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 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 Freundlich 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 stem, 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 °C 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 $C_{V}$ vs. $C_{Q}$ for Langmuir and log $Q_{e}$, Log $q_e$ for Freundlich isotherms were drawn using the absorbance values, and the constants were calculated using equation 1 and equation 2.

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} = \frac{1}{Q_m}C_e$$  \text{Eq. 1}

$$\log Q_e = \log k + \frac{1}{n} \log C_e$$  \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 $K_e$ with change in temperature. Free energy of adsorption ($\Delta G$) can be related with the equilibrium constant $K$ (L mol⁻¹) corresponding to the reciprocal of Langmuir constant, b by the following equation:

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

Where, R is Gas universal constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature, and b (L mol⁻¹) is the Langmuir constant. The enthalpy change ($\Delta H$) and entropy change ($\Delta S$) was calculated using the following equation:

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

$\Delta H$ and $\Delta S$ was estimated from the slope and intercept of the straight line plot of $\ln b$ against $1/T$. 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 $1/T$ is plotted and using equations 3, 4 and $\Delta G$, $\Delta H$ and $\Delta S$ 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 % decolourisation was obtained as response dependent variable by the experimental design obtained by full factorial Central Composite design (CCD). A $2^4$ full factorial experimental design with 30 experiments were employed which includes 8 trails for each axial point and 6 trails for replication of central
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:

\[ x_i = \frac{(X_i - X_0)}{d_{xi}} \]  

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](image-url)
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. $C_e/q_e$ vs. $C_e$ 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 $\Delta G$, $\Delta H$, and $\Delta S$ are presented in Table 2. The values of $\Delta G$ were negative at all the temperatures studied, which confirms the feasibility of the process and spontaneous nature of adsorption. The values of $\Delta G$ were low, suggesting a physical adsorption process (Silva et al., 2004). The estimated enthalpy change ($\Delta H$) and entropy change ($\Delta S$) of adsorption were 32.195 kJ mol$^{-1}$ and 115.44 J mol$^{-1}$ K$^{-1}$, respectively. A positive value of $\Delta H$ indicated that the adsorption of melanoidin is an endothermic process. A positive value $\Delta S$ 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

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**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

<table>
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<th>T (K)</th>
<th>$Q_m$ (mg g$^{-1}$)</th>
<th>$b$ (L mg$^{-1}$)</th>
<th>$b$ (L mol$^{-1}$)</th>
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<th>RL</th>
<th>$K_f$</th>
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**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: 2hr 75min

<table>
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<tr>
<th>T (K)</th>
<th>($\Delta G$) (kJ mol$^{-1}$)</th>
<th>($\Delta H$) (kJ mol$^{-1}$)</th>
<th>($\Delta S$) (J mol$^{-1}$ K$^{-1}$)</th>
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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 (P(model) < 0.0001) 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 imply 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 (Xiaodong Ren, 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

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

<table>
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<tr>
<th>pH</th>
<th>Contact time (h)</th>
<th>Melanoidin concentration (g/l)</th>
<th>Biomass (g)</th>
<th>Color removal (% actual)</th>
<th>Color removal (% predicted)</th>
<th>ANN prediction</th>
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Fig. 4(a): Contour plot between pH and contact time

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

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

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

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

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

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

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

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

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

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

Predicted Vs Actual - color removal
"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:

\[ F(x) = \frac{1}{1+e^{-x}} \] \hspace{1cm} 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.

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 \( C/C_0 \) 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 \( R^2 \) 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 - 2 hr 75 min and biosorbent quantity - 1.63 g 100 ml\(^{-1}\). The value of coefficient 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 melanoidin pigment removal was obtained in continuous fixed bed column study.

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**References**


