MATHEMATICAL MODELLING BASED ON THE RESPONSE SURFACE METHODOLOGY (RSM) OF LEAD REMOVAL IN SYNTHETIC WASTEWATER USING *CORIANDRUM SATIVUM* AS BIO-SORPTION

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ABSTRACT

Water pollution is a serious environmental issue that needs urgent concern from the government and the non-government board. There is the necessity to treat wastewater with high heavy metal content concentration to the permissible standard limit to protect the aquatic ecosystem. This study investigated the optimum condition for lead removal from synthetic wastewater (industrial wastewater) using the Coriandrum Sativum as a medium for lead extracting. Response surface methodology (RSM) by central composite design (CCD) was employed as the experimental design, in which three operational variables including the pH (4-10), retention time (30-180 minutes), and agitation speed (100-300 rpm). The focus of the study was lead removal. Through the optimization and validation process of the data, the highest removal efficiency of the lead was 74.68% (initial concentration of the lead for synthetic wastewater = 20 mg/L) was obtained at the following optimum condition: pH 6.16, the retention time of 180 minutes, and the agitation speed was at 254rpm. The values predicted from the models agreed satisfactorily with the experimental values, which implied that RSM was reliable and practical for experimental design developed using optimization of the lead removal in the wastewater.

Keywords: *Adsorption, Industrial wastewater, Design Expert 11, Atomic Absorption Spectrometry (AAS), central composite design (CCD).*

1. INTRODUCTION

The socio-environmental issues due to globalization and rapid industrialization are becoming a nuisance for human beings and the ecosystem. Therefore efficient and effective methods are needed, especially for chemical industries. Heavy metals present in wastewater and industrial effluent are the primary concern of environmental pollution. Heavy metals are generally considered those whose density exceeds five g per cubic centimetre. Most of the elements that fall into this category are highly water-soluble, well-known toxics, and carcinogenic agents. Heavy metals are considered the following elements: Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Molybdenum, Cobalt, Manganese, and Aluminum [1]. The pH of water controls the heavy metal compounds solubility in surface waters, the type and amount of ligands on which the metal could adsorb the redox environment of the system, and the oxidation state of the mineral constituents. The various water treatment technologies widely used as coagulation, filtration, ion exchange, solvent extraction, electrolysis, microbial reduction and activated sludge, foam flotation, etc., adsorption are favourable in terms of convenience, ease of operation simplicity of design [2] The practical process of removal of heavy metal pollutants is offered by biosorption. The exploration of natural adsorbents which can eliminate dyes from aqueous solutions is an important field of research due to being environmentally

friendly and ecologically acceptable [3].

The present research investigates the potential of Coriandrum sativum leaves as a low-cost bio-sorbent to remove lead from the aqueous medium; in this research, the synthetic water content of lead prepared to replace the industrial wastewater. A study of adsorption kinetics and equilibrium isotherms has been carried out in the previous research to get an insight into the adsorption behaviour and make the adsorption mechanism more intelligible for the theoretical evaluation and interpretation of thermodynamic parameters. The adsorption capacity was determined through various kinetic models. The experimental parameters, namely the pH, agitation speed and times of adsorption between the *Coriandrum sativum* and synthetic wastewater, have been optimized to remove the metal ion efficiently.

2. MATERIALS AND METHODS

Preparation of adsorbent from Coriandrum sativum

Figure 1a: Fresh Coriandrum Salivum purchased from a shop.
Figure 1b: *Coriandrum Salivum* after washed and chopped.

Based on Figures 1a and 1b, the *Coriandrum sativum* leaves were purchased from the nearby market and washed with tap water to remove any foreign particles and materials. The leaves were then chopped with the standard size, 1.0 to 2.0 cm in length.

Figure 2a: Coriandrum Salivum after a dried overnight at 60^{o}C
Figure 2b: Coriandrum Salivum kept in a tight container for further use.

Figures 2a and 2b show the *Coriandrum sativum* leaves after drying in the oven overnight at 60oC or until the dry weight basis was constant (≈ 95%). The dry weight basis equation used is shown as Equation

1. The dried leaves are then ground with the dry blender to get a good mesh of the size and kept in a tight container for further use as an adsorption agent.

$$Mass\ (dry\ basis) = \frac{w-d}{d} \times 100, \quad (1)$$

where:
w = wet weight of the leaves
d = dry weight of the leaves at a certain temperature.

Preparation of synthetic wastewater for replacing industrial wastewater sample

Figure 3: Preparation of synthetic wastewater in laboratory

In preparing the synthetic wastewater to replace and acted as industrial wastewater, 1000.0 mg of the $Pb(NO_3)_2$ in HNO_3 was add into the de-ionized water (1000.0 mL). This aqueous solution is prepared with a safety procedure and mix well. This solution was kept in an Erlenmeyer flask until further used and covered with aluminium foil to avoid any reaction of the solution and the light. Figure 3 shows the laboratory procedure to work with the aqueous solution.

Adsorption experiments

Figure 4a and 4b: Adsorption process of *Coriandrum sativum* and synthetic wastewater

In this project, the ratio between the C*oriandrum sativum* leaves and the aqueous solution were constant with a ratio of 5.0 gm of *Coriandrum sativum* leaves and 250.0 mL of the aqueous solution (lead content). Before the adsorption agent and aqueous solution were mixed, the pH of the solution was taken to observe the pH changes at the end of the reaction. This flask was placed on the stirrer plate to control the agitation speed of the response. This work was placed in the fume hood for safety purposes. All the experiments planned were done before proceed with the sample analysis using the AAS [4]. Dilutions of the aqueous solution were prepared, and the calibration curve was generated to generate an equation for determining lead concentration. The AAS was stated at 283.0 nm using hollow-cathode lamp type.

Central composite design (CCD) from Design Expert 11.

The first step is to design and run the experiments to set up the factors using Design expert software, version 11. The details of the start-up show in Figure 5 below. For this research, the significant factors chosen are pH, retention time (minutes) and agitation speed (rpm). At the same time, the ratio between the weight of the *Coriandrum sativum* and the volume of the aqueous solution is fixed. Central composite design (CCD) is selected in this research since the factors are only three and all the factors are in numeric type. Besides CCD, the experiment also can be designed using Box-Behnken, or optimal design.

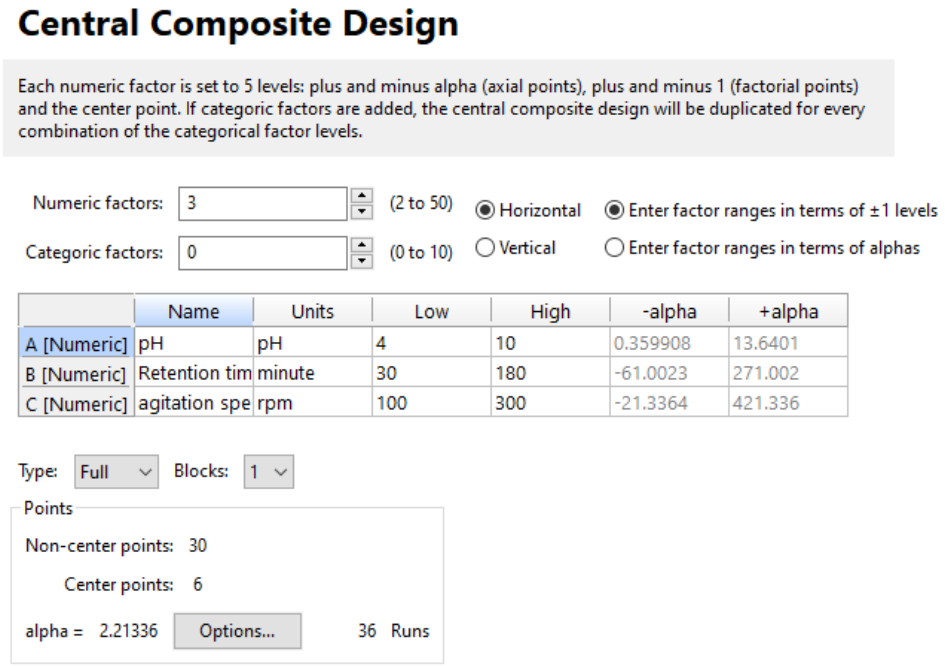

Figure 5: Set up the factors using the central composite design (CCD) from Design-Expert software, version 11.

Table 1 below shows the number of experiments that need to be run. This is the second step after the factors are created, as shown in Figure 5. The software made these arrangements, and from the list, the experiment numbers 4, 7, 9, 12, 31 and 36 were neglected since the magnitude of the factors is out of the spectrum and in the software, this row will be neglected to run the ANOVA analysis.

Table 1: The arrangement of an experiment designed from software.

No of experiment	pH	Retention time (minutes)	Agitation speed (rpm)
1	7.00	105.00	200.00
2	10.00	30.00	300.00
3	4.00	30.00	100.00
4	7.00	271.00	200.00
5	4.00	30.00	300.00

6	10.00	30.00	300.00
7	0.36	105.00	200.00
8	4.00	30.00	300.00
9	7.00	105.00	-21.34
10	4.00	180.00	300.00
11	4.00	180.00	100.00
12	7.00	105.00	421.34
13	10.00	30.00	100.00
14	10.00	180.00	300.00
15	10.00	180.00	100.00
16	10.00	30.00	100.00
17	10.00	30.00	100.00
18	7.00	105.00	200.00
19	10.00	180.00	300.00
20	7.00	105.00	200.00
21	4.00	30.00	300.00
22	10.00	30.00	300.00
23	10.00	180.00	100.00
24	10.00	180.00	300.00
25	7.00	105.00	200.00
26	4.00	30.00	100.00
27	4.00	180.00	300.00
28	4.00	180.00	300.00
29	4.00	180.00	100.00
30	7.00	105.00	200.00
31	13.64	105.00	200.00
32	4.00	180.00	100.00
33	10.00	180.00	100.00
34	7.00	105.00	200.00
35	4.00	30.00	100.00
36	7.00	-61.00	200.00

3. RESULT AND DISCUSSION

Analysis of Variance (ANOVA)

Table 2: The Analysis of Variance (ANOVA) result for the data set.

Source	Sum of squares	df	Mean square	F-value	P-value	
Model	324.4349698	7	46.34785283	2356.181956	4.07E-30	*a
A-pH	1.042083375	1	1.042083375	52.97630624	2.73E-07	
B-Retention time	40.58860504	1	40.58860504	2063.399553	3.04E-23	
C-agitation speed	144.417922	1	144.417922	7341.761944	2.85E-29	
AB	2.421255375	1	2.421255375	123.089159	1.77E-10	
AC	6.033045375	1	6.033045375	306.7014281	2.10E-14	
BC	14.10513338	1	14.10513338	717.0614974	2.77E-18	
AA	115.8269252	1	115.8269252	5888.283805	3.20E-28	

BB	0	0	-	-	-	
CC	0	0	-	-	-	
Residual	0.432756375	22	0.019670744	-	-	
Lack of Fit	0.038640375	1	0.038640375	2.058906198	1.66E-01	*b
Pure Error	0.394116	21	0.018767429			
Cor Total	324.8677262	29				

*a = the P-value is significant for the model

*b = the P-value is not significant for the lack of fit.

Table 2 shows the Model F-value of 2356.18 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, B, C, AB, AC, BC, A^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The Lack of Fit F-value of 2.06 implies the Lack of Fit is not significant relative to the pure error. There is a 16.60% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good and indicates the acceptance of the model. Table 3 shows the R-squared value, and this value indicates the model's equation is reasonable and very fixed with the model. The adjusted R-squared also indicates the percentage is nearest to 100%. This is meant; every factor is very significant with others.

Table 4 shows the coded equation created from the ANOVA and the R-squared value. This equation can be converted to the actual values by replacing the unknown of the A with the pH, while B with the retention time (minutes) and the C is an agitation speed (rpm).

Table 3: The value of the R-squared for the data set.

Std. Dev.	0.1402524	R^2	0.99867
Mean	12.971833	Adjusted R^2	0.99824
C.V. %	1.0812075	Predicted R^2	0.99785
		Adeq Precision	126.26673

Table 4: The coded equation created from the ANOVA.

Lead removal	=
16.901667	
-0.208375	A
1.300458	B
2.453042	C
-0.317625	AB
-0.501375	AC
0.766625	BC
-4.912292	A^2
0	B^2
0	C^2

Figure 6 shows the normal plot of residuals for the ANOVA analysis. The tabulated data from the normal plot residuals shows one data is recommended to be neglected since the value was too far and precise from the other value. This point is experiment number 33; the pH value was 10, retention time was 180 minutes, and agitation speed was 100 rpm.

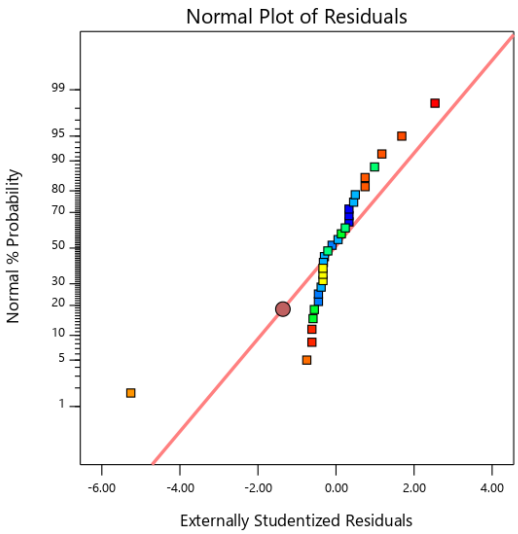

Figure 6: The graph of the Normal Plot of Residuals for the ANOVA

The residuals vs predicted graph shown in Figure 7 also proves the normal plot of residuals acceptable, and experiment number 33 should be ignored during the ANOVA processing.

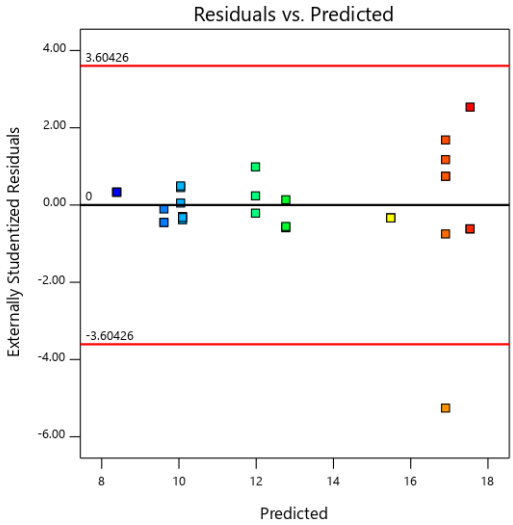

Figure 7: The graph of the Residuals vs Predicted from the ANOVA.

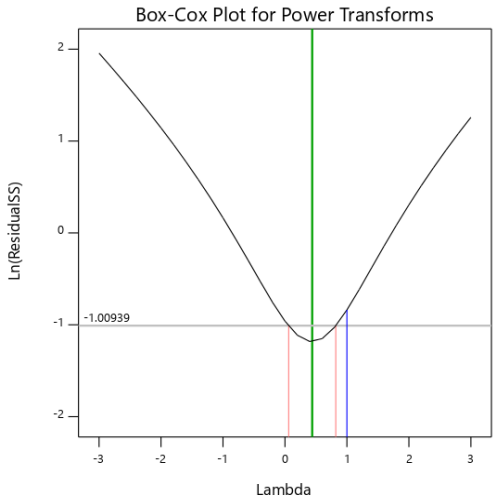

Figure 8: The graph of the Box-Cox for Power Transforms

Figures 9, 10 and 11 show the interaction between both factors; AB, AC, and BC. AB is an interaction between pH and retention time (minutes). At the same time, AC is an interaction between pH and agitation speed (rpm), and BC is an interaction between agitation speed (rpm) and retention time (minutes). From the 3D graph, the interaction between agitation speed and retention time need to reduce the range to fixed the model for achieving the optimum condition. One factor (agitation speed or retention time) is not very significant to the model and can be replaced by other factors.

The condition can be fixed by one factor at a time (OFAT) study before continuing with the central composite design (CCD). From the interaction graph (Figure 11), the communication between the agitation speed and retention time of the reaction is not in good condition; this is because the shape of the graph is not quadratic but more to the linear graph. This shows the relationship for both factors (agitation speed and retention time) is not quite good, and the factors should be replaced with other significant factors in the following research [5].

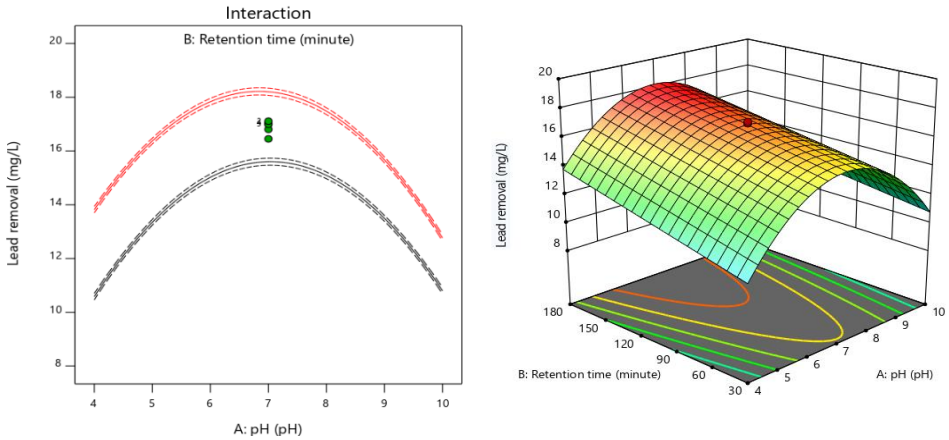

Figure 9: Interaction between pH and retention time (minutes) towards lead removal

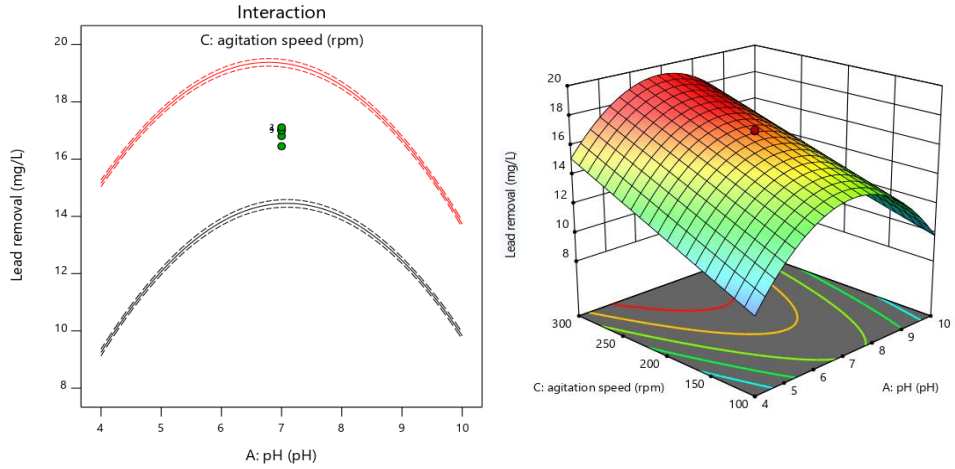

Figure 10: Interaction between pH and agitation speed (rpm) towards lead removal.

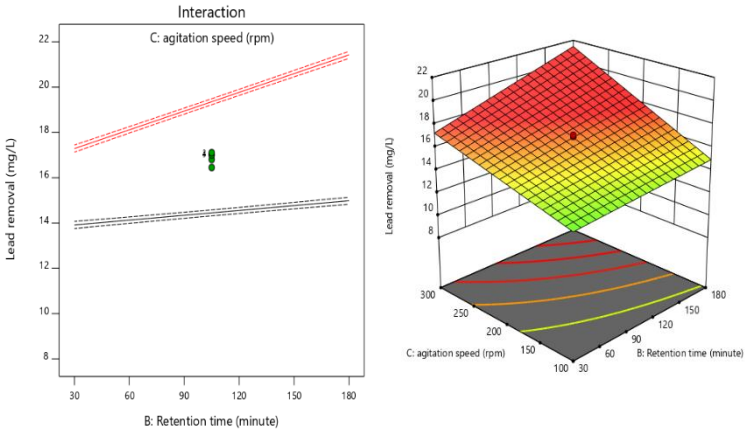

Figure 11: Interaction between retention time (minutes) and agitation speed (rpm) towards lead removal.

Optimization value

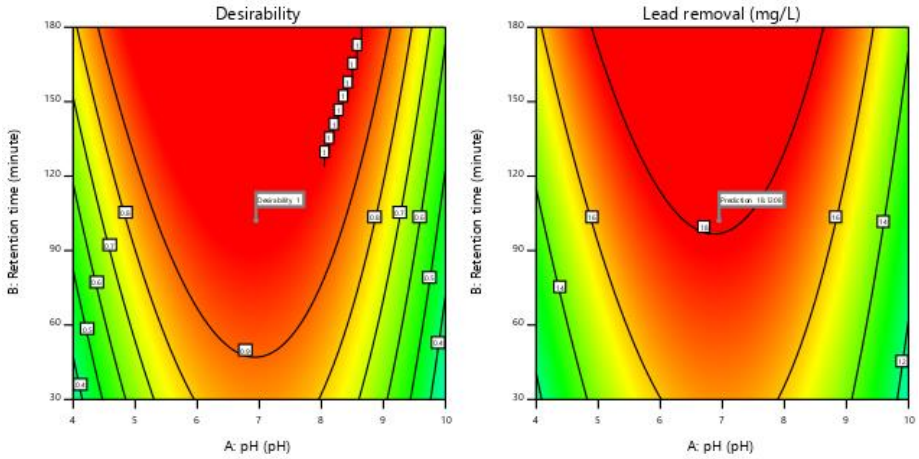

Figure 12: Optimization of the lead removal based on the desirability of the pH and retention time (minutes)

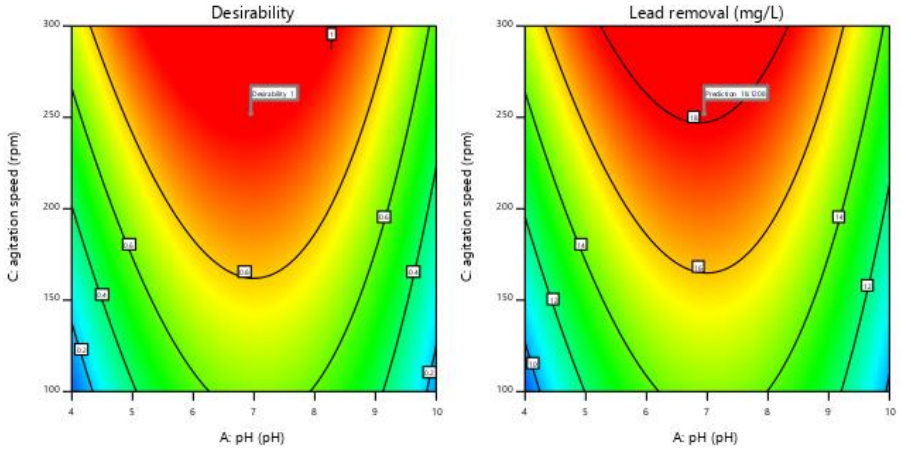

Figure 13: Optimization of the lead removal based on the desirability of the pH and agitation speed (rpm)

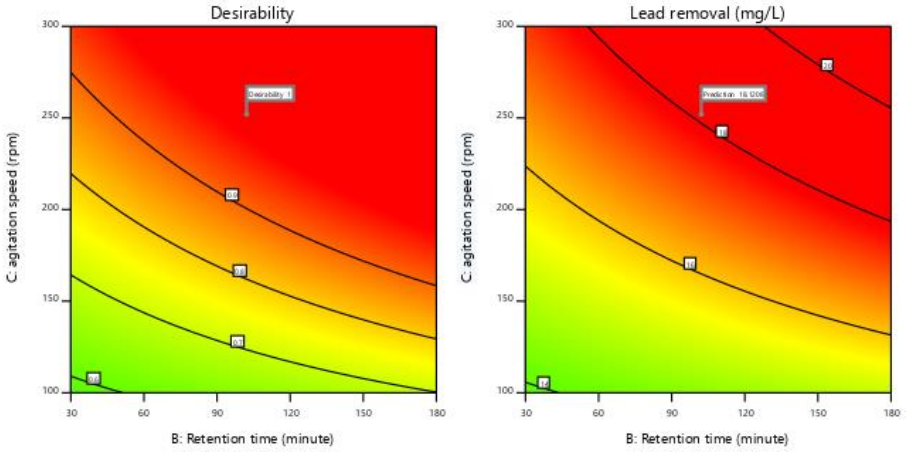

Figure 14: Optimization of the lead removal based on the desirability of the retention time (minutes) and agitation speed (rpm).

Figures 12, 13 and 14 revealed the optimal condition for the model (pH, retention time and agitation speed). The optimization values were extracted from the desirability of the factors, and the three contour shows all the interaction of the factors. Figure 14 shows the incomplete contour since the interaction between the agitation speed and the retention time is not good in terms of the significance to the lead removal. The lead removal from synthetic wastewater was significant to the optimization graph's pH and agitation speed or retention time.

Validation of the predicted vs actual value.

The suggested value or predicted value should be validated by re-do the experiment and run the actual analysis. From the analysis done, the percentage of the error (average) is only 95%. This percentage shows the model is good enough and

Table 5: Validation experiments to validate the actual value suggested from the software.

No	pH	Time (minutes)	Agitation speed (rpm)	Predicted	Actual	% Error
1	7	105	200	16.9017	15.003	0.12
2	10	30	300	11.9832	14.853	23.95
3	4	30	300	12.7675	14.995	17.45
4	4	180	100	14.0948	14.893	5.67

4. CONCLUSION

The adsorption of lead from the synthetic wastewater was best explained using optimization by the Design Expert. The validation of the coded and predicted value proved that the actual value was not far from the suggested utilizing the software. This is only 95% as the average percentage.

5. RECOMMENDATION

To enhance the design's capability, the study for every factor at a time is recommended to narrow down the error percentage. At the same time, very significant factors can be studied. At the same time, the physical characteristics of the *Coriandrum sativum* should be reviewed to differentiate the condition of the leaves before and after the reaction occurred.

6. REFERENCES

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