International Journal of Applied Science and Engineering
2019. 16, 3: 187-200

Optimization of Process Parameters for the Removal of Chromium (VI) from Waste Water Using Mixed Adsorbent

Darapureddi Krishna*, Gantala Santhosh Kumar and Dandu Radha Prasada Raju

Department of Chemical Engineering, MVGR College of Engineering, Vizianagaram, India

Abstract: Use of mixed adsorbent (Borasus Flabellifer coir powder and Ragi Husk powder) for the removal of chromium (VI) from waste water has been investigated in a batch mode process wherein influences of parameters like initial Cr (VI) concentration (20-60 mg/L), pH (1-3) and mixed adsorbent dosage (10-14 g/L) on Cr (VI) adsorption were tested by adopting both Box-Behnken Design (BBD) in response surface methodology and Feed Forward Artificial Neural Network (ANN). Optimum conditions for maximum removal of Cr (VI) from waste water of 20 mg/L have been analyzed by both the models, viz, mixed adsorbent dosage (12.3099 g/L in BBD and 12.1928 g/L in ANN), pH (1.6162 in BBD and 2.0912 in ANN) and initial Cr (VI) concentration (20.0261 mg/L in BBD and 20 mg/L in ANN). An ANN model was also developed in which 6 neurons were used in the hidden layer. The SEM and EDS photographs have indicated the surface morphology of mixed adsorbent and confirmation of metal ions adsorption.

Keywords: Box-behnken design (BBD); artificial neural network (ANN); mixed adsorbent, Cr (VI) removal and adsorption.

1. Introduction

Large amount of waste is generated due to ever increasing standards of living and tremendous growth in urbanization and industrialization and also from leather, tanneries, and electroplating, mining, steel and petrochemical industries. Heavy metals are present in wastewater streams that are often discharged into water bodies without following discharge limits specified as per environmental regulations. As heavy metals in wastewater seriously affect on well being of people, aquatic species and other living organisms, such discharges needs to be treated effectively [1]. Among heavy metals present in wastewater, chromium assumes significance for removal because of its toxicity, carcinogenic and mutagenic nature [2]. Typical tolerance limit for Cr (VI) in wastewater streams is 0.05 mg/L [3].

Treatment methods used for Cr (VI) removal from wastewater includes mainly ion exchange technique, chemical precipitation, electrochemical process, reduction technique, extraction technique, membrane processes, etc [4]. While several merits exist for these processes, primary limitations of these techniques are expensive or not found to be very effective at lower concentrations. An alternative process considered for the removal of Cr (VI) from wastewater streams is the bio-sorption which has gained credibility during last two decades and also recognized as a low cost process due to low cost of naturally available agricultural waste materials.

Corresponding author; e-mail: d_krishna76@rediffmail.com
Received 9 May 2018
doi:10.6703/IJASE.201911_16(3).187
Revised 30 September 2019

Accepted 4 October 2019

The interaction and effect of various operating parameters, such as pH, initial Cr (VI) concentration and mixed adsorbent dosage were investigated in a batch mode experimental set up. The conventional optimization techniques, one factor at a time in multivariable system have been used. Such classical methods require a lot of experimental data and also long time. Otherwise it could not represent the combined effects between various components. Many statistical experimental design methods have been used in chemical process optimization as it helps in understanding the interactions among parameters [5]. Some of such processes that are popular are response surface methodology (RSM) which is followed for developing, improving and also in optimizing processes in more so when it involves complex interactions. Response surface methodology includes Box-Behnken design and central composite design. Box-Behnken design generally require fewer design points than the central composite design, hence it is less expensive to run with same number of factors. It can estimate the first and second order coefficients effectively. The main objective of RSM is to determine the optimum operational parameters for the system [6]. Some applications of Box-Behnken Design (BBD) in RSM have been reported for the removal of heavy metals by various adsorbents like mixed culture of Pseudomonas Aeruginosa & Bacillus Subtillis [7], borasus flabellifer coir powder [8] and ragi husk powder [9].

Major water pollution causes due to organic and inorganic pollutants like nutrients, heavy metals etc. Artificial Neural Network (ANN) was used as important techniques in the design of experiments which can generate optimum parameters for modeling and optimization of pollutants removal [10]. Artificial Neural Networks has been used for the adsorption process which is highly complex and non-linear. The conventional mathematical modeling fails to simulate the mechanism of adsorption [11]. The ANN technique has been successfully applied in environmental modeling as it has been used in tracking the non-linear relationships of variables in complex system [12]. Trial and error procedure in ANN has been used to find out the architecture of ANN and training algorithm to get best solution of the given problem within acceptable limits of error [13]. To get optimum process parameters in ANN, pattern search algorithm in Genetic Algorithm (GA) has been applied by the fitter solutions in a population surviving and passing their traits to offspring which replace the poorer solutions [14]. A proportion of such population has been selected to breed and produce new chromosomes. The selection has been according to fitness of individual solutions by roulette selection and deterministic sampling [15]. The response surface methodology coupled with artificial intelligence like ANN, GA and particle swarm optimization (PSO) has been used for the removal of heavy metals such as copper, cadmium, mercury and selenium (IV), from aqueous solutions using various nanocomposite materials [16-19].

In the present investigation, batch experimental studies [20] have been conducted for the removal of Cr (VI) from waste water using mixed adsorbent (Ragi husk powder and Borasus flabellifer coir powder). The experimental values have been analyzed to obtain the mathematical model for the BBD in RSM and also train the ANN model with 6 neurons in hidden layer with feed forward back propagation algorithm. Both the models have been tested for validation of the experimental data which was not followed earlier for the input parameters (Initial Cr (VI) concentration, mixed adsorbent dosage and pH). The process optimization has been carried out using both the BBD and ANN coupled with GA to optimize the input parameters in the adsorption process for maximum Cr (VI) removal.

2. Experimental methods and techniques

2.1 Adsorbate: Chromium (VI) solution preparation

Stock solution of 1000 mg/L was prepared by adding distilled water in measured quantity of $K_2Cr_2O_7{\cdot}5H_2O$ placed in 1 L volumetric flask. The $K_2Cr_2O_7{\cdot}5H_2O$, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were procured from reputed manufacturers. Various concentrations of test solution of chromium (VI) ranging from 20-100 mg/L were prepared by subsequent dilution of the stock solution. All chemicals used in the experimentation were analytical reagents (AR) and pure.

2.2 Adsorbent: Borasus flabellifer coir powder and Ragi husk powder

Borasus flabellifer coir and Ragi husk, collected from agriculture forms in the close region of college were used as mixed adsorbents. These materials were washed with pure water and dried to increase the purity of material by removal of moisture. After this process, materials have been crushed in a roll crusher. The powders so obtained were screened through British Standard Screen (BSS) meshes of required particle sizes (63µm-125µm). The powders so obtained without any pre-treatment were kept in air tight bottles for carrying out experiments.

2.3 Batch studies

The adsorption studies in a batch mode for individual metal components have been carried out to find out the effect of different parameters, such as initial metal ion concentration (20-100 mg/L), mixed adsorbent dosage (0.1-1.0 g in 50 mL solution), agitation time (0 -120 min), pH (1-7) and adsorbent size at 63µm-125µm. The prepared solution containing known quantity of metal ion and adsorbent has been taken in 250 mL capacity conical flasks and agitated at 180 rpm in a mechanical shaker at predetermined time intervals. The adsorbent was filtered and separated from the solution using filter paper. Final residual metal ion concentration after adsorption was measured by Atomic Absorption Spectrophotometer (PinAAcle, 500, Perkin Elmer Pvt Ltd).

2.4 Experimental design and procedure followed for response surface methodology

The experimental data has been used to find out the analysis of variance and regression models and also the optimum process parameters in (RSM) which is one of the mathematical and statistical techniques [6]. BBD in RSM has been applied in this work to get the optimum process parameters for adsorption process. Experimental work covered three variables (initial Cr (VI) concentration, pH and mixed adsorbent dosage), each with the minimum and the maximum levels. The advantage of BBD in RSM allows the utilization of few combinations of process parameters for determining the complex response model [21]. A total of 15 experiments have been conducted to determine 10 coefficients of second order polynomial equation [22]. In the present statistical experimental design model, initial Cr (VI) concentration (20-60 mg/L), pH (1-3) and mixed adsorbent dosage (10-14 g/L) have been considered as input variables. Percentage removal of Cr (VI) has been taken as the response of the system. Three factors were studied and their ranges, low levels and high levels have been given in Table 1. The experimental design matrix obtained from BBD has been given in Table 2.

Table 1. The experimental design parameters ranges and its levels.

Input parameters		Various parameters levels		
		-1.00	**0**	**1.00**
Initial Cr (VI) concentration (mg/L)	X_1	20	40	60
pH	X_2	1	2	3
Mixed adsorbent dosage (1:1)(g/L)	X_3	10	12	14

The optimization of Cr (VI) removal from wastewater has been carried out using three input process parameters by BBD with 12 different runs including 3-replicates at center points and the same was shown in Table 2. MATLAB software has been used for obtaining model regression and graphical analysis. The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots. The model has been explained based on the regression coefficient (R^2) which was used to predict the optimum values and the interaction between the various input parameters within the specified range.

3. Results and Discussions

3.1 Characterization of mixed adsorbent (Ragi husk and Borasus Blabellifer coir powders)

The carbon component present in the mixed adsorbent was evaluated and it was analyzed to be organic in nature; namely, it contains the components such as carbon, oxygen and silica. The organic nature of mixed adsorbent indicates porous nature to the mixed adsorbent as observed in SEM photographs shown in Figures 1 and 2. Both the figures indicated that mixed adsorbent surface has the nature of most irregular and highly porous and thus it promotes the adsorption of metals on the surface of mixed adsorbent. Furthermore, the EDS spectra of selected zone of mixed adsorbent before adsorption and after adsorption has indicated the chemical components present in the adsorbent (refer to Figure 3). It was observed from Figure 3a that mixed adsorbent having the carbon, oxygen and silica on its surface before interaction with Cr (VI) ions, whereas in Figure 3b new chromium peak has been found along with the surface bearing groups of carbon, oxygen and silica, which indicated the adsorption of Cr (VI) on mixed adsorbent.

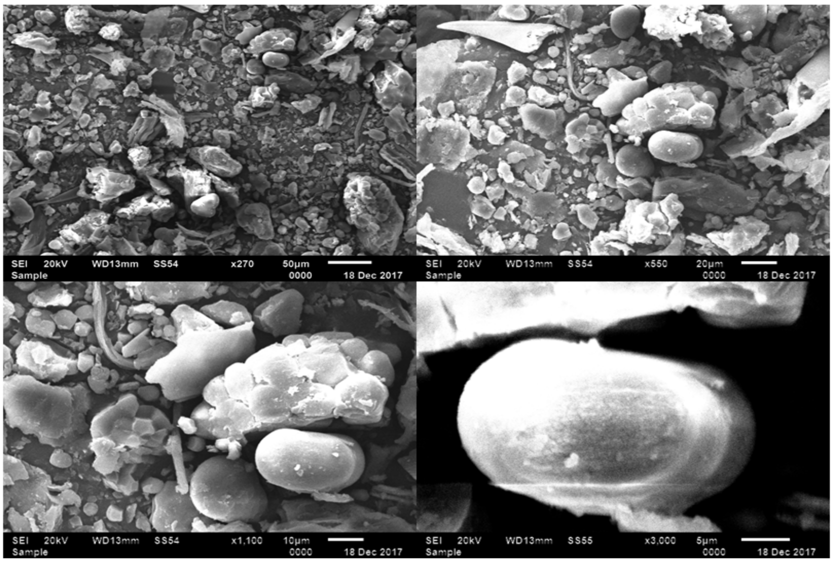

Figure 1. Scanning Electron Micrograph (SEM) of mixed adsorbent before adsorption.

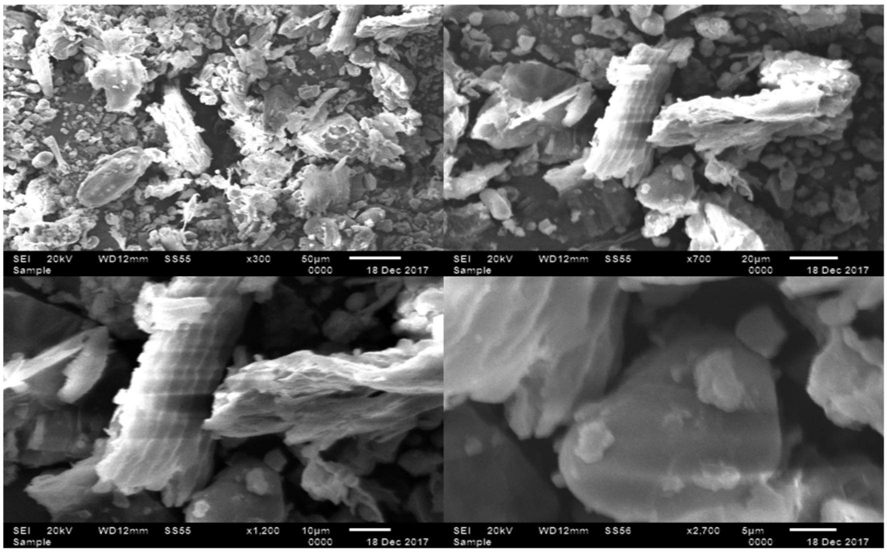

Figure 2. Scanning Electron Micrograph (SEM) of mixed adsorbent after adsorption.

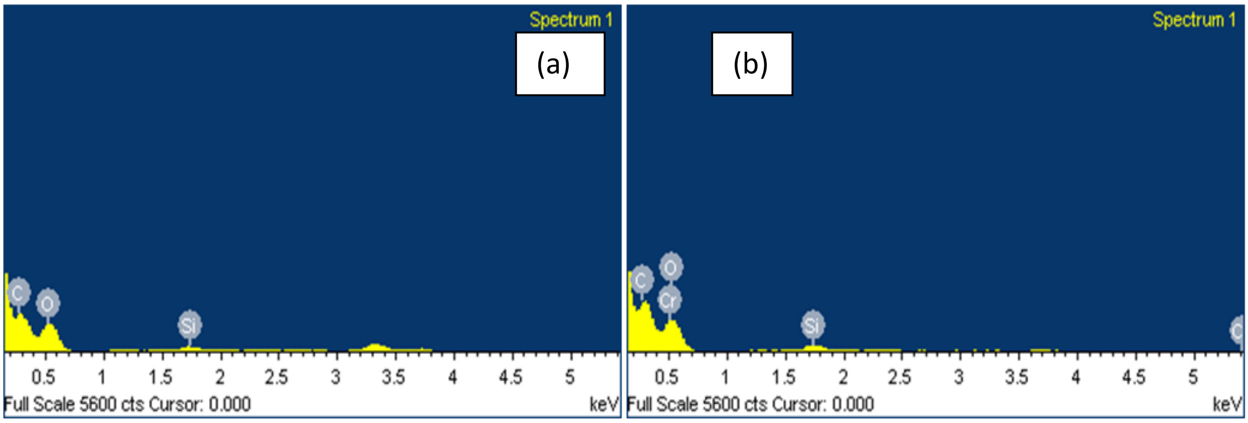

Figure 3. Energy Disperse Spectra of mixed adsorbent (a) before chromium (VI) adsorption (b) after chromium (VI) adsorption.

3.2 BBD experimental results

The results of the each experiment carried out conformity with the MATLAB software have been depicted in Table 2. The quadratic empirical equation relating between the output and the input parameters have been expressed as under.

$$Y = 73.18 - 1.6812X_1 - 11.9612X_2 + 0.9275X_3 - 0.8387X_1^{\ 2} - 15.5587X_2^{\ 2} - 2.9962X_3^{\ 2} - 0.0175X_1X_2 - 0.005X_1X_3 + 0.01X_2X_3 \quad (1)$$

Y is the percentage removal of Cr (VI).

Table 2. Results of chromium (VI) removal by response surface methodology.

Run	Parameter levels			Parameter values			Cr(VI) removal		Relative error
	X1	X2	X3	X1	X2	X3	Experimental	Predicted	
1	-1	-1	0	20	1	12	70.39	70.41	-0.02
2	-1	1	0	20	3	12	46.35	46.52	-0.17
3	1	-1	0	60	1	12	67.25	67.08	0.17
4	1	1	0	60	3	12	43.14	43.12	0.02
5	-1	0	-1	20	2	10	70.21	70.09	0.12
6	-1	0	1	20	2	14	72.03	71.96	0.07
7	1	0	-1	60	2	10	66.67	66.74	-0.07
8	1	0	1	60	2	14	68.47	68.58	-0.12
9	0	-1	-1	40	1	10	65.57	65.67	-0.09
10	0	-1	1	40	1	14	67.45	67.50	-0.05
11	0	1	-1	40	3	10	41.78	41.73	0.05
12	0	1	1	40	3	14	43.70	43.60	0.09
13	0	0	0	40	2	12	71.25	73.18	-1.93
14	0	0	0	40	2	12	74.33	73.18	1.15
15	0	0	0	40	2	12	73.96	73.18	0.78

Table 3 shows the regression coefficient of full polynomial model. The analysis of variance (ANOVA) for the output to analyze the accessibility of the model has been shown in Table 4. To evaluate the best fitness of the model, F-value tests have also been carried out. The larger the F value assumes high priority for best fit model. As per thumb rule, if P-value is less than 0.05, model parameter is significant (refer to Table 3). Based on ANOVA, the chosen model satisfactorily represents the data for Cr (VI) removal from wastewater using mixed adsorbent. The regression coefficient (R^2) value of 0.99 indicates that the experimental values and predicted values are in perfect match (refer to Figure 4). Hence the present statistical method has been successfully employed to study the importance of individual, cumulative and interactive effects of the process parameters. The optimum values of initial concentration of Cr (VI), pH and mixed adsorbent dosage from BBD were found to be 20.02 mg/L, 1.62 and 12.31 g/L respectively. The maximum predicted adsorption of Cr (VI) was found to be 79.59%.

Table 3. The model regression coefficient values.

Regression Coefficient	Parameter estimate	P-Value
β0	73.18	0.00*
β1	-1.68	0.00*
β2	-11.96	0.00*
β3	0.93	0.06*
β11	-0.84	0.19
β22	-15.56	0.00*
β33	-2.99	0.00*
β12	-0.02	0.97
β13	-0.005	0.99
β23	0.01	0.98

***significant, if P<0.05**

Table 4. Analysis of variance results.

Source of variation	Degrees of Freedom	Sum of squares	Mean square	F-Value	P-Value
Regression	9	2080.79	231.19	200.11	0
Residual	5	5.77	1.15		
Total	14	2086.57			

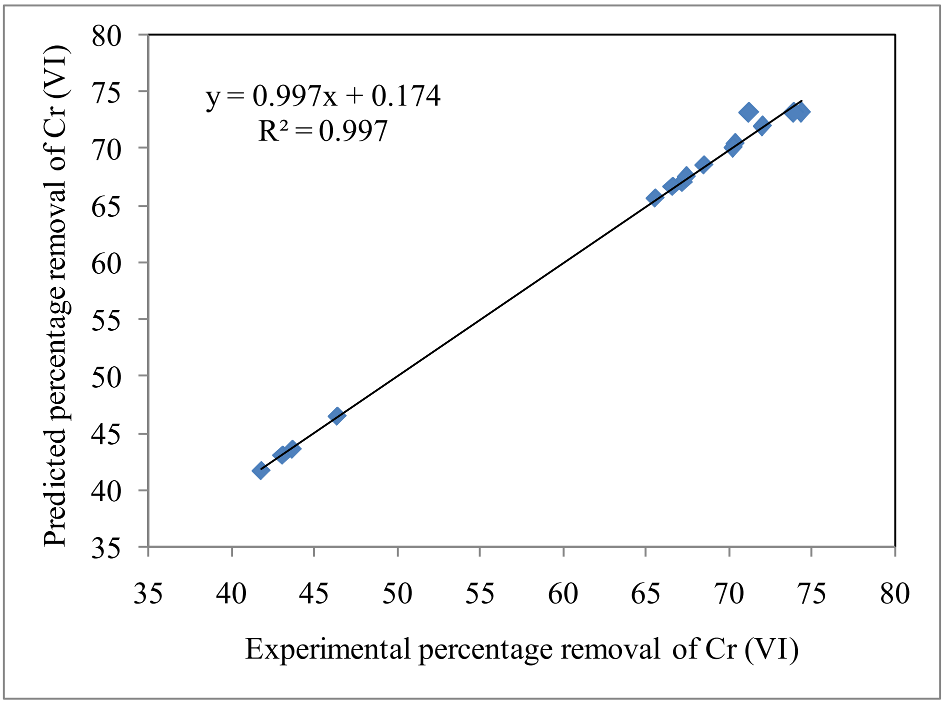

Figure 4. The experimental values vs predicted values for the percentage removal of Cr (VI) from BBD.

3.3 Effect of pH, initial concentration and mixed adsorbent dosage on removal of Cr (VI) by mixed adsorbent in 3D graph

The percentage adsorption of Cr (VI) with mixed adsorbent powder has been studied by chosen range of pH, initial concentration of Cr (VI) and mixed adsorbent dosage. The results have been depicted in Figures 5, 6 and 7. The results reveal that the maximum adsorption has occurred in the acidic range and at low initial concentration of Cr (VI) i.e. adsorption of chromium (VI) increased when pH values varied from 1 to 1.62 and then which decreased when pH was greater than 1.62. The maximum percentage removal of chromium (VI) has been noticed at pH 1.62. The percentage removal of adsorption decreased when concentration increased from 20 mg/L to 100 mg/L. It was noticed that the percentage removal of chromium (VI) increased with an increase in the mixed adsorbent dosage from 10 g/L to 12.31 g/L afterward it decreased.

The maximum adsorption of Cr (VI) metal ions was found to be 79.59 % at pH 1.62 and mixed adsorbent dosage 12.31 g/L.

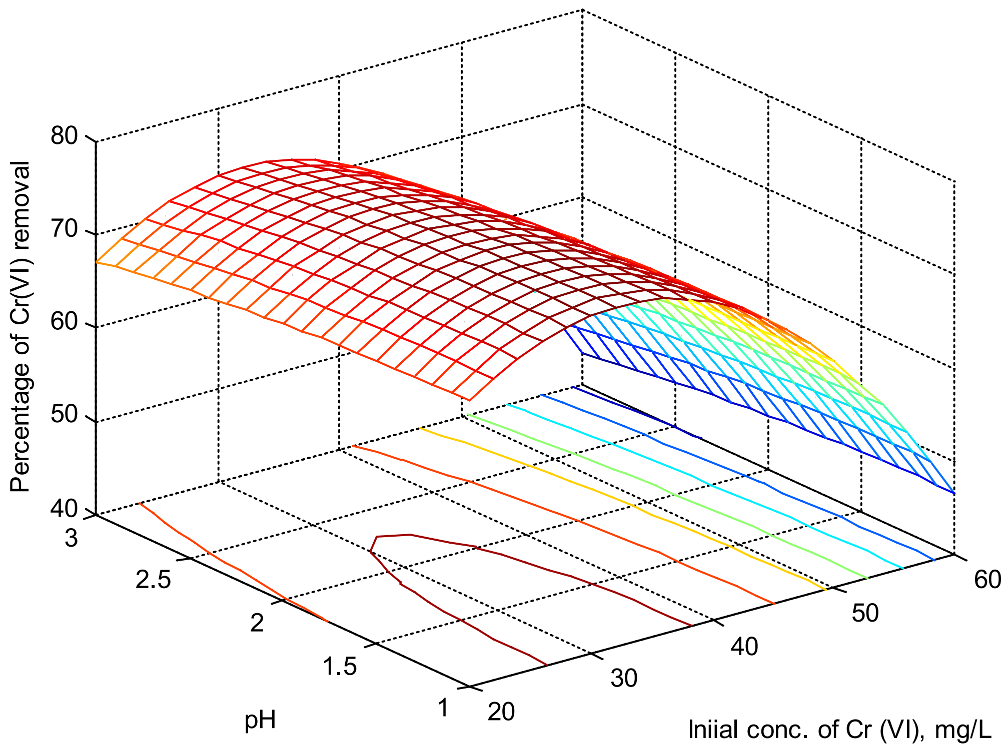

Figure 5. Effect of interaction between initial concentration and pH on removal of Cr (VI) (mixed adsorbent dosage at 12.31 g/L).

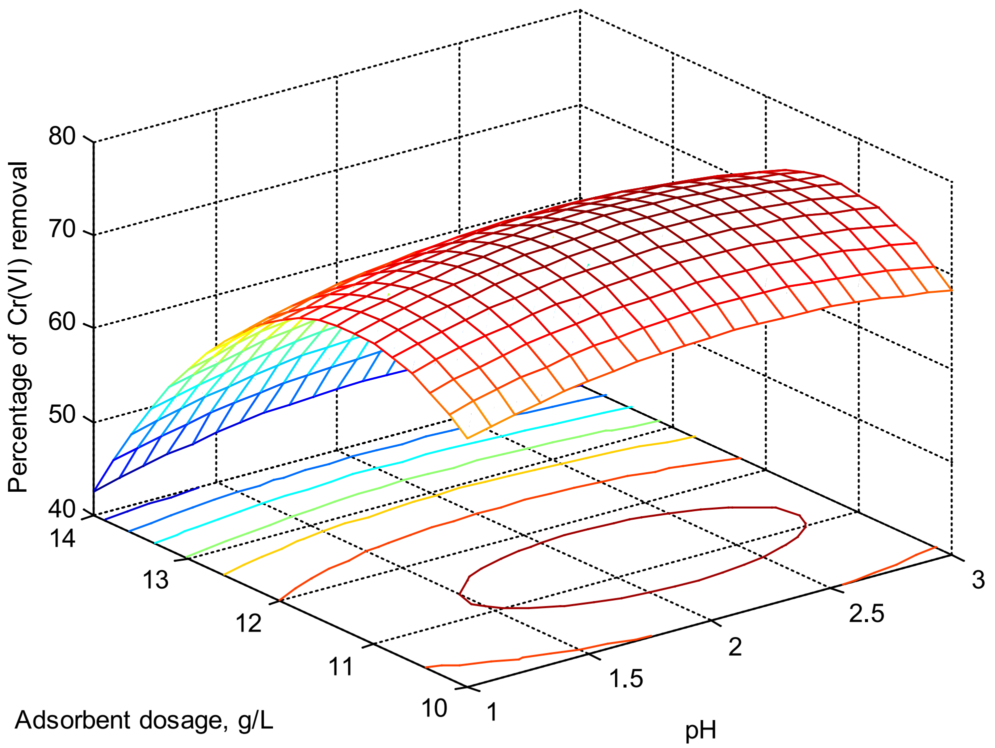

Figure 6. Effect of interaction between mixed adsorbent dosage and pH on removal of Cr (VI) (initial concentration at 20.02 mg/L).

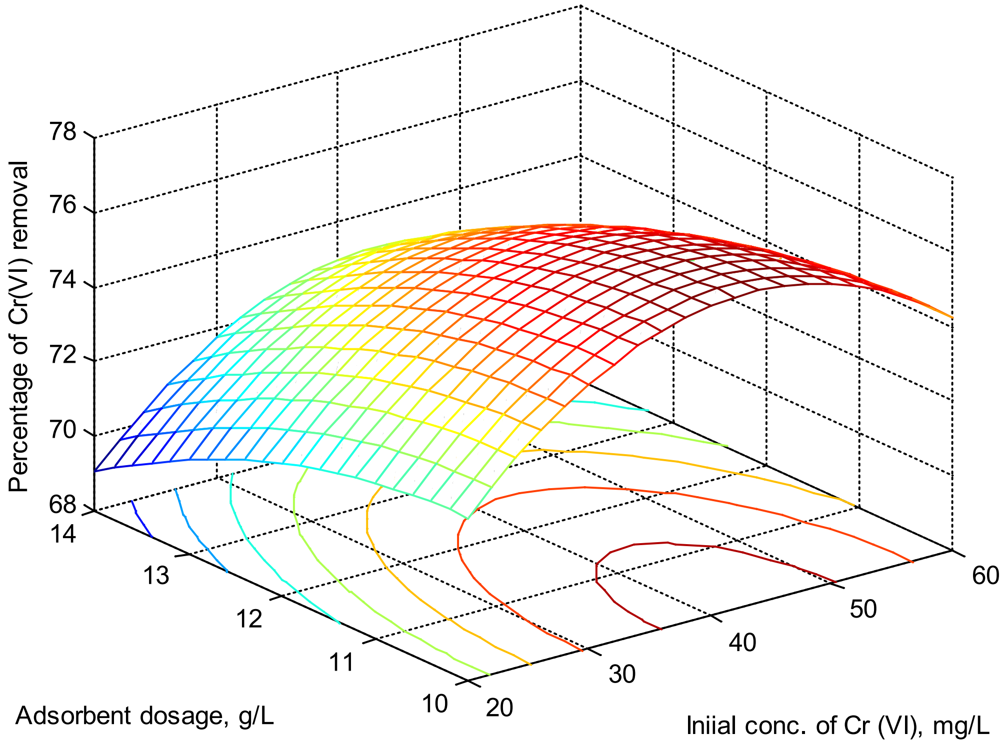

Figure 7. Effect of interaction between mixed adsorbent dosage and initial concentration of Cr (VI) on removal of Cr (VI) (pH value at 1.62).

3.4 ANN model

In this work, Feed-forward ANN with one hidden layer was followed. Optimized ANN model structure has been depicted in Figure 8. Sigmoid transfer function in the hidden layer and a linear transfer function in the output node in the development of ANN model have been used. The back propagation algorithm has been used in the ANN training. MATLAB software has been used to get ANN model data. Initial concentration of Cr (VI) (over range of 20-100 mg/L), pH (over range 1-7) and mixed adsorbent dosage (over range of 2-20 g/L) have been used as inputs of ANN model. The percentage removal of Cr (VI) was the output variable. 54 experimental points have been referred to for the both the training (41 data points) and test sets (13 data points).

ANN topology was one of the important steps in the development of ANN model by means of number of nodes in layers and nature of transfer functions. Based on the minimum Mean Square Error (MSE), the number of neurons in the hidden layer has been calculated. Various topologies namely, number of nodes in hidden layer (varied from 2 to 23 for the determination of optimum number of neurons) have been tested. Each topology has been repeated minimum thrice. The performance of the network as per MSE has been assessed as per following equation:

$$MSE = \frac{1}{N}\sum_{i=1}^{i=N}(y_{i,pred} - y_{i,\exp})^2 \tag{2}$$

N is the number of data points, $y_{i,pred}$ is predictive values $y_{i,\exp}$ is the experimental values and i is an index of data.

The network MSE has been achieved as minimum at six nodes in the hidden layer (refer to Figure 9). Hence, number of hidden neurons equal to six and a single layer feed forward backpropagation neural network have been adopted according to minimum MSE for the modeling of the process.

The weights and bias values obtained by ANN have been given in Table 5. The predicted output values have been compared with experimental values using test data for examining the ANN network (refer to Figure 10). Based on high correlation coefficient (R^2=0.99) values, the model values have closely matched with the experimental values.

Table 6 shows the comparison of experimental and predicted removal efficiency by ANN model on testing data. It shows that predicted removal efficiency by ANN model and experimental values were almost equal with low relative as well as percentage errors. Finally it was concluded that present ANN model has been suitable for the removal of Cr (VI) from waste water using mixed adsorbent with 3 input variables (pH, mixed adsorbent dosage and initial concentration of Cr (VI)). Further it was found to be good interpolation tool for the prediction of data for most experimental values in waste water treatment techniques, as ANN model has favorable features of simplicity, generalization and efficiency.

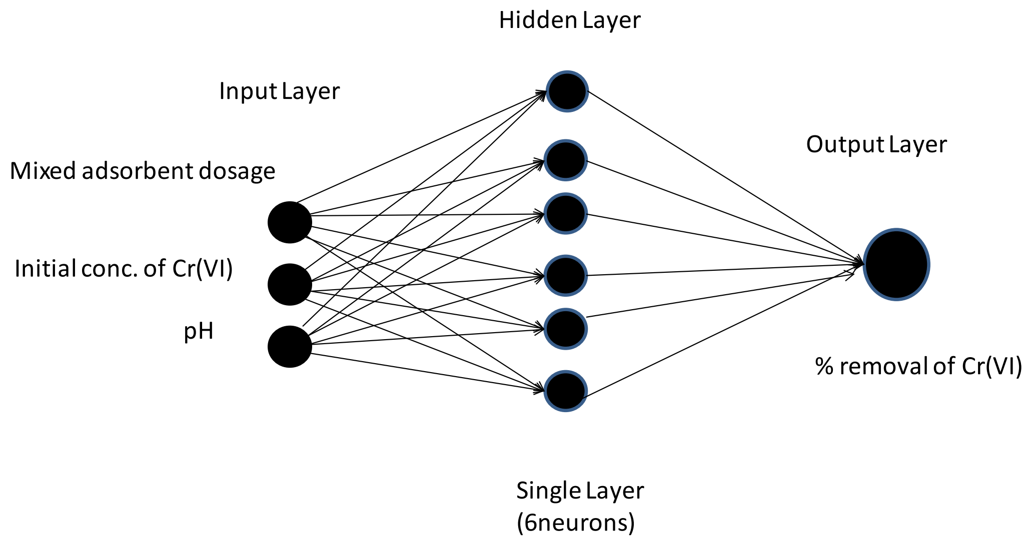

Figure 8. ANN optimized structure.

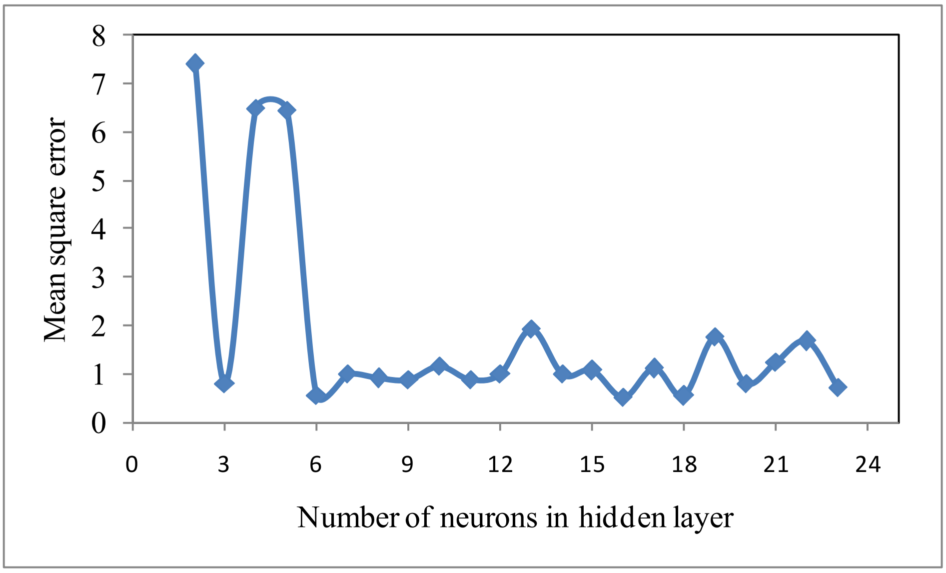

Figure 9. Mean Square Error versus number of neurons in hidden layer.

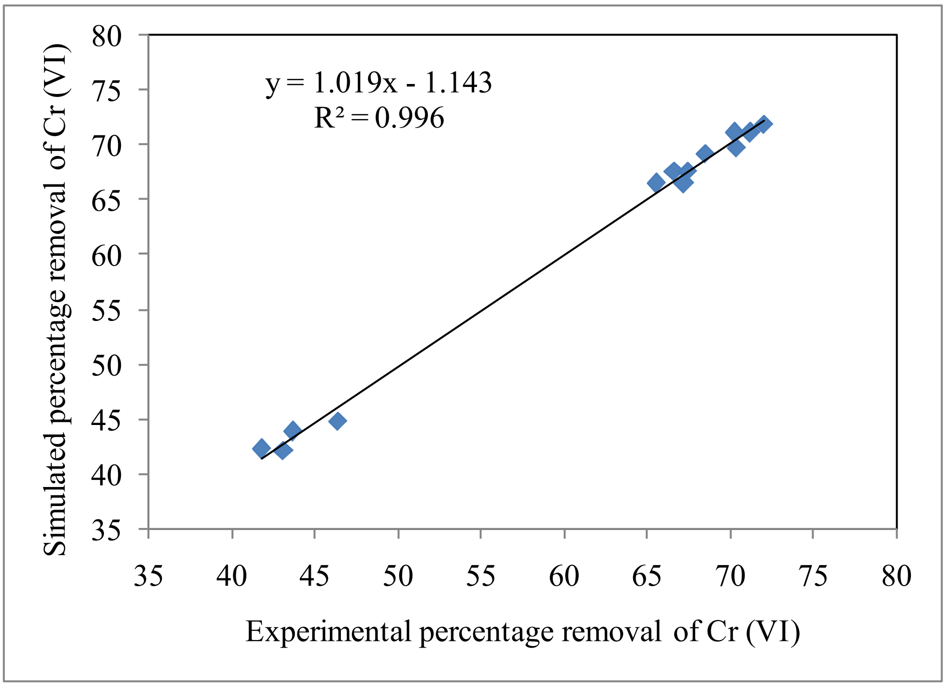

Figure 10. Experimental versus predicted values of percentage removal of Cr (VI).

Table 5. Weights and biases of the neural networks.

W_1 (6×3 matrix)			W_2 (1×6 vector)	b_1(6×1 vector)	b_2(scalar)
0.33	1.17	0.82	[-14.76, -12.46, 0.92, -5.14, 13.97, -15.49]	-4.64	15.87
0.16	2.46	-0.41		-1.86	
-1.07	0.61	0.77		4.33	
0.23	-0.34	-4.60		-1.07	
-0.43	-8.03	3.01		-0.51	
0.22	-0.35	0.38		-0.67	

Table 6. Comparison of experimental and predicted removal efficiency on testing data by ANN.

Run	Initial concentration of Cr (VI), mg/L	pH	Mixed adsorbent dosage g/L	Experimental % efficiency	Predicted % efficiency	Relative error
1	20	1	12	70.39	69.81	0.58
2	20	3	12	46.35	44.93	1.41
3	60	1	12	67.25	66.52	0.73
4	60	3	12	43.14	42.24	0.90
5	20	2	10	70.21	71.13	-0.92
6	20	2	14	72.03	71.90	0.13
7	60	2	10	66.67	67.61	-0.94
8	60	2	14	68.47	69.19	-0.72
9	40	1	10	65.57	66.48	-0.91
10	40	1	14	67.45	67.62	-0.17
11	40	3	10	41.78	42.31	-0.53
12	40	3	14	43.70	43.91	-0.21
13	40	2	12	71.25	71.12	0.13

Optimization of the process parameters for the removal of Cr (VI) from waste water using mixed adsorbent has been carried out with application of GA. The optimum values of variables evaluated from pattern search method in GA were as follows (1) initial concentration of Cr (VI)-20 mg/L (2) mixed adsorbent dosage-12.19 g/L (3) pH-2.09. The residual sum of squares has been 0.57. The maximum percentage removal of Cr (VI) has been 72.45% at the optimum process parameters.

4. Conclusions

The optimum process parameters using both BBD in RSM and ANN for the maximum percentage removal of Cr (VI) from waste water using mixed adsorbent have been evaluated in the present study. The BBD proved to be effective as time saving model for studying the interactions among process parameters on response which significantly reduces the number of experiments and also facilitating to find out the optimum values with regression coefficient (R^2) value of 0.99, the experimental values and the predicted values closely matched with each other. The BBD method has been successfully employed to find out the importance of individual, cumulative and interactive effects of the process parameters. The optimal adsorption of Cr (VI) was obtained at the optimum initial concentration of Cr (VI), pH and mixed adsorbent dosage and these were found to be 20.02 mg/L, 1.62 and 12.31 g/L respectively, resulting in 79.59% of maximum predicted adsorption of Cr (VI).

A multilayer feed forward neural network having one hidden layer, three input parameters, one out parameter and 6 neurons has been applied to predict the percentage removal of Cr (VI) with the minimum MSE. Back propagation algorithm was used to train the network. The model and the test data were in closely matched at R^2 value of 0.99. ANN successfully tracked the non-linear behavior of percentage removal of Cr (VI) versus the initial concentration of Cr (VI), pH and mixed adsorbent dosage with low relative percentage error.

A pattern search solver in GA has been used to optimize the ANN model. The optimization has been achieved at the input parameters of pH-2.09, mixed adsorbent dosage-12.19 g/L and initial concentration of Cr (VI)-20 mg/L. BBD requires 15 experiments as compared to 41 experimental data points in case of ANN model. Hence BBD could be chosen as better on comparison with GA coupled with ANN.

Acknowledgment

The authors are thankful to Department of Science and Technology (DST), Government of India, New Delhi for grant award (No.DST/TM/WTI/2K15/210) for carrying out this research. The authors are thankful to the management and Principal, MVGR College of Engineering for extending the support and encouragement in implementing the project work.

References

[1] Gupta, V. K., Rastogi., A. and Nayak, A. 2010. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost ferilizer industry waste material. *J. Colloid Interface Sci*, 342, 1: 135-141. doi: 10.1016/j.jcis.2009.09.065.

[2] Baral, A. and Robert, D. E. 2002. Chromium based regulations and greening in metal finishing industries in USA, *Environmental Science & policy*. 5, 2: 121-133. doi: org/10.1016/S1462-9011 (02)00028-X.

[3] World Health Organization (WHO). 2004. *Guidelines for Drinking water quality*, 3rd ed., WHO, Geneva, 1:334.

[4] Sud, D., Mahajan, G. and Kaur, M. P. 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions- a review. *Bioresour. Technol*, 99, 14: 6017-6027. doi: 10.1016/j.biortech.2007.11.064.

[5] Md.Zahangir, A., Suleyman, A. M. and Juria, T. 2007. Statistical optimization of adsorption processes for removal of 2, 4-dichlorophenol by activated carbon derived from oil palm empty fruit bunches, *J. Environ. Sci.,* 19: 674-677.

[6] Montgomerry, D. C. 2001. *Design and Analysis of Experiments*, 5th ed., John Wiley Sons, New York, USA.

[7] Tarangini, K., Arvind, K., Satpathy, G. R. and Vikas Kumar, S. 2009. Statistical optimization of process parameters for Cr (VI) biosorption onto mixed cultures of Pseudomonas aeruginosa and Bacillus subtilis. *Clean-Soil,Air, Water*, 37, 4-5: 319-327. doi: org/10.1002/clen.200900033.

[8] Krishna, D., Siva Krishna, K. and Padma Sree, R. 2013. Response surface modeling and optimization of chromium (VI) removal from aqueous solution using borasus flabellifer coir powder. *International Journal of Applied Science and Engineering,* 11, 2: 213-226.

[9] Krishna, D. and Padma Sree, R. 2013. Artificial neural network (ANN) and Response Surface Methodology (RSM) approach for modeling and optimization of chromium (VI) adsorption from waste water using a ragi husk powder. *Indian chemical Engineer,* 55, 3: 200-222. doi: org/10.1080/00194506.2013.829257.

[10] Fan, M., Hu, J., Cao, R., Ruan, W. and Wei, X. 2018. A review on experimental design for pollutants removal in water treatment with the aid of artificial intelligence. *Chemosphere*, 02, 330-343. doi: 10.1016/j.chemosphere.2018.02.111.

[11] Prakash, N., Manikandan, S. A., Govindarajan, L. and Vijayagopal, V. 2007. Prediction of biosorption efficiency for the removal of copper (II) using artificial neural networks. *J. Hazard. Mater,* 152, 3: 1268-1275. doi: 10.1016/j.jhazmat.2007.08.015.

[12] Young-Seuk, P., Tai-Soo, Ch., Inn-Sil, K. I. S. and Sovan, L. 2004. Hierarchical community classification and assessment of aquatic ecosystems using artificial neural networks. *Science of the Total Environ,* 327, 105-122.

[13] Gamze Turan, N., Basak, M. and Okan, O. 2011. Artificial neural network (ANN) approach for modeling of Zn(II) adsorption from leachate using a new biosorbent. *Chem. Eng. J,* 173, 1: 98-105. doi: 10.1016/j.cej.2011.07.042.

[14] Buckeles, B. P. and Petry, F. E. 1992. *Genetic Algorithms*, IEEE Computer Society Press, Los Alamitos, CA.

[15] Bundy (Ed), A. 1997. *Artificial Intelligence Techniques; A Comprehensive catalogue*, Fourth Ed., Springer-Verlag, New York.

[16] Fan, M., Hu, J., Cao, R., Xiong, K. and Wei, X. 2017. Modeling and prediction of copper removal from aqueous solutions by nZVI/rGO magnetic nanocomposites using ANN-GA and ANN-PSO. *Scientific Reports*, 7, 1: 18040-18054. doi: 10.1038/s41598-017-18223-y.

[17] Fan, M., Li, T., Hu J., Cao R., Wei, X., Shi, X. and Ruan, W. 2017. Artificial neural network modeling and genetic algorithm optimization for cadmium removal from aqueous solutions by reduced graphene oxide-supported nanoscale zero-valent iron (nZVI/rGO) composites. *Materials*, 10, 5: 2-22. doi: 10.3390/ma10050544.

[18] Cao, R., Fan, M., Hu, J., Ruan, W., Xiong, K. and Wei, X. 2017. Optimizing low-concentration mercury removal from aqueous solutions by reduced graphene oxide-supported Fe3O4 composites with the aid of an artificial neural network and genetic algorithm. *Materials,* 10, 11: 2-17. doi: 10.3390/ma10111279.

[19] Cao, R., Fan, M., Hu, J., Ruan, W., Wu, X. and Wei, X. 2018. Artificial intelligence bas ed optimization for the Se(IV) removal from aqueous solution by reduced graphene oxid e-supported nanoscale zero-valent iron composites. *Materials,* 11, 3: 1-19. doi: 10.3390/ ma11030428.

[20] Krishna, D., Santhosh Kumar, G. and Prasada Raju, D. R. 2017. Removal of chromium (VI) from waste water using mixed adsorbent. *International Journal of Current Engineering and Scientific Research,* 4, 10: 28-42.

[21] Goel, J., Kadirvelu, K., Rajagopal, C. and Garg, V. K. 2005. Removal of lead (II) from a queous solution by adsorption onto carbon Aerogel using Response surface methodolog yapproach. *Ind. Eng. Chem. Res,* 44, 7: 9354-9362. doi: org/10.1021/ie0490684.

[22] Yetilmezsoy, K., Demirel, S. and Vanderbei, R. J. 2009. Response surface modeling of Pb(II) removal from aqueous solution by Pistacia Vera L: Box-Behnken Experimental Design. *J. Hazard. Mater,* 171, 1-3: 551-562. doi: org/10.1016/j.jhazmat.2009.06.035.