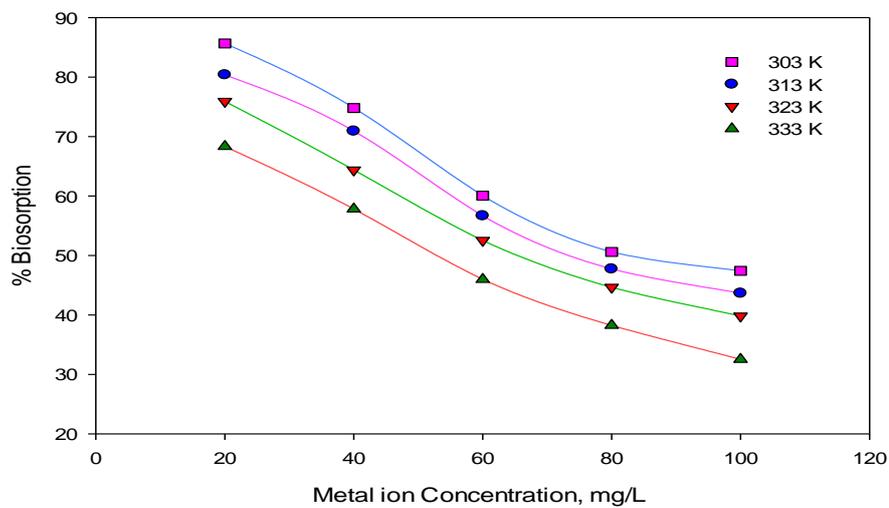


Fig.6. Effect of temperature on biosorption of Lead by *Mimusops elengi* for 0.1 g/30 mL of biosorbent concentration.

Equilibrium Studies to fit experimental data

Freundlich Isotherm

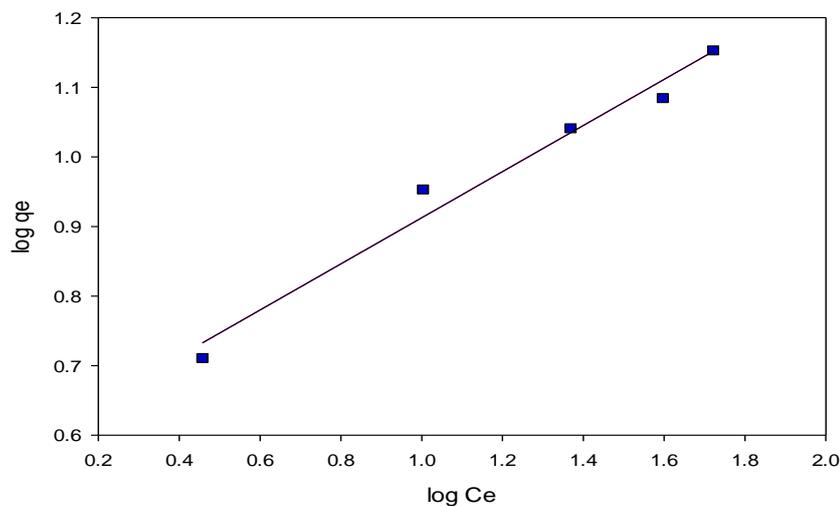


Fig.7. Freundlich adsorption isotherm at 0.1 g/30 mL of biosorption concentration.

Logarithmic plot of sorbed and equilibrium concentration gives a straight line with a coefficient of determination close to unity (0.9766). The value of $1/n$ (0.331 g/L) and K_f (1.392 mg/g) were derived from the slope and intercept of the straight line which is shown in Figure 7 and tabulated in Table 1. The magnitude of K_f and $1/n$ shows easy separation of lead ions from aqueous solutions with high adsorptive capacity of *Miliusa tomentosa*, especially at 303 ± 1 K and pH = 5.0.

Table-1. Equilibrium constants for Lead onto *Mimusops elengi*

Langmuir Isotherm			
$Q_{max} (mg / g)$	$b(L/mg)$	R^2	--
15.408	0.1338	0.984	--
Freundlich Isotherm			
$K_f (mg / g)$	$1/n (g / L)$	R^2	--
1.392	0.331	0.9766	--
Redlich-Peterson Isotherm			
$A (L/g)$	$B (L/mg)$	g	R^2
5.805	3.261	-0.3582	0.1206
Temkin Isotherm			
$A_T (L/mg)$	b_T	R^2	--
2.03	865.71	0.982	--
D-R Isotherm			
$K_d (Mol^2 kJ^{-2})$	$Q_0 mg / g$	R^2	$E kJ / mol$
0.0099	29.18	0.7874	7.106

Langmuir Isotherm

In Figure 8, C_e/q_e was plotted against $C_e q$ yielding a straight line with R^2 (0.984) indicating that sorption data fitted well with the Langmuir model. The value of Q_{max} (15.408 mg/g for lead) was calculated from the slope of the linear plot, whereas the value of b (0.1338 for lead) was derived from the intercept. From the value of b , a dimensionless parameter, K_R was estimated using the following equation

$$K_R = \frac{1}{1 + bC_i} \tag{12}$$

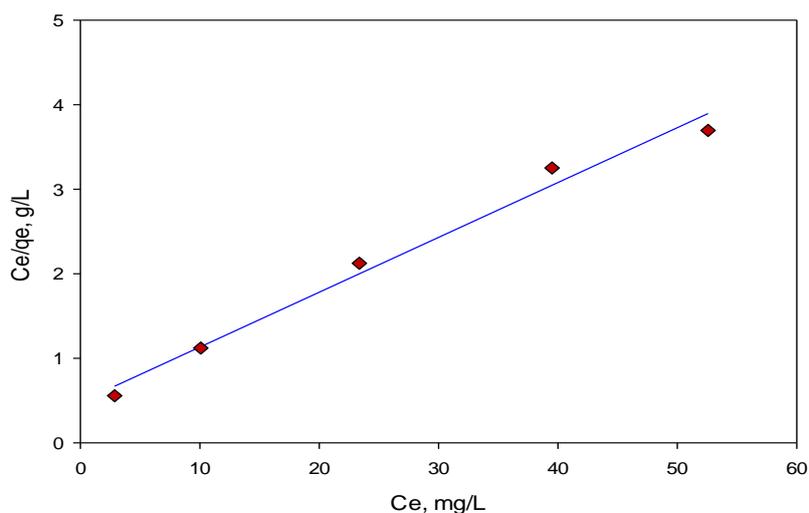


Fig.8. Langmuir adsorption isotherm at 0.1g/30mL of biosorption concentration.

The values of K_R at different concentrations are shown in Figure 9 and Table 2. The K_R values indicated that adsorption is higher at lower concentrations than higher concentrations. However, the *Mimusops elengi* would be an effective biosorbent for removing lead from solution.

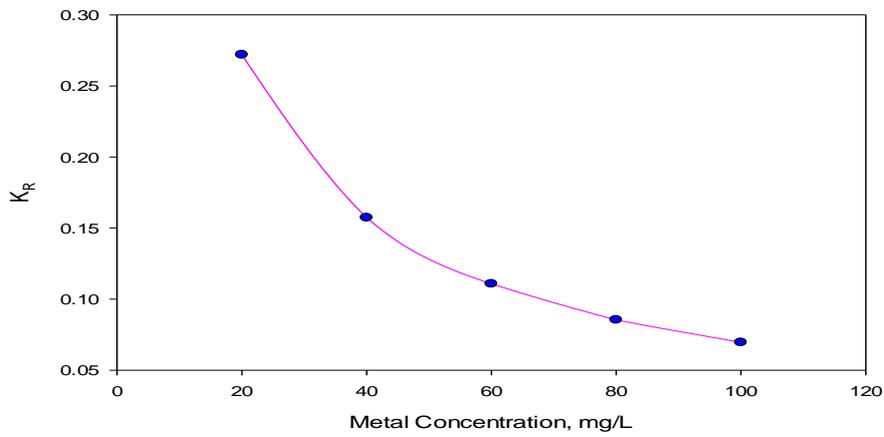


Fig.9. Values of the separation factor, K_R for the biosorption of Lead using *Mimusops elengi*.

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					
Lead	0.271932	0.157362	0.110715	0.0854	0.069507

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.

$$\ln \left(\frac{AC_{eq}}{q_{eq}} - 1 \right)$$

Figure 10, show 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 are shown in Table 1.

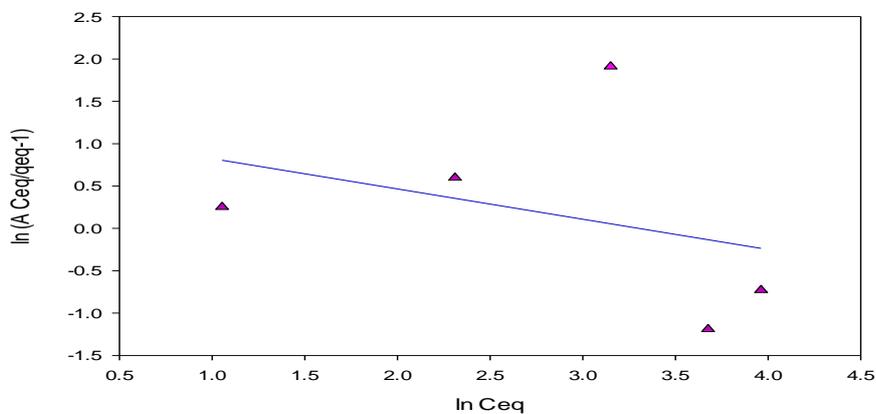


Fig.10. Redlich-Peterson adsorption isotherm at 0.1 g/30 mL of biosorbent concentration.

Temkin Isotherm

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions [23]. The adsorption data were analyzed according to the linear form of the Temkin isotherm and the linear plots are shown in Figure 11. Examination of the data shows that the Temkin isotherm provides a close fit to the lead adsorption data. The linear isotherm constants and coefficients of determination are presented in Table 1.

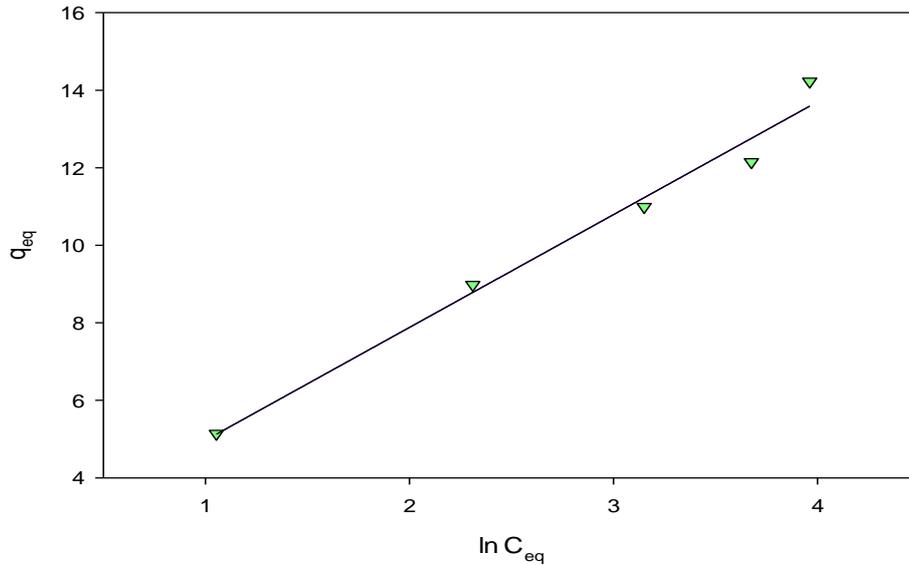


Fig. 11. Temkin adsorption isotherm at 0.1 g/30 mL of biosorbent concentration.

D-R Isotherm

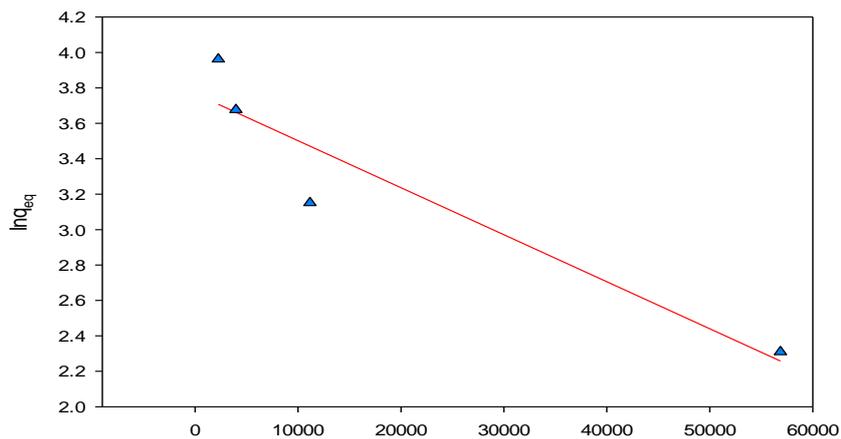


Fig.12. Dubinin-Radushkevich (D-R) adsorption isotherm at 0.1 g/30 mL of biosorbent concentration

The mean free energy change of adsorption (E) can be calculated using equation 8. The magnitude of E can be used for estimating the type of adsorption. The adsorption behavior can be described as the physical adsorption when the mean adsorption energy (E) is between 1.0 and 8.0 kJ/mol. However, the chemical adsorption is more than 8.0 kJ/mol of the mean adsorption energy [24]. The mean adsorption energy to lead was presented in Table 1. E value was calculated as 7.106 kJ/mol for lead and found to be in the range of a

typical free energy attributed to physical adsorption and chemical interactions. Similar observations were reported in other studies [25, 26, 27]. One of the remarkable feature of the D–R isotherm model lies on the fact that it is temperature-dependent, which, when adsorption data at diverse temperatures are plotted as a function of the logarithm of the amount adsorbed (ln qe) vs ϵ^2 the square of potential energy (Figure 12), all suitable data will lie on the same curve, named as the characteristic curve [28]. The equilibrium data were fitted to all the four equilibrium models. The calculated isotherm constants are given in Table 1. The best fit equilibrium model was determined based on the linear regression correlation coefficient R². From the table it was observed that the sorption data were very well represented by Langmuir isotherm for the lead with an average higher correlation coefficient of 0.984, followed by Temkin, Freundlich and Redlich-Peterson with a correlation coefficient of 0.9817, 0.9766 and 0.1206 respectively. The higher adsorption capacity Q_{max} (>>1) indicates the strong electrostatic force of attraction [29].

EXPERIMENTAL DESIGN USING THE CCD MODEL

Development and Statistical analysis

In the present study RSM was used to optimize different parameters which include pH, metal ion concentration and biosorption dosage as shown in Table 3. CCD is applied to obtain a correlation between the biosorption of Lead from the wastewater and the process variables investigated. The quadratic model suggested by the software was selected. Experiments were planned to obtain a quadratic model consisting of 16 trials and 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 lead biosorption. The coded values of variables in equation 13 represent % lead biosorption (Y) as a function of pH (X₁), concentration (X₂), dosage (X₃). The information 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 Lead:

$$\begin{aligned} \% \text{ biosorption} = & -50.347 + 39.223X_1 + 0.466X_2 + 203.338X_3 - 4.324X_1^2 - 0.007X_2^2 \\ & - 335.919X_3^2 + 0.019X_1 X_2 + 6.901X_1 X_3 - 0.242X_2 X_3 \end{aligned} \quad (13)$$

Where X₁, X₂ and X₃ are the code values for the independent variables, X₁ X₂, X₁ X₃, X₂ X₃, X₁², X₂² and X₃² are the significant model terms for the biosorption of Lead.

The significance of the second–order polynomial equation is estimated by the F-test of ANOVA as represented in Table 5. Probability>F value indicates the adequacy 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 [30] whereas a low p-value (<0.05) indicates that the model is considered to be statistically significant [28]. The F-value of 1389.007 and p-value of <0.0001 represent that the model is statistically significant. The interrelationship of the free variables and response can be clarified by the regression model as shown in Table 6. The model is best suited by determination of correlation R², 99.7% (0.997) value which is close to 1 [31]. In this model X₁, X₂ and X₃ represents the pH, Concentration, Dosage respectively. Table 7 gives a correlation between the experimental values and predicted values by establishing the validity of the model and also indicates that they are in a close agreement with each other. The actual and the predicted percentage biosorption of lead are shown in Figure 13.

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	% Biosorption
1	-1.00000	-1.00000	-1.00000	76.25
2	-1.00000	-1.00000	1.00000	80.02
3	-1.00000	1.00000	-1.00000	60.95
4	-1.00000	1.00000	1.00000	63.45
5	1.00000	-1.00000	-1.00000	70.79
6	1.00000	-1.00000	1.00000	80.03
7	1.00000	1.00000	-1.00000	59.14
8	1.00000	1.00000	1.00000	64.12
9	-1.68179	0.00000	0.00000	68.93
10	1.68179	0.00000	0.00000	64.9
11	0.00000	-1.68179	0.00000	85.66
12	0.00000	1.68179	0.00000	62.25
13	0.00000	0.00000	-1.68179	66.33
14	0.00000	0.00000	1.68179	75.36
15	0.00000	0.00000	0.00000	84.6
16	0.00000	0.00000	0.00000	83.93

Table-5. ANOVA for the biosorption of Lead

Source	SS	DF	Mean Square	F Value	p-value Prob > F
X1	13.085	1	13.0845	25.427	0.002351
X2	359.187	1	359.1865	697.998	0.000000
X3	714.776	1	714.7760	1389.007	0.000000
X12	129.422	1	129.4222	251.503	0.000004
X22	93.200	1	93.2000	181.113	0.000010
X32	216.770	1	216.7696	421.243	0.000001
X1 X2	2.322	1	2.3220	4.512	0.077828
X1 X3	7.900	1	7.9003	15.352	0.007818
X2 X3	3.823	1	3.8226	7.428	0.034390
Error	3.088	6	0.5146		
Total	1255.274	15			$R^2 = 0.99754; R^2 (Adj) = 0.99385$

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 biosorption of Lead

Term	Coefficient	SE Coefficient	t-value	p-value
Constant	-50.347	6.78468	-7.4206	0.000308
X1	39.223	1.80777	21.6970	0.000001
X12	-4.324	0.16367	-26.4197	0.000000
X2	0.466	0.07239	6.4391	0.000664
X22	-0.007	0.00042	-15.8588	0.000004
X3	203.338	14.31761	14.2019	0.000008
X32	-335.919	16.36695	-20.5242	0.000001
X1 X2	0.019	0.00888	2.1242	0.077828**
X1 X3	6.901	1.76127	3.9182	0.007818
X2 X3	-0.242	0.08880	-2.7255	0.034390

**insignificant ($P \geq 0.05$)

Table-7. The experimental values vs predicted values for biosorption of Lead

S.No.	Experimental values of biosorption	Predicted values of biosorption
1	76.25	75.94
2	80.02	80.56
3	60.95	61.77
4	63.45	63.63
5	70.79	70.92
6	80.03	79.51
7	59.14	58.91
8	64.12	64.74
9	68.93	68.33
10	64.9	65.04
11	85.66	85.89
12	62.25	61.56
13	66.33	66.22
14	75.36	75.01
15	84.6	84.30
16	83.93	84.30

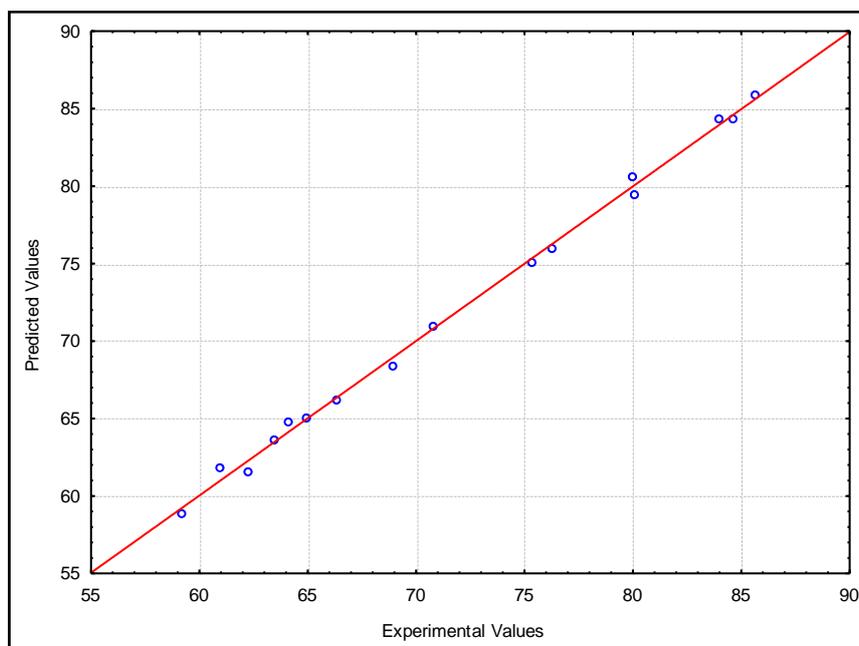


Fig.13. Correlation plot of experimental values vs predicted values for the biosorption of Lead

Interaction effects of biosorption variables

The % biosorption of lead with the distinct consolidation of free variables is visualized through three-dimensional view of response surface plots (Figures.14-16). All the response surface plots reveal that at low and high tiers of the variables, the % biosorption by the biosorbent is maximal; however, there exists a part where neither an expanding nor a diminishing pattern in the % biosorption is noticed. This exception confirms that there is a presence of ideal condition for the biosorption variables to encourage the % biosorption. The pH assumes an imperative in % biosorption as is apparent from the plots (Figures.14-16). A relatively strong association was observed between pH with CO, pH and w which is reflected by the corresponding P values 0.077828, 0.007818 and 0.034390 respectively as deduced from the curvature of the contour. The 'w' of the biosorption has appreciable amounts of interaction effect with pH (P = 0.007818) from Figure.15.

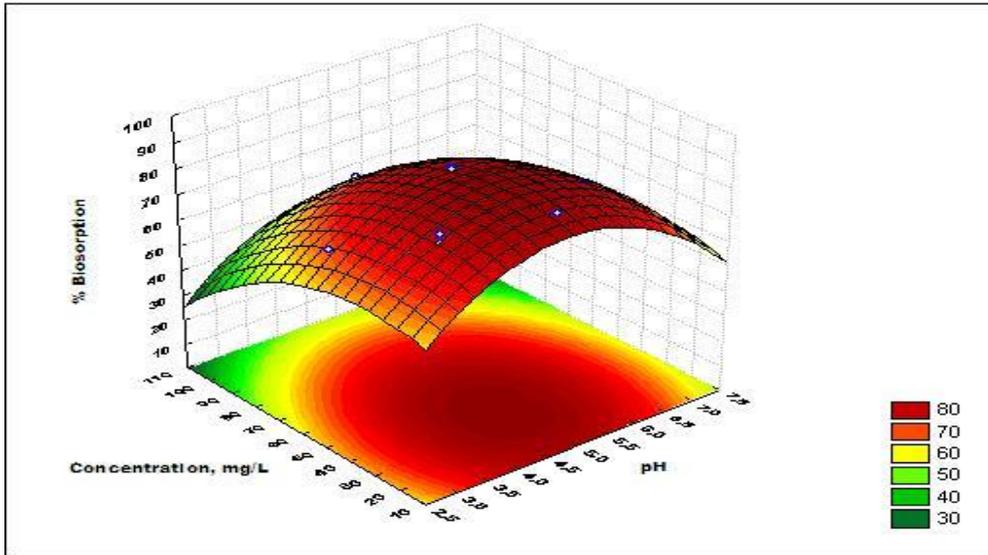


Fig.14. Response surface plot of pH vs concentration for the biosorption of Lead

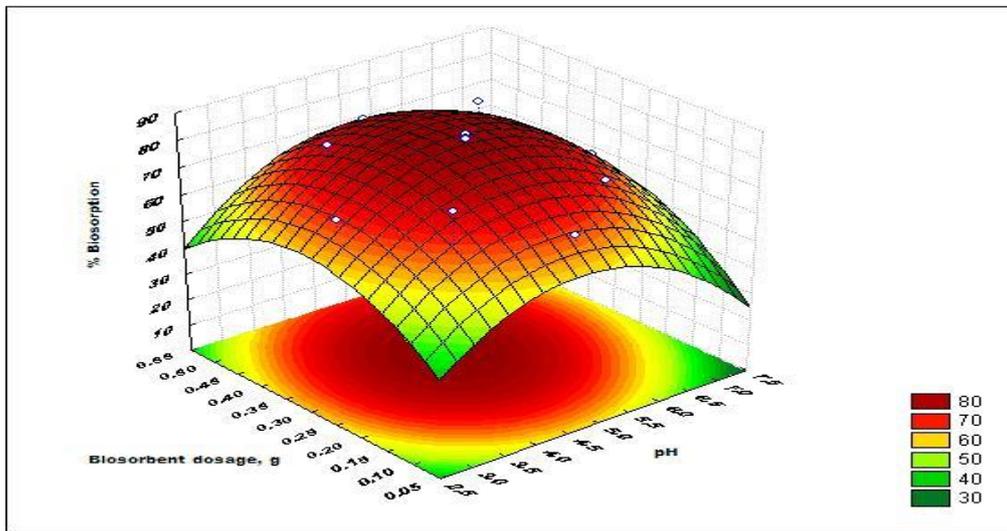


Fig.15. Response surface plot of pH vs dosage for the biosorption of Lead

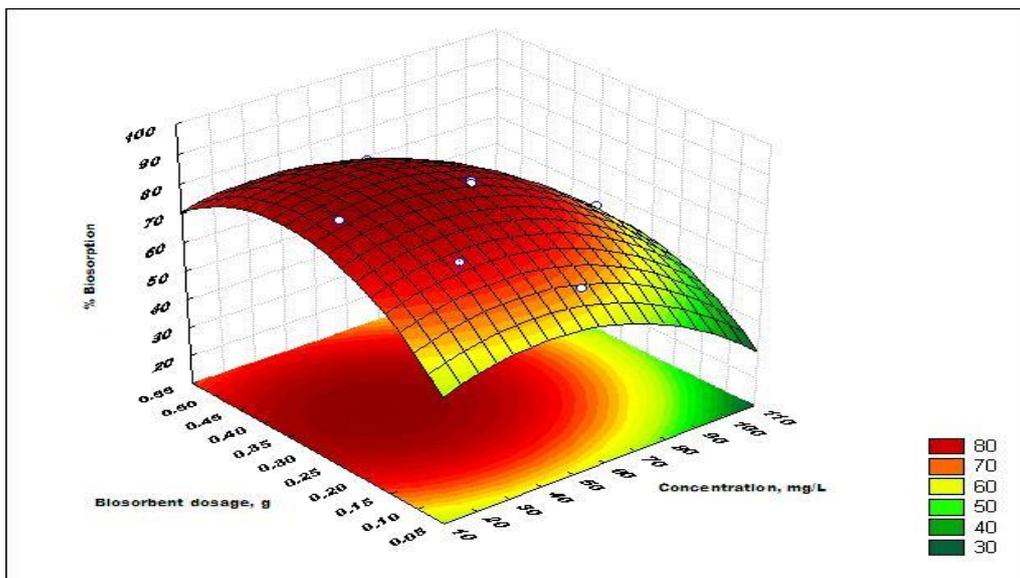


Fig.16. Response surface plot of concentration vs dosage for the biosorption of Lead

Optimization by response surface modeling

The optimum biosorption conditions determined for the biosorbent *Mimusops elengi* in batch studies are pH 4.8, metal ion concentration 36.07 mg/L, biosorbent dosage 0.33g. The model approval has been characterized at optimum levels of the process variables, anticipated by the model to accomplish the maximum % biosorption of 88.42.

CONCLUSION

The leaves of *Mimusops elengi* were evaluated as one of the possible biosorbents for the removal of Lead from industrial effluents. The Lead biosorption was influenced by pH, contact time, initial metal ion concentration, biosorbent dosage and biosorbent size and temperature. The maximum biosorption was at pH 5.0, contact time 180 min with the percentage removal of 85.67%. The experimental data were fitted well with Langmuir isotherm with R² value of 0.984. RSM was used to determine the optimum conditions for the maximum percentage removal of Lead. The optimum conditions were pH 4.8, metal ion concentration 36.07 mg/L, bioorbent dosage 0.33g and correlation coefficient of 0.997 with the percentage removal of 88.42%. Henceforth, this model can be effectively utilized to concentrate on the significance of the individual, combined and intuitive effects of distinctive test variables of biosorption.

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