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Applications of response surface methodology and artificial neural network for decolorization of distillery spent wash by using activated *Piper nigrum*

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Abstract

Ethanol production from sugarcane molasses yields large volume of highly colored spent wash as effluent. This color is imparted by the recalcitrant melanoidin pigment produced due to the Maillard reaction. In the present work, decolourization of melanoidin was carried out using activated carbon prepared from pepper stem (*Piper nigrum*). The interaction effect between parameters were studied by response surface methodology using central composite design and maximum decolourization of 75 % was obtained at pH 7.5, Melanoidin concentration of 32.5 mg l^{-1} with 1.63 g 100ml^{-1} of adsorbent for 2hr 75min. Artificial neural networks was also used to optimize the process parameters, giving 74 % decolourization for the same parameters. The Langmuir and Freundich isotherms were applied for describing the biosorption equilibrium. The process was represented by the Langmuir isotherm with a correlation coefficient of 0.94. The first-order, second-order models were implemented for demonstrating the biosorption mechanism and, as a result, Pseudo second order model kinetics fitted best to the experimental data. The estimated enthalpy change (ΔH) and entropy change (ΔS) of adsorption were 32.195 kJ mol^{-1} and 115.44 J mol^{-1} K which indicates that the adsorption of melanoidin was an endothermic process. Continuous adsorption studies were conducted under optimized condition. The breakthrough curve analysis was determined using the experimental data obtained from continuous adsorption. Continuous column studies gave a breakthrough at 182 mins and 176 ml. It was concluded that column packed with *Piper nigrum* based activated carbon can be used to remove color from distillery spent wash.

Key words

Activated carbon, Ann model, Distillery spent wash, Melanoidin, Pepper steam, RSM model

Introduction

Disposal of wastes from industrial sources are turning into a major issue all over the world. The major problem prevailing in ethanol production industry is release of large quantity of dark brown colored distillery effluent which is known as spent wash. It was reported that spent wash discharge is 15 times of the total amount of ethanol production (Raghukumar *et al.,* 2004). Synthetic activated carbon commonly used as an adsorbent in industrial effluent treatment is expensive. Replacement of activated carbon with cheaper alternative natural materials such as peanut shells (liu *et al*., 2010), barks and dry tree leaves (Patnukao *et al*., 2008, Chen *et al*., 2010), tea waste (Auta *et al*., 2011), makes the process economically compatible.

In real systems, the modeling of complex process with simple linear multivariate correlation is tedious. These limitations can be overcome using artificial neural networks (ANNs) model to simulate the solid–liquid adsorption *via* simple, reliable, and robust approaches. Recently, optimization via chemometrics approaches is used extensively in almost all these areas of decision making. Various efficient and flexible meta-heuristics optimization algorithm such as Genetic algorithms, particle swarm optimization, Bees Algorithm (BA), back propagation (BP) algorithm have been implemented to solve complex optimization problems. Dynamic adsorption process using ANN model for the removal of crystal violet from aqueous solution using citric-acid-modified rice straw as adsorbent has been reported (Chakraborty *et al*., 2013). Hosseini *et al*. (2013) investigated Cr (VI) adsorption from aqueous solution by zeolite prepared from raw fly ash (ZFA) and developed the model using artificial neural network (ANN) approach. Report stated that a three-layer ANN model using a back propagation (BP) algorithm to predict the efficient adsorption of methyl violet using a low-cost adsorbent, an activated carbon prepared from putrescible vegetable waste treated with phosphoric acid (Sundari *et al*., 2014). Based on various studies, the ANN model proves to be the most appropriate modeling technique for describing the dynamic dye adsorption process. In the present study, RSM and ANN was used to optimize the process parameter in Batch Method. Optimized conditions were used for continuous column study to describes the adsorption potential of melanoidin pigment by activated carbon prepared from pepper stem.

Materials and Methods

Anaerobically treated distillery spent wash (ATDSW): The molasses spent wash after biomethanation from anaerobic digester was collected aseptically from the discharge stream of distillery industry situated in Theni District, Tamil Nadu (India). The effluent sample was collected in well cleaned plastic bottle. The spent wash collected were centrifuged for 4200 x g for 30 min before discarding the suspended solids and stored at 4 °C. The stored Anaerobically Treated Distillery Spent Wash (ATDSW) was filtered and diluted using distilled water for further studies.

Preparation of activated carbon : Pepper stem is a part of Black pepper plant (*Piper nigrum*) were obtained from the agricultural farm at Dindigul District. The solid waste was cut into small pieces and washed 5 times with distilled water to remove the dust particles. The materials were dried in sunlight for 48 hrs, until the residual moisture was completely removed. This dried biomass was then carbonized in muffle furnace at 800 ºC for 30 min and was converted to activated carbon. After drying, materials were ground to fine powder and sieved through 425-600µm.

Isotherms and kinetics: Batch experiment was conducted in a 250 ml conical flask with a fixed quantity of 1.5 g 100 ml^{-1} adsorbent for varying concentration (10-100 mg l^{-1}) of spent wash in an orbital shaker at 120 rpm for 6 hrs. Isothermal studies for melanoidin adsorption by activated carbon were performed, and the absorbance was obtained before and after adsorption at 475 nm for regular time interval (Ravikumar *et al*., 2013a). The plot of C_e V_s. C_e/q_e for Langmuir and log $C_e v_s$. Log q_e for Freundlich isotherms were drawn using the absorbance values, and the constants were calculated using equation 1 and equation 2.

$$\frac{Ce}{Qe} = \frac{1}{bQm} = \frac{1}{Qm} Ce \qquad \text{Eq. 1}$$

$$\text{Log } Q_e = \log k_f + 1/n \log C_{e\cdot} \qquad \text{Eq.2}$$

Thermodynamic parameters : During the batch experiment, the standard free energy change, enthalpy change and entropy change were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the adsorption process. Thermodynamic parameters was calculated from the variation of the thermodynamic equilibrium constant K_0 with change in temperature. Free energy of adsorption (ΔG) can be related with the equilibrium constant K (L mol^{-1}) corresponding to the reciprocal of Langmuir constant, b by the following equation:

$$\Delta G = -RT \ln b \qquad \text{Eq.3}$$

Where, R is Gas universal constant (8.314 J mol^{-1} K), T is the absolute temperature, and b (L mol^{-1}) is the Langmuir constant. The enthalpy change (ΔH) and entropy change (ΔS) was calculated using the following equation:

$$\ln b = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad \text{Eq.4}$$

ΔH and ΔS was estimated from the slope and intercept of the straight line plot of ln b against 1 T^{-1}. To study the thermodynamic parameters, isothermal studies for adsorption were performed at three different temperatures (303 K, 309 K and 313 K) (Ravikumar *et al*., 2013a). A graph between ln b and 1/T was plotted and using equations 3, 4 and ΔG, ΔH and ΔS were calculated.

Response surface methodology (RSM) : Optimization of process parameters using single factorial experimental design will not explain the interaction among the parameters and the regression fit for the experimental values. The only method to overcome this drawback is to utilize Response Surface Methodology (RSM). Therefore, batch experiments were designed with three independent variables pH (X_1), contact time (X_2), melanoidin concentration (X_3) and adsorbent quantity (X_4) at three coded levels (-1, 0, 1). The % decolourization was obtained as response dependent variable by the experimental design obtained by full factorial Central Composite design (CCD). A 2^3 full factorial experimental design with 30 experiments were employed which includes 8 trails for each axial point and 6 trails for replication of central points based on the pattern generated through software (Ravikumar *et al*., 2013b).

Experiment was conducted as per design matrix with 100 ml of synthetic melanoidin in 250 ml Erlenmeyer flasks at room temperature at 120 rpm. During the process, equal volume of sample was collected at regular intervals and centrifuged. The supernatant was collected and absorbance was read at 475 nm. The ANOVA table and regression information were generated by Design Expert 8.0.3.1 software. Further based on the 'P' and 'T' value, significant factors were determined. For statistical calculation independent variables were coded as:

$$x_i = \frac{(Xi - XO}{dxi} \qquad \text{Eq.5}$$

where, x_i - coded value of the i^{th} variable, X_i – uncoded value of the i^{th} test variable and X_0 - uncoded value of the i^{th} test variable at center point. The experiment design was tabulated along with the experimental data and predicted responses. Regression analysis was performed to estimate the response function as a second order polynomial.

Artificial neural network (ANN): ANN with back propagation algorithm was used in MATLAB 7.6 with four input neurons (for the four independent variables), and one output neuron (for the dependent variable of interest). The basic problem in constructing the neural network is to find the optimal number of hidden neurons. In the present study four neurons (n1,n2,n3,n4) were used in the input layer, four in the hidden layer (w1,w2,w3,w4) and one in the output layer(O) as transfer function to model the dependency of decolorization process (Ravikumar *et al*., 2013b). A single hidden layer with 4 neurons was used, and a combination of tan-sigmoid, log- sigmoid and linear functions was employed. Four input variables were pH, contact time, melanoidin concentration and biomass. Once the ANN was performed the experimental value and the output from ANN was fitted to explicate the result using regression value of R^2. Training parameter goal was set at 0.001, Epochs at 26000 and learning rate of 0.9 were used. Network was trained and experimental results were validated. (Ravikumar *et al*., 2013b).

Continuous column studies: Fixed bed column studies were carried out in a glass column (diameter: 2.5 cm; length: 58 cm). Activated carbon was packed in the column with glass beads at the bottom (7.5 cm). Spent wash was prepared at the optimized concentration from RSM and ANN. The melanoidin pigment was prepared in such a manner that the initial concentration was held at 30.5 mg l^{-1} and pH was maintained at 7.5 which was charged from the top of the column in down flow method at a fixed inflow rate of 2.5 ml min^{-1} using peristaltic pump. Effluent samples were collected at an interval of 5 min. Samples were analyzed for residual dye concentration using UV-Vis spectrometer by fixing wavelength of 475 nm. The column studies were terminated when the column reached exhaustion. In order to determine the capacity of packed bed column for biosorption of melanoidin pigment, column was characterized by plotting the breakthrough curve.

Results and Discussion

A mixture of adsorbent after pre-treatment and also after conversion to activated carbon analyzed for Scanning Electron Microscopy. The SEM images (Fig. 1 a and 1 b showed that biosorbent after pretreatment was porous in nature as compared to untreated, which indicates the capability of pepper stem to act as best biosorbent for decolorization of melanoidin pigment. It was also observed from SEM analysis that after pre-treatment, the particle size was distributed, whereas for raw biosorbent, it was clustered and agglomerated.

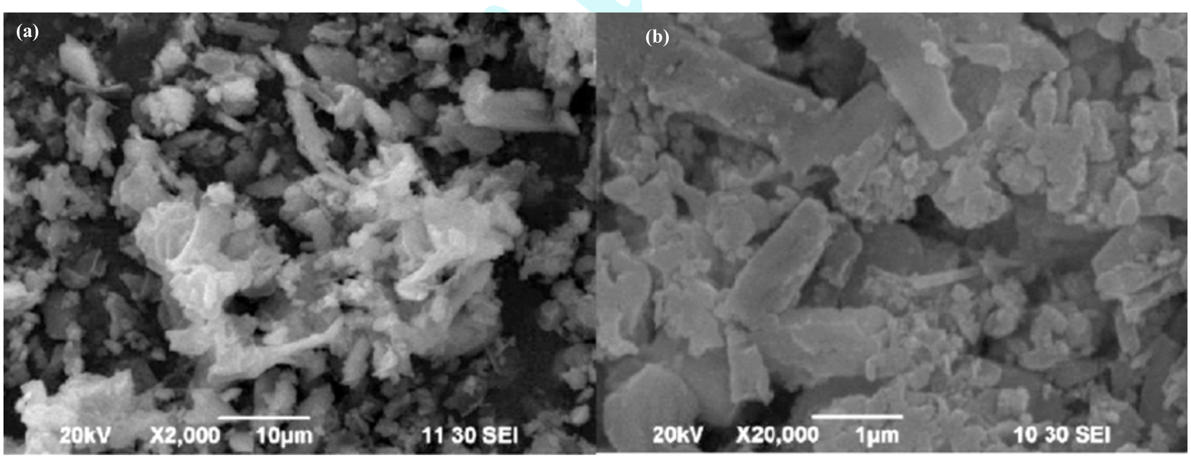


Fig. 1: (a) SEM image of biosorbent before treatment; (b) SEM image of biosorbent after treatment

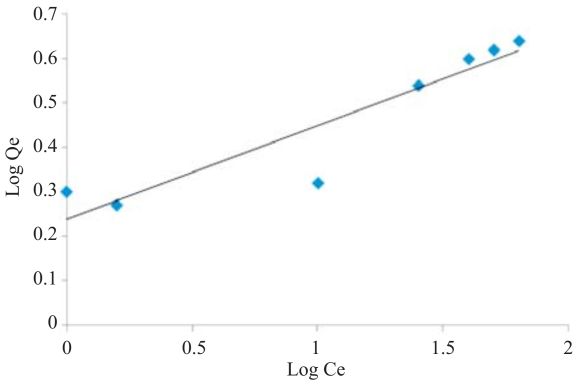


Fig. 2 : Plot for the Freundlich Isotherm

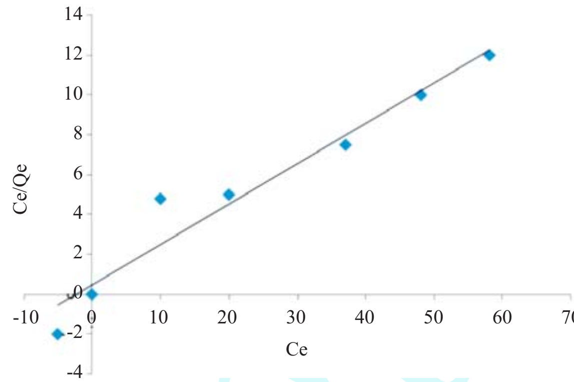


Fig. 3 : Plot for the Langmuir Isotherm

Table 1 : Langmuir and Freundlich Isotherms parameters for the adsorption of melanoidin at different temperatures from synthetic effluent under optimum pH: 7.5; Melanoidin concentration: 32.5 mg l^{-1}; Biomass:1.63 g; Contact time: 2hr 75min

	Langmuir constants					Freundlich constants		
T (K)	Qm (mg g^{-1})	b (L mg^{-1})	b (L mol^{-1})	R^2	RL	Kf	N	R^2
306	3.203	1.579	465.75	0.9444	2.2×10^{-5}	1.357	4.277	0.864
309	1.716	0.127	41.134	0.9517	2.0×10^{-3}	1.342	4.166	0.8388
3.13	1.788	2.553	805.124	0.922	1.5×10^{-4}	1.004	5.424	0.6683

Table 2 : Values of the thermodynamic parameters for adsorption of melanoidin at different temperatures from synthetic effluent under optimum pH: 7.5; Melanoidin concentration: 32.5 mg l^{-1}; Biomass:1.63 g;, Contact time: 2h 75min

T (K)	(kJ mol^{-1})	(kJ mol^{-1})	(J mol^{-1} K)
300	-12.684		
305	-7.41	32.195	115.44
310	-14.45		

Equilibrium studies on biosorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain isotherm constant values, which express the surface properties and affinity of the adsorbent, and could also be used to compare the adsorptive capacities of the adsorbent for different adsorbates. A plot of log C_e vs. log q_e at 303 K is depicted in Fig. 2. R^2 value was 0.85 for the plot of Freundlich isotherm. C_e/q_e v_s. C_e was plotted at 303 K to obtain Langmuir isotherm is depicted in Fig. 3, giving an R^2 value of 0.94. This R^2 values indicated that the Langmuir Isotherm predicted, the existence of monolayer coverage of adsorbate at the outer surface of the adsorbent, which was assumed to be homogeneous. The Langmuir and Freundlich constants are given in Table 1. The RL values lied between 0 and 1, indicating favorable adsorption conditions. Similar results were reported by Li *et al*. (2011) in their study on adsorption of cationic red X-GRL from aqueous solutions by graphene: equilibrium, kinetics and thermodynamics study.

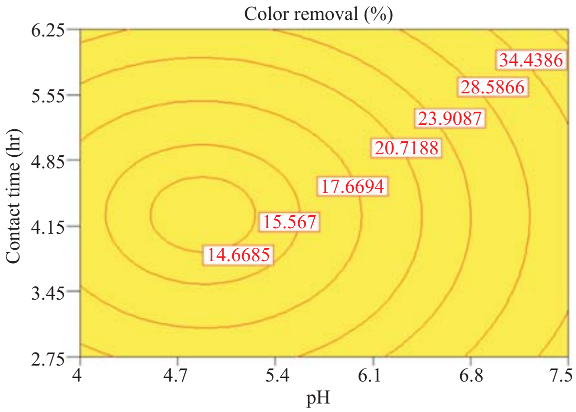
Thermodynamic parameters are usually used to determine the adsorption nature. The standard free energy change, enthalpy change and entropy change were calculated to evaluate the thermodynamic feasibility, and the spontaneous nature of the adsorption process in the present study.The estimated values of ΔG, ΔH, and ΔS are presented in Table 2. The values of ΔG were negative at all the temperatures studied, which confirms the feasibility of the process and spontaneous nature of adsorption. The values of □G were low, suggesting a physical adsorption process (Silva *et al*., 2004). The estimated enthalpy change (ΔH) and entropy change (ΔS) of adsorption were 32.195 kJ mol^{-1} and 115.44 J mol^{-1} K, respectively. A positive value of ΔH indicated that the adsorption of melanoidin is an endothermic process. A positive value ΔS reflect the affinity of the adsorbent for the pigment and increased randomness at the solid-solution interface during adsorption. Similar results were reported by Emmanuel *et al*. (2011) in a study on removal of methylene blue from aqueous solution using alkali-modified malted sorghum mash.

Experiments were performed according to the CCD experimental design given in Table 3 in order to search for the optimum combination of parameters for decolourization of

Table 3 : Experimental design, observed yields in CCD experiments in term of color removal efficiency by activated carbon prepared from *Piper nigrum*

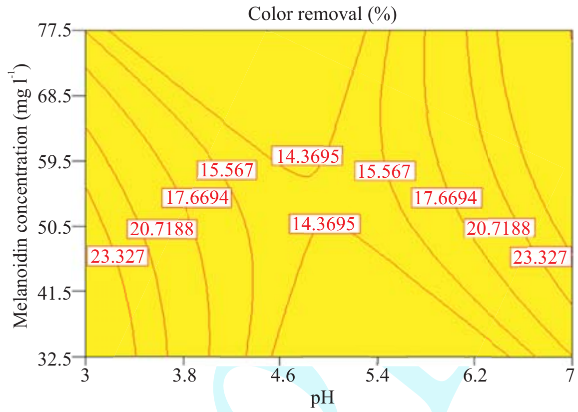
pH	Contact time (h)	Melanoidin concetration (g l^{-1})	Biomass (g)	Color removal (%) actaul	Color removal (%) predicted	ANN prediction
4.5	2.75	32.5	3.875	24.40	26.32	25.12
6	4.5	55	2.75	17.12	17.70	16.45
4.5	6.25	32.5	3.875	25.03	23.01	24.53
4.5	6.25	32.5	1.625	23.74	22.77	21.67
6	4.5	55	0.5	37.68	37.43	38.46
7.5	6.25	77.5	1.625	49.94	49.12	48.24
6	8	55	2.75	50.08	49.61	47.16
3	4.5	55	2.75	20.80	23.62	22.25
6	4.5	55	2.75	17.99	17.70	16.70
6	4.5	100	2.75	15.52	17.77	17.42
4.5	6.25	77.5	3.875	22.30	24.30	23.65
4.5	2.75	32.5	1.625	41.04	39.40	38.75
6	1	55	2.75	39.20	41.81	42.31
4.5	6.25	77.5	1.625	44.12	42.75	41.26
4.5	2.75	77.5	1.625	30.84	32.25	31.65
6	4.5	55	2.75	17.88	17.70	18.70
4.5	2.75	77.5	3.875	7.59	7.47	6.45
7.5	6.25	32.5	3.875	52.63	52.32	53.42
7.5	2.75	77.5	3.875	46.90	48.97	47.78
6	4.5	55	5	46.24	48.64	47.65
7.5	2.75	32.5	1.625	26.27	25.37	24.35
7.5	2.75	32.5	3.875	56.90	55.02	54.06
6	4.5	55	2.75	17.27	17.70	18.47
6	4.5	55	2.75	17.80	17.70	17.46
6	4.5	55	2.75	18.12	17.70	18.45
7.5	2.75	77.5	1.625	39.24	38.01	37.01
9	4.5	55	2.75	59.37	58.70	59.70
6	4.5	10	2.75	3.94	3.83	4.8
7.5	6.25	77.5	3.875	75.01	73.41	74.63
7.5	6.25	32.5	1.625	5.47	9.34	8.54

mealnoidin. Six replicates at the central point were used to determine experimental error. Four factors, namely pH, contact time, melanoidin pigment concentration and biosorbent dosage weight were used to determine the key variable that significantly influences % decolourization of melanoidin. Each factor was examined at two levels: -1 for low level and +1 for high level. Table 3 shows the predicted RSM values for % decolourization. Table 4 shows ANOVA analysis for the experiments. A Model F-value of 12.13288 and P value of 0.0001 implied that second order polynomial model was developed. There is only 0.01% chance variation in "Model F-Value" . The Fisher F-test with a very low probability value (Pmodel> F = .0001) demonstrated high significance for the regression model. Similar results were observed in the Central Composite design optimization for dye removal in the presence of Macroalgae Charasp (Khataee *et al*., 2010). The goodness of fit of the model was checked by determination coefficient (R^2). The coefficient of determination (R^2) was 0.9288. This implie that more than 92% of the experimental data was compatible with the data predicted by the model, and only less than 9% of total variations were not explained by the model. The R^2 value was always between 0 and 1, and a value >0.75 indicated aptness of the model. For a good statistical model, R^2 value should be close to 1.0 (XiaodongRen, *et al*., 2005). The adjusted R^2 value corrects the R^2 value for the sample size and for the number of terms in the model. The value of Adj R^2 (0.8231) was also high to advocate for a high significance of the model. If there are many terms in the model and the sample size is not very large, the adjusted R^2 may be noticeably smaller than the R^2 (Jiangya *Zhou et al*., 2010). The adjusted R^2 value was lesser than the R^2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. In the present study, the ratio was found to be >14, which indicates an adequate signal. The experimental results were analyzed through RSM to obtain an empirical model for best response. The significance of each coefficient was determined by Student's t-test and p-values, which are listed in Table 5. Larger the magnitude of t-value, smaller the p-value, the more significant is the corresponding coefficient. Values of



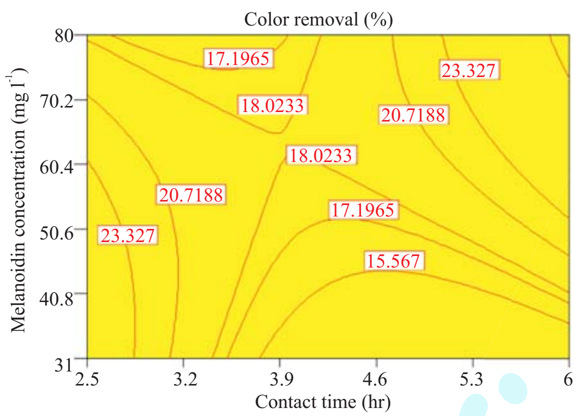
Hold Values : Melanoidin Con (mg l^{-1})- 55; Biomass (g)- 2.75

Fig. 4(a) : Contour plot between pH and contact time



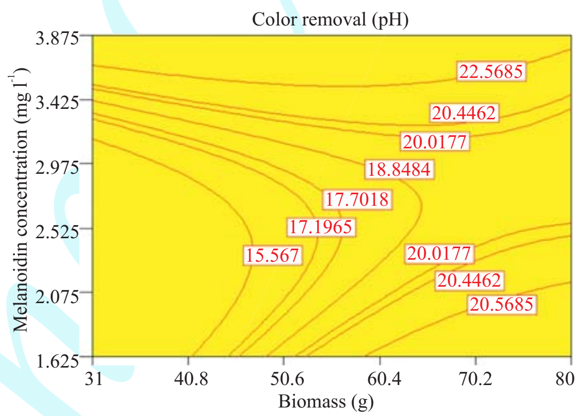
Hold Values : contact time (h)- 4.5; Biomass (g)- 2.75

Fig. 4(b) : Contour plot between pH and Melanoidin Concentration



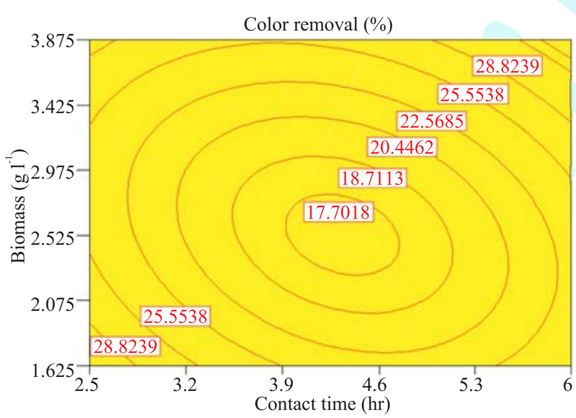
Hold Values : Melanoidin Con (mg l^{-1})- 55; Biomass (g)- 2.75

Fig. 4(c) : Contour plot between contact time and Melanoidin Concentration



Hold Values : pH – 6; contact time (h)- 4.5

Fig. 4(d) : Contour plot Contour plot between Biomass and Melanoidin Concentration



Hold Values : pH – 6; Melanoidin Con (mg l^{-1})- 55

Fig. 4(e) : Contour plot between contact time and Biomass

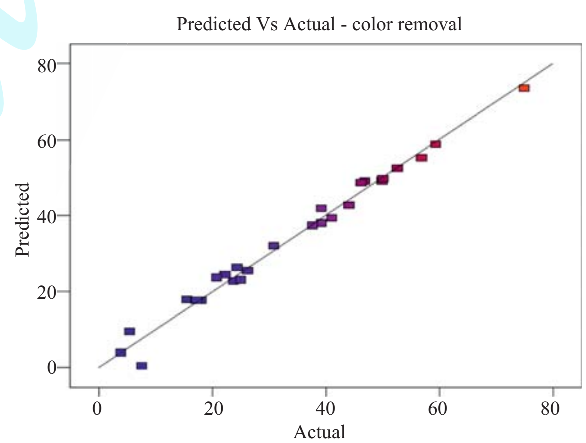


Fig. 5 : Plot of actual vs. predicted response values by the Design Expert 8.0.3

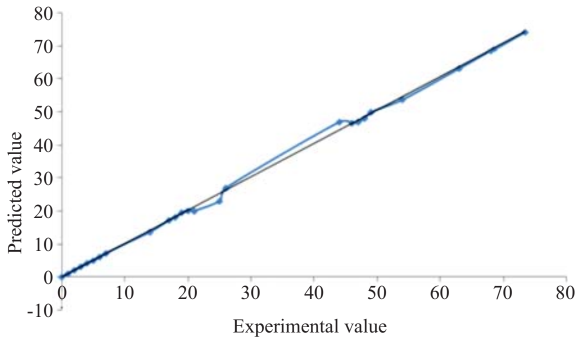


Fig. 6 : Plot of Experimental value vs. predicted response values by ANN

Table 4 : Regression coefficients obtained by the response surface model for removal of melanoidin from synthetic effluent

Term constant	Color removal (%)
Intercept	17.70
X_1	8.77
X_2	1.95
X_3	3.48
X_4	2.80
X_1X_2	0.15
X_1X_3	4.95
X_1X_4	10.68
X_2X_3	6.78
X_2X_4	3.33
X_3X_4	-4.67
X_1X_1	5.87
X_2X_2	7.00
X_3X_3	-1.72
X_4X_4	6.33

X_1: pH, X_2:Contact time (h), X_3:Melanoidin Concentration (g l^{-1}), X_4: Biomass (g)

"Prob> F" less than 0.0500 indicated that model terms were significant. Lack of Fit F-value of 18.068 implied that the Lack of Fit was significant (Rajasimman *et al*., 2011).The response surface curves and contour plots for the melanoidin decolourization are shown in Fig. 4. It was observed that the elliptical nature of the contour in 3D-response surface graphs depicted the mutual interactions of all the variables.

In the study, number of independent variables was the number of input neurons, and the response was the number of output neurons. Here, a sigmoidal transfer function was used in the hidden layer and given by:

$$F(x) = 1/1+e^{-x} \quad \text{Eq.6}$$

Where, f(x) is the hidden neuron output. Training was done by Training Scaled Conjugate. The number of epochs was set to 25000 and the iterations involved for optimization were 88. The learning rate was fixed at 0.8, and the goal was 0.001.

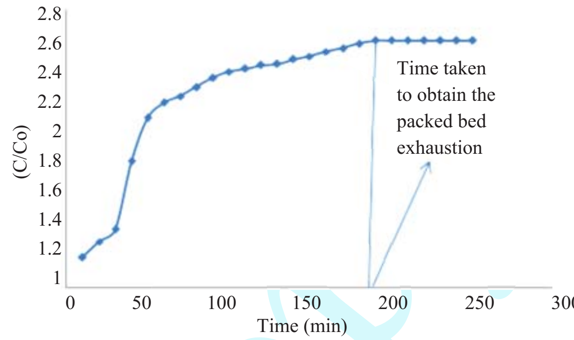


Fig. 7 : Breakthrough curves for adsorption of melanoidin at optimized condition (pH 7.5, Melanoidin concentration 32.5 mg l^{-1}, Biomass 1.63 g, Contact time 2hr 75min)

Table 5 : ANOVA for responses

Source	Color reduction (%)	
	F value	p Value
Model	76.57	<0.0001
X_1	220.54	<0.0001
X_2	10.91	0.0048
X_3	34.82	<0.0001
X_4	22.50	0.0003
X_1X_2	0.044	0.8369
X_1X_3	46.84	<0.0001
X_1X_4	218.27	<0.0001
X_2X_3	87.98	<0.0001
X_2X_4	21.22	0.0003
X_3X_4	41.77	<0.0001
X_1X_1	112.78	<0.0001
X_2X_2	160.81	<0.0001
X_3X_3	9.74	0.0070
X_4X_4	131.53	<0.0001
R^2	0.9862	
Adj-R^2	0.9733	

X_1: pH, X_2: Contact time (hr), X_3:Melanoidin concentration (g l^{-1}), X_4: Biomass (g)

The values predicted by ANN are included, making it very clear that ANN was a better option for optimization of melanoidin adsorption as deviation from experimental values was less. Fig. 6 shows the significance of ANN with regression coefficient value of 0.99.Similar results were observed by Khataee *et al*., (2010) bioremediation of malachite green from contaminated water by three microalgae: Neural Network Modeling

The performance of packed bed column was explained by the concept of breakthrough curve. The breakthrough curve showed the loading behavior of melanoidin pigment removed from the solution in a fixed bed. It is usually explained as normalized concentration defined as the ratio of melanoidin concentration in effluent to the initial concentration of melanoidin pigment (C/C_o) as a function of time or volume of effluent for the given bed height (Sivakumar *et al.,* 2009). Fig. 7 is a plot of breakthrough curve. It was found that increase in the flow rate led to early breakthrough. Binding sites became saturated more quickly at high concentration and was indicated by early breakthrough time. In a continuous column mode, contact between the adsorbate and the biosorbent was less when compared with batch mode, which ultimately resulted in lesser equilibrium sorption capacity in the column mode (Fu *et al.,* 2003). Removal efficiency of melanoidin mainly depends on the influent concentration, flow rate and bed height.

The isothermal curves showed that the process followed the Langmuir isotherm. The R_L values lay between 0 and 1, indicating favorable adsorption, and the thermodynamic parameters classified this melanoidin adsorption as a physical adsorption, which was endothermic in nature. The optimized parameters from RSM and ANN were as follows : pH- 7.5; melanoidin concentration-32.5 mg l^{-1}; contact time- 2hr 75 min and biosorbent quantity- 1.63 g 100 ml^{-1}. The value of co efficient regression (R^2=0.92) indicated good fitness of the experimental values. Continuous column studies gave a breakthrough at 182 min and 176 ml^{-1}. Various adsorbate were used for the treatment of distillery spent wash was discussed (Agarwal *et al*., 2010).

Thus, it can be concluded that the activated pepper stem can be effectively used for the removal of melanoidin pigment (75%), and also considerable amount of melanodin pigment removal was obtained in continuous fixed bed column study.

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