

Optimization of Cr (VI) Removal Efficiency of Waste Tire Adsorbent from Aqueous Solution by Response Surface Methodology

¹Gaurav Kumar Meena*, ²N. R. Rawal

^{*1}Department of Civil Engineering, Motilal Nehru National Institute of Technology Allahabad, Prayagraj, Uttar Pradesh, India

²Department of Civil Engineering, Motilal Nehru National Institute of Technology Allahabad, Prayagraj, Uttar Pradesh, India

ABSTRACT: The aim of the present study is to optimize the adsorption parameters with the help of response surface methodology for increasing the Cr (VI) removal efficiency of Waste Tire Adsorbent (WTA). The effect of four independent adsorption parameter such as Adsorbent dose (4–8g/l), Cr (VI) concentration (60–100 mg/l), duration (60–300 min), and temperature (30–50 °C), was investigated. Second-order polynomial regression model for fitting experimental data was suggested by ANOVA, and the coefficient of determination ($R^2 = 0.979$) of the suggested model showed a good correlation between the predicted and experimental responses. The optimal conditions for removing Cr (VI) were found to be 5.4 g of adsorbed dose, 60.09 mg/l of Cr (VI) concentration, 30 °C temperature, and 140.15 minutes of adsorption time. The maximum removal efficiency of Cr (VI) using WTA was 62.22% at the optimum condition. The surface morphology, function group and element proportion of WTA were obtained using SEM, FTIR and XRF.

Keywords: RSM, WTA, SEM, FTIR, ANOVA.

INTRODUCTION

The widespread and indifferent discharge of heavy metals such as cadmium, lead, mercury, and chromium (Cd, Pd, Hg, and Cr) into water bodies by industry results in an accumulation of these metals in water resources, which in turn lowers the quality of the water and poses significant risks to the health of both people and animals. [1]. Heavy metals are hazardous to human health because they do not decompose in their natural environments and instead build up in food chains [2]. One of these potentially dangerous metals, chromium (Cr), finds widespread application in a variety of industries, such as electroplating, mining, the manufacture of paint and pigment, textile dyeing, preservation of wood, cement, metal finishing, stainless steel, alloys, and photographic material [3,4]. It is common to find chromium in either the Cr (VI) or Cr (III) oxidation states. the Cr(VI) oxidation state is considered more dangerous than Cr(III) due to its greater agility [5]. Cr (VI) ions can irritate human skin and induce a variety of other medical conditions when they come into touch with human beings. Some of these conditions include vomiting, hepatic sickness, bronchitis, nausea, severe diarrhoea, epigastric discomfort, ulceration, pulmonary congestion and hemorrhage[6]. According to the guidelines established by the "United States Environmental Protection Agency (USEPA)," the concentration of Cr in drinking water must be lower than 0.1 mg/l. Total chromium served as the foundation for the development of these recommendations. On the other hand, studies have determined that the concentrations of Cr (VI) in normal wastewaters range from 50 to 100 mg/l. [7], which is almost 1000 times greater than the previous value. Because of this, it is absolutely necessary to make use of the appropriate technology in order to lessen the amount of chromium to a level that is tolerable before discharging it into the environment.

Chromium rich water and wastewater treatment can be accomplished through a variety of processes that have been affirmed as effective and are currently in use. These processes include "chemical reduction and precipitation", "ion-exchange", "solvent extraction", "membrane separation", reverse osmosis, coagulation, and adsorption[8–11]. These technologies, despite their widespread application in water and wastewater treatment, are not without their drawbacks.. These include insufficient metal removal, high operational costs, creation of hazardous sludge, high energy needs etc[12–14]. According to the recommendations of the WHO and EPA[15], adsorption technology is developing as an effective and ubiquitous approach of water treatment. Its increasing momentum and broader applicability are a result of its affordability and environmental friendliness. The utilization of efficient adsorbents from solid industrial and agricultural/municipal wastes accounts for the technology's low cost[16–19] [20]. The creation of more effective adsorbents from low valued solid waste products is still being explored.

Waste rubber tyres, which make up the largest portion of all waste polymers worldwide, are difficult to break down because of their crosslinked structure and the addition of stabilizers and other chemicals. As a result, they are typically disposed of by landfill or incinerated [21]. However, this creates two issues: environmental contamination and the waste of expensive rubber. Carbon black, which has a carbon content as high as 70–75 weight percent, makes up about 32 percent by weight of the waste tyre[22]. The only obvious physical difference between this carbonaceous adsorbent and activated carbon is that

carbon black has significantly smaller surface area [23]. As a result, the untreated rubber tyre pyrolysis-produced carbon black can be heated in an environment of air, carbon dioxide, or steam to increase its surface area and porosity [24,25] and so enhance its adsorption behavior. As a result, discarded tyres are an interesting and cost-effective substrate for the adsorption of hazardous pollutants from aqueous solutions. The recycling of scrap tyres into activated carbon for possible uses such as waste water treatment for the sorption of hazardous contaminants is quickly becoming a significant. Waste rubber tyres have been successfully used as an adsorbent for a variety of contaminants, including dyes [26], insecticides [27], phenols [28], and metal ions [29–33], according to numerous studies.

Response surface methodology is a statistical method that uses different statistical and mathematical techniques to find the best way to improve a process in which the response of interest is affected by several different factors. In contrast to the conventional approach, which permits variation of only one parameter at a time while keeping all other parameters constant, thereby limiting the ability to examine the combined impact of all influencing parameters, Response Surface Methodology (RSM) permits simultaneous investigation of the interaction between two or more variables. One variable at a time is a tedious procedure that needs several tests to find the optimal value. As a further advantage, RSM increases yield percentage, decreases process variability, more closely verifies the output response to the objective, and requires less time and money to implement. When the number of factors exceeds two, the Box-Behnken (BBD) design is a cost-effective alternative to the central composite design and a significant improvement over three-level full factorial designs. Another benefit of BBD is that it doesn't have any combinations where all the factors are at their best or lowest points at the same time. So, it helps to avoid doing tests that aren't necessary under extreme conditions, which could lead to poor results. These characteristics prompted the use of BBD and RSM in this investigation.

In this study, the effect of various factors, such as doses, concentration, time, and temperature, on the adsorption efficiency of Cr (VI) by WTA from aqueous solution was analyzed. So, RSM was used to evaluate the adsorption efficiency of Cr (VI) and the impacts of individual components and their interactions were evaluated using a Box-Behnken experimental design. A second-order polynomial model was used to analyze the experimental data. This model was subsequently tested by means of statistical analysis, which ultimately used to the optimization of the process.

MATERIALS AND METHODS

Materials

All reagents were analytical-grade and purchased from the Uma Scientific store in Prayagraj. Stock and other solutions were made with double-distilled water. 144 milligrammes of potassium dichromate ($K_2Cr_2O_7$) in 100 ml of distilled water gives 500 mg/l Cr (VI) stock solution. A stock solution was used to make a Cr (VI) solution of the desired concentration. Waste tyres for developing WTA were procured from a nearby tyre repair shop. Tyres were cut into 10–12 mm pieces and shocked in diluted HCl for 24 hours to remove dirt, then thoroughly washed in distilled water and dried for 24 hours in a 100 °C hot air oven. Hence, dried tyres were carbonised in a muffle furnace at 400 °C for 4 hours. After carbonization, the obtained tyre char was activated by chemical and thermal treatment. For chemical treatment, tyre char and H_2SO_4 were mixed in a 250-mL crucible at a 1:2 weight ratio and left to react for one hour in a shaker with constant stirring, then the thermal treatment was done by an hour-long heating of the mixture at 400 °C. The developed activated carbon (WTA) was placed in a glass container once it had cooled.

Characterization of Adsorbent

The small portion of adsorbents were intended for morphological characterization. The environmental scanning electron microscope (ESEM) images were obtained by (Model: JSM-6010LA; JEOL) instrument. FT-IR was used to identify chemical bonds, functional groups, and oxygen-containing groups. FT-IR Spectrum2 (Perkin Elmer) spectrophotometer was used to capture the WTA IR spectra from 4000–400 cm^{-1} using KBr pellets. Handheld XRF analyzer (ProSpector 3) was used to find the element present in the WTA.

SEM

The surface morphology of the WTA by scanning electron microscopy (SEM) at 200X and 2000X magnifications, as shown in Figure 1. There are two unique morphologies of WTA that can be seen in the image. One of the morphological sections is granular in texture, and the other is composed of pores. A higher magnification of the image shows that there are various pore sizes in WTA. The fundamental characteristics of an efficient adsorbent are a large surface area and a porous structure. The media is porous, then the adsorbent's surface area will be greater.

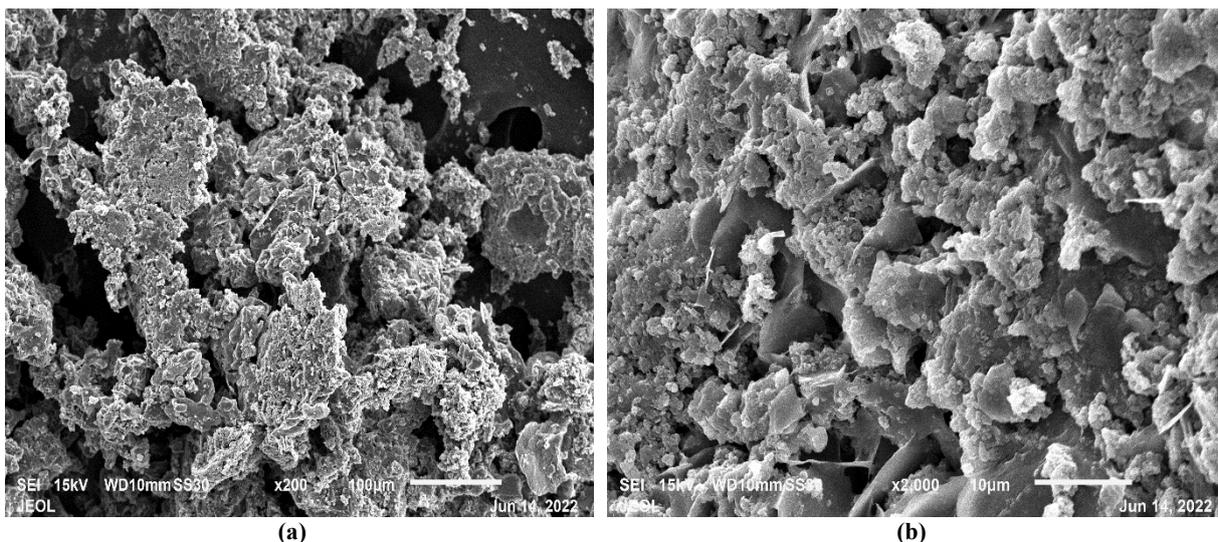


Figure 1. SEM illustration of WTA

FTIR

The IR spectra of WTA were measured in the region of 4000–400 cm^{-1} . The FTIR spectrum of WTA consists of a number of bands, as shown in Figure 2. A prominent band in the C-O stretching region at 1164 cm^{-1} confirms the ester identification of the carbonyl band. The bands at 1625 cm^{-1} are caused by stretching (C=O) vibrations of carboxyl and carbonyl in acidic oxygen surface groups. Generally, it is assumed that the carboxylic acid group participates in the adsorption of metal ions from aqueous solution. The peak at 3415 cm^{-1} is indicating stretching (-OH) vibrations in hydroxyl groups, while the peak at 2475 cm^{-1} is indicating the C≡C stretching vibration of the alkyne group.

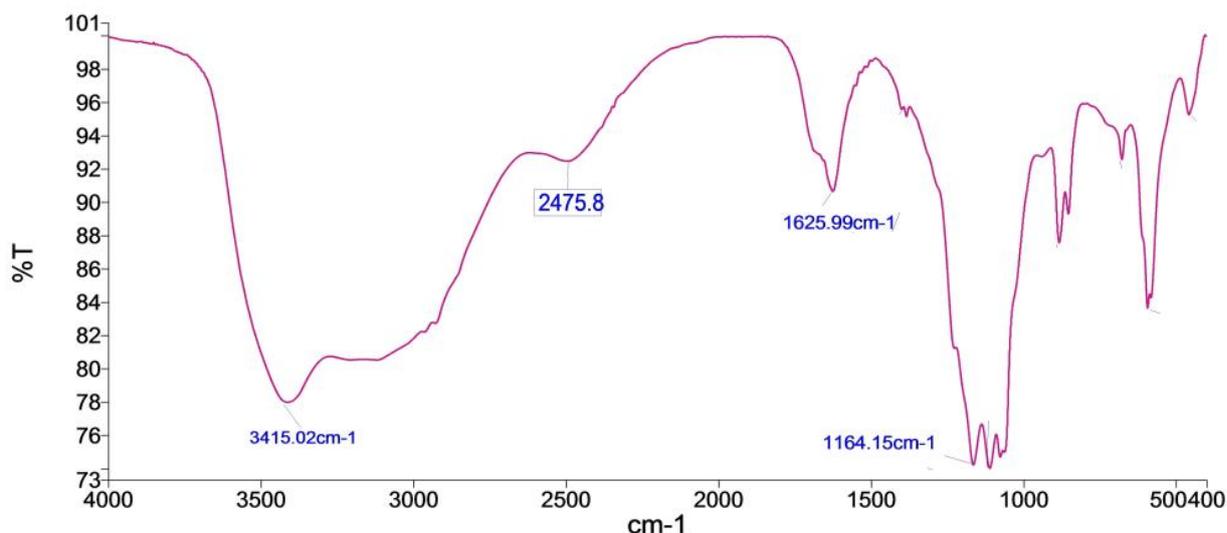


Figure 2. FTIR Spectra of WTA

XRF

The elements in the waste tire adsorbent were identified using an XRF spectrometer. The X-ray fluorescence (XRF) technique measures the concentration of elements by comparing the fluorescence intensity of individual spectral lines with the X-ray peaks of each element that are located at slightly different wavelengths. Elements of WTA, both before and after adsorption, are summarized in Table 1, which was measured by X-ray fluorescence (XRF) spectra. The XRF analysis demonstrates that the Cr (VI) concentration increased from .07% to 3.69% due to the adsorption of Cr (VI) by the WTA.

Table 1: Element of WTA by XRF

Element	Before Adsorption (%Wt.)	After Adsorption (%Wt.)
Ag	0.03	0.02
As	0.02	-
Br	0.01	0.01
Ca	27.65	12.25
Cr	0.07	3.69

Cu	0.07	0.07
Fe	7.53	4.54
Ga	0.10	0.01
K	3.79	4.55
Mn	0.07	-
Ni	0.10	0.05
Pb	0.42	0.34
Rb	0.02	0.02
Se	0.00	-
Si	23.86	62.19
Sn	0.05	0.03
Ti	4.44	3.64
V	0.55	0.43
Zn	31.11	8.03
Zr	0.11	0.13

Experimental design

The effects of dose, concentration, time, and temperature on Cr(VI) removal efficiency of WTA from aqueous solution were investigated using a 4-factor, 2-level factorial Box-Behnken (BB) design of experiment (DOE). Response surface methodology (RSM) with BB is used with three levels, which are represented by the codes -1, 0 and +1. Two-level factorial and incomplete block designs are combined to create BB designs, whose geometry suggests the presence of a sphere within the process space with a surface that protrudes through each face and is perpendicular to each edge of the space. Using this method, statistically robust models can be developed with a small number of the experiments that are usually needed for two-level factorial (2k-p) designs. Since this is only a two-level factorial problem, the linear or quadratic model gives a better result for this method. The following second-order polynomial equation was used to fit the observations:

$$Y = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^k b_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k b_{ij} x_i x_j \quad \text{Eq.-1}$$

Where Y is the predicted value, b₀ is constant, b_i is linear coefficient of x_i factor, b_{ii} is the quadratic coefficient of x_i factor, and b_{ij} is the 2-way linear by linear interaction coefficient of x_i and x_j factor. Where x_i and x_j is the coded values of independent factors and the value of k represents the total number of independent factor. The doses, the concentration of Cr (VI), time, and temperature have been chosen as the four factors for the BB design. These have been labelled x₁, x₂, x₃, and x₄, respectively. The Cr (VI) removed by WTA is taken as the dependent variable (Y_i). A coded list of factors and experimental runs and their outputs are shown in Tables 2 and 3.

Table 2: Coded value of factors used

Fctor	Unit	Low Level		Center Level		High Level	
		Coded	Uncoded	Coded	Uncoded	Coded	Uncoded
Doge	gm	4	-1	0.6	0	8	1
Concentration	mg/l	60	-1	80	0	100	1
Time	min	60	-1	180	0	300	1
Temperature	oc	30	-1	40	0	50	1

Table 3: Experimental Run summary

		Factor 1	Factor 2	Factor 3	Factor 4	Response
Std	Run	A: Doge	B: Concentration	C: Time	D: Temp	Adsorption Efficiency
21	1	6	60	180	30	73.25
12	2	8	80	180	50	88
26	3	6	80	180	40	62.06
1	4	4	60	180	40	58.56

17	5	4	80	60	40	41.5
8	6	6	80	300	50	96.45
11	7	4	80	180	50	62.74
20	8	8	80	300	40	97.56
2	9	8	60	180	40	85.18
25	10	6	80	180	40	62.8
6	11	6	80	300	30	76.92
23	12	6	60	180	50	86
16	13	6	100	300	40	78.5
28	14	6	80	180	40	64.14
5	15	6	80	60	30	47.55
24	16	6	100	180	50	64.5
9	17	4	80	180	30	56.8
19	18	4	80	300	40	61.23
27	19	6	80	180	40	62.48
4	20	8	100	180	40	72.64
3	21	4	100	180	40	52.8
13	22	6	60	60	40	55.5
18	23	8	80	60	40	60.46
29	24	6	80	180	40	66.85
14	25	6	100	60	40	48.5
7	26	6	80	60	50	58.56
10	27	8	80	180	30	75.58
22	28	6	100	180	30	60.17
15	29	6	60	300	40	92.14

Statistical analysis and model fitting

The analysis of variance, also known as ANOVA, has been implemented for graphical analyses of the data to estimate the statistical parameters and identify the interaction that exists between the process factors and responses. The statistical software program Design Expert 13 has been utilized for the regression analysis of the experimental data, the plotting of the response surfaces, and the contour plotting of the optimal condition. The F-test in the same software was utilized to examine the level of statistical significance. The coefficient R² was used to assess how accurately the fitted polynomial model represented the data. At the 95% confidence interval, the significant model terms were judged based on their probability value, or P-value.

Adsorption study

A number of combinations of adsorption experiments were conducted based on Box-Behnken (BB) design of experiment (DOE). The total treatment combination for BB design was 29 for the given factor and level in Table 2 and Table 3. In 250 mL conical flasks, adsorption studies were conducted at various doses, concentrations, times, and temperatures while maintaining constant shaker speed. The flasks were agitated in temperature control orbital shaker at 120 rpm and samples were taken out at a given time interval. Whatman filter paper was used to filter the samples, and a double beam spectrophotometer (LABINDIA UV 30000+) was used to analyse the filtrate. Cr (VI) adsorption of WTA were computed with the help of the relationships presented in Equations 2 below

$$R(\%) = \left(\frac{C_0 - C}{C_0} \right) \cdot 100 \quad \text{Eq.-2}$$

Where V represents the volume of the solution in millilitres, C₀ represents the initial concentration, and C represents the concentration of Cr (VI) at time t in milligrammes per litre.

RESULT AND DISCUSSION

The dose (A), concentration (B), time (C), and temperature (D) are the important parameter that affect the adsorption efficiency of adsorbate. So dose (A), concentration (B), time (C), and temperature (D) were considered independent variables, and the Cr (VI) removal efficiency of WTA was considered the response (dependent variable). A series of

experiments were carried out using the Box-Behnken design to investigate the effects of parameters. The Box-Behnken model does not include combinations of all factors at their highest or lowest values at the same time, and thus can prevent extreme treatment combinations in a particular case.

Generally, a multivariate process is driven by its key factors, which interact with each other on a low-order level. In this study, only two-way interactions were explored. The experimental data were analyzed using linear, two-factor interaction (2FI), quadratic, and cubic models, respectively, in order to find the suitable regression equations. Two tests were used to assess the model adequacy of the removal efficiency of Cr (VI) by WTA. The first is the sequential model sum of squares, and the second is the model summary statistics. Results of the sequential model sum of squares and statistics summary of the model are shown in Table 4 and Table 5, respectively. The fitness and statistical significance of the model were determined by R² and F-test, respectively. A value of R² close to one indicates a better model. From the statistics summary of the model in Table 5, it can be seen that the "Predicted R²" and "Adjusted R²" for the quadratic model are 0.8899 and 0.9582, respectively. So the quadratic model is better at describe the relationship between the independent and dependent variables. Therefore, the quadratic model was used to investigate the design space and selected as the most appropriate model for further analysis.

The relationship between the dependent and independent variables is shown by the following quadratic model in equation 3. Equation 3 can be encoded as follows, based on statistical significance:

$$Y = 63.016 + 12.38 * A - 6.13 * B + 15.89 * C + 5.69 * D - 1.69 * A * B + 4.34 * A * C + 1.62 * A * D - 1.66 * B * C - 2.11 * B * D + 2.13 * C * D + 2.94 * B^2 + 1.23 * C^2 + 5.19 * D^2 \quad \text{Eq. (3)}$$

Where Y removing efficiency of Cr (VI) and adsorbent dose (A), initial concentration (B), time (C), and temperature (D) are the independent variables. This equation describes the effect of the linear or double interaction (quadratic) of variables with the removal of Cr (VI) by WTA.

Table: 4 Sequential Model Sum of Squares of Response

Source	Sum Squares	Df	Mean Square	F-value	p-value	
Linear	< 0.0001	0.0468	0.9099	0.8876	< 0.0001	
2FI	0.2947	0.0500	0.9168	0.8613	0.2947	
Quadratic	0.0074	0.1526	0.9582	0.8899	0.0074	Suggested
Cubic	0.1076	0.3283	0.9798	0.7299	0.1076	Aliased

Table 5: statistics summary of the model

Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	
Linear	4.42	0.9228	0.9099	0.8876	
2FI	4.25	0.9465	0.9168	0.8613	
Quadratic	3.02	0.9791	0.9582	0.8899	Suggested
Cubic	2.10	0.9957	0.9798	0.7299	Aliased

Table 6 shows the results of the analysis of variance (ANOVA) for the quadratic response surface model in Eq. 3 for the Cr (VI) adsorption efficiency of WTA. ANOVA included F-value, probability, and the correlation coefficient R² to measure the significance of coefficient terms parameters and the fitness of the regression model. For significant corresponding coefficient terms, the F-value should be larger than the p-value. In this analysis, the F-value was 446.79, the p-value was less than 0.0001, the R² was 0.979, and the coefficient of variation was 4.4%, which shows the significance of the model and the accuracy and consistency of the experiment. Further, the adequacy of the quadratic regression model was also verified by the accuracy-precision ratio. The value of the adequate precision ratio should be greater than 4. In the present study, the adequate precision ratio is 25.8586, which indicates the suitability of the model. Lack of fit should be 'not significant' for a well-fit model. The F and p values for lack of fit were 0.4243 and 0.8762 (probability > F), respectively, which indicate 'not significant'. The linear effects of dose (A), concentration (B), time (C), and temperature (D) were found to be significant since the p values were less than 0.0001 for the factors. Quadratic terms, viz. AC, B² and D² were found to be significant because of their high F values and low p values, while a higher P-value (0.05) makes the combined effect of dose AB, AD, BC, BD, CD, A² and C² less significant. Therefore, it can be concluded that dose, concentration, time, and temperature are important parameters for Cr (VI) removal by WTA.

Figure 3 illustrates the correlation between the experimental and predicted values of Cr (VI) removal. The data presented in the figure indicates an excellent fit between the experimental and predicted values, suggesting a high degree of correlation between the input and output variables.

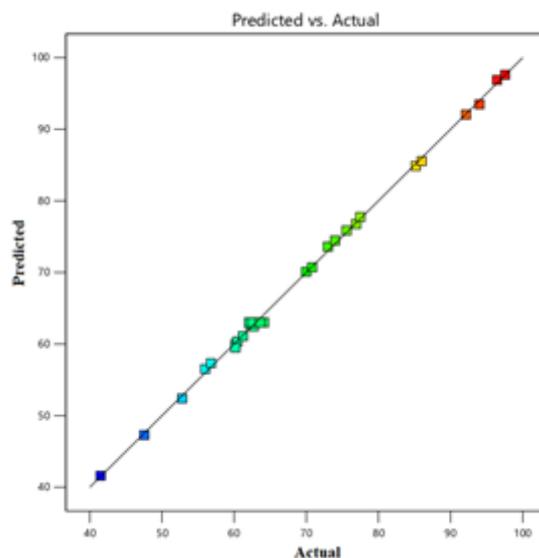


Figure 3: Plot of experimental data (line) vs predicted data (symbols)

Table 6: Analysis of Variance of Quadratic model

Source	Sum Squares	of	df	Mean Square	F-value	p-value	
Model	5958.48		14	425.61	46.79	< 0.0001	significant
A-Doge	1771.23		1	1771.23	194.74	< 0.0001	
B-Concentration	450.43		1	450.43	49.52	< 0.0001	
C-Time	3031.49		1	3031.49	333.30	< 0.0001	
D-Temp	362.78		1	362.78	39.89	< 0.0001	
AB	11.49		1	11.49	1.26	0.2799	
AC	75.43		1	75.43	8.29	0.0121	
AD	10.50		1	10.50	1.15	0.3008	
BC	11.02		1	11.02	1.21	0.2895	
BD	17.72		1	17.72	1.95	0.1845	
CD	18.15		1	18.15	2.00	0.1796	
A ²	6.52		1	6.52	0.7172	0.4113	
B ²	52.28		1	52.28	5.75	0.0310	
C ²	9.82		1	9.82	1.08	0.3164	
D ²	174.49		1	174.49	19.18	0.0006	
Residual	127.33		14	9.10			
Lack of Fit	112.24		10	11.22	2.97	0.1526	not significant
Pure Error	15.10		4	3.77			
Cor Total	5855.02		28				
Std. Dev.	3.02			R²			0.9791
Mean	67.91			Adjusted R²			0.9582
C.V. %	4.44			Predicted R²			0.8899

			Adeq Precision			25.8586
--	--	--	-----------------------	--	--	---------

The normal residual plot shown in Figure 4 indicates that residuals were normally distributed, so no transformation of the data was required.

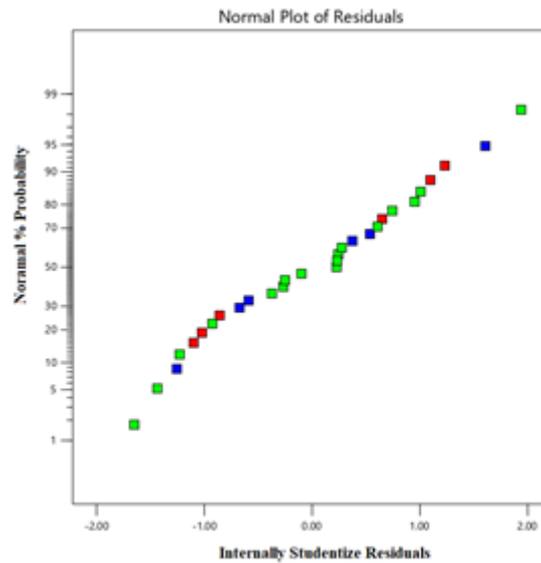
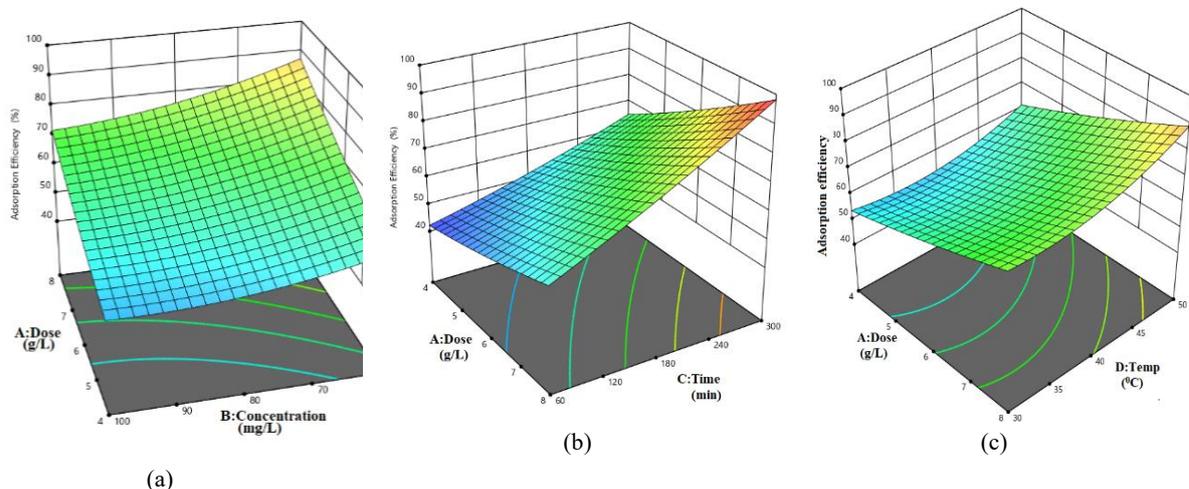
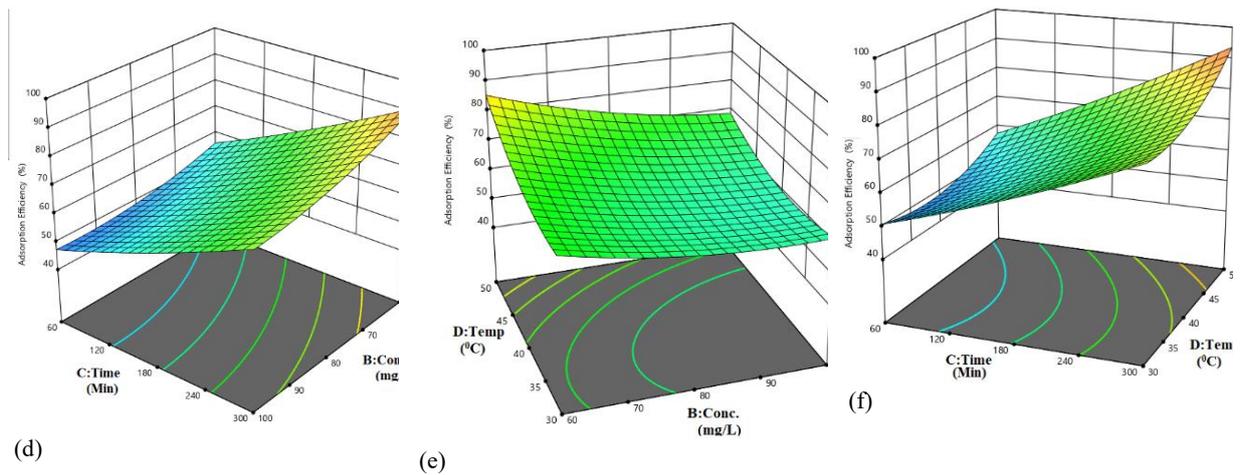


Figure 4: internally studentized residuals vs Normal plots of residuals

Effect of variable on the Response

3D response surface plots as a function of two parameters while other parameters are kept constant help to understand the effects of these two parameters on the response. The contour plots, which are the response surfaces projected in the x–y plane, show the effects of independent variables on the response. Figure 6 shows all the three-dimensional response surfaces for dose, concentration, time, and temperature. Maxima and minima on the response surface can be used to determine the optimum values of both variable parameters, such as dose concentration, time and temperature. Figure 6(a, b, c) show the effect dose with concentration, time and temperature of Cr (VI) removal efficiency of WTA. It can be seen in Figure 6(a) that the removal efficiency increases 51% to 87 % with increasing the dose from 4 g to 8g and decreasing the concentration from 100 mg/l to 60 mg/l and keeping other parameter constant. As dose increases, the surface area also increases, which leads to an increase in removal efficiency. Similarly, The removal efficiency increases from 42% to 97% with increasing time from 60 min to 300 min and from 54% to 84% with increasing temperature from 30°C to 50 °C when the dose increases from 4 g to 8 g, as shown in Figure 6(b,c). Figure 6 (d, e) shows the effect of concentration on Cr (VI) removal efficiency with time and temperature. Removal efficiency increases 47% to 90 with increasing time from 60 to 300 min and 61% to 85% with increasing temperature from 30°C to 50 °C as concentration decreases from 100 mg/l to 60 mg/l. This observation is due to the fact that the available adsorbent site is sufficient when concentration is low. Figure 6 (d) shows the effect time and temperature on Cr (VI) removal efficiency. Removal efficiency increases from 50% to 92% as time increase from 60 to 300 min and temperature increase from 30 to 50 °C simultaneously while keeping other parameters constant.





(d) (e) (f)
Figure 6. 3D surface plots of adsorption parameter (a) Dose vs Con. (b) Dose vs Time (c) Dose vs Temp. (d) Con. Vs Time (e) Con. Vs Time (f) Time vs Temp.

Optimization

The crucial aspect of the experimental investigation was to ascertain the optimal condition for the adsorption parameter, ensuring the maximum removal of Cr (VI) from WTA. Optimization of the dose, concentration of Cr (VI), time, temperature, and removal of Cr (VI) were all possible outcomes of this statistical optimization process, which used a multiple response method. The software determined 100 different conditions where the maximum Cr (VI) adsorption efficiency of WTA can be achieved without adversely affecting economic viability. The optimum was found at a dose of 5.44 g, a concentration of 60.1 mg/l, a time of 140.16 min, and a temperature of 30 °C. At the optimum, Cr (VI) removal is 62.23% and desirability is 0.6951, as shown in figure 8.

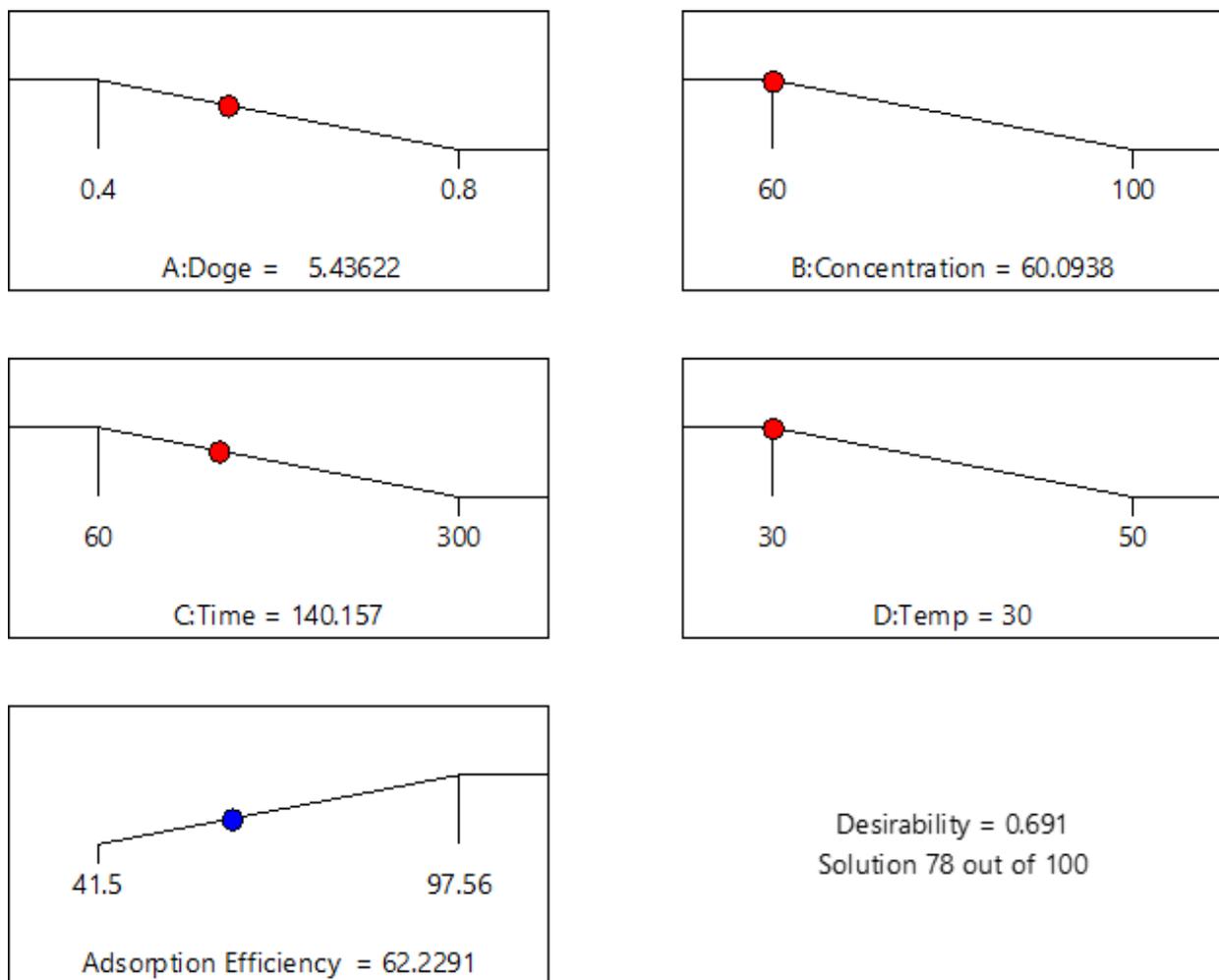


Figure 8. RAMP plots optimization of response variable

CONCLUSIONS

In this study, response surface modeling was successfully implemented to optimize Cr (VI) removal using WTA, which was developed and analyzed by SEM, FTIR, and XRF. SEM of WTA exhibits unique surface morphologies, with one granular texture and the other composed of pores. Its efficient adsorbent characteristics include a large surface area and a porous structure. The FTIR spectrum of WTA consists of several bands, including the carbonyl band at 1164 cm⁻¹, carboxyl and carbonyl in acidic oxygen surface groups, and hydroxyl and alkyne groups. The X-ray fluorescence (XRF) spectrometer identified elements in WTA, revealing an increase in Cr (VI) concentration from 0.07% to 3.69% due to adsorption. ANOVA revealed that the second-order regression model was well fitted to the experimental data, with high coefficients of determination ($R^2 = 0.979$ and $Adj-R^2 = 0.95$). Process optimization was performed, and the highest adsorption efficiency of Cr (VI) was 62.23 % at an optimal dose of 5.44 g, concentration of 60.1 mg/l, a time of 140.15 min, and a temperature of 30 °C. According to the findings of the current research, applying RSM in conjunction with a Box-Behnken design produces an extremely robust methodology for optimizing trials for the adsorption-based removal of Cr (VI) from aqueous solutions.

STATEMENTS AND DECLARATIONS

I hereby certify that I have no financial or interpersonal conflicts that would have appeared to have an impact on the research presented in this paper.

REFERENCES

1. Božić D, Gorgievski M, Stanković V, Štrbac N, Šerbula S, Petrović N. Adsorption of heavy metal ions by beech sawdust - Kinetics, mechanism and equilibrium of the process. *Ecol Eng.* 2013;58:202–6.
2. Maksin DD, Nastasović AB, Milutinović-Nikolić AD, Suručić LT, Sandić ZP, Hercigonja R V., et al. Equilibrium and kinetics study on hexavalent chromium adsorption onto diethylene triamine grafted glycidyl methacrylate based copolymers. *J Hazard Mater.* 2012;209–210:99–110.
3. Anirudhan TS, Nima J, Divya PL. Adsorption of chromium(VI) from aqueous solutions by glycidylmethacrylate-grafted-densified cellulose with quaternary ammonium groups. *Appl Surf Sci [Internet]. Elsevier B.V.;* 2013;279:441–9. Available from: <http://dx.doi.org/10.1016/j.apsusc.2013.04.134>
4. AL-Othman ZA, Ali R, Naushad M. Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies. *Chem Eng J [Internet]. Elsevier B.V.;* 2012;184:238–47. Available from: <http://dx.doi.org/10.1016/j.cej.2012.01.048>
5. Owlad M, Aroua MK, Wan Daud WMA. Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine. *Bioresour Technol [Internet]. Elsevier Ltd;* 2010;101:5098–103. Available from: <http://dx.doi.org/10.1016/j.biortech.2010.01.135>
6. Gueye M, Richardson Y, Kafack FT, Blin J. High efficiency activated carbons from African biomass residues for the removal of chromium(VI) from wastewater. *J Environ Chem Eng [Internet]. Elsevier B.V.;* 2014;2:273–81. Available from: <http://dx.doi.org/10.1016/j.jece.2013.12.014>
7. Zhao YG, Shen HY, Pan SD, Hu MQ, Xia QH. Preparation and characterization of amino-functionalized nano-Fe₃O₄ magnetic polymer adsorbents for removal of chromium(VI) ions. *J Mater Sci.* 2010;45:5291–301.
8. Sharma YC, Srivastava V, Singh VK, Kaul SN, Weng CH. Nano-adsorbents for the removal of metallic pollutants from water and wastewater. *Environ Technol.* 2009;30:583–609.
9. Religa P, Kowalik A, Gierycz P. Application of nanofiltration for chromium concentration in the tannery wastewater. *J Hazard Mater [Internet]. Elsevier B.V.;* 2011;186:288–92. Available from: <http://dx.doi.org/10.1016/j.jhazmat.2010.10.112>
10. Wang G, Chang Q, Han X, Zhang M. Removal of Cr(VI) from aqueous solution by flocculant with the capacity of reduction and chelation. *J Hazard Mater [Internet]. Elsevier B.V.;* 2013;248–249:115–21. Available from: <http://dx.doi.org/10.1016/j.jhazmat.2013.01.001>
11. Sharma YC, Srivastava V, Weng CH, Upadhyay SN. Removal of Cr(VI) from wastewater by adsorption on iron nanoparticles. *Can J Chem Eng.* 2009;87:921–9.
12. Jung C, Heo J, Han J, Her N, Lee SJ, Oh J, et al. Hexavalent chromium removal by various adsorbents: Powdered activated carbon, chitosan, and single/multi-walled carbon nanotubes. *Sep Purif Technol [Internet].* 2013;106:63–71. Available from: <http://dx.doi.org/10.1016/j.seppur.2012.12.028>
13. Ouaisa YA, Chabani M, Amrane A, Bensmaili A. Removal of tetracycline by electrocoagulation: Kinetic and isotherm modeling through adsorption. *J Environ Chem Eng [Internet]. Elsevier B.V.;* 2014;2:177–84. Available from: <http://dx.doi.org/10.1016/j.jece.2013.12.009>
14. Sun X, Yang L, Xing H, Zhao J, Li X, Huang Y, et al. Synthesis of polyethylenimine-functionalized poly(glycidyl methacrylate) magnetic microspheres and their excellent Cr(VI) ion removal properties. *Chem Eng J [Internet]. Elsevier B.V.;* 2013;234:338–45. Available from: <http://dx.doi.org/10.1016/j.cej.2013.08.082>
15. Ali I, Gupta VK. Advances in water treatment by adsorption technology. *Nat Protoc.* 2007;1:2661–7.
16. Gupta VK, Rastogi A, Nayak A. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. *J Colloid Interface Sci [Internet]. Elsevier Inc.;* 2010;342:135–41. Available from: <http://dx.doi.org/10.1016/j.jcis.2009.09.065>
17. Bhatnagar A, Jain AK, Minocha AK, Singh S. Removal of lead ions from aqueous solutions by different types of industrial waste materials: Equilibrium and kinetic studies. *Sep Sci Technol.* 2006;41:1881–92.
18. Mohan S, Gandhimathi R. Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent. *J Hazard Mater.* 2009;169:351–9.
19. Gupta VK, Carrott PJM, Ribeiro Carrott MML, Suhas. Low-Cost adsorbents: Growing approach to wastewater treatment review. *Crit Rev Environ Sci Technol.* 2009;39:783–842.

20. Akhtar M, Iqbal S, Kausar A, Bhanger MI, Shaheen MA. An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk. *Colloids Surfaces B Biointerfaces*. 2010;75:149–55.
21. Merchant AA, Petrich MA. Environmental and Enerav Enaineerina Pyrolysis of Scrap Tires and Conversion of Chars to Activated Carbon. 1993;39:1370–6.
22. Murillo R, Aylón E, Navarro M V., Callén MS, Aranda A, Mastral AM. The application of thermal processes to valorise waste tyre. *Fuel Process Technol*. 2006;87:143–7.
23. Knocke WR, Hemphill LH. Mercury(II) sorption by waste rubber. *Water Res*. 1981;15:275–82.
24. Betancur M, Martínez JD, Murillo R. Production of activated carbon by waste tire thermochemical degradation with CO₂. *J Hazard Mater*. 2009;168:882–7.
25. Suuberg EM, Aarna I. Porosity development in carbons derived from scrap automobile tires. *Carbon N Y*. 2007;45:1719–26.
26. San Miguel G, Fowler GD, Sollars CJ. Adsorption of organic compounds from solution by activated carbons produced from waste tyre rubber. *Sep Sci Technol*. 2002;37:663–76.
27. Hamadi NK, Swaminathan S, Chen XD. Adsorption of Paraquat dichloride from aqueous solution by activated carbon derived from used tires. *J Hazard Mater*. 2004;112:133–41.
28. Tanthapanichakoon W, Ariyadejwanich P, Japthong P, Nakagawa K, Mukai SR, Tamon H. Adsorption-desorption characteristics of phenol and reactive dyes from aqueous solution on mesoporous activated carbon prepared from waste tires. *Water Res*. 2005;39:1347–53.
29. Alexandre-Franco M, Fernández-González C, Macías-García A, Gómez-Serrano V. Uptake of lead by carbonaceous adsorbents developed from tire rubber. *Adsorption*. 2008;14:591–600.
30. Hamadi NK, Chen XD, Farid MM, Lu MGQ. Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust. *Chem Eng J*. 2001;84:95–105.
31. Manchón-Vizúete E, Macías-García A, Nadal Gisbert A, Fernández-González C, Gómez-Serrano V. Adsorption of mercury by carbonaceous adsorbents prepared from rubber of tyre wastes. *J Hazard Mater*. 2005;119:231–8.
32. Alexandre-Franco M, Fernández-González C, Alfaro-Domínguez M, Gómez-Serrano V. Adsorption of cadmium on carbonaceous adsorbents developed from used tire rubber. *J Environ Manage* [Internet]. Elsevier Ltd; 2011;92:2193–200. Available from: <http://dx.doi.org/10.1016/j.jenvman.2011.04.001>
33. Calisir F, Roman FR, Alamo L, Perales O, Arocha MA, Akman S. Removal of Cu(II) from aqueous solutions by recycled tire rubber. *Desalination* [Internet]. Elsevier B.V.; 2009;249:515–8. Available from: <http://dx.doi.org/10.1016/j.desal.2008.07.029>
34. Diagnostics R, Data II, Belsley BDA, Wiley J, York N. 0 1989. 1989;4:97–9.