

ADSORPTIVE REMOVAL OF HEXAVALENT CHROMIUM USING RESPONSE SURFACE METHODOLOGY AND ARTIFICIAL NEURAL NETWORK

P. Roy✉

Department of Chemistry, B.N Mahavidyalaya, Itachuna, Hooghly-712147 (West Bengal) India.

✉Corresponding Author: palaschem@gmail.com

ABSTRACT

Fe-SCC adsorbent was used in a batch procedure to remove Cr(VI) from an aqueous solution. An RSM and an ANN model were developed using data gathered from 30 batch trials, which were then utilized to optimize and accelerate the absorption processes. As a result of a three-level, four-factors central composite design (CCD) in RSM, the impacts of operational factors such as Cr(VI) concentration, contact duration, the dosage of adsorbent, and pH of solution were evaluated. The suggested quadratic model had a coefficient of determination (R^2) value of 0.996 and a Fisher F -value of 264.18, which indicated an excellent match of the experimental data. When it came to figuring out how important the various variables were in determining the best process conditions, response surface plots came in handy. Assuming ideal operating circumstances, the maximum removal of Cr(VI) was determined to be 98.3% when the test variables stayed unchanged at a maximum desirable value of 0.978: 20 mg/L initial Cr(VI) concentration plus 0.1 g Fe-SCC dosage, pH 8, and 13 min of contact time. The same architecture was used to construct an ANN model that predicted Cr(VI) adsorption with acceptable accuracy ($R^2 = 0.962$). The R^2 coefficient of determination and the order of relevance of the operational parameters were used to compare the two models. The experimental datasets were well-suited to both models, as seen by the overall findings.

Keywords: Chromium, Adsorption, Removal, RSM, ANN.

RASAYAN J. Chem., Vol. 15, No.2, 2022

INTRODUCTION

The significant toxicity and harmful influence on human health that heavy metals have on the environment make it a critical concern. The mutagenic and carcinogenic consequences of chromium (Cr) in its hexavalent form have drawn attention to this heavy metal.¹⁻⁴ Metal finishing, iron and steel industries, and the manufacture of inorganic compounds all lead to the emission of Cr(VI) into the environment. Compared to the WHO acceptable limit of 0.05 mg/L in wastewater systems, industrial effluents have substantially higher concentrations. Large amounts of Cr(VI) effluent from these businesses end up in the soils and waterways, where they build up in the food chain and pose serious health risks to humans.⁵⁻⁸ Chromium-containing industrial effluents must be treated to decrease Cr(VI) to permissible limits before they are discharged into the environment to comply with these regulatory requirements.^{1,9}

Adsorption technology is the most used removal method since it is both simple and affordable.^{10,11} Commercially available activated carbon is the most widely used adsorbent for the removal of Cr(VI) because of its vast surface area, micro/mesoporous structure, and significant adsorption capabilities.^{12,13} Activated carbon is expensive and difficult to get, so researchers are focusing on generating less expensive but similarly efficient adsorbents produced from agricultural and industrial waste sources.¹⁴⁻¹⁶ Char carbon from various agricultural and industrial waste sources is anticipated to be a useful substitute for activated carbon because of its physical activity.¹⁶⁻¹⁹ Carbonized sugarcane bagasse, known as sugarcane carbon (SCC), is an alternate adsorbent for this application. In addition, iron implanted into char carbon increases the adsorption capacity of Cr(VI) by providing more reactive sites.²⁰ There are a number of potential applications for Fe-SCC, such as the removal of Cr(VI) from water, that might be explored. The current research focuses on batch studies to determine if Fe-SCC can eliminate Cr(VI) from polluted water and see if it is effective. RSM and ANN were used in conjunction to improve the

process parameters for the adsorption experiment. The models have also been used to investigate the effects of different factors on the adsorption process individually and in combination. Statistical comparison was made between RSM and ANN using the coefficient of determination (R^2) and the relevance of operational parameters. The findings of this research are presented and analyzed.

EXPERIMENTAL

Reagent and Apparatus

Purchased and used AR-grade chemicals were provided by M/S Merck India Ltd. Double-distilled water was used to make all reagents and standards. To achieve the required Cr(VI) concentrations, a stock solution of hexavalent chromium (100 mg/L) was serially diluted by double-distilled water. 0.1 M HCl and NaOH solutions were used to alter the pH of Cr(VI) solution. Before usage, all of the glassware was washed with double-distilled water after being immersed in 15% HNO₃.

Instruments and Software

Sets of the batch experiments were stirred using a temperature-controlled magnetic stirrer (Spinot, Cat No. 6030). The concentration of Cr(VI) in solution was measured by UV-visible spectrophotometer (Systronics, Vis double beam Spectro 1203) with a 1-cm quartz cell. A digital pH meter (Eutech, pH 700 Meter) with an accuracy of 0.01 unit was used to determine the pH. An electrical balance (Denver, SI-234) was used to measure the weight.

By employing SPSS-17 and Design-Expert software, the data was analyzed and feature sets were constructed from it.

General Procedure

In a batch adsorption experiment, iron impregnated sugarcane carbon (Fe-SCC) was used to study the adsorption of Cr(VI) from water. The specifics of the Fe-SCC preparation and characterization are described in Roy et al., Journal of Environmental Chemical Engineering, 2(2014): 585–597. Cr(VI) concentrations ranging from 5 to 20 mg/L, pH ranging from 4.0 to 8.0, as well as the dosages of adsorbent ranging from 0.1 to 0.25 g, and contact time ranging from 5 to 20 min were used to study the impact of these variables in the batch tests.

Cr(VI) solution was taken in Erlenmeyer flask. Each Erlenmeyer flask had a capacity of 250 mL, and each contained 50 mL of Cr(VI) solution. After pH adjustment, an amount of dried Fe-SCC adsorbent with a monoparticle size of 250 μ m was added to the Cr(VI) containing suspensions under magnetic stirring at 500 rpm until equilibrium was established. The suspension was allowed to settle after it had been stirred for some time, and then filtered using a Whatman-42 grade. With an excitation wavelength of 540 nm, the content of Cr(VI) in the filtrate was measured after it had been subjected to the 1,5-diphenyl carbazide technique. To calculate the adsorption (removal) percentage, it was necessary to record Cr(VI) levels before and after adsorption.

$$\% \text{ Adsorption (Removal)} = \frac{(C_i - C_e) \times 100}{C_i}$$

Where, C_i and C_e are the initial and final concentrations of Cr(VI) in the solution.

The average percentage removal of Cr(VI) at 30°C room temperature was reported in all studies, with a 5% experimental error limit. To ensure the accuracy of each test, a new Cr(VI) standard was used each day for calibration. The adsorbent showed no signs of releasing Cr(VI) in a control experiment. It was necessary to do blank tests to make certain that no adsorption had occurred on the equipment walls.

RESULTS AND DISCUSSION

Response Surface Methodology (RSM) Modeling

Experimental Design of RSM

To create, improve, and optimize complicated processes, response surface methodology (RSM) is increasingly being used to analyze operational factors.^{18,19,21} Four independent factors were studied for their impact on Cr(VI) adsorption in a batch process using Fe-SCC adsorbent, and the most beneficial central composite design in RSM was adopted. These were the initial Cr(VI) concentration, contact

duration, adsorbent dose, and solution pH. Table–1 shows the experimental range of the variables utilized in CCD, as well as their unit and notation.

Table–1: Independent Variables Selected for CCD

Factors	Units	Notations	Level of variables	
			Low	High
Initial Cr(VI) concentration	mg/L	A	5	20
Contact time	min	B	5	20
Adsorbent dose	g	C	0.1	0.25
pH		D	4.0	8.0

"Design–Expert" software was used to build the three–level, four–factor CCD. The CCD matrix was used for 30 trials in which the most effective quadratic model, from the sequential model sum of squares; (Table–2) was selected to continue the progress of the experimentation.

Table–2: Sequential Model Sum of Squares

Source	Sum of squares	df	Mean square	F value	p–value, Prob >F	
Mean vs Total	254121.50	1	254121.50			
Linear vs Mean	300.76	4	75.19	5.68	0.0021	
2FI vs Linear	168.72	6	28.12	3.29	0.0215	
Quadratic vs 2FI	159.65	4	39.91	234.64	< 0.0001	<i>Suggested</i>
Cubic vs Quadratic	0.53	7	0.08	0.30	0.9359	<i>Aliased</i>
Residual	2.02	8	0.25			
Total	254753.18	30	8491.77			

Table–3: ANOVA and Model Statistics for CCD

Source	Coefficient estimate	Sum of squares	Standard error	F value	p–value, Prob >F
Model		629.13		264.18	
A	0.98	3.27	0.224	19.22	< 0.0001
B	0.67	1.73	0.209	10.16	0.0005
C	6.42	79.48	0.297	467.26	0.0061
D	0.75	3.39	0.169	19.91	< 0.0001
AB	0.71	1.91	0.211	11.22	0.0005
AC	–0.19	0.10	0.251	0.58	0.0044
AD	3.07	61.13	0.162	359.35	0.4584
BC	6.09	88.00	0.268	517.34	< 0.0001
BD	–2.87	52.68	0.163	309.70	< 0.0001
CD	–4.51	108.70	0.178	639.04	< 0.0001
A ²	–1.09	5.87	0.185	34.53	< 0.0001
B ²	1.75	16.45	0.178	96.70	< 0.0001
C ²	9.91	138.22	0.348	812.56	< 0.0001
D ²	0.54	5.55	0.095	32.65	< 0.0001
Residual		2.55			
Lack of Fit		0.65		0.300	0.9433
Pure Error		1.90			
Cor. Total		631.68			
Std. Dev.	0.4124	Mean	92.036	C.V.%	0.4481
PRESS	4.4715				
R–Squared	0.9960	Adj. R ²	0.9922	Pred. R ²	0.9929
Adeq. Precision	61.087				

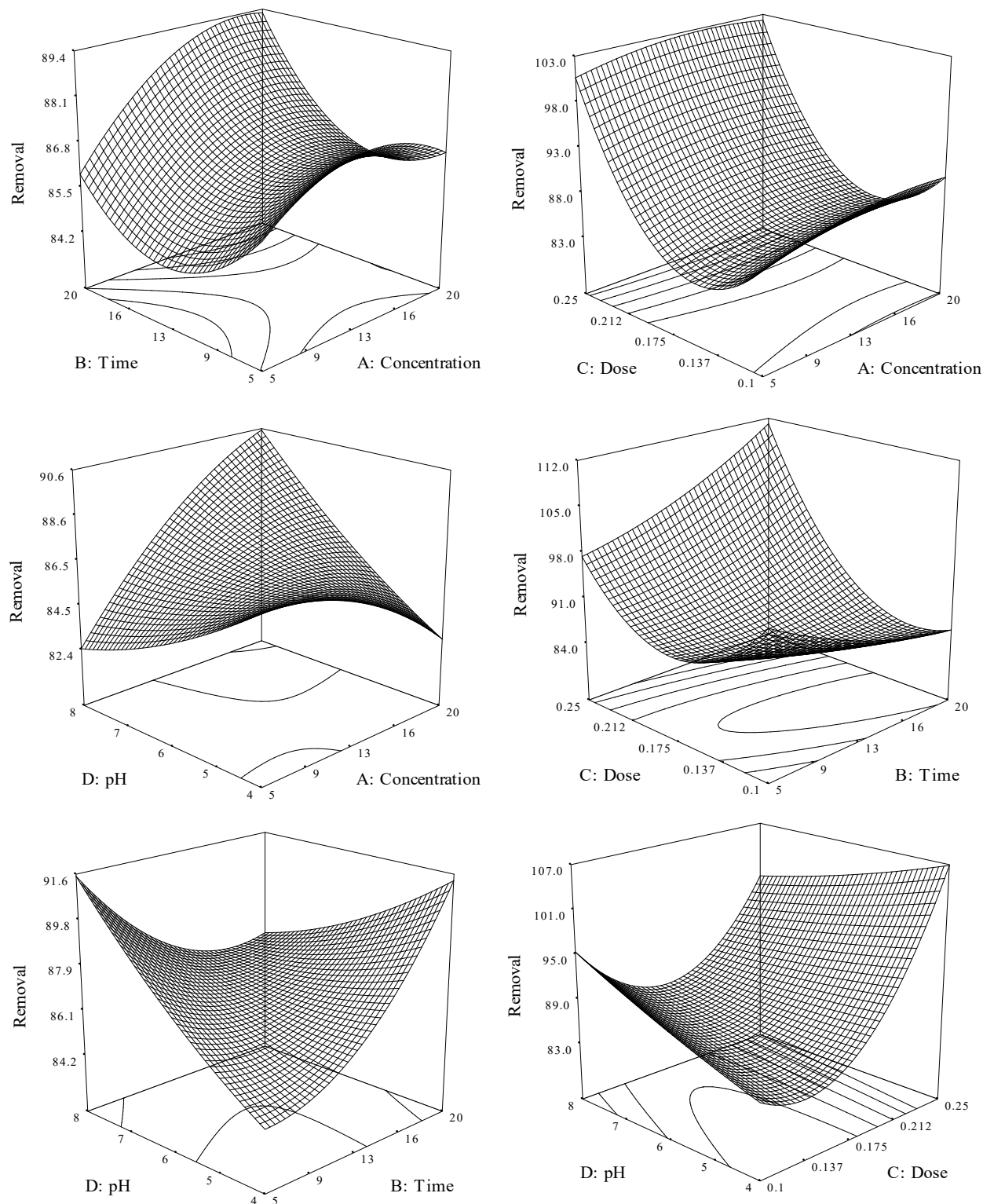


Fig-1: Response Surface Plots Showing the Effect of Tested Variables on Cr(VI) Removal by Fe-SCC

Evaluation of the CCD Model

The analysis of variance (ANOVA) proved that the quadratic model was adequate and significant. The Fisher variation ratio (F -value), probability value (p -value), lack of fit, coefficient of determination R_d^2 , R_{Adj}^2 , R_{Pred}^2 , and adequate precision were all evidence of it. A signal-to-noise ratio of at minimum 4 is

desired for adequate precision. The higher F -value and R^2 values close to 1 indicate that the model is extremely important in the adsorption process.^{11,22-24} The selected quadratic model was validated by ANOVA (Table-3) which provided evidence such as a high F -value (264.18), very low p -value (< 0.0001), non-significant lack of fit (0.30), as well high values for the coefficient of R -squared ($R_a^2 = 0.9960$), adjusted R -squared ($R_{Adj}^2 = 0.9922$), predicted R -squared ($R_{Pred}^2 = 0.9929$), and the adequate precision (61.09).

The following equation expresses the empirical relationship between the response and the tested independent variables expressed in terms of unit less regression coefficient by the chosen model:

$$\text{Response (\% removal)} = + 86.27 + 0.98A + 0.67B + 6.42C + 0.75D - 0.71AB - 0.91AC + 3.07AD + 6.09BC - 2.87BD - 4.51CD - 1.09A^2 + 1.75B^2 + 9.91C^2 + 0.54D^2$$

where A (initial Cr(VI) concentration), B (contact time), C (adsorbent dose), and D (pH of the solution) are coded factors.

Positive coefficient results showed that factors increased Cr(VI) adsorption in the measured range, while negative coefficient values suggested that factors decreased the percentage of removal. A, B, C, D, AB, AD, BC, BD, CD, A^2 , B^2 , C^2 , and D^2 are key model terms in this instance (Table-3). To investigate the interaction between the independent components and their influence on the response, 3D plots (Fig.-1) were created. While keeping all other factors constant, the 3D graphs provide a clearer understanding of the effect of two variables and their interactions on the answer.

Optimization on Cr(VI) Adsorption/Removal Using the Desirability Functions

An object's desirability can be measured on a scale from zero at the margins to one at the apex.^{18,24} This is the goal of the program. It was decided to use an optimization process in which initial Cr(VI) concentration was set to "maximum", Fe-SCC dosage was set to "minimum", and contact time and pH of the solution were adjusted to parameters that were all "in range". For the sake of determining the most economically advantageous state, the term "maximum" was used. The idea behind this procedure was to have the best adsorptive removal of Cr(VI) while using the least amount of adsorbent. The desirability value (Fig.-2a) for each variable varies from 0.942 to 1, and the total desirability value is 0.978.

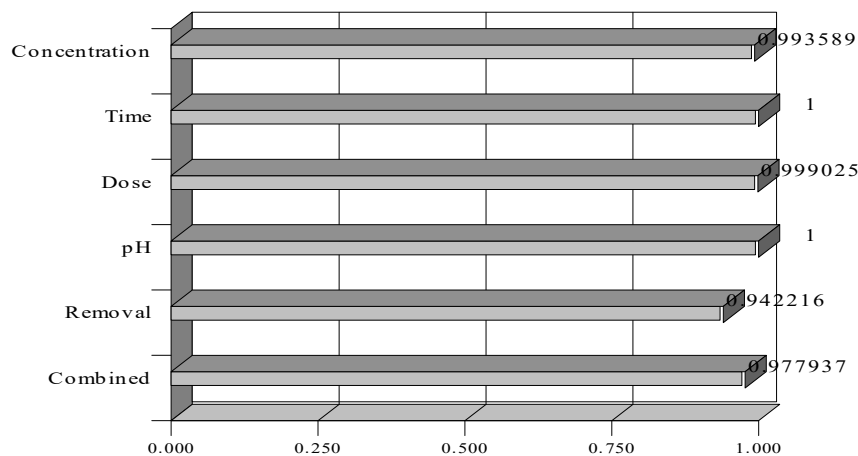


Fig.-2a: Bar Plot for Optimization Procedure

By seeking 10 starting points and solutions in the response surface changes, the best local maximum removal of Cr(VI) was found at 98.3 percent when the variables tested remained at 20 mg/L initial Cr(VI) concentration, 0.1 g Fe-SCC dose, pH 8, and 13 min of contact time at a maximum desirable value of 0.978 (Fig.-2b).

Artificial Neural Network (ANN) Modeling

ANN stands for artificial neural network, and it is a type of advanced statistical or computer modeling process that is analogous to biological neural networks.^{25,26} Using the present data, this model may

construct a mapping from the input parameters to the output parameters without knowing exactly how the input and output parameters relate to one another.

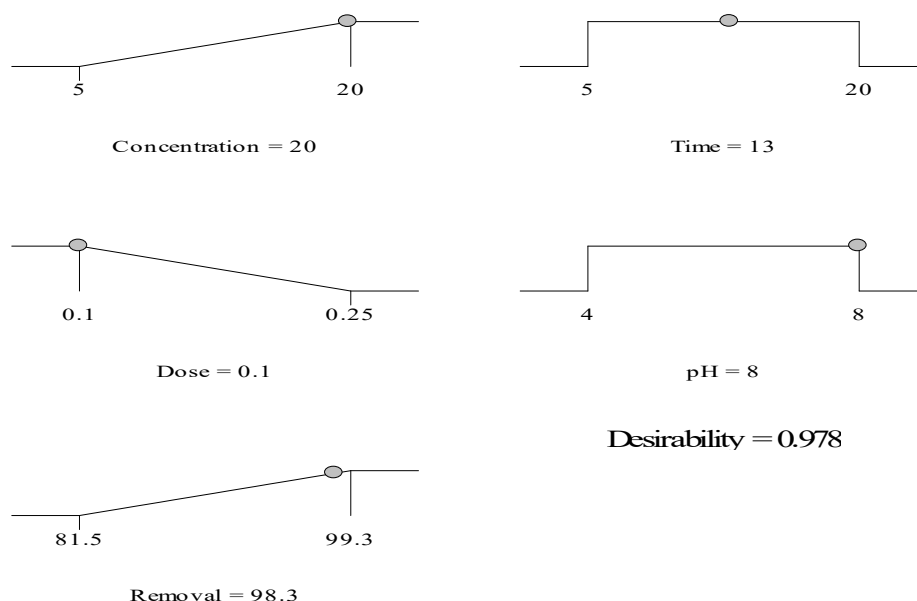


Fig.-2b: Desirability Ramp for Numerical Optimization

ANN may be taught to discover patterns and extract trends from non-linear data that is difficult to interpret.^{27,28} Cr(VI) adsorption parameters can be anticipated and estimated using a neural network since adsorption is a complicated non-linear process. SPSS-17 statistical program was used to forecast the adsorption process of Fe-SCC during batch investigation using the Neural Network Toolbox. Figure-3 depicts the study's basic ANN architecture.

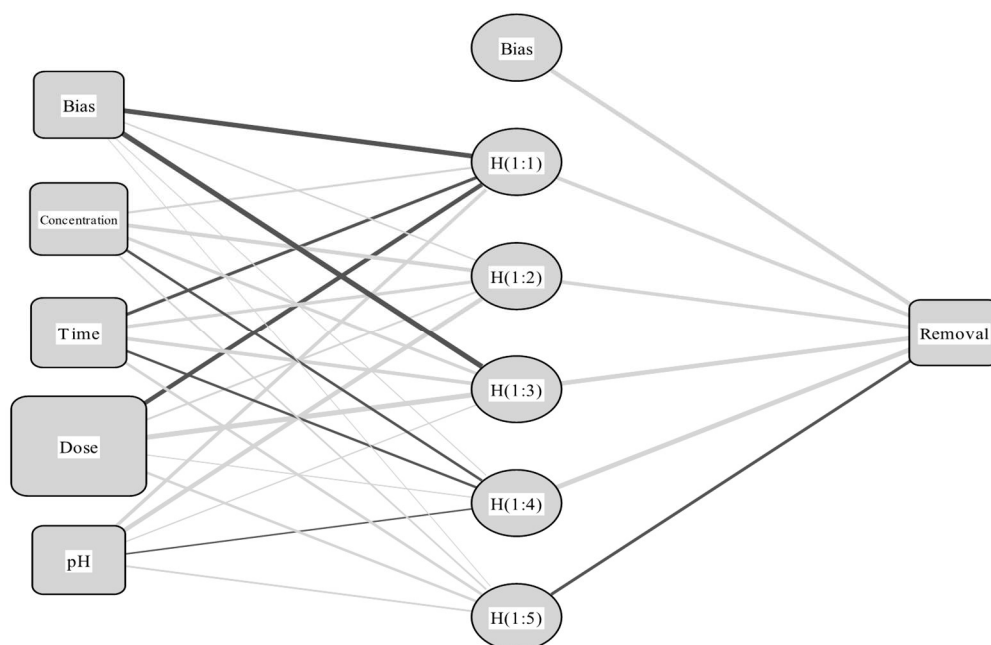


Fig.-3: Neural Network Architecture of Cr(VI)

On 30 experimental datasets acquired from CCD's experimental design, a three-layer feed-forward neural network model was created using the standardized hyperbolic tangent function. The network was trained

with 76.7% of the datasets, while the remaining 23.3 percent were utilized to test and verify the ANN model. The input layer had four neurons (i.e., initial Cr(VI) concentration, contact time, adsorbent dosage, and solution pH), but the output layer only had one neuron (i.e., percent removal). Adsorption processes may be predicted with fair accuracy using the 5–6–1 ANN (with bias neuron) model. The model was found to be performing satisfactorily throughout the testing phase with a sum square error of 0.083% and an average relative error of 0.023%. The value of R^2 (0.962), which is quite near 1, indicates that the experimental and the ANN-predicted values are in good agreement. When it came to determining the most important variables, an importance analysis revealed that adsorbent dosage had the highest effectiveness.

Comparison of RSM and ANN Models

In today's adsorption research, RSM and ANN are two of the most commonly used methodologies. RSM and ANN both present a system where the mathematical relationship between both the parameters/variables and the response is unclear. It is possible to capture and describe complicated non-linear correlations between the tested variables and the system response using one of these extremely powerful data modeling methods.^{22,29} A batch adsorption process using Fe–SCC adsorbent was modeled and optimized using RSM and ANN techniques in light of these characteristics. RSM and ANN outcomes were tested using 30 identical experimental datasets.

Perturbation Plot of RSM

A perturbation plot is akin to a one factor at a time experiment in that it does not display the impact of interactions. Figure-4 shows plots made by CCD in RSM to compare the impact of all independent variables at a certain position in the design space. Only one element is modified across its range to depict the response, while the other factors remain fixed. The reaction is sensitive to the factor if the slope or curve is steep. The lack of response to a change in that particular element is demonstrated by a very flat line. Because of this, the graphical plot demonstrated that adsorbent dose is more sensitive for Cr(VI) adsorption than other studied variables.

Importance Analysis of ANN

The created ANN was also subjected to an important analysis to determine the most effective parameter. The degree of efficiency for Cr(VI) adsorption was discovered in the order of adsorbent dose > initial Cr(VI) concentration > contact duration > pH of the solution in the present situation (Fig.-5). These input factors had a percentage effect on the output response of 100.0, 58.3, 56.0, and 53.2 percent, respectively.

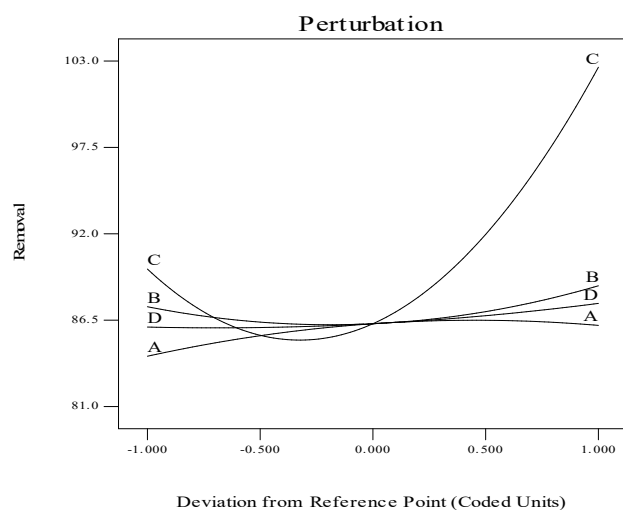


Fig.-4: Perturbation Plot Showing The Effect of Tested Variables

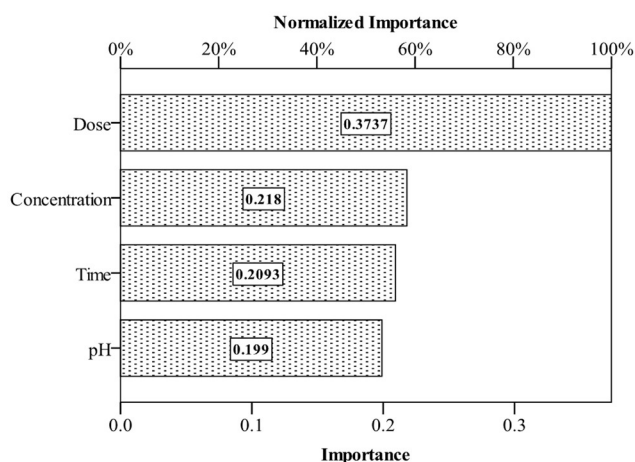
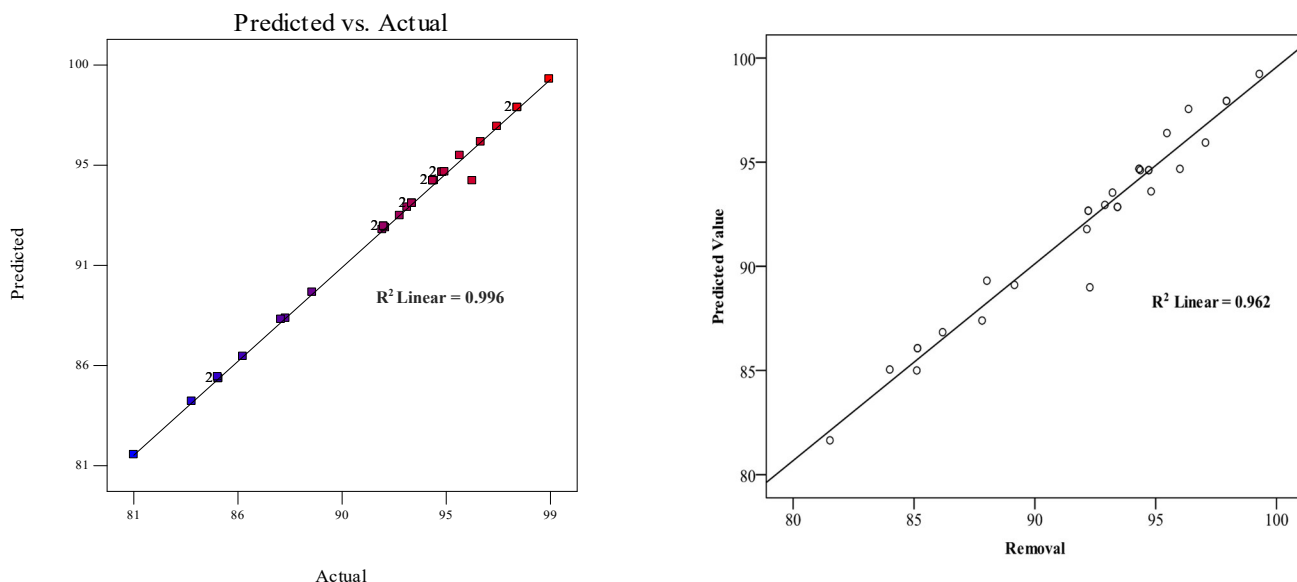


Fig.-5: Importance Analysis of Experimental (input) Parameters

A comparison of the optimized RSM and ANN models' performance is shown in Figure-6. Figures-6a and 6b show actual and predicted values for the adsorptive elimination of Cr(VI). R^2 values of (0.996;

0.962) both of which are quite close to 1, show that there are judgments to be made between experimental and model-predicted values.



(a) Plot of Actual vs. Predicted response by RSM

(b) Plot of Actual vs. Predicted response by ANN

Fig.-6: Comparison of Experimental data and Predicted data by RSM and ANN models

An RSM model and an ANN model were found to be equally effective in this study at making correct predictions. In addition to providing a regression equation for prediction, RSM shows the impact of operational variables and their interactions on response. You don't need to conduct a standard design experiment to build a model using an ANN. RSM and ANN models, thus, may both accurately represent the adsorptive removal of Cr(VI) by Fe-SCC.

CONCLUSION

Adsorbent Fe-SCC was used to remove Cr(VI) from the water, and the effectiveness of the process was explained using RSM and ANN statistical models. Importance analysis and perturbation plots demonstrate that adsorbent dosage is the most important parameter for adsorbing Cr(VI). Based on the adjusted determination coefficient ($R_{Adj}^2 = 0.9922$) and the adequate precision ratio (61.09), the quadratic model adequately characterizes the response surface space. When comparing the RSM and ANN models, the coefficient of determination R^2 (the difference between the actual and predicted values) is employed. More accurate predictions are made using the RSM model than the ANN model. Accordingly, the use of statistical models for optimization, modeling, and design of the Cr(VI) adsorption process appears to be the most effective technique. By executing a column operation to remove Cr(VI), the results of this study can be further applied in the industrial sector.

ACKNOWLEDGEMENT

The author is grateful for financial support from the UGC (ERO) of the Government of India's Minor Research Projects Scheme [F.No.PSW-010/014-15(ERO)]. Thank you to the editor and anonymous reviewers for their valuable suggestions and comments, which helped to enhance the research.

REFERENCES

1. M. Jain, V.K. Garg and K. Kadirvelu, *Journal of Environmental Management*, **91**(4), 949(2010), <https://doi.org/10.1016/j.jenvman.2009.12.002>
2. T. Ravi and S. Sundararaman, *Rasayan Journal of Chemistry*, **14**(2), 1105(2021), <http://dx.doi.org/10.31788/RJC.2021.1426220>
3. M. Varga, M. Takács, G. Záray and I. Varga, *Microchemical Journal*, **107**, 25(2013), <https://doi.org/10.1016/j.microc.2012.08.009>

4. X.J. Wang, Y. Wang, X. Wang, M. Liu, S.Q. Xia, D.Q. Yin, Y.L. Zhang and J.F. Zhao, *Chemical Engineering Journal*, **174**(1), 326(2011), <https://doi.org/10.1016/j.cej.2011.09.044>
5. S. Mitra, A. Sarkar and S. Sen, *Nanotechnology for Environmental Engineering*, **2**, 11(2017), <https://doi.org/10.1007/s41204-017-0022-y>
6. R.M. Muthuraman, A. Murugappan and B. Soundharajan, *Rasayan Journal of Chemistry*, **14**(3), 2024(2021), <http://doi.org/10.31788/RJC.2021.1436129>
7. H. Oliveira, *Journal of Botany*, **2012**, 375843(2012), <https://doi.org/10.1155/2012/375843>
8. R.A. Wuana and F.E. Okieimen, *ISRN Ecology*, **2011**, 402647(2011), <https://doi.org/10.5402/2011/402647>
9. X.S. Wang, L.F. Chen, F.Y. Li, K.L. Chen, W.Y. Wan and Y.J. Tang, *Journal of Hazardous Materials*, **175**(1–3), 816(2010), <https://doi.org/10.1016/j.jhazmat.2009.10.082>
10. V.E. Pakade, N.T. Tavengwa and L.M. Madikizela, *RSC Advances*, **9**(45), 26142(2019), <https://doi.org/10.1039/C9RA05188K>
11. M.P.S. Kumar and B.R. Phanikumar, *Environmental Science and Pollution Research*, **20**(3), 1327(2013), <https://doi.org/10.1007/s11356-012-0981-2>
12. S. Parlayici, V. Eskizeybek, A. Avcı and E. Pehlivan, *Journal of Nanostructure in Chemistry*, **5**(3), 255(2015), <https://doi.org/10.1007/s40097-015-0156-z>
13. M.K. Rai, G. Shahi, V. Meena, R. Meena, S. Chakraborty, R.S. Singh and B.N. Rai, *Resource–Efficient Technologies*, **2**(S1), S63(2016), <https://doi.org/10.1016/j.reffit.2016.11.011>
14. H. Li, X. Dong, E.B. da Silva, L.M. de Oliveira, Y. Chen and L.Q. Ma, *Chemosphere*, **178**, 466(2017), <https://doi.org/10.1016/j.chemosphere.2017.03.072>
15. H. Lyu, J. Tang, Y. Huang, L. Gai, E.Y. Zeng, K. Liber and Y. Gong, *Chemical Engineering Journal*, **322**, 516(2017), <https://doi.org/10.1016/j.cej.2017.04.058>
16. M. Nazar, N.M. Aulya, Syahrial and K. Puspita, *Rasayan Journal of Chemistry*, **15**(1), 221(2022), <http://dx.doi.org/10.31788/RJC.2022.1516546>
17. N.K. Amin, *Desalination*, **223**(1–3), 152(2008), <https://doi.org/10.1016/j.desal.2007.01.203>
18. N.K. Mondal, A. Samanta, P. Roy and B. Das, *Sustainable Water Resources Management*, **5**(4), 1627(2019), <https://doi.org/10.1007/s40899-019-00322-5>
19. P. Roy, N.K. Mondal and K. Das, *Journal of Environmental Chemical Engineering*, **2**(1), 585(2014), <https://doi.org/10.1016/j.jece.2013.10.014>
20. W. Liu, J. Zhang, C. Zhang, Y. Wang and Y. Li, *Chemical Engineering Journal*, **162**(2), 677(2010), <https://doi.org/10.1016/j.cej.2010.06.020>
21. S. Chowdhury, S. Chakraborty and P.D. Saha, *Environmental Science and Pollution Research*, **20**(3), 1698(2013), <https://doi.org/10.1007/s11356-012-0989-7>
22. S. Chattoraj, N.K. Mondal, B. Das, P. Roy and B. Sadhukhan, *Applied Water Science*, **4**(1), 79(2014), <https://doi.org/10.1007/s13201-013-0132-z>
23. P. Roy, U. Dey, S. Chattoraj, D. Mukhopadhyay and N.K. Mondal, *Applied Water Science*, **7**(3), 1307(2017), <https://doi.org/10.1007/s13201-015-0339-2>
24. B. Sadhukhan, N.K. Mondal and S. Chattoraj, *Clean Technologies and Environmental Policy*, **16**(6), 1015(2014), <https://doi.org/10.1007/s10098-013-0701-8>
25. P. Roy, *Journal of Materials and Environmental Sciences*, **9**(12), 3206(2018)
26. K. Sinha, P.D. Saha and S. Datta, *Industrial Crops and Products*, **37**(1), 408(2012), <https://doi.org/10.1016/j.indcrop.2011.12.032>
27. K.R. Raj, A. Kardam, J.K. Arora and S. Srivastava, *Waste and Biomass Valorization*, **4**(2), 401(2013), <https://doi.org/10.1007/s12649-012-9164-0>
28. P. Roy, N.K. Mondal, S. Bhattacharya, B. Das and K. Das, *Applied Water Science*, **3**(1), 293(2013), <https://doi.org/10.1007/s13201-013-0082-5>
29. A. Witek–Krowiak, K. Chojnacka, D. Podstawczyk, A. Dawiec and K. Pokomeda, *Bioresource Technology*, **160**, 150(2014), <https://doi.org/10.1016/j.biortech.2014.01.021>

[RJC-6930/2021]