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Optimization Studies for Chromium (VI) Removal using Agro-Industrial Wastes

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Abstract

The heavy metals released from various industries are toxic to the environment even at minute concentration. Box-Behnken design is the Response Surface Methodology (RSM) tool used to model higher order response surfaces using lesser experimental trials than a normal factorial technique. The current study, involves the application of Box-Behnken experimental design in evaluating and optimizing the Hexavalent Chromium [Cr(VI)] removal using agricultural industrial wastes as adsorbents. The effect of process variables such as pH (2-9), adsorbent dosage (0.1-3g) and initial Cr(VI) concentration (50-100 mg/L) on the industrial wastes are evaluated. The saw palmeto extract exhibited maximum chromium removal at a pH of 2 with 1g biomass dosage and at an initial metal ion concentration of 100 ppm. Similarly, the maximum Cr(VI) removal efficiency using waste of black cumin extract was observed with 2g biomass dosage at an initial metal ion concentration of 60 ppm for a pH value 2. The maximum chromium removal using waste of ginger root extract was observed with 2g biomass dosage at an initial metal ion concentration of 60 ppm for a pH value 2. The RSM technique provided a mathematical model which helped in determining the interactions between various process variables which affected the removal efficiency of Cr(VI).

Keywords: *Hexavalent chromium, Optimization, Box-Behnken design, Biomass dosage, Chromium(VI)*

1.0 Introduction

Chromium, lead, cadmium, zinc, copper, arsenic, and mercury are a few examples of heavy metals that harm people, even at low concentrations[1,2]. Under normal circumstances, all tissues and cells contain non-essential metals, and individuals can tolerate chromium concentrations between 100 and 200 times their body's total without experiencing negative consequences. As a result, several methods have been created in an effort to clean wastewater that has been polluted with heavy metals, especially chromium. While more recent methods used microbiological processes, some of these technologies were based on physical-chemical processes such chemical reduction, precipitation, coagulation and focculation. The latter includes biosorption, a technique for pollutant removal that shows a promising results and has a number of benefits over conventional physical-chemical ones[3].

Agro-industrial wastes are utilized in various fields including biofuels, enzymes, vitamins, antioxidants, animal feed, antibiotics, and other chemicals production[4]. Agricultural waste products are implied to be some of the typical renewable resources that are accessible worldwide and may be employed as sustainable adsorbents[3]. Experimental designs are far more effective when compared to one factor at a time designs. The interactive effects of the variables can be determined using the experimental designs. One of the most effective experimental designs are Box-Behnken

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response surface methodology[5]. In turn, it generates empirical equations that correlate the relationship between variables and responses[6].

The present study involves the removal of chromium ions using industrial wastes such as saw palmeto extract, black cumin extract and ginger root extract as adsorbents. It carries out optimization studies to better understand the relationships between the factors (biomass dosage metal ion concentration and pH) and percentage biosorption using RSM based Box-Behnken (BB) experimental design.

2.0 Materials and Methods

The spent biomass used as adsorbent for removal of heavy metals was obtained from MS. Sami Labs Pvt Ltd, Nelamangala, Bangalore viz., wastes from, ginger root extract (GRE), saw palmetto extract (SPE) and black cumin extract (BCE). The powdered samples collected were sieved with a 100µm mesh to maintain uniformity and used without any pretreatment. Stock solution of chromium (1000 ppm) was prepared by dissolving 0.283g of $K_2Cr_2O_7$ in 100 ml of distilled water. Studies were conducted using 100 ml of the solution at different concentrations 20, 40, 60, 80 and 100 ppm. Initial Cr(IV) concentration, pH and adsorbent dosage are considered for Box-Behnken experimental design. The percentage absorption of Cr(VI) measured for wastes from ginger root, saw palmetto and black cumin extracts fitted a second order polynomial model as suggested[5]. The responses are outlined in the Table 1.

3.0 Results and Discussion

The batch studies were carried out to estimate the percentage biosorption using wastes of ginger root extract, saw palmetto extract and black cumin extract varying the initial metal ion concentration, biomass dosage and pH at room temperature (25±5ºC) for 1 hour. The maximum percentage adsorption was observed at 1 hour.

3.1 Wastes from Ginger Root Extract (GRE)

The second order polynomial model of the Box-Behnken design response for waste from ginger root extract is given in equation 2 and Y is the percentage adsorption.

$$Y_{GRE} = 81.8509 + 95.3166\,x_1 - 28.6428\,x_1^2 - 1.8428\,x_2 + 0.0045x_2^2 + 2.5238x_3 - 0.9748x_3^2 + 0.1003x_1x_2 - 3.1993x_1x_3 + 0.1480x_2x_3 \quad \ldots (2)$$

Pareto chart (Figure 1) and P-value[5] in Table 1 indicates that ginger root extract is the major influential parameter for adsorption. The multiple coefficient of determination, R^2 is found to be 0.89156 showing close relation between the predicted and experimental values.

Table 1: Box-Behnken experimental design for ginger extract extract, saw palmetto extract and black cumin extract

	Agro-Industrial Wastes	Chromium (ppm)	pH	Percentage Adsorption	
	Ginger Extract (g)			Experimental	Predicted
1	0.1	50	7	16.95	30.07235
2	2	50	7	69.56	63.86795
3	0.1	100	7	25.26	23.65223
4	2	100	7	72.8	66.97747
5	0.1	60	2	25.38	15.43745
6	2	60	2	84.23	81.53247
7	0.1	60	9	19.56	17.98797
8	2	60	9	27.32	41.53211
9	1	50	2	74.1	82.08912
10	1	100	2	38.52	43.17096
11	1	50	9	69.54	54.12058
12	1	100	9	64.24	67.01934
13	1	60	7	69.38	69.69667
14	1	60	7	70.21	69.69667
15	1	60		69.5	69.69667

	Saw Palmetto (g)	Chromium (ppm)	pH	Percentage Adsorption	
				Experimental	Predicted
16	0.1	50	7	48.75	53.86283
17	2	50	7	79.6	76.53322
18	0.1	100	7	53.68	53.61212
19	2	100	7	82.15	80.17183
20	0.1	60	2	68.05	64.33132
21	2	60	2	91.96	91.35187
22	0.1	60	9	47.28	45.95373
23	2	60	9	62.32	67.97307
24	1	50	2	89.52	92.39686
25	1	100	2	92.42	93.86995
26	1	50	9	76.54	71.61709
27	1	100	9	72.66	73.25610
28	1	60	7	80.22	80.15333
29	1	60	7	79.66	80.15333
30	1	60	7	80.58	80.15333
	Black Cumin (g)	Chromium (ppm)	pH	Percentage Adsorption	
				Experimental	Predicted
31	0.1	50	7	31.32	35.36656
32	2	50	7	50.04	48.70296
33	0.1	100	7	28.95	28.17906
34	2	100	7	77.64	75.70142
35	0.1	60	2	62.62	63.19853
36	2	60	2	81.18	83.47887
37	0.1	60	9	29.27	25.41585
38	2	60	9	44.57	45.54675
39	1	50	2	75.08	72.00393
40	1	100	2	80.94	81.13867
41	1	50	9	33.82	34.18655
42	1	100	9	40.63	43.14085
43	1	60	7	37.17	37.08333
44	1	60	7	36.97	37.08333
45	1	60	7	37.11	37.08333

The results are shown in the graph (Figures 2,3,4) which shows the interactive effects of the independent process parameters on the Cr(VI) removal.

The effect of initial chromium ion concentration and waste from ginger root extract on percentage biosorption (Figure 3) was studied at a constant pH of 2^2. At low biomass dosage of less than 0.4g, the biosorption varied between 20 to 50%. However, the biosorption increased with increase in biomass dosage. The maximum chromium removal efficiency was 81%. This may be due to low surface area and less number of active sites.

The effect of waste from GRE and pH on percentage biosorption (Figure 4) was studied at a constant initial chromium ion concentration of 50ppm. At low biomass dosage of less than 0.4g, the biosorption varied between 20 to 50% with pH being less effective. The biosorption increased with

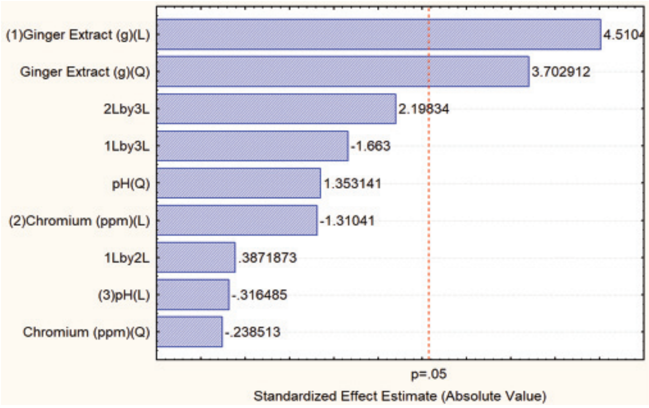

Figure 1: Pareto chart for waste from GRE

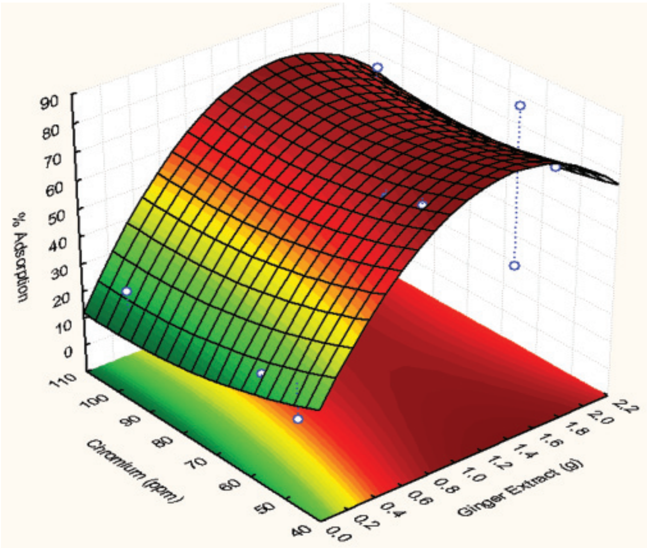

Figure 2: Effect of waste from GRE and initial Chromium ion concentration on percentage biosorption

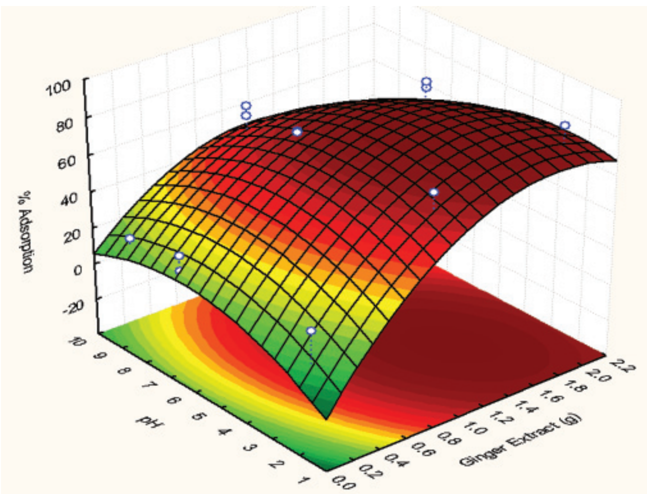

Figure 3: Effect of waste from GRE and pH on percentage ebiosorption

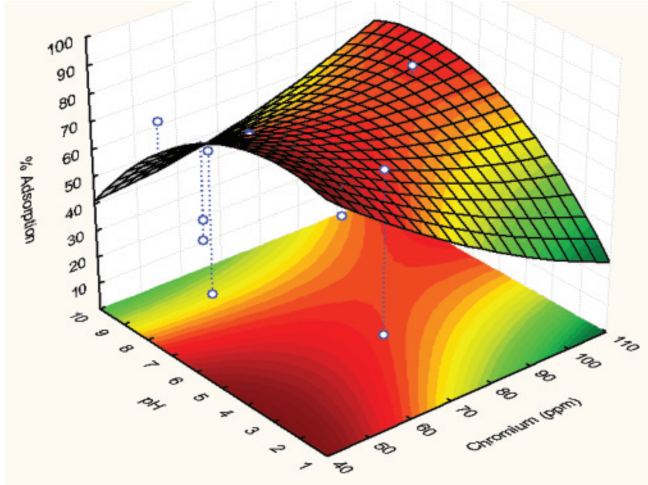

Figure 4: Effect of initial Chromium ion concentration and pH on percentage biosorption

increase in biomass dosage as well as pH. The maximum Cr(VI) removal efficiency was observed at 80% for a pH of 2.

At a constant biomass dose of 1g, the impact of the initial chromium ion concentration and pH on percentage biosorption (Figure 5) was investigated. The biosorption was found to be at its maximum at a pH of 2 and an initial concentration of chromium ions of 50 ppm. As long as the biomass dose is steady, the initial increase in chromium ion concentration has little impact.

3.2 Waste from Saw Palmetto Extract (SPE)

Pareto chart (Figure 6) and P-value (Figure 5) indicates that waste from SPE is highly influential on percentage biosorption and pH comparatively to a lesser extent.The second order polynomial model of the Box-Behnken design response for waste from SPE is given by equation 3 and Y is the percentage biosorption.

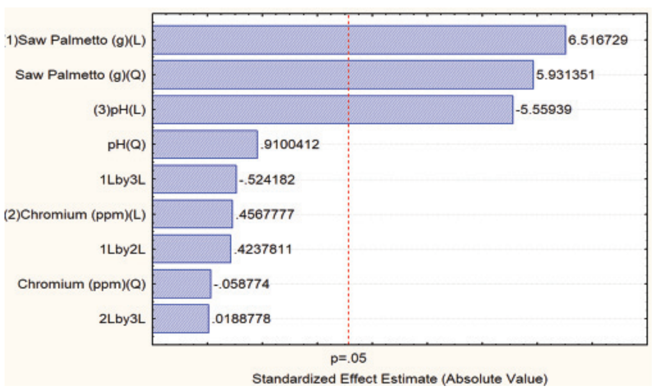

Figure 5: Pareto chart for waste from SPE

$$Y_{SP} = 63.2183 + 48.4439x_1 - 17.1081x_1^2 - 0.0738x_2 + 0.0004x_2^2 + 0.0728x_3 - 0.2445x_3^2 + 0.0409x_1x_2 - 0.3760x_1x_3 + 0.0005x_2x_3 \quad \text{... (3)}$$

The experimental and the predicted Cr(VI) percentage biosorption are almost close as shown in Figure 5.

The multiple coefficient of determination, R^2 is found to be 0.95985 showing close relation between the predicted and experimental values. The maximum chromium ion removal efficiency was observed at 92% for waste from SPE with 1g biomass dosage, an initial metal ion concentration of 50 ppm and at a pH value of 2. The effect of initial chromium ion concentration and waste from saw palmetto extract on percentage biosorption (Figure 6) was studied at a constant pH of 2. At low biomass dosage of less than 0.4g, the maximum biosorption was found to be 70%. However, the biosorption increased with increase in biomass dosage.

The maximum Cr(VI) removal efficiency was 90%. This may be due to low surface area and less number of active sites.

The effect of waste from SPE and pH on percentage biosorption (Figure 7) was studied at a constant initial chromium ion concentration of 50 ppm. At low biomass dosage of 0.2g, the biosorption was about 70% but increased with increasing biomass dosage as well as pH. The maximum Cr(VI) removal efficiency was observed at 90% for a pH of 2.

The effect of initial chromium ion concentration and pH on percentage biosorption (Figure 8) was studied at a constant biomass dosage of 1g. The maximum biosorption was at a pH value of 2, 50 ppm initial chromium ion concentration. The maximum biosorption was observed with increase in initial chromium ion concentration for a pH value of 2. The increase in pH was less effective due to the weakening of electrostatic force of attraction between the oppositely charged sorbate and biosorbent[6].

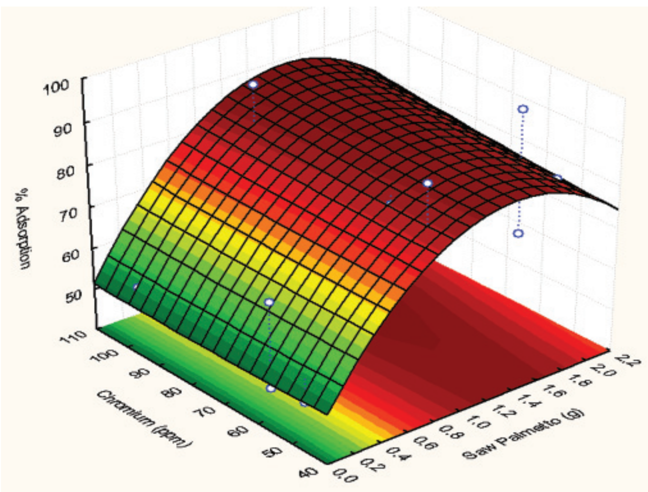

Figure 6: Effect of waste from SPE and initial chromium ion concentration on percentage biosorption

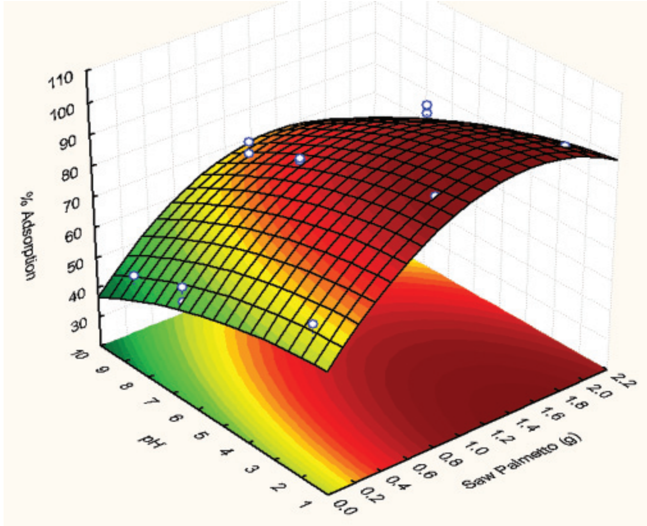

Figure 7: Effect of waste from SPE and pH on percentage biosorption

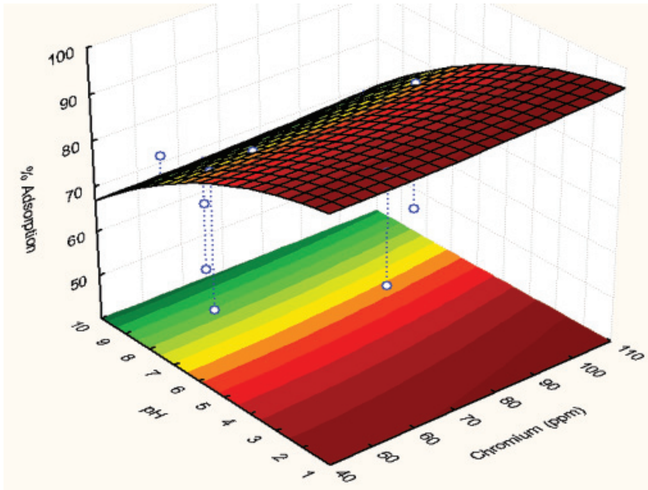

Figure 8: Effect of initial Chromium ion concentration and pH on percentage biosorption

3.3 Waste from Black Cumin Extract (BCE)

The second order polynomial model of the Box-Behnken design response for waste from BCE is given by equation 4 and Y is the percentage biosorption.

$$Y_{BC} = 145.0166 - 17.1665x_1 + 2.9865x_1^2 - 1.5688x_2 + 0.0093x_2^2 - 11.9606x_3 + 0.5996x_3^2 + 0.3599x_1x_2 - 0.0112x_1x_3 - 0.0005x_2x_3 \quad \text{... (4)}$$

Pareto chart (Figure 9) and P-value Table 3, indicates that pH along with BCE and Cr to some extent are influential on adsorption. The multiple coefficient of determination, R^2 is found to be 0.98927 showing close relation between the predicted and experimental values. The 3D response surface plots (Figures 10 to 12) were used to study the interactive effects of the independent parameters on the chromium removal efficiency. The effect of waste from BCE and initial chromium ion concentration on percentage biosorption at a constant pH value of 2 (Figure 10) is not so effective compared to wastes from GRE and SPE.

The maximum Cr(VI) removal efficiency observed was not greater than 50%. The pH variation is least effective (Figure 14) on percentage biosorption. The maximum Cr(VI) removal efficiency was observed between 40 to 50%. The effect of initial chromium ion concentration and pH on percentage biosorption (Figure 11) was studied at a constant biomass dosage of 1g.

The increase in chromium ion concentration was significant when compared to that of pH on biosorption which was observed to vary between 40 to 50% (Figure 12).

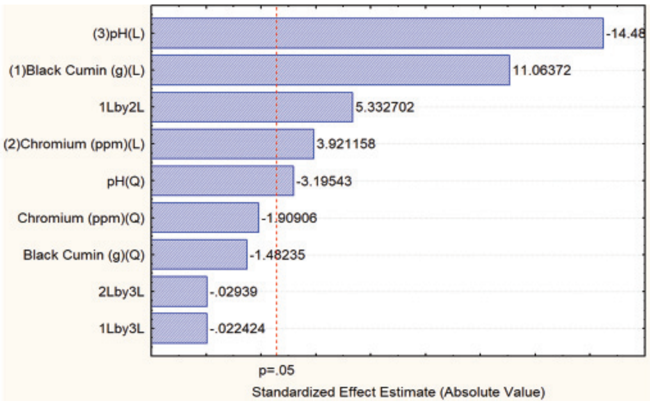

Figure 9: Pareto chart for waste from BCE

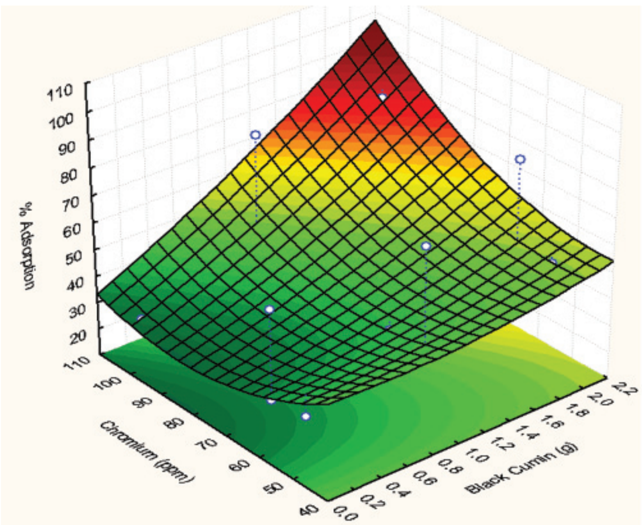

Figure 10: Effect of waste from BCE and initial Chromium ion concentration on percentage biosorption

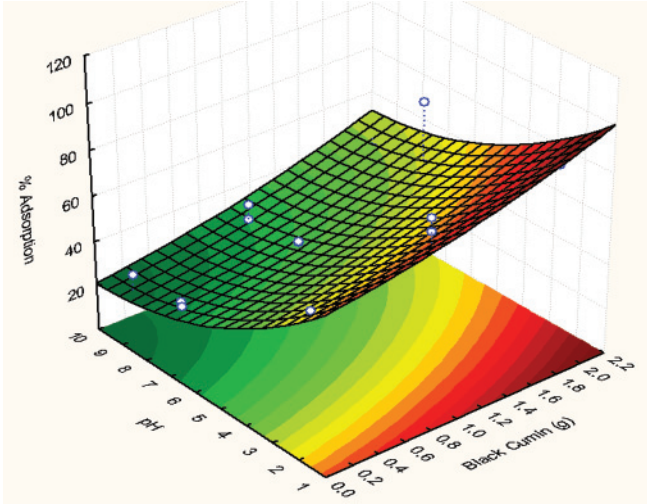

Figure 11: Effect of waste from BCE and pH on percentage biosorption

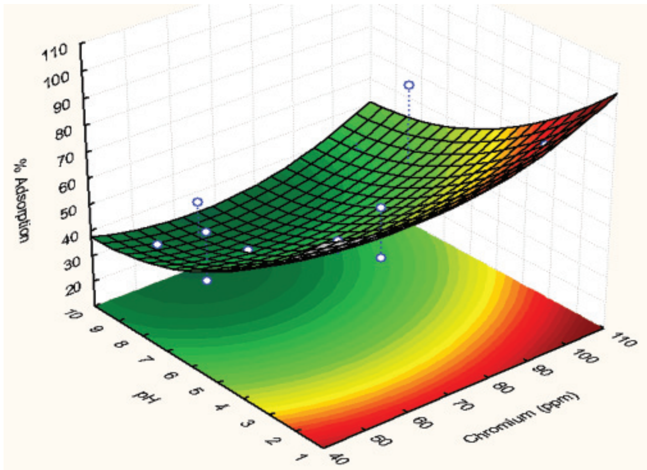

Figure 12: Effect of initial Chromium ion concentration and pH on percentage biosorption

4.0 Conclusions

The Box-Behnken design for the three biosorbents saw palmeto extract, black cumin extract and ginger root extract were used to derive the polynomial expression for Cr(VI) removal. The model is helpful in predicting the percentage adsorption for other industrial wastes as adsorbents and thus eliminates the conduction of batch studies. A relation between the predicted and the experimental variables for Chromium removal is observed for all three biosorbents. The optimized value of the parameters was observed at 1g biomass with a pH of 2 and an initial chromium ion concentration of 50 ppm for the three biosorbents. The maximum chromium removal efficiency was estimated at 81%, 92% and 72% for the wastes from GRE, SPE and BCE respectively. The optimized value of the parameterswas observed at 1g biomass with a pH value of 2 and an initial chromium ion concentration of 50 ppm for the three biosorbents. The maximum chromium removal efficiency was estimated at 81%, 92% and 72% for the wastes from GRE, SPE and BCE respectively.

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