

Design of optimum Response Surface Model for the Treatment of Chromium Contaminated Groundwater at TCCL Site of Ranipet, TamilNadu, India

Vanitha Murugaiyan¹, Saif Ullah Khan²

Tamilnadu Pollution Control Board, Chennai-600 037 and Aligarh Muslim University, Uttar Pradesh, India

E-mail ID: vanithapcb[at]gmail.com

Abstract: A statistical model using Central Composite Design (CCD) of surface response analysis was employed for the optimization of parameters in the removal of Cr (VI) from contaminated ground water at laboratory scale. Different concentrations of Sodium dithionite have been used in synthetic chromium water to optimize the initial concentration, pH and dosage for complete removal of Cr (VI). Analysis of variance showed a high coefficient of determination value ($R^2 = 0.9670$) and a satisfactory prediction quadratic regression model was derived. The optimum reduction pH, dosage and the maximum removal of Cr (VI) from the initial concentration of 1335.4 mg/L of synthetic contaminated water were found to be 2.80, 3.68 g/L and 99.62 %, respectively. Based on the optimized conditions, trials have been extended to chromium contaminated groundwater. The results are compared. Ex-situ treatment using $\text{Na}_2\text{S}_2\text{O}_4$ for treating the groundwater is a suitable choice for effective field implementation.

Keywords: TCCL, Ranipet, hexavalent Cr (VI); reduction and precipitation; response surface methodology

1. Introduction

The continuous leaching of chromium from dumping of COPR over two decades at the Ranipet industrial area in Vellore district, Tamil Nadu is an evidence of chromium contamination in groundwater. Due to the dissolution and mobile characteristic of Cr (VI) from the COPR dumpsite migrates to the water body through underground leakage and even contaminate the surrounding soil by surface runoff during monsoon. A preliminary field investigation has shown the concentration of Cr (VI) varied in the range of 0.87 to 2016 mg/L in and around the dumpsite. Thus the continuous leaching of Cr (VI) from the dumpsite has been growing interest among the various researchers to carryout study at the site [1-8]. Though number of technologies have been developed for remediation of contaminated groundwater, chemical reduction and precipitation processes offer significant potential to remove the soluble ionic species from contaminated water particularly containing heavy metals [9].

Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) is a reducing agent has the potential to reduce the activity of Cr (VI) from any wastewater [10-12]. Earlier study has shown a field investigation on in-situ Cr (VI) reduction using combination of sodium dithionite and ferrous sulphate [13]. The solid or powder form of dithionite is classified as spontaneously combustible material, whereas the liquid form of sodium dithionite, a powerful reducing agent, is classified as non-hazardous by U. S. Department of Transportation (DOT) [14].

The main objective of the present work is to investigate and demonstrate the performance of $\text{Na}_2\text{S}_2\text{O}_4$ as reducing agent for reduction of Cr (VI) in the contaminated groundwater at TCCL study area. The process variables are optimized using

Response Surface Methodology (RSM), which is simple and efficient in terms of time and resource utilization as well as giving insights into the process mechanism involved [15]. The optimization of the treatment process in remediating Cr (VI) at batch scale may prove beneficial for such contaminated sites having practical significance as it results in lower consumption of the reducing agent for such higher concentration of Cr (VI) leading to complete removal in shorter duration as compared to other conventional technologies.

2. Materials and Methods

All the chemicals used in this study were of analytical grade and procured from E-Merck India Ltd. The important chemicals used were Sodium Dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), Sodium Hydroxide (NaOH), and Sulphuric Acid (H_2SO_4). Distilled water of highest purity was used for optimization. The lower pH was adjusted with H_2SO_4 and higher pH was adjusted with NaOH. The pH was determined using pH meter 240 (Elico L1614). The concentration of Cr (VI) was determined by recording the absorbance at 540 nm using UV-Visible Spectro photometer (UV-3200, Lab India). The total Cr and major heavy metal concentrations were determined on an Atomic Adsorption spectrophotometer (Shimadzu 6800). APHA method was adopted to analyze other parameters [16].

The reactions were performed in a batch of experiments using a jar test apparatus stirred at 100 rpm. The percentage removal of hexavalent chromium was calculated as

$$\% \text{Cr(VI) removal} = \frac{C_i - C_f}{C_i} \times 100$$

Where, C_i and C_f represent initial and final Cr (VI) concentrations respectively.

Upon optimizing the variables from synthetic contaminated water (SCW), the optimized conditions were executed in the real contaminated groundwater sample which was collected from TCCL dumpsite, Ranipet Industrial Area, Vellore Dt, Tamilnadu, India. The optimization of variables using RSM is discussed below.

3. Experimental design

The conditions of initial concentration, pH and dosages were optimized using RSM by the Central Composite Design (CCD) method in the software "design-expert 12.0" [17]. CCD was adopted, with 3 factors in total and each factor at 3 levels. The 3-factor was the initial concentration, dosage of

the reducing agent and pH of the solution and the response surface variable was the percentage removal of Cr (VI). The reduction of Cr (VI) on desired concentrations were performed in Jar apparatus using $\text{Na}_2\text{S}_2\text{O}_4$ as reducing agent stirring at 100rpm. After reduction and precipitation the supernatant was analysed to measure the residual Cr (VI). A total of 20 experiments were performed. The first 14 experimental runs were performed in triplicates, and the Coefficient of variation (CV) was calculated to check the uncertainty. Results of the last 6 experimental runs that representing central points were used to check the reproducibility of results as per CCD. Table 1 shows the level and coding of the experimental design.

Table 1: Real and coded values of the factors adopted for CCD

Factors	Units	Code	Real Values				
			$-\alpha$	-1	0	+1	$+\alpha$
Initial concentration	mg/L	A	200	565	1100	1635	2000
pH	-	B	2	2.4	3	3.59	4
Dosage	g/L	C	1	1.81	3	4.19	5

In this design, the Cr (VI) removal efficiency was used as the response, and the model developed was validated through chemical process.

4. Results and Discussion

It is important to examine the fitted model if the model provides an adequate approximation of the true response surface. For the selected process parameters of experimental design, the model obtained using central composite design shows the suggested model as quadratic for the chosen response in terms of percentage Cr (VI) removal.

Response surface analysis of influencing factor

The analysis of variance (ANOVA) was carried out to check the model significance. Significant terms were identified at 95% confidence level. Non-significant terms were eliminated, based on the F values. ANOVA results have been shown in table 3. A significant model was obtained with F-Value of 32.61 and the corresponding probability <0.0001 . Coefficient of determination or R squared value of 0.9670 was obtained for the fitted model. Adequate precision ratio was obtained as 19.47.

Table 2: Analysis of variance for Cr (VI) removal efficiency

Source	Sum of Squares		Mean Square	F-value	p-value	
Model	1787.45	9	198.61	32.61	<0.0001	significant
A-Initial. Conc	234.40	1	234.40	38.48	0.0001	
B-pH	48.72	1	48.72	8.00	0.0179	
C-Dosage	1006.97	1	1006.97	165.32	<0.0001	
AB	13.52	1	13.52	2.22	0.1671	
AC	147.92	1	147.92	24.28	0.0006	
BC	11.04	1	11.04	1.81	0.2078	
A ²	0.8788	1	0.8788	0.1443	0.7120	
B ²	4.39	1	4.39	0.7209	0.4157	
C ²	324.01	1	324.01	53.19	<0.0001	
Residual	60.91	10	6.09			
Lack of Fit	54.70	5	10.94	8.81	0.0161	significant
Pure Error	6.21	5	1.24			
Cor Total	1848.37	19				

Std. Dev.	2.47	R ²	0.9670
Mean	92.73	Adjusted R ²	0.9374
C. V. %	2.66	Predicted R ²	0.7666
		Adeq Precision	19.4769

The first 14 experimental runs were performed in triplicates, and the coefficient of variation (C. V) was calculated to check the uncertainty. Results of the last experimental runs, representing central points were used to check the reproducibility of the results as per CCD. The data was fitted into second order quadratic model using multiple regression.

The regression model equation of chromium removal efficiency in the coded form was obtained as follows:

$$\% \text{ Removal} = +96.54 - 4.14 * A - 1.88 * B + 8.54 * C - 1.29 * AB + 4.26 * AC + 1.15 * BC - 0.2468 * A^2 - 0.5497 * B^2 - 4.72 * C^2$$

Where, A, B & C are coded values of chosen process parameters (initial conc., pH & dosage).

% removal = +71.33370 - 0.013791 * Initial. Conc + 5.72732 * pH + 14.95098 * Dosage - 0.004050 * Initial. Conc * pH + 0.006698 * pH * Dosage - 8.61723E-07 * Initial. Conc² - 1.55469 * pH² - 3.33867 * Dosage².

According to the results of variance analysis, the model is shown to be significant, in which the Initial concentration, pH and Dosage are shown to be very significant, indicating that the fitting accuracy is good, and the response surface model can be approximated for subsequent optimization design

Actual vs predicted Plot

Actual vs predicted values were plotted against each other to check the model suitability as shown in Figure 1. The Figure shows a close agreement between the actual and predicted values and hence the model can be suitably used to navigate the chosen design space. The actual vs predicted plots suggested that the model predictions agreed with the experimental data within 10% error

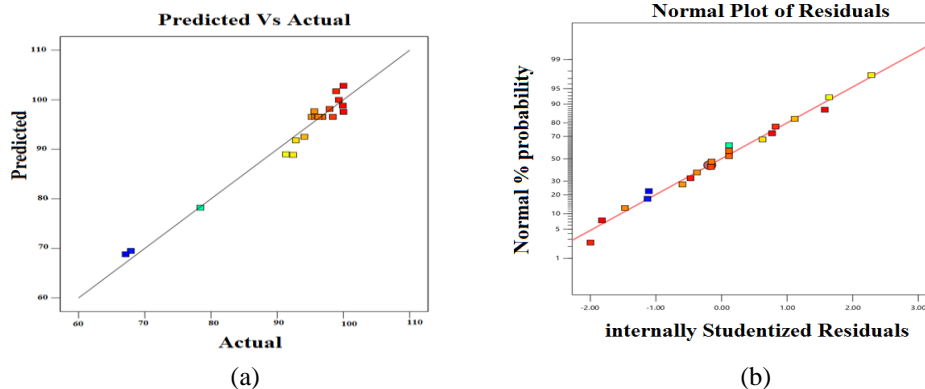


Figure 1: (a) Plot signifying agreement between actual & predicted value. (b). Normal plot of residuals

The residual plot was used to ascertain as to whether the actual data and established model and fit well. The straight line shows the normal probability distribution of the residuals and the actual value are as close as possible to a straight line. From Fig.1 (a), it can be observed that the data points are basically linear, indicating that the model conforms to the normal hypothesis and the experimental data is well fitted. Fig.1 (b) explains the distribution of data points along the line Y=X, which indicates that the simulated value is close to actual value and the reduction and precipitation of Cr (VI) in SCW can effectively predict the response results.

Process Optimization as evident from 3D Surface Interactive Plots

Process optimization was done using differential calculus to determine the global maxima by employing design expert. This was done by calculating the successive steepest slopes. Optimization was subjected to suitable constraints to resolve the final solution. Design-expert software takes the inputs for optimization with predefined values as maximum, minimum, target, within range and none for process variable from the ranges selected for the design. Our goal in optimization of reduction and precipitation process was kept at 100% removal of Cr (VI) for the process variables set “within range”. The optimum conditions as obtained by RSM for 99.99% Cr (VI) removal were obtained for desirability function value of 1 (as shown in Figure 2).

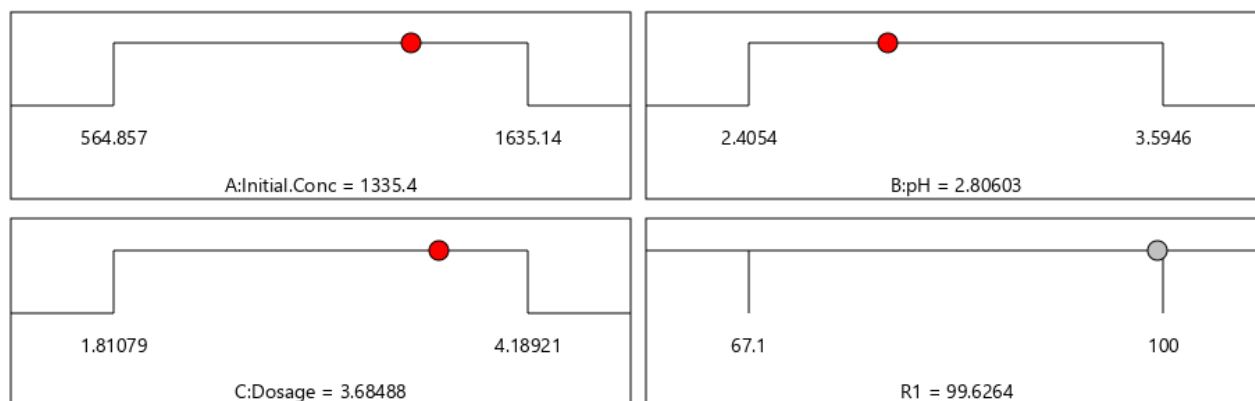


Figure 2: Optimum conditions as obtained by RSM for 99.62 % Cr (VI) removal for desirability function value of 1

The process optimization for maximizing the Cr (VI) removal was carried out by keeping the variables or factors within range. The theoretical optimum conditions obtained were confirmed by performing 3 experiments at these values to compare the theoretical and experimental results. This comparison has been shown in Table 3. The resemblance in

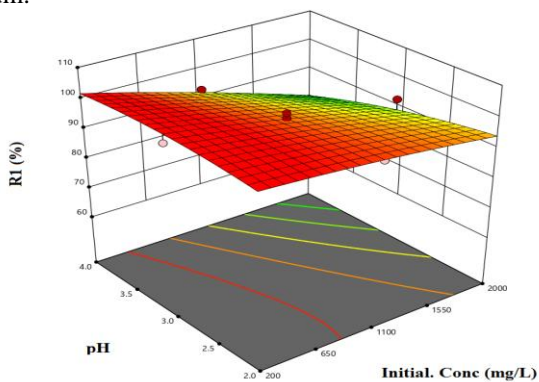
these values suggests that RSM can suitably be used to optimize the process.

Table 3: Optimal values of the adopted variables.

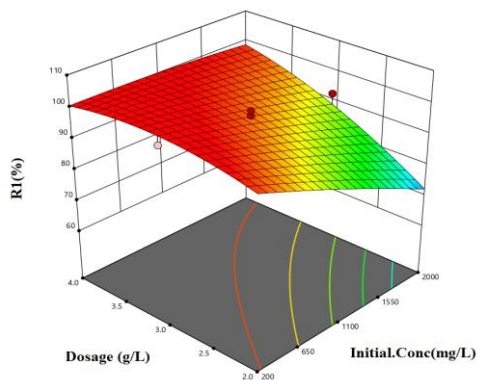
Process Variables	Optimal values	Avg. experimental values
Cr (VI) removal (%)	99.62	97.4
Initial Cr (VI) conc. (mg/L)	1335.4	1335.4
pH	2.80	3
Dosage (g/L)	3.68	3.67

3-D Plots explaining the effect of process

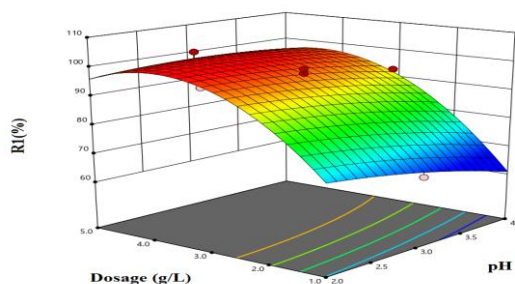
It is evident from the 3D plot in Figure 3 (a) that on keeping pH fixed and varying initial concentration in the range from 200 to 2000 ppm results in lowering down the removal efficiency of Cr (VI) at the maximum initial Cr (VI) concentration of 2000 ppm at pH around 4, whereas the removal efficiency increases with the higher acidic values at pH value around 2 signifying the role of pH as a deterministic factor and is in accordance with several past studies. This can be attributed from the fact that reduction of Cr (VI) to Cr (III) consumes protons therefore Cr (VI) removal rate is higher at low pH values because reduction of Cr (VI) to Cr (III) is favored at low pH values. Although Cr (VI) was reduced proportionally at all the pH levels assayed which indicates that Cr (VI) removal rate was also affected in accordance with pH. From 3D plot in Figure 3 (b), we can infer that dosage of reducing agent has a significant effect over the % Cr (VI) removal. The consumption of reducing agent is directly proportional to the initial Cr (VI) concentration and adding beyond the optimum level there seems to have a slight negative or negligible effect on Cr (VI) removal with further increase in dosage beyond this value. However from Figure 3 (c) it is evident that at pH 4, as we increase the dosage of reducing agent from 1 to 5 g/L, the % Cr (VI) removal increases only at the higher dosage and hence it is necessary to bring the pH at higher acidic medium.



(a)



(b)



(c)

Figure 3: Surface plots (a, b & c) in 3-D presenting the effect of factors: initial conc., pH & dosage of reducing agent on % Cr (VI) removal

Response optimization of Cr (VI) removal from CGW.

The treatment of contaminated groundwater is very significant to make it suitable either for drinking or irrigation purposes and the treatment option depends on the quality of groundwater. Upon analysing the composition of groundwater sample, the results have shown that the sample is very high in chromium concentration (2016 mg/L), chloride (285 mg/L), sulphate (2539 mg/L) and nitrate ions (215 mg/L).

The optimum values obtained for 99.99 % reduction of Cr (VI) using Na₂S₂O₄ are: Initial concentration of Cr (VI) in synthetic prepared water-1100 mg/L, pH-2.66 and dosage-5.67 mg/L; whereas the contaminated ground water treated at these conditions shows a maximum reduction of 99.4%.

Experiments were also conducted at single variate level along with multivariate analysis to ascertain the role of process parameters even beyond chosen design range on Cr (VI) reduction using Na₂S₂O₄ at different pH values such as 2, 2.5, 3 and 4. To ascertain the situation different dosages of Na₂S₂O₄ were added to the contaminated ground water of required strength. The effect of pH and dosage of Na₂S₂O₄ on the reduction of Cr (VI) in CGW containing 1617 mg/L of Cr (VI) was investigated. The experimental results reveal that maximum reduction of Cr (VI) at pH-2 (99.98%), pH-2.5 (100%) and pH-3 (100 %) at constant precipitation pH-9 at the dosage of 4.5 g/L. Overall results of all the data, expose that Na₂S₂O₄ appears to be the best, and pH 2.5 is the optimum pH for complete reduction of Cr (VI) and pH 9 is the optimum pH for precipitation of Cr (III) in time duration of just thirty minutes signifying the utility of reducing agent with the lowest residual total chromium concentration of 0.2772 mg/L within the regulatory level.

5. Conclusion

This paper discusses the remediation of Cr (VI) present in the contaminated groundwater collected from the COPR at Ranipet industrial site at laboratory scale. The surface models obtained were checked and found with a reasonable good fit having high values of coefficient of determination as 0.967 for removal efficiency. Reduction in concentration of hexavalent chromium, total chromium, chloride, and other heavy metals have been taken as the benchmark for efficacy of the process adopted. Direct application of sodium dithionite in this treatment indicates that the concentration of Cr (VI) can be successfully reduced to zero level

concentration within 30 min, at pH 2.5 and its reduced form Cr (III) can be precipitated at pH 9. It is suggested to adopt, pump and treat method for restoration of the groundwater.

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7. Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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