ISSN : 0974 - 7443 Volume 7 Issue 1

CHEMICAL TECHNOLOGY

An Indian Journal

Trade Science Inc.

Full Paper

CTAIJ 7(1) 2012 [9-15]

Application of artificial neural networks and response surface methodology for dye removal using a novel adsorbent

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Received: 11th January, 2012 ; Accepted: 4th February, 2012

ABSTRACT

Experiments were conducted to study the efficiency of green carbon prepared from natural source for removal of a basic dye Methylene Blue (MB). The effect of various process parameters such as temperature, initial pH, contact time, adsorbent dosage and initial dye concentration of the solution were studied by running batch experiments in Erlenmeyer flasks. Modeling equation was developed to study the effects of all the parameters on dye removal by Response Surface Methodology to optimize the process parameters. ANOVA analysis was also studied to know the interaction effect of dye and adsorbent. This experiment revealed that the adsorbent exhibited high adsorption capacities and this adsorption capacity was affected by the changes in temperature, initial pH, contact time, adsorbent dosage and initial dye concentration of the solution. The results obtained were also modeled by using Artificial Neural Networks (ANN). High values of correlation coefficients indicated the best fit of experimental results with that of values obtained from modeling. From these studies, it may be concluded that green carbon adsorbent prepared is efficient and economical for Methylene blue removal from aqueous solutions.

KEYWORDS

Adsorption;
Dye;
CCD;
RSM;
ANN.

INTRODUCTION

Dye pollutants from various industries are an important source of environmental contaminations. Most industries use dyes and pigments to color their products, which include textile, tannery, food, paper and pulp, printing, carpet, and mineral processing industries. Color is a visible pollutant and the presence of even very minute amount of coloring substance makes it undesirable due to its appearance. Disposal of dye effluents into the water streams causes damage to aquatic life as well as humans by mutagenic and carcinogenic effects[7, 8, 27].

Biosorption process is one of the most promising method used for dye removal because of its simplicity, high efficiency, and wide ranging availability[19, 24, 27]. The researchers studied the feasibility of low cost materials such as peat, pinus bark, orange peel, banana pith, cotton waste, rice husk, bentonite clay, neem leaf powder, bamboo dust, coconut shell, ground nut shell, cassava peel, duck weed industrial waste, zeolites, etc for removal of dyes from effluents[6, 13, 19, 20]. But still there is a need to develop economical and highly effective adsorbent to treat dye effluents. Hence, the present work is aimed to develop a simple, cost effective and environmentally benign method for removal of methylene blue from aqueous solution using carbon prepared from Acacia Arabica seeds (AAS) as sorbent.

Neural network is a new class of information processing techniques. The most basic components of neural networks are modeled after the structure of the human brain; like human information processing systems artificial neural systems or networks acquire, store and utilize knowledge. It has been applied in solving wide varieties of problems. The most common is the use of neural network to forecast what will most likely happen. It has a unique ability to recognize relationship before input and output events. Numerous researches have applied neural networks in the modeling of various systems in which no explicit scientific solutions were available[5, 11, 15, 16, 21, 25, 31]. The present study is focus on development of efficient models for predicting percentage of removal of dye by using RSM and ANN methods.

MATERIALS AND METHODS

Materials

Methylene blue, HCl and NaOH used in this study were purchased from lotus enterprises, visakhapatnam, India. Deionized water was used to prepare the dye solutions. All the glassware was washed thoroughly with deionized water before use.

Preparation of biosorbent

The AAS material was collected from nearby forest area in steel plant, Visakhapatnam, Andhra Pradesh, India. The AAS were separated from the waste material and washed with deionized water till no color was obtained in effluent water. Then it was dried in sunlight for overnight, crushed in roll crusher and grounded in a ball mill for 20 minutes. The grounded material was placed in a muffle furnace at 500^0C for 3 hr and resulted activated carbon (AASC) was screened using a sieve shaker for 30 minutes then different sized particle mixtures were collected separately from the sieve analysis and stored in a dessicator for further use.

Experimental procedure

The stock solution of dye at desired concentration was prepared by dissolving accurately weighed amount of MB dye in deionized water in 1000 ml volumetric flask. It was diluted to the required concentrations of dye (0 ppm - 150 ppm) in 250 ml Erlenmeyer flasks by mixing with appropriate volumes of deionized water. Dye solutions of 50 ml were taken in a 100 ml Erlenmeyer flasks and required pH's were maintained by using 0.1N HCl or 0.1N NaOH. Dye solutions were contacted with the appropriate amounts of biosorbents and kept at 200 rpm in an orbital shaker. The solutions pH was measured by using a pH meter. Dye concentrations were determined by using UV-Vis Spectrophotometer at a wavelength corresponding to the maximum absorbance of dye.

Experimental Design and Data Analysis

A Central Composite Design[2] was used to evaluate the effects of process parameters on dye removal efficiency. Temperature (x_1), pH (x_2), time (x_3), adsorbent dosage (x_4) and initial dye concentration (x_5) were chosen as the independent variables. Percentage of dye removal (Y) from water was selected as the dependent output variable. A half fraction factorial Central Composite Design (CCD), with sixteen cube point runs, ten axial point runs and 6 replications at the centre point leading to a total number of 32 experiments were employed for the optimization of parameters for removal of MB dye from aqueous solution. For statistical calculations, the variables x_i were coded as X_i according to equation-1.

$$\mathbf{X_i = \frac{X_i - X_{oi}}{\Delta X_i} \quad i = 1,2,3...k} \qquad (1)$$

Where X_i is the dimensionless value of an independent variable, x_i is the real value of an independent variable, x_{oi} is the real value of the independent variable at the centre point, and Δx_i is the step change. All independent variables were coded to five levels.

A second degree polynomial (Equation-2) was developed to estimate the response of the dependent variable.

$$\mathbf{Y = b_o + \Sigma_{i}^{k} = 1 b_i X_i + \Sigma_{i=1}^{k-1}}$$
$$\mathbf{\Sigma_{i=2}^{k} b_{ij} X_i X_j + \Sigma_{i=1}^{k} b_{ii} X_i^2} \qquad (2)$$

Where Y is the measured response, b_0 was the intercept term, b_i were linear effects, b_{ij} were the squared effects and b_{ij} were the interacting effects.

RESULTS AND DISCUSSION

Central Composite Design is a very useful tool to determine the optimal level of various growth parameters and its constituents and their interaction. The CCD design matrix and the observed responses were given in TABLE-1. All experimental runs were conducted at three replicates and average values were shown in TABLE-1.

TABLE 1 : CCD plan matrix in coded values and Responses

Run Order	X_1	X_2	X_3	X_4	X_5	% Removal of dye	
						Observed	Predicted
1	0	0	0	0	0	81.72	81.7380
2	-1	-1	1	-1	-1	80.74	80.7344
3	-1	1	-1	-1	-1	83.73	83.7144
4	-1	-1	-1	-1	1	71.60	71.6019
5	0	0	0	0	0	81.70	81.7380
6	0	0	0	-2	0	73.36	73.4345
7	1	1	-1	1	-1	82.50	82.5778
8	1	-1	-1	1	1	72.65	72.7453
9	-1	-1	1	1	1	78.34	78.3728
10	1	1	1	-1	-1	86.90	86.8853
11	2	0	0	0	0	78.69	78.5778
12	0	0	0	2	0	82.15	81.9778
13	0	0	2	0	0	85.29	85.3028
14	0	0	0	0	0	81.70	81.7380
15	0	0	0	0	-2	83.50	83.4045
16	-1	1	1	-1	1	82.54	82.4703
17	-1	1	1	1	-1	93.60	93.6153
18	-1	1	-1	1	1	88.50	88.5228
19	0	0	0	0	2	76.90	76.8978
20	0	0	0	0	0	82.12	81.7380
21	1	1	1	1	1	89.60	89.6236
22	-2	0	0	0	0	84.50	84.5145
23	1	-1	-1	-1	-1	73.80	73.8569
24	1	-1	1	1	-1	78.70	78.7878
25	0	-2	0	0	0	72.14	72.0095
26	-1	-1	-1	1	-1	76.29	76.3769
27	1	1	-1	-1	1	78.72	78.7128
28	0	0	0	0	0	81.82	81.7380
29	1	-1	1	-1	1	68.47	68.4728
30	0	0	0	0	0	81.27	81.7380
31	0	2	0	0	0	93.27	93.3028
32	0	0	-2	0	0	77.70	77.5895

The RSM analysis for the optimization of parameters shows that dye removal percentage was a function of temperature, pH, time, adsorbent dosage and initial dye concentration. The main effects of each of the parameter on dye removal efficiency were determined and shown in Figure -1. A plot of temperature versus percentage removal of MB shows that the percentage removal of dye decreased with increased temperature. This indicates the exothermic nature of the process. Similar temperature effects were obtained with other adsorbents also[17]. The present study reveals the fact that in general increasing of temperature leads to decrease of adsorption.

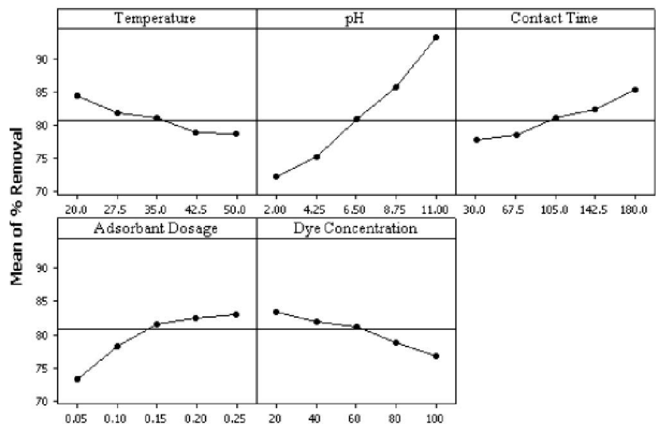

Figure 1 : Main effects plot for percentage removal of MB dye

One of the important factors that effect adsorption process is pH thus the effect of pH on MB removal was studied in the range of pH 2-11. It is clear from the Figure -1 that percentage removal increased with increased pH and reached maximum at pH of 11. Similar observations were noticed for biosorption of dye from aqueous solution[9, 23, 24]. Time course profile of Figure-1 shows that removal efficiency increased with time up to 52.5 minutes thereafter dye removal rate proceeds at slower rate till equilibrium is reached. This might be attributed that increased time allowed the particles to reach equilibrium hence, removal efficiency increased. These results are in accordance with the results obtained by other researches on dye removal[4, 30].

The effect of biosorbent's dose on removal of MB dye from solution was significant as seen in Figure-1. It was noticed that percentage removal of MB increased significantly with increased adsorbent dosage up to 0.2 g. However, beyond the dosage of 0.6 g changes in percentage removal of MB is marginal. Similar trends were reported in case of other adsorption processes on dye removal[1,26]. The effect initial dye concentration plot indicated that the effect of dye concentration on removal of dye is modest. The removal efficiency gradually decreased. This might be due to the non availability of active sites to the dye particles[26].

From the results of the experiments the following second order polynomial equation (3) was developed to represent the percentage removal of MB dye.

$$Y_1 = 80.009 - 0.183X_1 - 0.976X_2 + 0.053X_3 + 23.949X_4 - 0.139X_5 - 0.001X_1^2 + 0.045X_2^2 + 0X_3^2 - 403.182X_4^2 - 0.001X_5^2 + 0.01X_1X_2 + 0X_1X_3 - 0.427X_1X_4 + 0X_1X_5 + 0.005X_2X_3 + 6.078X_2X_4 + 0.015X_2X_5 + 0.317X_3X_4 - 0.001X_3X_5 + 1.365X_4X_5 \quad (3)$$

The predicted values of percentage removal using the above equation (3) were given along with experimental data (TABLE-1). Response Surface Method (RSM) analysis gives the information about quadratic and interaction effects along with the normal linearised effects of the parameters. The regression equation-3 for percentage removal of dye was evaluated by regression coefficients, standard error, t-values, p-values, correlation coefficient (R) and the determination coefficient, R^2, (TABLE-2). The proposed model suggests that the dye concentration and pH had a strong effect; linear and quadratic terms had more influence in comparison to the interaction term. Here, the value of correlation coefficient (R= 0.998) indicates a high agreement between the experimental and predicted values. The fitted full quadratic model of percentage removal of MB dye was tested for its adequacy using ANOVA (TABLE-3). P-value of for regression model equation from ANOVA implies that the second-order polynomial model fitted to the experimental results well.

The graphical representations of the regression equation (3) could be exhibited by the 3D response surfaces. All these response surfaces were presented in Figures: 2-11, from which the optimum combination of all parameters for percentage removal of dye was predicted by using prediction profiler of the software. The maximum removal efficiency was predicted to be 95% which was obtained at a temperature of 20^{0}C, pH of 11, contact time of 180 min, adsorbent dose of 0.05 g and initial dye concentration of 20 ppm (Figure -12).

TABLE 2 : Response Surface Regression of percentage removal efficiency of MB dye

Term	Constant	SE	t	p
b0	80.009	2.1978	36.403	0
b_1	-0.183	0.0648	-2.83	0.016
b_2	-0.976	0.1939	-5.035	0
b_3	0.053	0.0116	4.616	0.001
b_4	23.949	8.7771	2.729	0.02
b_5	-0.139	0.0219	-6.356	0
$b_1 * b_1$	-0.001	0.0007	-1.213	0.25
$b_2 * b_2$	0.045	0.0078	5.809	0
$b_3 * b_3$	0	0	-1.846	0.092
$b_4 * b_4$	-403.182	15.8075	-25.506	0
$b_5 * b_5$	-0.001	0.0001	-10.038	0
$b_1 * b_2$	0.01	0.0032	3.154	0.009
$b_1 * b_3$	0	0.0002	1.051	0.316
$b_1 * b_4$	-0.427	0.1427	-2.99	0.012
$b_1 * b_5$	0	0.0004	1.075	0.306
$b_2 * b_3$	0.005	0.0006	8.503	0
$b_2 * b_4$	6.078	0.4756	12.778	0
$b_2 * b_5$	0.015	0.0012	12.965	0
$b_3 * b_4$	0.317	0.0285	11.096	0
$b_3 * b_5$	-0.001	0.0001	-18.852	0
$b_4 * b_5$	1.365	0.0535	25.51	0

TABLE 3 : Analysis of Variance for Removal of MB dye using CCD

Source	DF	SS	MS(Adj)	F	p
Linear	20	1102.52	55.12597	1203.34	0
Square	5	995.21	1.04997	22.92	0
Interaction	5	36.12	7.22355	157.68	0
Residual Error	10	71.2	7.11954	155.41	0
Lack of Fit	11	0.5	0.04581		
Pure Error	6	0.13	0.02177	0.29	0.917
Total	5	0.37	0.07466		

S = 0.2148 R = 0.9854 R-Sq = 98.7% R-Sq(adj) = 98.1%

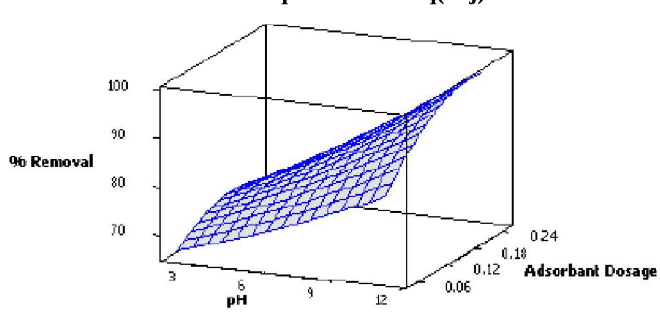

Figure 2 : Surface plot of percentage removal of MB dye, pH and Adsorbent dose

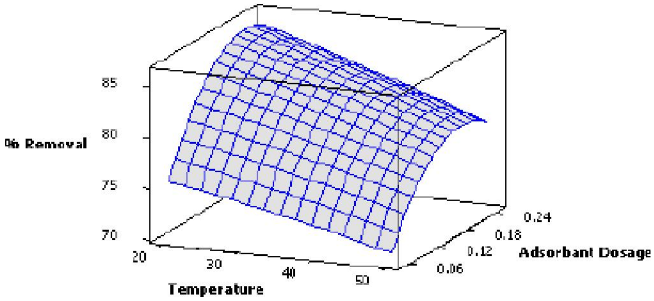

Figure 3 : Surface plot of percentage removal of MB dye, Temperature and Adsorbent dose

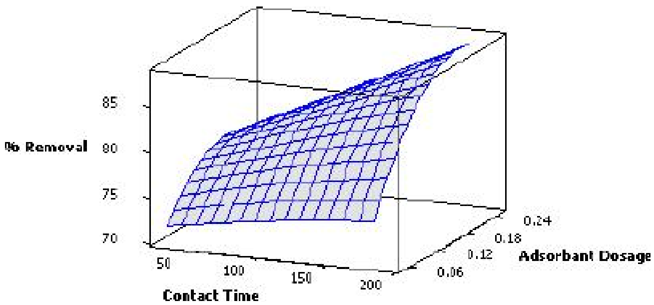

Figure 4 : Surface plot of percentage removal of MB dye, time and Adsorbent dose

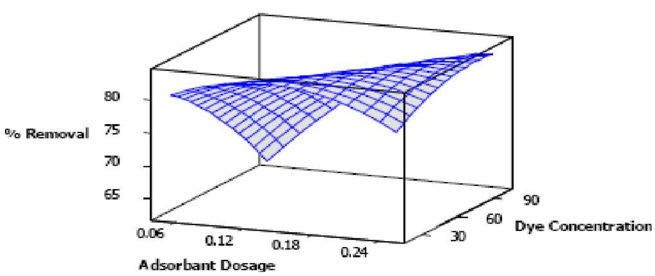

Figure 5 : Surface plot of percentage removal of MB dye, Adsorbent dose and Dye concentration

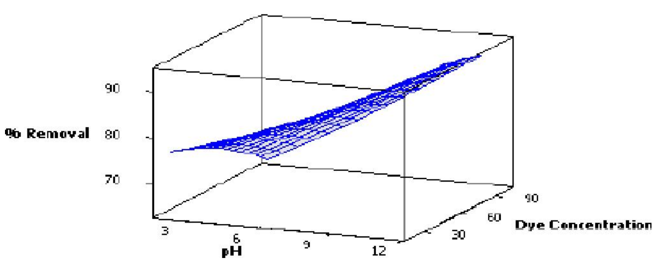

Figure 6 : Surface plot of percentage removal of MB dye, Dye concentration and pH

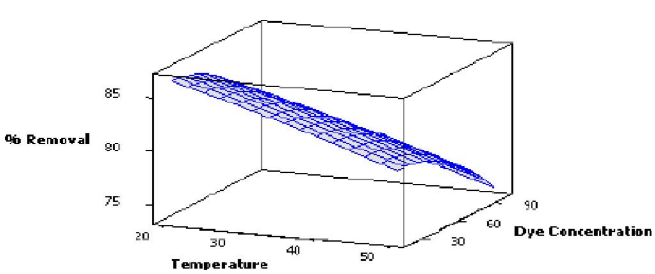

Figure 7 : Surface plot of percentage removal of MB dye, Dye concentration and Temperature

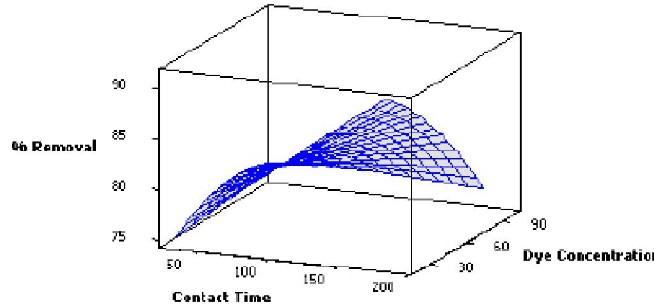

Figure 8 : Surface plot of percentage removal of MB dye, Dye concentration and Time

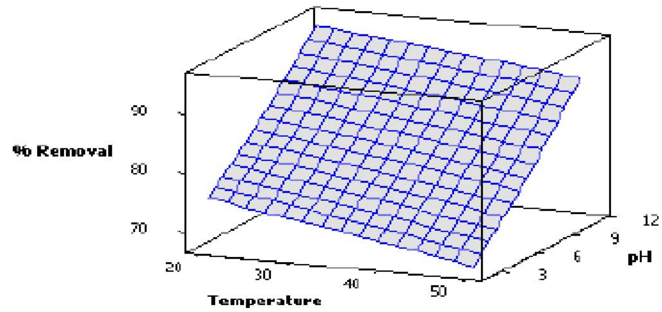

Figure 9 : Surface plot of percentage removal of MB dye, Temperature and pH

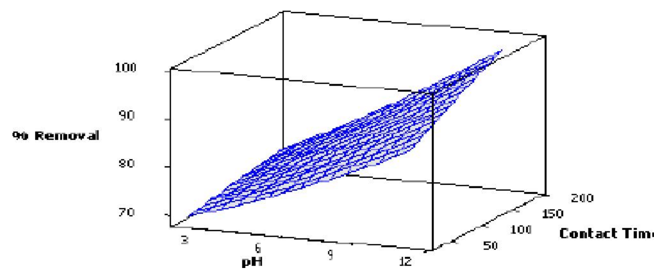

Figure 10 : Surface plot of percentage removal of MB dye,

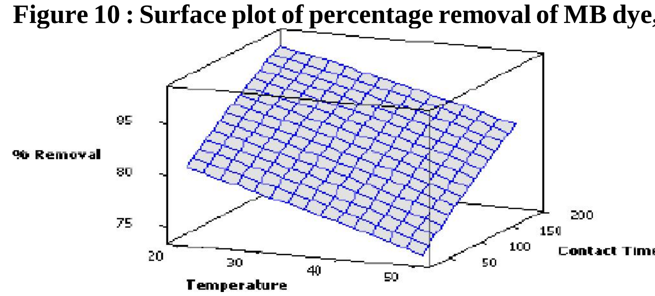

Figure 11 : Surface plot of percentage removal of MB dye, Temperature and Time

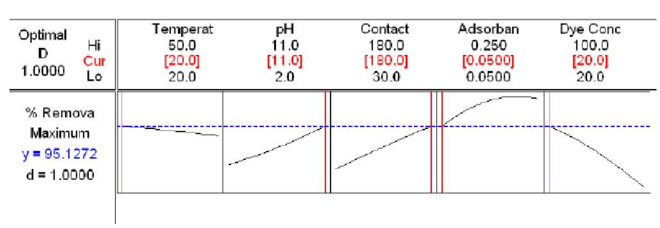

Figure 12 : Response surface optimization plots for percentage removal of MB dye

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TABLE 4 : ANN Information about % Removal

Network Name	Training Performance	Test performance	Training Error	test error	Training Algorithm	Error function	Hidden activation	Output activation
MLP 5-7-1	0.992095	0.991269	0.000539	0.004629	BFGS 45	SOS	Tanh	Identity

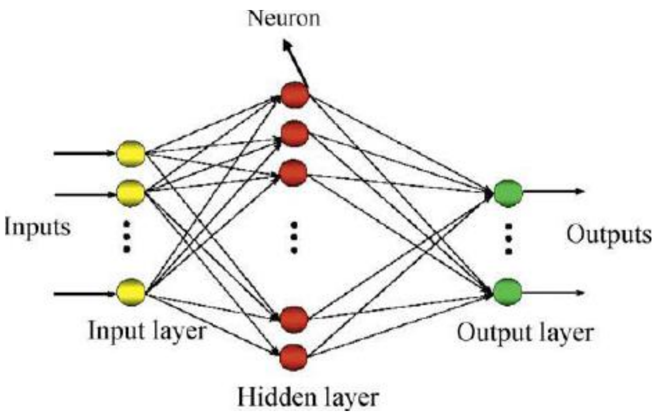

Figure 13 : Multilayer Perceptron Neural Network

In achieving the set goal of the study, an artificial neural Network (ANN) was trained and validated. A total of 96 data sets obtained from the experimental work was used in this study. About 60 sets of these data sets we assigned the training set while the remaining 36 sets were used as the validation sets. There are five input variables, which are: applied pressure, pressing time, moisture content, heating temperature and heating time. The desired output is the oil yield from the coconut kernel. The ANN was trained using standard back propagation architecture with BFGS training algorithm and this architecture used was comprised of two layers. Figure 13 shows the architecture of the network used. The tansigmod function was used as the transfer function in the hidden layer due to its suitable application for the data set of this kind. The output layer was made up of pure lineartransfer function. The optimal hidden layer was determined by varying the total number of neurons from 1 to 20. The results of ANN during training and testing were given in TABLE-4. The stop criteria were based on mean square error (MSE) on the validation set for model generalization. The optimum hidden layer comprised of 7 neurons. Incremental training style is used where the weights and biases of the network are updated each time an input is presented to the network.

CONCLUSIONS

In this work, statistical methods were successfully applied for optimization of process variables for the removal of MB dye from aqueous solutions. With the application of Central Composite Design a high removal efficiency design was successfully developed. Highly significant quadratic polynomials were also obtained. The results clearly showed that the MB removal efficiency was highly influenced by initial pH and dye concentration. However the effects of temperature, contact time and adsorbent dosage were marginal.

Response Surface Method was employed to determine the optimum combination parameters for higher removal efficiency. The optimum temperature of 20^0C, pH of 11, contact time of 180 min, adsorbent dose of 0.05 g and initial dye concentration of 20 ppm were obtained which resulted 95% of MB dye from solutions. The above studies proved that the RSM could be effectively used to optimize various parameters in MB removal process. Careful Experimental design has resulted the less number of replicates and number of observations. In overall the results suggest that activated carbon prepared from AAS could be used to remove the MB dye from aqueous solutions effectively. This method may results in reduction of environmental problems without compromising plant productivity.

Effect of various parameters on percentage of dye removal could be predicted well by both response surface method and ANN. Prediction ability of both the methods were very high (>99%) however, ANN gave more accurate results. Back propagation neural network model was designed, trained and validated for the prediction of MB removal. The network had five input variables. The network performed well during validation. The accuracy of prediction was significantly improved compared to statistical model. The neural network model developed could better predict the properties than the previously regression model. The network model had R = 0.999 which showed that the neural network model was capable of learning the relationships among the input and output variables for given data set.

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