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Application of Response Surface Methodology for Optimization of Heavy Metals Biosorption on Natural Gum of Acacia Nilotica

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***Abstract* - In the present study, application of response surface methodology (RSM) was used for optimization of cadmium (Cd) and lead (Pb) removal from wastewaters using the gum of *Acacia nilotica* as an adsorbent material. The influence of various process parameters such as contact time, solution pH and temperature on the removal process was investigated.**

Response surface plots were used to determine the interaction effects of main factors and optimum conditions of process, respectively for the simultaneous removal of cadmium and lead .From the experimental result, maximum of lead (II) removal of 60% was obtained at the optimum condition of contact time (20 min), pH (4) and temperature (50°C), while maximum of cadmium (II) removal of 100% was obtained at the optimum condition of contact time (25 min) , (pH 5) and temperature (70°C).

***Keywords* - Gum of *Acacia nilotica*, Adsorption, cadmium, lead, Response surface methodology (RSM)**

I. INTRODUCTION

Nowadays, the problem of contamination by heavy metals in water, and wastewater are important environmental pollutants, particularly in areas with high anthropogenic pressure. In addition to these metals, copper, manganese, iron, and zinc are also important trace micronutrients. The presence of trace heavy metals in the atmosphere, soil, and water can cause serious problems to all organisms, and the ubiquitous bioavailability of this heavy metal can result in bioaccumulation in the food chain which especially can be highly dangerous to human health [1].

Heavy metals cannot be biodegraded and thus remain in the environment for long periods. The environmental protection requires limiting the contents of these heavy metals in the permitted maximum.

Several types of methods can be applied for removal and recovery of metals present in the effluent [2],[3],[4] precipitation and coprecipitation, electrodeposition and electrocoagulation, cementation, membrane separation, solvent extraction, ion exchange [5] and reverse Osmosis [6]. Several studies using adsorption and bio different sorption systems, developed from various materials of industrial waste, for the removal of heavy metals [6]. However, most of these techniques have high operating costs and in some cases are limited in terms of efficiency of metal removal [7]. The use of organic and inorganic inexpensive adsorbent to remove heavy metals from contaminated waters and industrial effluents has shown its worth as alternatives to traditional physicochemical methods a new method of removing heavy metals in solution to effectively and economically based on the use of materials of natural origin.

Their use is to propose the addition or as an alternative to conventional methods .These materials are characterized by their adsorption capacity, a high specific surface and abundance in nature. Among these natural materials are cited gums of *Acacia nilotica*.

Response surface methodology (RSM) is a collection of mathematical and statistical approach for experimental design useful for analyzing and evaluating the effects of variable as well as searching optimum conditions of variable to predict targeted responses [8], [9]. RSM has been proven to be successfully implemented in some researches, such as engineering, food processing, biotechnology and adsorption processes for optimization [7], [8], [9], and [10], [11], [12], [13]

The main purpose of this study is to evaluate the gum *of Acacia nilotica* adsorption capacity that is abundant and inexpensive materials for the removal of ions of cadmium and lead in water using response surface methodology. Besides, investigation to the effect of pH, temperature, and contact time was done.

II. MATERIALS AND METHODS

II.1. Materials

All chemicals used were of analytical reagent grade which were purchased from Sigma Aldrich. All solutions were prepared using Milli-Q water. Lead (II) and cadmium (II) stock solutions of 1000 m/ L were prepared by dissolving $Cd(NO3)_2.4H2O$ and $Pb(NO3)_2$, respectively. All metal solution used in the experiments were obtained by stock solution dilution.

II.2. Adsorbent

The adsorbent of acacia gum is harvested manually every ten days during the dry season (October to May to June). It is first spread in the shade for a period of at least one week to allow drying (the ressuyage). Then is cleaned with a small knife for removing sticky peel and other impurities.

After it is placed on a tarp in the sun for weeks it was covered with a thin white film whose fall during the screening provides better clarity and purity that is: bleaching. Finally the sun and bleached Gum is packed in new bags of 50 kg.

II.3. Batch adsorption procedure

To evaluate the performance of adsorbent material, batch experiments were carried out. The adsorbent material 2.5g was placed in 250 ml flasks containing 50 ml of standard solutions of Pb and Cd (50 ppm).

Then, adjusted (pH 0–11.71) by adding 0.01M HCl or 0.01 M NaOH solutions. The flasks were shaken at different temperatures (13–97°C) on an electrical shaker at 100 rpm for a designated time intervals (0–65.3 min). The time required for reaching the equilibrium condition was estimated by analyzing the samples at regular intervals of time. The gum of acacia was separated from the solution by filtration and resulting solutions were

Analyzed.

Batch experiment was carried out with variation of the three factors including pH, contact time and temperature as shown in Table.1. The 15 runs with all combinations of factors for each adsorbent were randomly performed according to a box-behnken statistical design (BBD), one of Response Surface Methodology experimental design under

Design Expert 6.0.8 stat ease software (Stat-Ease Inc., Minneapolis, MN, USA) for linear, quadratic and interaction effects of three factors. All the experiments conducted in duplicate and mean values were presented. The removal efficiency of cadmium and lead solution was defined as equation 1:

$$Y= ((C_0-Ce)/C_0)*100 \qquad (1)$$

Where C_0 and Ce are the initial and final concentration of metal ions.

II.4. Experimental design

The applied optimization approach is based on a central composite design and RSM, this method is one of the most important experimental designs used in process optimization studies [14] in order to describe the nature of the response surface in the optimum region, a central composite design with five coded levels was performed (-1.68, --1, 0, 1, 1.68) and three factors (contact time (min), temperature (T) and (pH)) were selected and processed simultaneously through the central composite design.

In general, central composite designs need a total of (2^k + 2k +N_0) runs where k is the number of studied factors, 2^k are the points from the factorial design, 2k the face centred points and N_0 the number of experiments carried out at the centre (Figure 1). As usual, the experiments were carried out in random order to minimize the effect of systematic errors.

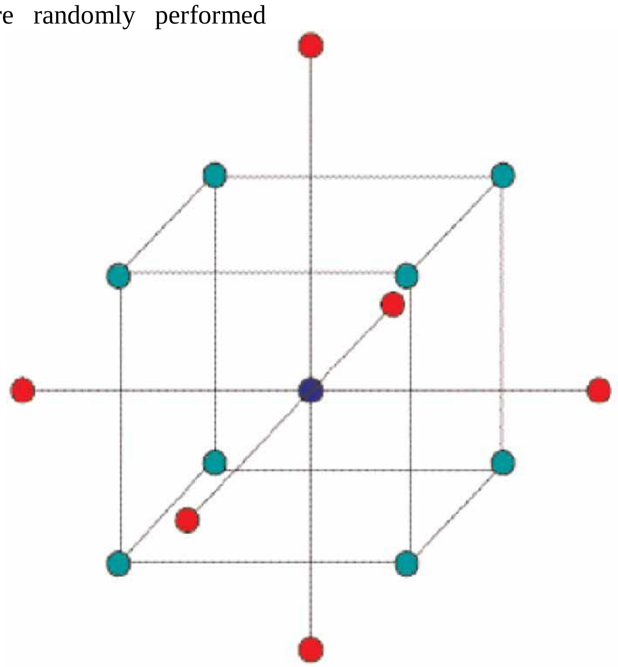

Figure 1.Spatial representation of a complete centred composite design with three factors.

A CCD with 15 experiments was used to optimize effective parameters with a minimum number of experiments, and for analyzing the interaction between the parameters. To determine the relationship between the preparation variables and responses to the study, the data must be analyzed by a statistical approach using the regression equations 2 and 3. For the regression equation, the preparation variables were coded according to the eq. (2): The coded values of the independent variables were determined by the following equation:

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$$X_i = (x_i - x_{0i})/\Delta x_i \quad i=1, 2, 3\ldots\ldots k \quad (2)$$

Where Xi is the coded value of the i^{th} variable, x_i is the uncoded value of the i_{th} test variable, x_{oi} denotes the uncoded value of the i_{th} test variable at the center point and Δx_i is the step change. The range and levels of independent process variables were summarized in Table 1. The behavior of the percentage removal of Cd (II) and Pb (II) was explained by the following second order polynomial equation 11, 12. This can be represented by following Eq. (3)

$$Y = \beta_0 + \sum_{i=1}^{n} bi\,xi + \sum_{i=1}^{n} bii\,xi^2 + \sum_{i-1}^{n-1}\sum_{j=i+1}^{n} bijxixij \quad (3)$$

Where Y is the response variable, β_0, β_i, β_{ij} and β_{ii} are the regression coefficients for intercept, linear effect, double interaction and quadratic effects respectively, x_i, x_j

Table 1.Parameter levels and coded values used in the experimental design

Variables	Code	Coded variable levels				
		-1,68	-1	0	+1	+1,68
pH	X1	0	1	5	9	11.71
Temperature(°C)	X2	13	30	55	80	97
Time (min)	X3	0	5	27.5	50	65.3

III. RESULTS AND DISCUSSION

III.1. Quadratic model for Cd(II) and Pb(II) adsorption process

To examine the combined effect of three different independent process parameters on percentage removal of Cd(II) and Pb(II) 15 experiments were performed. The experimental design is given in table 2, along with experimental data and predicted responses.

Table 2.Experimental design and response value

Run order	Coded Value			Removal (%)	
	pH	Temperature (°C)	Time (min)	Cd(II)	Pb(II)
1	1	30	5	67.5	93.66
2	9	30	5	71.78	95.66
3	1	80	5	68.5	95.33
4	9	80	5	72.78	95.66
5	1	30	50	68.66	94.33
6	9	30	50	72.95	94.66
7	1	80	50	69.66	96
8	9	80	50	73.95	96.33
9	5	55	27.5	76.8	97.66
10	0	55	27.5	71.48	97.33
11	11.71	55	27.5	75.48	97.66
12	5	13	27.5	76.8	97.66
13	5	97	27.5	76.13	96.66
14	5	55	0	73.31	95.33
15	5	55	65.3	72.65	95.33

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The complete design matrix for 15 experimental runs, including the coded and actual factors of variables together with the results obtained for removal percentage of Cd(II) and Pb (II) is listed in table 2.

The quadratic model was selected by the software for both the responses. Multiple regression analysis was used to correlate the responses of removal percentage with the three variables studied using a second order polynomial as shown above by Eq. (3). The quadratic regression models for removal percentage of Cd (II) ions and removal percentage of Pb (II) ions, can be represented by following equations of (4) et (5):

$$\% Cd(II) = 130.862 - 4.5pH - 1.618T - 2.016t + 0.2pH^2 + 0.01233T^2 + 0.0266t^2 + 0.05pH*T + 0.0021T*t + 0.04pH*t \quad (4)$$

$$\%Pb(II) = 80.575 - 1.071pH - 1.4588T - 1.0096t + 0.1550pH^2 + 0.01433T^2 + 0.00886t^2 - 0.0018pH*T + 0.00402T*t - 0.001876pH*t \quad (5)$$

Positive sign in front of these three terms represents synergistic effect, while negative sign represents antagonistic effect.

The coefficients with two factors and others with second order terms show the interaction between the two factors and quadratic effect, respectively.

Table 3.Statistical parameters obtained from the analysis of variances (ANOVA) for the models for Pb (II) and Cd (II) removal % from gum of acacia nilotica

Variable	Removal of Cd (II)	Removal of pb (II)
Standard deviation	2.41	0.807
Mean	70.36	94.88
Coefficient of variation, CV	1.55	0.89
R- squared (R^2)	0.9748	0.9512
R^2 adjusted	0.9433	0.9061
Adeq. precision	10.33	18.63

Table 4.Analysis of variance (ANOVA) for removal Cd (II)

Variation source	coefficient	sum of squares	DF	mean square	value F	prob>F
Intercept	130.862		1			
X_1	- 4.5	58.5	1	58.5	9	<0.0001
X_2	-1.618	11.32	1	11.32	2.03	<0.0001
X_3	-2.016	26.208	1	26.208	4.12	<0.0001
X_1X	0.05	0.4	1	54	0.035	<0.0001
X_1X_3	0.04	0.32	1	0.32	0.03	<0.0001
X_2X_3	0.002	0.016	1	0.016	0.0045	<0.0001
X_1^2	0.2	82	1	82	0.046	<0.0001
X_2^2	0.01233	14	1	14	3.33	<0.0001
X_3^2	0.0266	0.2	1	0.26	0.00201	<0.0001

Table 5.Analysis of variance (ANOVA) for removal Pb (II)

Variation source	coefficient	sum of squares	DF	mean square	value F	prob>F
Intercept	80.575					
X_1	-1.071	11.41	1	11.41	2.15	<0.0001
X_2	-1.4588	23.62	1	23.62	5.02	<0.0001
X_3	-1.0096	8.66	1	13.42	2.85	<0.0001
X_1X_2	-0.0018	8.62	1	8.62	0.96	<0.0001
X_1X_3	-0.001876	0. 41	1	0.41	0.0015	<0.0001
X_2X_3	0.00402	2.8	1	2.8	0.051	<0.0001
X_1^2	0.1550	63	1	63	6.89	<0.0001
X_2^2	0.01433	25	1	25	3.02	<0.0001
X_3^2	0.00886	0.36	1	0.36	0.004	<0.0001

The accuracy of the model developed can be understood by the value of R^2, adjusted R^2 and standard deviation. R^2 indicates the ratio between sum of the squares (SSR) with total sum of the square (SST) and it describes up to what extent perfectly the model estimated experimental data points.

Determination of CV value is essential as it indicates the ratio between standard error of estimate with the mean value of the observed response as percentage. It measures the reproducibility of the model. If the value is less than 10% the model used can be considered reproducible.

It was found that the CV values obtained for the removal of gum percentages of Cd (II) and Pb (II) were 1.55 and 0.89 showing reproducibility of the models. The correlation coefficient R^2 and adjusted R^2, CV and standard deviation is listed in table 3. The competence and significance of the model was justified by analysis of variance (ANOVA).

Analysis of variance (ANOVA) for the model to elimination percentage of Cd (II) and Pb (II) is listed in the table 4. The values of Prob > F below 0.05 reflects the terms of the model were significant. Here, pH, temperature and time.

The regression parameters and graphic interpretation for each response with statistical significance were calculated using Design-Expert software (version 6, Stat-Ease, Inc., Minneapolis, USA). The relationship between the experimental variables and responses were assessed by generating response surface and contour plots.

III.2. Effect of pH

The heavy metal ions adsorption is strictly pH dependent. The distribution of Pb (II) and Cd (II) ions in aqueous water is mainly dependent on pH conditions. PH dependent behavior for removal of lead from waste water using bagasse Fly Ash also has been reported earlier by Gupta [15]

The uptake of Pb (II) by adsorbent material was increasing from pH 1 to 3 and maximum at pH 4 and after that became constant, when the pH value was exceeded to 5 shown in Fig.2. Maximum removal efficiency was 100% at pH 4. Hence, for further experiment pH 4 was selected as an optimum pH value.

The uptake of Cd (II) by adsorbent material was increasing from pH 1 to 4 and maximum at pH 5, after that adsorption decreased, when the pH value was exceeded to 6 as in Fig.2. Maximum removal efficiency was 75.95% at pH 5. Hence, for further experiment pH 5 was selected as an optimum pH value.

The decrease in adsorption at a higher pH may be attributed due to the hydrolysis of lead and cadmium.

A similar behavior has been reported earlier [16] for the adsorption of Hg (II) and also by Gupta et al., for the removal of Pb (II) by fly ashes [15]

So, finally it was concluded that, adsorbent functional groups on which adsorption of lead and cadmium ions takes place provide the active sites for the binding of the metal ions when solutions were acidic.

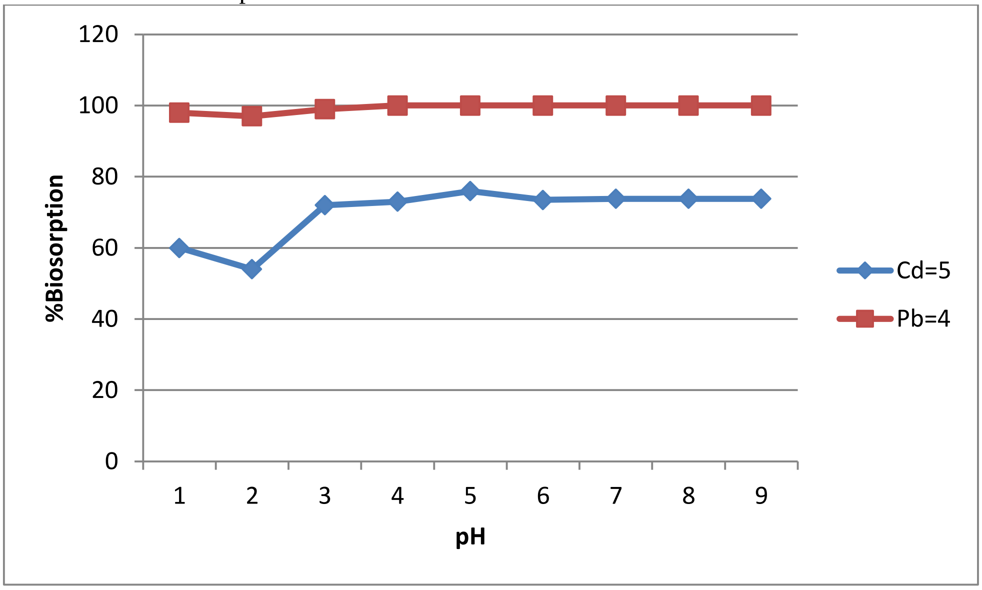

Figure 2.Effect of pH on adsorption of Pb (II) and Cd (II) by gum of *Acacia nilotica*

III.2. Effect of temperature

In lead solutions maximum adsorption was observed at 50° C and removal efficiency was 96% and in case of cadmium solutions, maximum adsorption was obtained at 70 °C and removal efficiency was 83%. But once the equilibrium has been established it remains constant or decreases.

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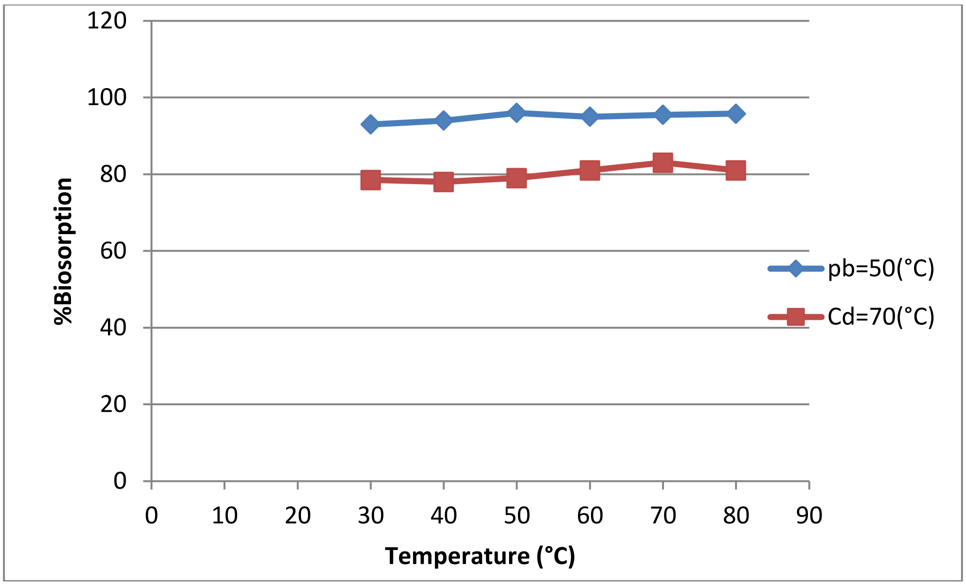

Figure 3.Effect of temperature on adsorption of Pb (II) and Cd (II) by gum of *Acacia nilotica*

III.3. Effect of contact time

For Pb (II), the minimum adsorption was 92% at 5 min and maximum adsorption was 97% at 20 min, which indicate the availability of the adsorption sites. Further increase in time up to 30 min, the adsorption was constant and after that increase in time contact decreased the removal of Pb(II). Therefore, further adsorption experiments for lead were carried out for a contact time of 20 min. For Cd(II), the minimum adsorption was 63.5% at 5 min and maximum adsorption was 72.45% at 25 min, which indicate the availability of the adsorption sites. Further increase in time contact decreased the removal of Cd(II). Therefore, further adsorption experiments for Cd (II) were carried out for a contact time of 25 min.

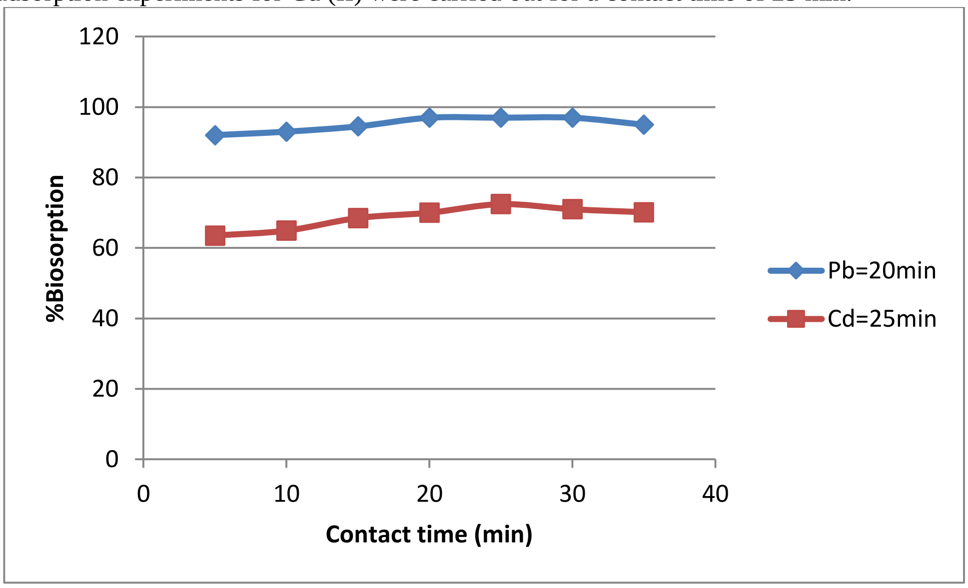

Figure.4.Effect of times on adsorption of Cd (II) and Pb (II) by gum of *Acacia nilotica*

IV. Determination of optimal conditions

The quadratic response surface for the three factors involved generates a four-dimensional response surface, which can be illustrated in a three-dimensional (3D) response surface. For this, we used the software MAPLE 9.5. The surfaces were obtained by varying an experimental factor each time while keeping the third constant at its central value.

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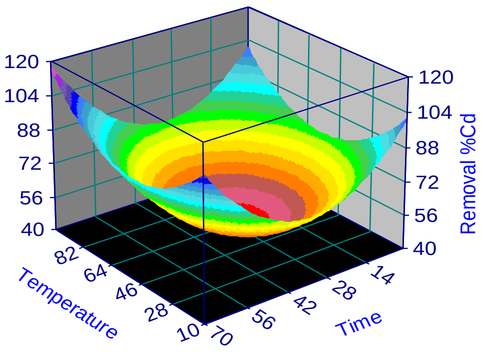

Figure 5.RSM 3D plot showing the effect of temperature and time for Cd(II) removal

The combined effect of temperature and contact time on removal efficiency of Cd (II) at constant pH (5) is depicted in Fig. 5. The percentage removal of Cd (II) ion increased with increasing the temperature of Cd (II) ions and lower value of time. It is also clear from Fig.5 that the removal efficiency with increasing in contact time and decreasing the temperature. The maximum biosorption (100 %) was observed at temperature (70°C) and contact time (25min).

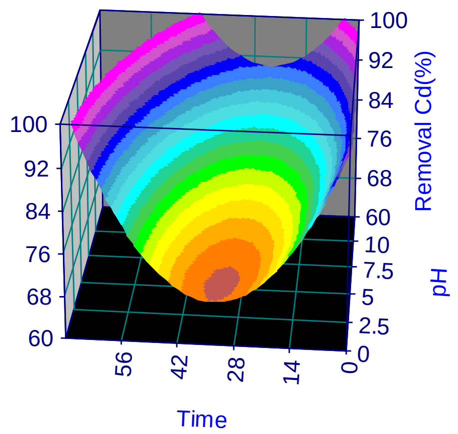

Figure 6.RSM 3D plot showing the effect of time and pH for Cd (II) removal

The effect of contact time and pH on Cd (II) removal at constant temperature T (55°C) is shown in Fig.6. Value of pH and contact time was highly significant in adsorption process; it was observed that percentage of Cd (II) ion removal increased with increase in contact time and pH. At time 25 min and pH =5 the removal of Cd (II) ions was 100%.

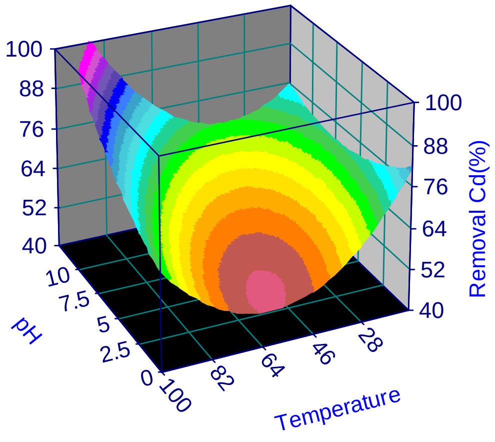

Figure 7.RSM 3D plot showing the effect of pH and temperature for Cd(II) removal

The interaction between pH and temperature on Cd (II) removal is presented in Fig.7
It was observed that a sharp increase in the Cd (II) ion removal occurred when the pH value of the solutions changed from 2.5 to 11.71 and the temperature decrease. The maximum adsorption of Cd (II) ions (100%) are obtained at pH =5.

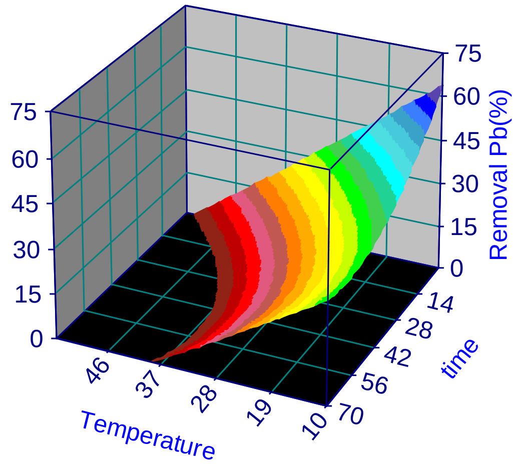

Figure 8.RSM 3D plot showing the effect of temperature and time for Pb(II) removal

The biosorption of Pb (II) shows the effect of pH and contact time. Fig.8 depicts the maximum removal of Lead in the optimized condition was at 20 min at temperature of 50°C. The percentage removal was 60%.

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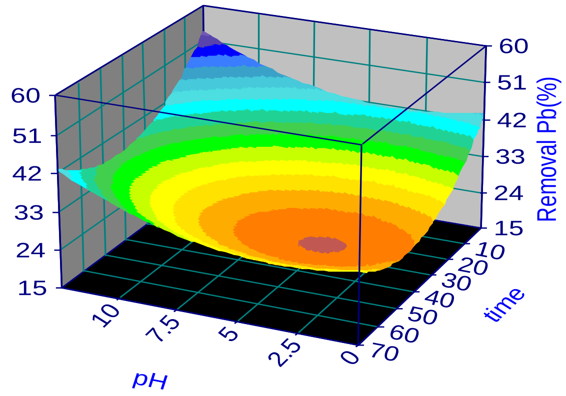

Figure 9.RSM 3D plot showing the effect of pH and time for Pb(II) removal

The biosorption of Pb (II) shows the effect of pH and contact time. Fig.9 depicts the maximum removal of Lead in the optimized condition was at 20 min at the pH of 4. The percentage removal was 51.42%.

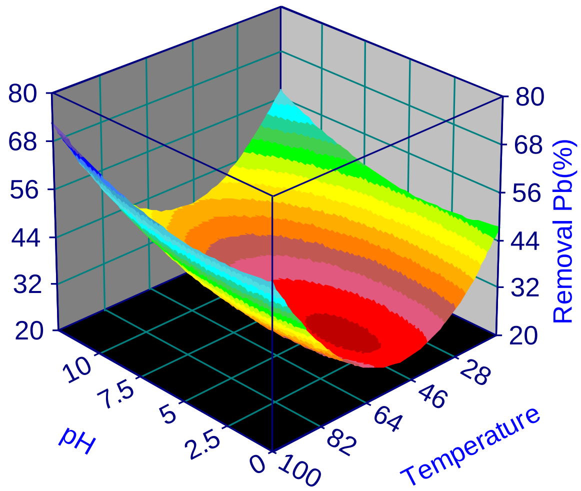

Figure 10.RSM 3D plot showing the effect of pH and temperature for Pb(II) removal

The RSM 3D plot shows the combined effect of pH and temperature for the removal of Pb (II). The results indicate that the maximum adsorption was at pH =4, at the temperature 50°C as shown in Fig 10.

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V. CONCLUSION

We conclude that the gums of *Acacia nilotica* were evaluated as one of the possible biosorbent for the removal of Lead (II) and cadmium from aqueous solution. The lead (II) and cadmium (II) biosorption was influenced by pH, contact time and temperature, the maximum biosorption of cadmium was at pH 5.0, contact time 25 min and temperature (70°C) with the percentage removal 97.5%,for the lead the maximum biosorption was at (pH 4) contact time (20 min) and temperature (50°C) with the percentage removal 80%.

Near 100% deleading was possible for a (pH 4) and 75.95% are removed to (pH 5) in the batch test conditions. Hence this method can be successfully employed to study the importance of individual, cumulative and interactive effects of different test variables of biosorption.

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