

Response surface Methodology and Kinetic studies: Biosorption of Lead (II) in aqueous solution using dry pods of *Prosopis spicigera*

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Abstract - An extensive attention has been taken on the management of environmental pollution caused by hazardous materials like heavy metals. In the present study biosorption of Lead (II) from aqueous solution which include the factors such as pH, contact time, biosorbent dose, size and metal ion concentration was carried out. Characterization of the biosorbent was carried out using Fourier Transform Infrared (FTIR) analysis and Scanning Electron Microscope (SEM). Biosorption kinetics was evaluated using pseudo first order and pseudo second order models. Response surface methodology was used to optimize the variables using the Design Expert Software (Version 8.0.7.1).

Key Words: Lead (II), *Prosopis spicigera*, Kinetic models, Isotherms and RSM

1. INTRODUCTION

Modern agricultural practices and rapid industrialization have adversely affected the environment by heavy metals. Various toxic heavy metals such as Chromium, Nickel, Lead, Zinc, Cadmium and Copper tend to accumulate and deteriorate the environment [1]. Among these heavy metals, Lead is one of the most dangerous heavy metals which is released into natural waters from various industrial activities like mining and smelting of metallic ferrous ores, oil refining, municipal wastes, paint and pigment production and battery manufacturing [2]. When Lead is exposed to human body it may enter through inhalation or dermal contact, which accumulate in living tissues like bone, brain, muscles and kidney and cause diseases such as anemia, nephropathy, blood and brain disorders and even may lead to death [3, 4]. Maximum permissible limit for lead in drinking water was established by World Health Organization (WHO) as 3-10 µg/L [5] and also concentration of lead in wastewater can be as high as several hundred micrograms per liter. There are different methods for the treatment of wastewater which include Precipitation, adsorption with activated carbon, ion exchange, membrane processes,

oxidation and reduction [6]. These conventional methods are not only costly but also require trained personnel, and use of chemicals that generate wastes which are either toxic or hazardous [7, 8]. Hence, use of green, low cost, easily available and highly efficient materials like seeds, pods, roots and bark of plants which are called as biomass or biosorbent and the process involved is Biosorption and these are very promising methods for the removal of heavy metals from wastewater.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables on the response [9]. RSM generates an experimental design for model preparation. An experimental design is a specific set of experiments defined by a matrix composed of different level combinations of the variables studied [10].

In the present study the dried pods of *Prosopis spicigera* which belongs to pea family, Fabaceae was used for the removal of Lead in aqueous solution. Its common name is Indian Mesquite, and it is native to arid and dry regions of Indian subcontinent including Afghanistan, Iran, India, Oman, Pakistan, Saudi Arabia, the United Arab Emirates and Yemen. It is the state tree of Rajasthan and the National tree of United Arab Emirates [11]. The pod is straight, smooth, 10 to 15 cm long, 0.6 cm thick which grows in dry and arid regions. Different parameters involved in the adsorption process have been studied which included such as pH, contact time, adsorbent dose, initial metal ion concentration and size variation for the biosorption of Lead (II). The biosorption kinetics and equilibrium isotherms were also investigated.

1.1 MATERIALS AND METHODS

Preparation of the biosorbent: The pods of *P. spicigera* were collected from Mysore district, Karnataka, India. Biosorbent was washed thoroughly with distilled water to remove the impurities and sun dried for several days. These dried biosorbent pods were ground and sieved to different sizes from 100 µm to 400 µm to get a fine

powder. Biosorbent size of 100 μm was selected, kept in an air tight plastic jar until it is used for further experiments.

Preparation of Adsorbate: Metal ion solution of Pb (II) was prepared from Lead nitrate (Merck- A.R. grade). About 1.598 g of lead nitrate was weighed and a standard stock solution of concentration 1000 mg/l- was prepared in double distilled water and further working solutions of lower concentrations were prepared as and when required. The pH of the solution was adjusted using 0.01 M HCl and 0.01 M NaOH. The final concentration of metal ions was analyzed by AAS.

Characterization of Biosorbent: A Fourier Transform Infrared (FTIR) spectrum of unloaded and metal bound *P. spicigera* samples were recorded by using standard KBr pellet method to obtain the spectrum using Jasco FT / IR-4100 in wave number range of 400-4000 cm⁻¹. The scanning electron micrograph was used to reveal the surface texture and morphology of the biosorbent by using ZEISS, EVO/LS 15-15-41, smart SEM version 5.05. Paragraph comes content here. Paragraph comes content here. Paragraph comes content here.

1.2 Optimization using Central Composite Design (CCD) model

To optimize different variables such as pH, contact time, biosorbent dose, metal ion concentration and particle size Response Surface Methodology (RSM) procedure was used [12,13]. In this process the three steps involved were experimental design, modeling and optimization. In this study Central Composite Design has been used for the optimization of Lead biosorption. The five independent variables of RSM are represented as:

$$Y = f(A_1, A_2, A_3, \dots, A_n) \tag{1}$$

Where, Y is the amount of metal adsorbed (mg L⁻¹), f is the response function and A₁, A₂, A₃, ..., A_n are independent variables.

In the linear manner, if the response varies, the linear function can be given by the following formula:

$$Y = b_0 + b_1A_1 + b_2A_2 + \dots + b_nA_n \tag{2}$$

Where b₀, offset term; A_i first order main effect; A_{ij} second order main effect and A_{ij} interaction effect.

Table -1: Different parameters chosen for the biosorption as independent variables.

Factor	Name	Units	Minimum	Maximum
A	pH		2	7
B	Time	Min	10	100
C	Size Variation	μm	100	400
D	Biomass taken	g/L	0.2	4
E	concentration	mg/L	25	300

If there is a curvature in the system, the higher order polynomial quadratic model which is used can be stated as:

$$Y = b_0 + \sum b_i A_i + \sum b_{ii} A_i^2 + \sum b_{ij} A_i A_j \tag{3}$$

In the present study, five parameters such as pH (2-7), contact time (10- 100 min), biosorbent dose (0.2-4.0 g/L), metal ion concentration (25-300 mg/L) and particle size variation (100-400 μm) were used as independent variables using CCD model as shown in Table 1. The correlation coefficient (R²) value was also calculated to analyze the variance whether this model is good and appropriate.

2. BATCH EXPERIMENTS

Batch process was carried out for the biosorption of Lead under varying experimental conditions like different pH (2-7), contact time (10- 100 min), biosorbent dose (0.2-4.0 g/L), metal ion concentration (25-300 mg/L) and particle size variation (100-400 μm). Dried *P. spicigera* (2 g/L) was taken with 20 ml of 1000 mg/L in a clean conical flask. The mixture was stirred at 180 rpm in a rotary shaker with time intervals of 10 - 100 min. The resultant solution was decanted and analyzed by AAS. Mean value was calculated by repeating the experiment. The adsorbed metal is based on the soluble metal concentration before and after the batch experiment. The percent removal can be calculated as:

$$R = (C_0 - C_f) \times 100 / C_0 \tag{4}$$

Where, C₀ and C_f are the initial and residual concentration of Lead respectively in solution in mg/L. The metal uptake capacity for initial and final concentration of Lead was calculated using the following formula:

$$q_e \text{ (mg/g)} = V (C_i - C_e) / M \tag{5}$$

Where, q_e is the Lead uptake (mg/g), C_i and C_e are the initial and final Lead concentration respectively in the

solution (mg/l). V is the solution volume (L) and m is the mass of adsorbent (g).

3. RESULTS AND DISCUSSION

Characterization of Biosorbent

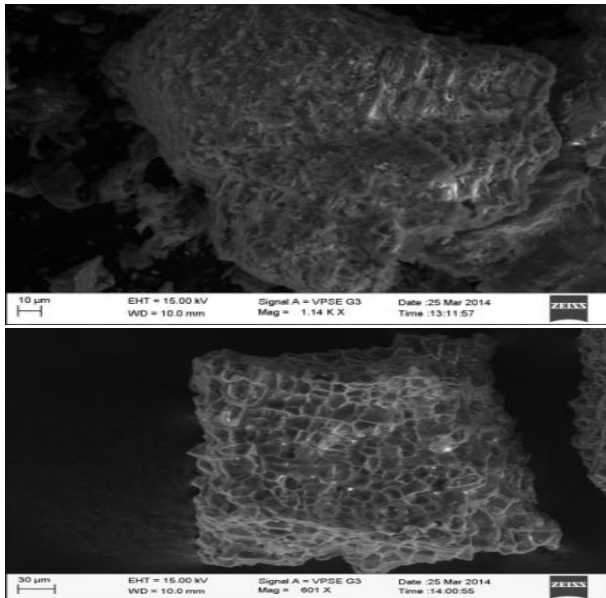


Fig - 1: (a) showing the SEM pictures of raw *P. spicigera*; (b) SEM pictures of loaded *P. spicigera*

Figures 1(a) and 1 (b) represent the SEM images of native and lead loaded biosorbent at 1.14 X and 601 X magnifications. In native biosorbent it was observed that the uneven texture with lot of irregular format. After the biosorption the morphology has undergone many changes with large surface area and opening of pores which as shown in Fig 1 (b) thereby confirming that biosorption has taken place with the biomass.

Chemical functional group is one of the most important mechanisms to understand the metal binding on the biosorbent surface. To analyze the functional groups FTIR analysis was carried out in the dried pods of *P. spicigera*. The dried pods powder of *P. spicigera* was sieved to different fractions of particle size ranging from 100 to 400 μm . To characterize the biosorbent 100 μm size was used for the adsorption studies as shown in Fig 2 (a) and (b) respectively. The peak ranging from 3634 and 3489 cm^{-1} indicates the presence of O-H (free) and -NH groups. Figure 2 (b) also represents stretching of -OH groups which are bound to methyl group radicals ranging between 2924 and 2855 cm^{-1} . The characteristics of carbonyl group stretching from aldehyde and ketones are located at the peak of 2711 cm^{-1} . The presence of -OH groups and carbonyl groups (C=O) confirms the carboxylic

group in the biosorbent. Presence of Nitroso N=O stretching and S=O sulfonyl groups at the peaks of 1461 and 1372 cm^{-1} is associated with stretching aromatic rings. Hence, -OH, -NH, carbonyl and carboxylic groups are important sorption sites for the binding of biosorbent and spectral data confirms that the presence of -OH, -NH, carbonyl and carboxylic groups in the biomass.

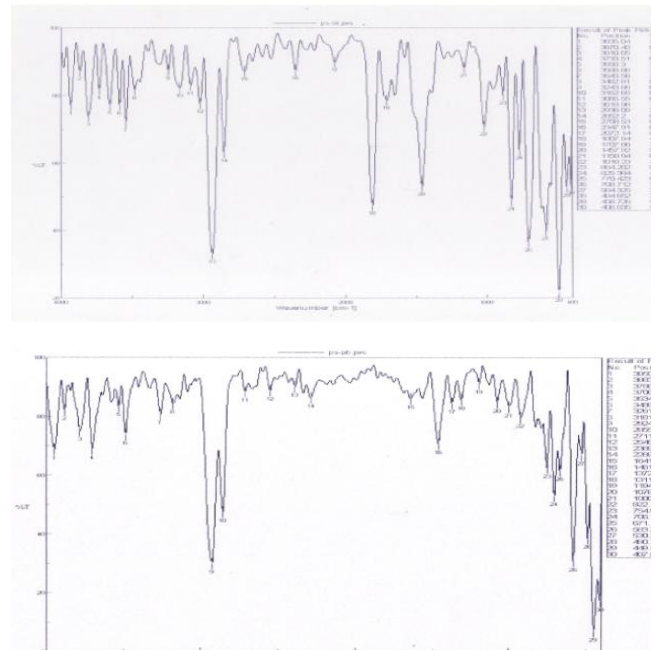


Fig -2: (a) FTIR spectra of unloaded *P. spicigera*; (b) FTIR spectra of Pb (II) loaded *P. spicigera*

3.1. Effect of pH

Figure 3 shows that the biosorption of heavy metal ions onto the biomass is affected by pH [14]. Batch studies with pH ranging from 2.0-7.0 were carried out in order to evaluate the effect of pH on metal uptake by the biosorbent. Results show that metal uptake was relatively slow at pH 2.0 which suddenly increased from pH 4.0-6.0 and attained maximum removal of 80% at pH 6.0. This may be due to large quantities of proton competing with metal cations for the biosorption sites [15]. Experiments carried out at pH higher than 6.0, resulted in the precipitation of Pb (II) [16]. Lead ions compete less with protons at low pH than at pH 5.0 for active binding sites on the biosorbent. Under acidic conditions biosorbent becomes more positively charged due to protonated active sites. Precipitation of lead hydroxide or hydrated oxide occurs at pH higher than 6.0 and hence, biosorption process is limited at higher pH solutions. Similar results were observed with *Albezia lebbek* pods powder [17] and *Chlorella vulgaris* [18].

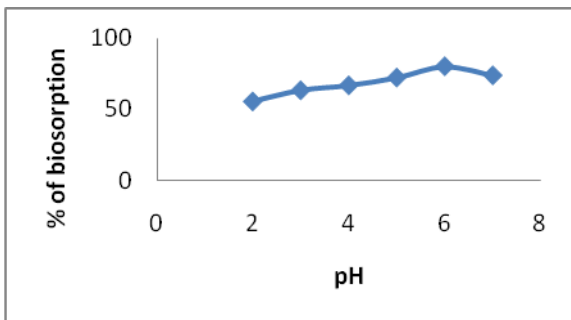


Fig -3: Effect of pH on biosorption of Pb (II) by *P. spicigera*

3.2. Effect of size variation

The effect of particle size on the removal of lead from aqueous solution was studied using different sizes varying from 100 μm to 400 μm . The rate of biosorption decreased from 80.0 % to 62.5 % as the particle size increased from 100 to 400 μm . This is due to that the smaller particles have more surface area with high binding sites and contact surfaces and thus there is more rapid sorption compared to larger surface area. Maximum lead biosorption achieved was found to be 80 % and 100 μm was best suited size compared to other particle sizes.

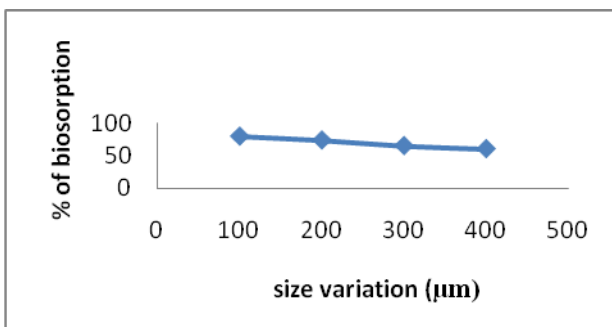


Fig - 4: Effect of particle size on biosorption of Pb (II) by *P. spicigera*

3.3 Effect of Contact time

Biosorption rate is very much important in designing batch experiments and hence effect of contact time on the biosorption was investigated. Biosorbent (2 g/L) with 200 mg/L of Pb (II) solution was taken in a clean conical flask with time intervals of 10 - 120 min at constant pH of 6.0. Figure 5 shows that the maximum biosorption of Pb (II) was attained at 70 min with percentage removal of 80. This may be due to more number of vacant negatively charged sites available initially on the surface of the biosorbent and the sites are gradually filled up while approaching equilibrium [19]. Further, there was no increase in contact time and reached the equilibrium.

Optimum time (70 min) obtained from the experiment was successfully used to evaluate the kinetics of adsorption process. Similar results were obtained by using non-living algal biomass *Oedogonium sp* and *Nostoc sp* [20].

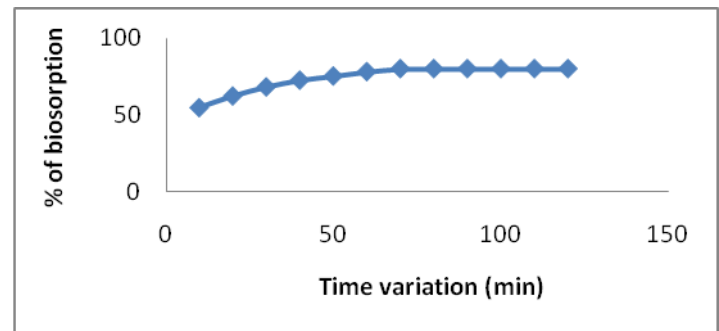


Fig - 5: Effect of contact time on biosorption of Pb (II) by *P. spicigera*

3.4 Effect of biosorbent dose

The effect of biosorbent dosage for the removal of lead is depicted in Figure 6 with dosages varying from 0.2 - 4.0 g/L. As the biosorbent dose increased, the percentage removal efficiency also increased from 52.5 - 80. Thus, maximum uptake capacity was at 2.0 g/L, above which the removal rate of metal ions remarkably decreased. This is because of the active sites available at higher dosage of the biosorbent, thus making easier penetration of the metal ions to the adsorption sites [21]. Hence, biosorbent dose of 2 g/L was considered to be more appropriate for the removal of Pb (II) in all batch experiments. Similar results were reported for the removal of Pb (II) by groundnut hull and by using rice husk and its ash [22, 23].

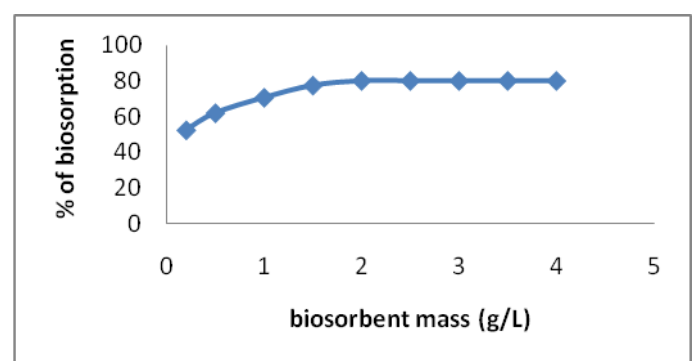


Fig - 6: Effect of biosorbent dose on biosorption of Pb (II) by *P. spicigera*

3.5 Effect of metal ion concentration

Figure 7 depicts the effect of ion concentration of Pb (II) in aqueous solution ranging from 25- 300 mg/L at constant pH 6.0, contact time 70 min and biosorbent dose of 2 g/L. Lead removal decreased from 91 % to 80 % as the metal concentration increased. Result shows that maximum percentage removal was at 80 with 200 mg/L of metal concentration. This may be due to the fact that at lower concentration the ratio of the initial Pb (II) surface area available was low and subsequently fractional sorption became independent of the initial concentration [24].

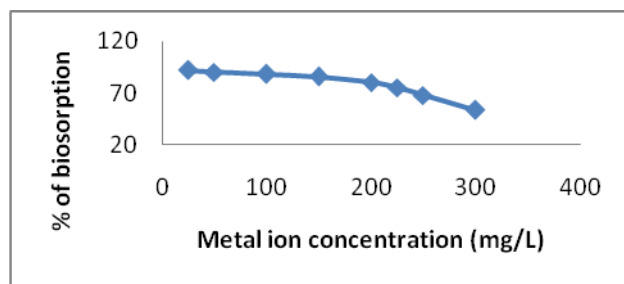


Fig -7: Effect of metal ion concentration on biosorption of Pb (II) by *P. spicigera*

3.6 Kinetic studies

To determine the sorption mechanism of lead onto pods of *P. spicigera* kinetic models like pseudo-first order and pseudo- second order were used and also rate controlling steps were involved in the process. Pseudo first- order equation was first suggested by [25] and the model integrated in linearized form is expressed as:

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (6)$$

Where, k_1 is the adsorption rate constant (min^{-1}), q_e metal biosorbed at equilibrium (mg g^{-1}), q_t metal biosorbed at any time t (mg g^{-1}). This model considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites [26]. The equation in the integrated form is as follows:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

Plot against t and $\log (q_e - q_t)$ shows the metal biosorption with straight line and data were fitted with poor correlation coefficient (R^2) of 0.973 (Fig 8) which indicates that pseudo first order equation did not fit with removal of lead from *P. spicigera*.

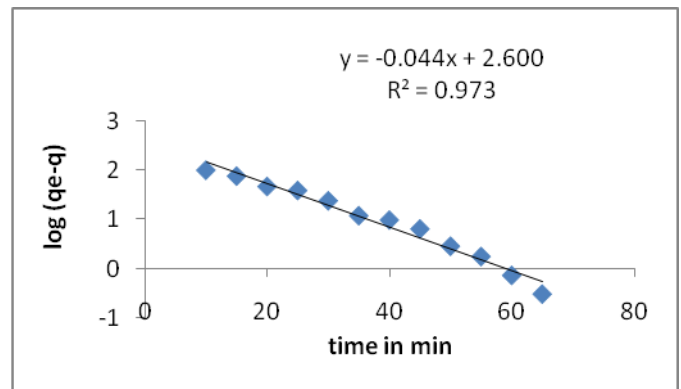


Fig - 8: Pseudo first – order biosorption Kinetics for Pb (II) by *P. spicigera*

Pseudo second order model is based on the assumption and the rate of biosorption is proportional to the square of the number of unoccupied sites [27]. The equation in the linearized form is as follows:

$$t / qt = 1 / k_2 qe_2 + 1 / qe t \quad (8)$$

Where, k_2 is equilibrium rate constant for second order model ($\text{g mg}^{-1} \text{min}^{-1}$), q_e is the equilibrium capacity and qt is the biosorption capacity at any time t . Fig 9 shows the plot against t and t/qt is straight line with R^2 value of 0.997 which fit the kinetic studies. The values of pseudo first order and pseudo second order are shown in Table 2. The biosorption rate, h (mg/g min) at $t=0$ is shown as:

$$h = K_2 qe^2 \quad (9)$$

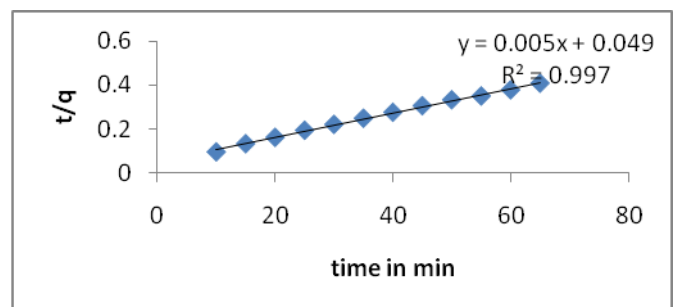


Fig - 9: Pseudo second- order biosorption Kinetics for Pb (II) by *P. spicigera*

Table - 2: Pseudo first- order and Pseudo second –Order constants for Pb (II) biosorption by *P. spicigera*

Metal	Pseudo first order			Pseudo second order			
	qe (mg/g)	K ₁ (min ⁻¹)	R ²	qe (mg/g)	K ₂ (g/mg ¹ min)	R ²	h
Pb (II)	2.0496	0.00230	0.973	0.0699	0.4375	0.997	8.015

3.7 Biosorption isotherms

The two different types of biosorption can be classified into Langmuir model in which the amount of metal uptake by the biomass reaches equilibrium and Freundlich model in which the amount of metal uptake by the biomass increases with effect of time [28]. The equilibrium between an adsorbate in the active site and the adsorbent remaining in aqueous phase is usually presented by adsorption isotherm [29].

Figure 10 depicts the regression coefficient of linearized isotherm of Langmuir model. Evaluation has been carried out from the slope and intercept, the Langmuir constant and maximum biosorption capacity and the values are 0.0792 L/mg, 12.5 mg/g and 0.964, respectively. Thus, Langmuir isotherm is monolayer in the biosorption and the linearized formula [30] is as follows:

$$C_e/q_e = 1/bq_{max} + C_e/q_{max} \quad (10)$$

Where, C_e and q_e are the residual and metal uptake capacity mg/L respectively, b is the adsorption equilibrium constant (mg/L) related to adsorption and q₀ is the maximum monolayer capacity of the adsorbent (mg/g). The values are shown in the Table 3.

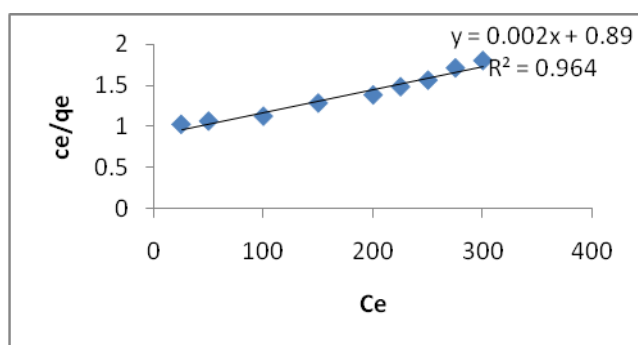


Fig -10: The linearized Langmuir adsorption isotherms of Pb (II) by *P. spicigera*

As Langmuir model describes a monolayer, Freundlich isotherm model describes a multi layer adsorption with

the assumption of heterogeneous surface in which the energy, a term in the Langmuir equation varies as a function of the surface area. The model can be represented as [31]

$$q = K_f C_e^{1/n} \quad (11)$$

And the linearized form can be represented as

$$\log(q) = \log(K_f) + 1/n \log(C_e) \quad (12)$$

Where, q is the amount of metal adsorbed per unit weight of the adsorbent at equilibrium (mg⁻¹), C_e is the equilibrium of metal concentration (mg L⁻¹), K_f is the measurement of adsorption capacity (mg/g) based on Freundlich isotherm, n is the adsorption equilibrium constant.

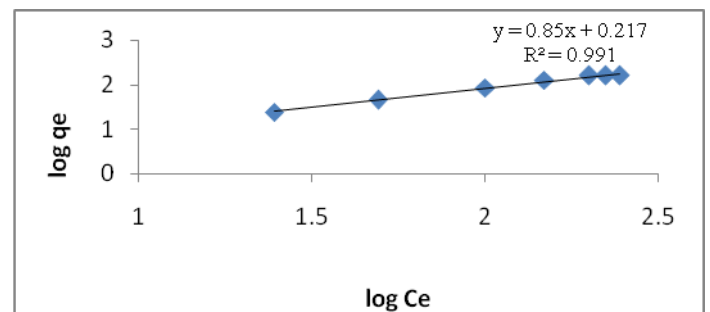


Fig -11: The linearized Freundlich adsorption isotherms for Pb (II) by *P. spicigera*

Metal	Langmuir			Freundlich		
	q _{max}	b	R ²	K _f	1/n	R ²
Pb (II)	12.5	0.0792	0.964	15.85	0.878	0.991

Table -3: Langmuir and Freundlich constants for Pb (II) biosorption by *P. spicigera*

4.0 CENTRAL COMPOSITE DESIGN MODEL FOR THE BIOSORPTION OF LEAD (II) BY RESPONSE SURFACE METHODOLOGY

The actual values and the predicted values of the variables like pH, contact time, biosorbent dose, metal ion concentration and particle size were used and the results of percentage removal by each factor is represented in Table 5. The significance of the variables and their interactions were studied using analysis of variance which was fitted to second polynomial equation [32].

$$\text{Biosorption of lead (II)} = 62.67 + 14.48*A + 11.65*B - 9.65*C + 11.57*D - 21.78*E - 2.69*A^2 - 9.85*B^2 + 0.11*C^2 - 13.82*D^2 - 13.56*E^2$$

Table - 4: Central composite rotatable quadratic polynomial model, experimental data, and actual and predicted values for response surface analysis.

Standard Order	A	B	C	D	E	Actual value (%)	Predicted value (%)
1	7	70	100	2	250	64	67.02
2	7	70	100	1	200	68.6	68.74
3	1	70	100	2	200	51.5	50.46
4	7	70	200	2	200	74	72.89
5	7	70	100	2	150	90.93	88.24
6	5	70	100	2	200	72.1	72.16
7	7	70	100	3	200	80	82.45
8	7	15	100	2	200	56.6	58.50
9	7	55	100	2	200	78.6	76.64
10	2	70	100	2	200	55.4	56.78
11	7	70	100	1.5	200	77.4	75.04
12	7	70	100	2.5	200	80	81.89
13	7	70	100	4	200	80	77.82
14	7	70	100	2	25	96.8	94.59
15	7	70	400	2	200	60.5	60.13
16	7	60	100	2	200	79.05	77.81
17	7	25	100	2	200	64.75	64.49
18	7	40	100	2	200	72.5	71.66
19	7	80	100	2	200	80	80.07
20	7	70	100	2	50	92.4	95.11
21	7	70	100	2	200	80	79.42
22	7	70	100	2	100	91.5	93.47
23	7	70	100	2	300	53.33	51.04
24	7	70	100	3.5	200	80	81.09
25	7	65	100	2	200	79.45	78.74
26	7	70	300	2	200	65.35	66.46
27	7	30	100	2	200	68.1	67.12
28	7	70	100	2	200	80	79.42
29	7	100	100	2	200	80	78.44
30	7	70	100	2	275	58.18	59.48
31	7	70	100	2	225	71.1	73.67
32	3	70	100	2	200	63.22	62.50
33	7	45	100	2	200	73.65	73.56
34	7	70	100	0.5	200	62	60.53
35	7	35	100	2	200	70.55	69.51
36	7	70	100	2	200	73.67	79.42
37	6	70	100	2	200	80	76.09
38	7	70	100	2	200	80	79.42
39	7	70	100	0.2	200	52.5	54.68
40	7	70	100	2	200	80	79.42

41	7	20	100	2	200	62.2	61.62
42	7	10	100	2	200	54.6	55.14
43	7	50	100	2	200	75.2	75.22
44	7	90	100	2	200	80	79.74
45	4	70	100	2	200	65.64	67.63

Table 5 shows the analysis of variance (ANOVA) for the biosorption of Lead (II) onto pods of *P. spicigera*. The adequacy (statistical significance) of quadratic model was tested through F- and P values. A large F- value indicates that most of the variations can be explained by a regression equation whereas low values of “Prob > F” less than 0.05 indicate model terms are statistically significant [33]. The Fisher’s F value of 122.3 depicts that the model is significant. The high R² value of 0.973 shows that the quadratic polynomial was highly significant and the percentage of biosorption was 98.84. Hence, the variables indicate low P value and are highly significant and it is used for further analysis. Regression analysis and ANOVA were performed using design expert software (Version 8.0.7.1)

Table - 5: ANOVA for biosorption of Lead (II)

Source	Degree of freedom	Sum of squares	Mean square	F value	P value
Model	10	5372.9	537.3	122.3	< 0.0001**
Residual	34	149.4	4.4		
Total	44	5522.3			
A	1	1071.6	1071.6	243.9	< 0.0001**
B	1	833.1	833.1	189.6	< 0.0001**
C	1	373.4	373.4	85.0	< 0.0001**
D	1	527.2	527.2	120.0	< 0.0001**
E	1	2001.9	2001.9	455.7	< 0.0001**
A ²	1	11.7	11.7	2.7	0.1115
B ²	1	197.1	197.1	44.9	< 0.0001**
C ²	1	0.0	0.0	0.0	0.9555
D ²	1	436.0	436.0	99.2	< 0.0001**
E ²	1	360.3	360.3	82.0	< 0.0001**

4.1 Optimization of selected parameters

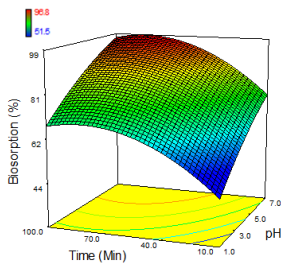


Fig- 12: RSM plot with effect of pH v/s time

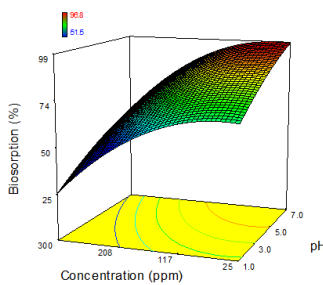


Fig -13: RSM plot with effect of pH v/s concentration

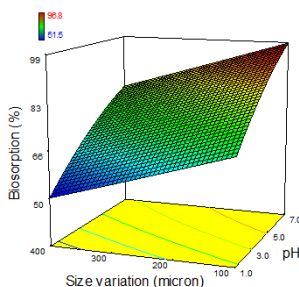


Fig - 14: RSM plot with effect of pH v/s size variation

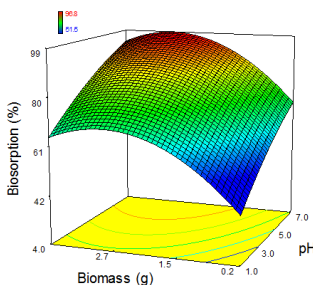


Fig- 15: RSM plot with effect of pH v/s biomass

Figures 12-14 show RSM plots with effect of contact time, biosorbent dose, metal ion concentration and particle size, keeping pH as common factor. Optimum conditions attained for biosorption was at pH 7.0, contact time 81.6 min, size variation of 100 μm , metal ion concentration of 52.26 mg/L and biosorbent dosage of 2.89 g/L. Using these optimum conditions maximum lead removal achieved 98.84 %. Similar percentage removal (98%) for of copper was achieved by using *Rhizopus arrhizus* [34]. The values obtained from response surface methodology confirm that CCD statistical design effectively optimizes the different parameters and also reveals the importance of individual, cumulative and interactive effects of the variables in the process of biosorption.

5. CONCLUSION

The present study shows that pods of *P. spicigera* can be used as biosorbent for the removal of Lead (II) from aqueous solution with maximum uptake capacity at pH 6.0, contact time 70 min, metal ion concentration of 200 mg/L, biosorbent dose 2 g/L and size variation of 100 μm with the percentage removal of 80 %. The CCD model shows the correlation of 0.973 with maximum adsorption of 98.84 %. Kinetics was also described in which pseudo second order fit well with experimental data. Freundlich isotherm model shows good results with R^2 value of 0.991 with maximum adsorption capacity (q_{max}) of 12.5 mg/g. Full factorial Central Composite Design (CCD) in RSM was used to determine the optimum conditions and the obtained results were pH 7.0, contact time 81.6 min, size variation of 100 μm , metal ion concentration of 52.26 mg/L and biosorbent dosage of 2.89 g/L to get maximum biosorption capacity.

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REFERENCES

- [1] M. Abbas, Z. Parveen, M. Iqbal, Riazuddin, S. Iqbal, M.Ahmed, R. Bhutto, Monitoring of toxic metals (cadmium, lead, arsenic and mercury) in vegetables of Sindh, Pakistan. Kathmandu University Journal of Science, Engineering and Technology, 6, (2010) 60-65.J.
- [2] N.R .Axtell, S.P.K. Sternberg and K. Claussen, Lead and Nickel removal using microspora and lemna minor, Bioresource Technol, 89(1) (2003) 41-48.
- [3] T.G .Kazi, N. Jalbani, N. Kazi, M.K. Jamali, M.B .Arain, H.I . Afridi, A. Kandhro and Z. Pirzado, Evaluation of toxic metals in blood and urine samples of chronic

- renal failure patients, before and after dialysis, Renal Failure 30(7) (2008) 737-745.
- [4] H.I Afridi, T.G Kazi, N. Kazi, M.K. Jamali and G.Q Shar, Essential trace and toxic element distribution in the scalp hair of Pakistani myocardial infarction patients and controls, Biol. Trace Elem. Res. 113(1) (2006) 19-34.
- [5] W.N.L dos Santhos, D.D Cavalcante, E.G.P da Silva, C.F. das Virgens and F.D . Dias, Biosorption of Pb (II) and Cd (II) ions by Agave sisalana (sisal fibre), Microchem J, 97(2) (2011) 269-273.
- [6] Wang Yuen-Hua, Lin Su-Hsia., Juang, and Ruey-Shin, Removal of heavy metals from aqueous solutions using various low-cost adsorbents. Journal of Hazardous materials, 102 (1993) 291-302.
- [7] T. Bannai, Y. Muramatsu, and S Amachi . Rate of iodine volatilization and accumulation by filamentous fungi through laboratory culture. Chemosphere 65 (2006) 2216-2222.
- [8] A. Cabuk, T. Akar, S. Tunali and S Gedikli,. Biosorption of Pb (II) by industrial strain of Saccharomyces cerevisiae immobilized on the biomatrix of cone biomass of *Pinus nigra*: Equilibrium and mechanism analysis. Chemical Engineering Journal 131 (2007) 293- 300.
- [9] G.E.P Box, N.R Draper, Empirical Model- Building and Response Surfaces, (John Wiley and sons, New York, 1987).
- [10] M. A Bezerra, R.E Santelli, E.P Oliveira, L.S Villar, and L.A.E Escal, Response surface methodology (RSM) as a tool for optimization in analytical chemistry, Talanta, 76, (2008) 965-977.
- [11] (<http://ecoheritage.cpreec.org/Viewcontall.php>)
- [12] M.J Anderson, and P.J Whitcomb, RSM simplified: optimizing processes using response surface methods for design of experiments (Productivity Press, New York 2005)
- [13] D.C Montgomery, Design and analysis of experiments (6th ed. John Wiley & Sons, Inc., USA 2005).
- [14] M. Iqbal and R.G.J. Edyvean, Loofa sponge immobilized fungal biosorbent: A robust system for cadmium and other dissolved metal removal from aqueous solution, Chemosphere, 61 (2005) 510-518.
- [15] C.P Huang, D. Westman, C. Huang and A.L. Morehart, The removal of Cadmium (II) from dilute aqueous solution by fungal biosorbent, Water Sci. technol. 20 (1998) 369-376.
- [16] J.C .P. Veghetti, E.C. Lima, B. Royer, B .M. da Cunha, and N. Cardoso,. 2009. Pecan nutshell as biosorbent to remove Cu(II), Mn (II) and Pb(II) from aqueous solutions. Journal of Hazardous Materials 162: 270-280.
- [17] Ch. A. I. Raju, R. Sarala Kumari, Ch. V. Satya, P. J. Rao and M. Tukaram Bai, Biosorption performance of *Albizia lebbek* pods powder for the removal of lead: Application of statistical method. International Journal of Modern Engineering Research (IJMER), 2 (3) (2012), 1297-1305.
- [18] Wai Lynn Aung, Dr. Nway Nay Hlaing, and Dr. Kyaw Nyein Aye, Biosorption of Lead (Pb²⁺) by using *Chlorella vulgaris*. International Journal of Chemical, Environmental & Biological Sciences (IJCEBS) 1(2), (2013) 408-412
- [19] B.V. Saradhi, Rao SRK, Y.P. Kumar, Vijetha P, K.V. Rao and G . Kalyami. Applicability of Langmuir and Freundlich theory for biosorption of chromium from aqueous solution using Test of Sea Urchins. International Journal of Chemical Engineering Research. 2(2) (2010) 139 – 148.
- [20] Vinod K. Gupta and Arshi Rastogi, Biosorption of lead (II) from aqueous solutions by non-living algal biomass *Oedogonium* sp. and *Nostoc* sp.—A comparative study, Colloids and Surfaces B: Biointerfaces, 64 (2) (2008) 170-178.
- [21] A. Sari, M. Tuzen, D. Citak and M. Soylak, Adsorption characteristics of Cu (II) and Pb (II) onto expanded Perlite from aqueous solution, J. Hazard. Mater. 148 (1-2) (2007) 387-394.
- [22] Suleman Kaiser, R. Anwar, Saleemi, Muhammad Umar, Biosorption of lead (II) and Chromium (VI) on groundnut hull: Equilibrium kinetics and thermodynamics study. Electronic Journal and Biotechnology, 12 (4) (2009).
- [23] A. G. El- Said, Biosorption of Pb (II) Ions from Aqueous Solutions Onto Rice Husk and its Ash. Journal of American Science, 6 (10), (2010) 143-150.
- [24] Nida M Salem, Akl M. Awwad, J Saudi Chem Soci, (2011), doi: 10.1016/ J.jses.2011.07.008.
- [25] Lagergren, "About the theory of so called adsorption of soluble substances, (K.Sven Vetenskapsakad Handle, 24: 1, (1898).
- [26] M. R. Sangi, A. Shahmoradi, J. Zolgharnein, G. H. Azimi, M. Ghorbandoost, J. Hazard. Mater. **155**, 513 (2008).
- [27] S. Schiewer, S. B. Patil, Bioresour. Technol. **99** (2008) 1896.
- [28] J.S Chang and J.Hong, Biosorption of mercury by the inactivated cells of *Pseudomonas aeruginosa* PU21.Biotech. Bioeng. 44: 999-1006, 1994.
- [29] C. N. Deepa, Jayadevappa and S. Suresha, Removal of Zn (II) ions from aqueous solution and industrial waste water using leaves of *Araucaria cookii*, Archives of Applied Science Research, 5 (4) (2013) 117-126.
- [30] Langmuir. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Amer. Chem.Soc., 40 (1918) 1361-1403.
- [31] H Freundlich, W. J. Helle,. Uber die adsorption in Lusungen. J. Amer. Chem. Soc., 61 (1939) 2- 28.
- [32] C. N. Deepa, A. A. Syed and S. Suresha , Kinetic and Isothermal Studies on the removal of Copper (II) from aqueous solution by *Araucaria cookii*: Response

Surface Methodology for the Optimization of Parameters, International Journal of Recent Scientific Research Research 5(4) (2014) 820-827.

- [33] R. H Myers and D C. Montgomery Response Surface Methodology. John Wiley and Sons, USA (2002).
- [34] Preetha and Viruthagiri, Application of response surface methodology for the biosorption of copper using *Rhizopus arrhizus*, Elsevier (2006)