final pH was utilized as input parameter for modelling the process using ANN.

2.6 Artificial Neural Network (ANN)

The ANN modelling was done with RSM-CCD data with additional data of final pH of solution after adsorption as shown in Table S2. A neural network tool (nntool) in MATLAB (R2017a), the MathWorks, Inc. was used in this study. It is used for nonlinear processes. It comprised of an input layer, a hidden layer and one or more than one hidden layer. The weighted sum of inputs arriving at each neuron is passed through activation function to get an output (Bhatti et al., 2011). The ANN structures are feed forward network trained from input using error back propagation algorithm. Input node takes independent variables and in return output nodes variables are dependent one. Hidden layers are used to perform nonlinear transformations function on the input which are further utilised for computation purpose. The model complexity increases with increase in the no of hidden layer. In this study neural network consisted of one input layer with four inputs, one hidden layer with 10 neurons and one output layer as shown in Figure S3. In this, 52 data sets of the experimental results were for modelling ANN network. The total data sets were divided as training (70%), validation (15%), and testing (15%). The performance was measured using mean square error (MSE).

Neuron transfer are used to transfer the input values to the next layers and strength of these connections are determined by weights. Modification on weights were performed to achieve minimum error between observed and predicted values for color removal efficiency. The validation of data was carried out till the error between the observes and predicted values reached to minimum. In present study, feed forward back propagation algorithm was selected with log sigmoidal (logsig) or tan sigmoid (tansig) function in hidden layer and output layer with linear transfer function (purelin) to achieve the best back propagation algorithm having minimum MSE and minimum relative error (MRE). The Levenberg–Marquardt (LM) and Gradient decent (GDA) back propagation algorithms were applied for training the model. The generalization ability of the observed values was assessed of the ANN model during the testing process. Further analysis of the trained network was carried out by linear regression between the observed and the predicted one.

3. Results and Discussion

Removal of color from synthetic dye wastewater was optimized using variable parameter *viz.* initial pH, dye concentration and adsorbent dose. All the combinations of the variable parameters were used for modelling the ANN. Experiments were conducted as per the design of RSM and results were reported as observed results. It was then analysed for removal prediction from RSM software.

3.1 WH Characterization

FTIR analysis was used to determine functional groups characteristics present on WH before and after dye adsorption as shown in Figure 1. The broad spectrum at peak 3330 cm^{-1} corresponds to O-H stretching vibrations of alcohols and carboxylic acid as in cellulose and lignin showing presence of free hydroxyl group on the adsorbent surface. Other peaks at 2918.28, 1619, 1414, 1321, 1025, and 512 cm^{-1} corresponds to N-H stretching, C-N, C-C, C-O, >C=O, and S-S respectively. After the dye adsorption onto WH, the peak is shifted to 3332, 2914, 1640, 1428, 1319, 1035, 541 cm^{-1} suggesting interaction of dye molecule with the functional groups. The presence of irregular and porous surface on water hyacinth indicates the possibility of adsorption as can be seen in Figure 2 (a) and therefore confirms its suitability for adsorption onto WH. It can be said that adequate surface is present on the WH for MB adsorption. After adsorption of MB dye (Figure 2 (b)), the surface of adsorbent became smooth showing the adsorption of dye onto the rough surface of the adsorbent.

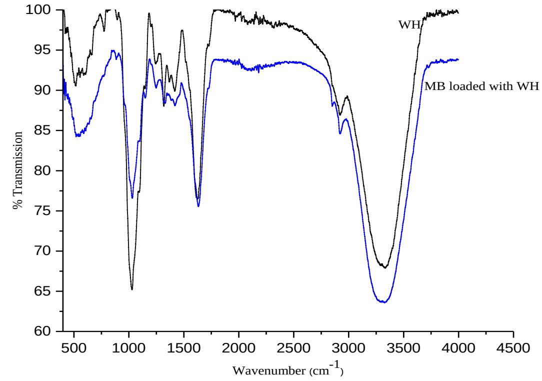

Figure 1: FTIR spectrum of water hyacinth

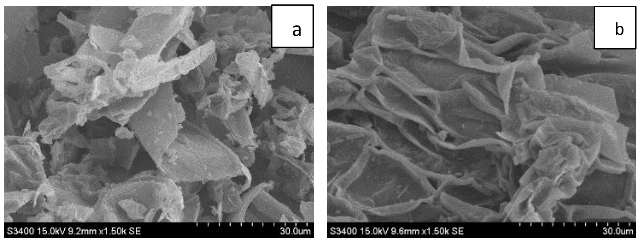

Figure 2: SEM image of WH before (a) and after adsorption (b) of MB dye

3.2 Effect of Operating Parameter

In this study, the effect of three parameters (initial pH, WH dose and dye concentration) was studied on the removal capacity of WH for MB removal through adsorption process. Experiments were conducted at different factors levels as per the design of Design Expert 11. The maximum color removal was obtained at higher dose of water hyacinth. Two-factor interaction (2FI) showed that colour removal was affected by two operating parameters. The presence of functional group -OH plays an important role in adsorption at higher dose of WH.

Figure 3 shows effect of initial pH and adsorbent dose on the color removal. It can be observed from the plot that with increase in pH and adsorbate dose, the color removal (%) increases. The maximum color removal was observed at pH of 10-12, adsorbent dose 3 g/L and dye concentration 300 mg/L as constant. Under acidic medium condition, removal was observed due to the fact of repulsion between the H^+ ions present in the solution and in the water hyacinth. The point of zero charge for the adsorbent was 6.65. The maximum adsorption was observed at pH > $pH_{ZPC,}$ because charge on the adsorbent surface changed to negative and there are probabilities of attraction between the cationic and anionic group present in the adsorbate. Similar results were reported by Roosta et al. (2014) for methylene blue removal by gold nanoparticle loaded on activated carbon.

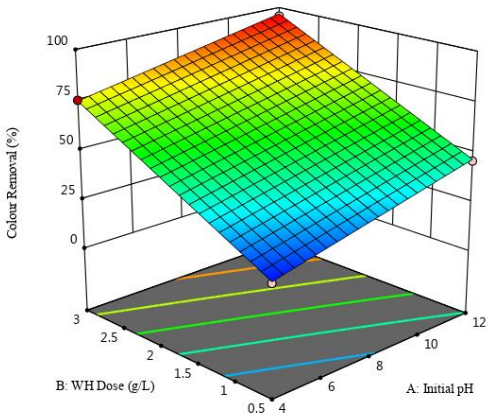

Figure 3: Interaction between water hyacinth dose and initial pH on the dye removal (at dye concentration of 300 mg/L)

Adsorbent dose plays a vital role in influencing the adsorption process by determining the adsorption capacity of the process under a given variable (Saha et al., 2010). Figure 4 shows the relation between the adsorbent dose and dye concentration of MB for adsorbent dose of 0.5-3 g/L. It can be seen that as dose of adsorbent increases, the removal also increases which can be attributed to the increase in the sorption surface area and more active adsorption sites available for adsorption of the dye molecule (Chowdhury and Saha, 2010)(Chowdhury et al., 2013). While color removal (%) increases, the adsorption capacity of the adsorbent decreases with increase in the adsorbent dose. This was attributed to the reduction in the total adsorption surface area and hence causes aggregations of adsorption sites (Chowdhury and Saha, 2010). Similar trend was observed by (Saeed et al., 2010) for adsorption of CV from grape fruit peel (Pathania et al., 2017) and for adsorption of MB onto activated Ficus carica bast.

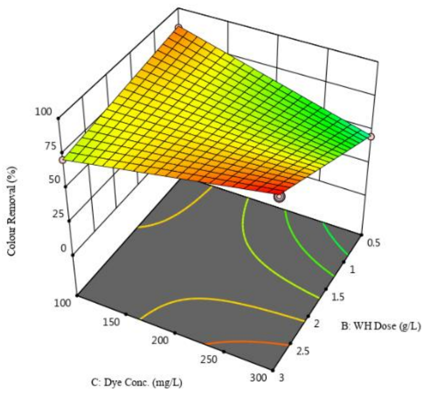

Figure 4: Interaction between water hyacinth dose and dye concentration on the dye removal (at initial pH of 12)

The rate of adsorption was also affected by the concentration of dye (Figure 5). The removal percentage decreases with increase in the dye concentration. This can be due to the saturation of adsorbent sites after a limit of number of active sites (Tsai and Chen, 2010). The dye concentration has contrary effect on the adsorption frequency (Marungrueng and Pavasant, 2007).

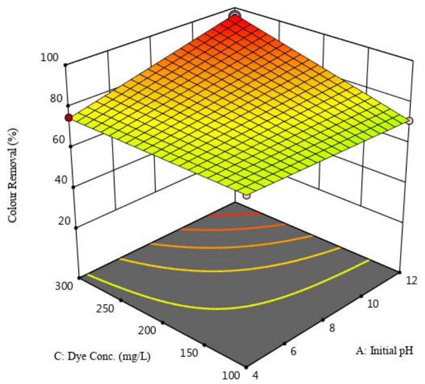

Figure 5: Interaction between water dye concentration and initial pH the dye removal (at adsorbent dose of 300 mg/L)

3.3 Modelling and Optimization using RSM

Different variables were selected to know the effect on colour removal using central composite design (CCD) were performed. Table S2 shows design matrix, experimental and predicted results. The second-order polynomial model was developed and analyzed from the observed data in terms of coded factor employing RSM. The two factor-interaction was suggested by the model as shown in Table S3. The two-factor interaction model (2FI) in terms of coded factors is expressed below to predict the response given as:

Colour Removal (%) = *69.98 + 5.59 x A + 9.28 x B – 9.81x C – 0.6837 x AB + 5.99 x AC + 16.31 x BC*

Analysis of variance shows model to be significant as shown in Table 1 (ANOVA). The significance of the model can be seen from p-value (0.99) which shows that the model was significant and can be used for prediction of color removal from aqueous medium.

Table 1: Analysis of variance (ANOVA) test results

Source	Sum of Squares	Degree of freedom	Mean Square	F-value	p-value
Model	5154.50	6	859.08	506.45	< 0.0001 (significant)
A-Initial pH	381.16	1	381.16	224.70	< 0.0001
B-WH Dose	1038.54	1	1038.54	612.24	< 0.0001
C-Dye Conc.	1314.39	1	1314.39	774.86	< 0.0001
AB	3.74	1	3.74	2.20	0.1614
AC	287.40	1	287.40	169.43	< 0.0001
BC	2127.80	1	2127.80	1254.39	< 0.0001
Residual	22.05	13	1.70		
Lack of Fit	10.94	8	1.37	0.6152	0.7424 (not significant)
Pure Error	11.11	5	2.22		

R^2: 0.99; Adjusted R^2: 0.99; Predicted R^2: 0.98; AP: 96.47

Table 2: Design matrix with experimental and predicted values

Sr. No.	A: pH	B: WH dose	C: Dye conc.	Color removal (%)	
		g/L	mg/L	Experimental	Predicted
1	1.2 (-1.682)	1.75 (0)	200 (0)	59.77	60.58
2	8 (0)	1.75 (0)	200 (0)	73.43	69.98
3	4 (-1)	3 (+1)	300 (+1)	75.22	74.86
4	8 (0)	0.35 (-1.118)	200 (0)	60.64	59.60
5	8 (0)	1.75 (0)	200 (0)	69.58	69.98
6	8 (0)	1.75 (0)	368.17 (1.682)	53.52	53.48
7	8 (0)	3.85(1.682)	200 (0)	85.32	85.58
8	8 (0)	1.75 (0)	31.82 (-1.682)	85.86	86.47
9	12 (+1)	0.5 (-1)	100 (-1)	85.77	87.09
10	12 (+1)	0.5 (-1)	300 (1)	45.98	46.84
11	8 (0)	1.75 (0)	200 (0)	69.61	69.98
12	4 (-1)	0.5 (-1)	300 (1)	21.54	22.31
13	8 (0)	1.75 (0)	200 (0)	69.66	69.98
14	12.7 (1.182)	1.75 (0)	200 (0)	78.22	76.58
15	12 (+1)	3 (+1)	300 (1)	95.45	96.65
16	4 (-1)	0.5 (-1)	100 (-1)	86.78	86.54
17	12 (+1)	3 (+1)	100 (-1)	71.48	71.66
18	8 (0)	1.75 (0)	200 (0)	70.20	69.98
19	8 (0)	1.75 (0)	200 (0)	70.16	69.98
20	4 (-1)	3 (+1)	100 (-1)	73.75	73.85

3.4 Optimization by RSM

Optimization of color removal was done using variables viz. WH dose, initial pH, and initial dye concentration. The favorable condition and its responses selected from the options provided to obtain optimum conditions. Desired goal was set to "maximise" and other parameters were set as "in range" as shown in Table S4. All other factors were given equal importance. A color removal of 96.649% was obtained with WH dose of 3 g/L, initial pH 12 and dye concentration 300 mg/L. To validate the predicted optimum condition, experiments were conducted at above optimize conditions and 93.86 % color removal efficiency was achieved as shown in Table S5. This shows that this model can be efficiently utilized for colour removal process. A statically significant model (P-value < 0.05) was developed using ANOVA, F-value (506.45) of the model implies the model was significant for the adsorption process.

The R^2 Pred. (0.987) and R^2 Adj. (0.993) values for MB biosorption capacity of water hyacinth biomass well satisfied the model. "Adequate precision" ratio of 96.474 showed an adequate signal for the model to be used for navigation in the design space. The $p < 0.050$ indicate model terms are significant, whereas $p > 0.100$ are not significant. In our study, all terms were significant except the interaction between the term AB i.e. initial pH and WH dose which had p-value of 0.161. Two-factor interaction was suggested by the model after using sequential model of square. Experimental responses are the responses measured for the specific run whereas predicted values are software assessed values using approximate functions of the model (Körbahti and Rauf, 2008). The adequacy of the model was confirmed by the responses obtained from experimental and predicted values.

3.5 ANN modelling

Artificial Neural Network was used to develop a mathematical model from the results obtained in RSM design. Artificial network was designed to train the neural network and to obtain the optimal number of neurons in hidden layer. Initial input data and results of central composite design were used to obtain the neural network model as show in Table 2. The original data sets with 50 data were divided into three sets viz. training, testing and validation of 70%, 15% and 15% respectively of the ANN model. The outliers were excluded from the data used for modelling in ANN. A feed forward network with three layers and back-propagation algorithm with log sigmoidal (logsig) or tan sigmoid (tansig) function in hidden layer including output layer with a linear transfer function (purelin) were developed. The no of hidden layer selected were 8 neurons (Dil et al., 2016). The Levenberg–Marquardt (LM) training function were used for ANN model training. The modelling was found to be satisfactory with mean square error of 5.705 during the analysis phase. This signifies the accuracy of adsorption process prediction. The value of R^2 (0.98) indicates excellent agreement between the experimental and predicted values of ANN.

3.6 RSM and ANN modelling

RSM and ANN are among the most widely used mathematical technique for adsorption study (Shojaeimehr et al., 2014;Ohale et al., 2017). Both methods provide a good relationship between the influencing input parameters involved in the process and the result outcome due to its nonlinear relations between responses of the system and independent variables (Witek-Krowiak et al., 2014). It allows output prediction on the basis of inputs without defining the interrelationship between them. The validity of both models was assessed using same data points but in ANN the number of data points used were 52 excluding the outliers. The comparisons of results are shown in Figure 6, where experimental and model predicted results are compared. The importance of operating parameter as per ANOVA analysis were as shown in Table 1.

Hence, both models (RSM and ANN) provided a good prediction for dye removal in this study. RSM allowed prediction by giving regression equation for result predicted and the interactions between the operating parameters. It needs a standard experimental design for prediction of results whereas, ANN does not require any standard results for its predictions. Hence, both models provide a reliable way to interpret MB dye removal from aqueous solution onto water hyacinth.

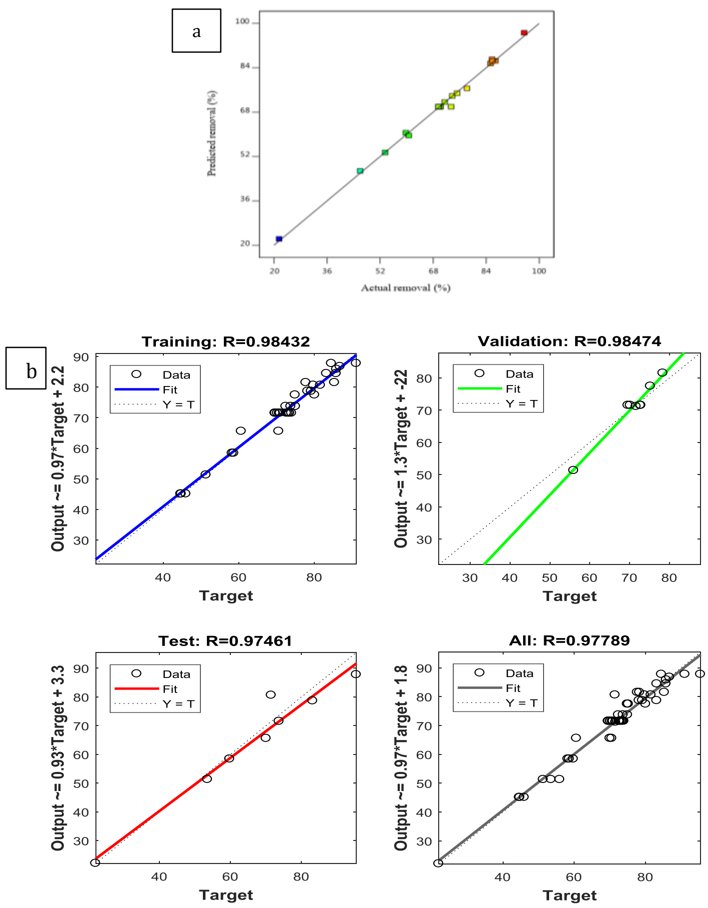

Figure 6: Comparison of the experimental (line) with predicted data (symbols) using (a) RSM and (b) ANN model

4. Conclusion

Two modelling approach, ANN and RSM were used to model the colour removal using water hyacinth. RSM provides an aid in visualization of the result obtained in interactions between the parameters with 99% variance (R^2=0.99). Both models provided good quality prediction for three independent variables. However, ANN gave good results due to its non-linear relations between the input parameters. The optimal conditions for 95.45% colour removal were initial pH of 12, dye concentration of 300 mg/L, and WH dose of 3 g/L.The results of both RSM and ANN methodologies showed that RSM (R^2 = 0.99) and ANN (R^2 = 0.977) are good method of prediction of colour removal process by adsorption. In this study RSM provided better removal efficiency and were in agreements with the experimental data. Feed forward BP with the Levenberg–Marquardt training algorithm was found best with highest R^2. The present adsorbent study showed WH as an economical and effective adsorbent for removal of MB dye.

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