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Adsorption of safranin onto chemically modified rice husk in a upward flow packed bed reactor: artificial neural network modeling

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ABSTRACT

The study reports the adsorption of safranin onto NaOH-modified rice husk in a upward packed bed column. Effects of the operating parameter such as flow rate, influent dye concentration were studied. To determine the characteristic parameters of the column, four models- Thomas, Adams–Bohart, BDST, and Yoon–Nelson models were applied to the experimental data. The results showed that Thomas model best fitted with the experimental data at various flow rates, while Yoon-Nelson model was suitable with data at various safranin concentrations. Moreover, it was observed that on increasing the concentration of safranin, adsorption capacity increased which in turn decreased on increasing the flow rate. Least sum of square (SS) and $\chi 2$ error analysis were applied to the models to find out the best fit model with the experimental data. An artificial neural network (ANN) model was developed to predict the decolorization of the dye solution in upward packed bed column. The model provided reasonable predictive performance (R^2 = 0.988).

Introduction

Textile industries consume a large amount of water for the dyeing processes and generate dye bearing effluents. The effluents generated by this type of textile industry are rated as most polluting among the all industrial effluents considering both the volumes discharged and the effluent composition (Kumari et al., 2007). The hazardous effects of these dyes come from their metabolites which are very toxic to the aquatic life and have carcinogenic and mutagenic effects on the environment (Ponnusami et al., 2009). Due to increasingly stringent restrictions on the effect of the industrial effluents, it is necessary to reduce the colourful dyes from wastewater before it is discharged (Crini G., 2006) to the environment. Therefore, the removal of these dyes is important for the industrialized countries of the world.

The reduction of dye from the solution can be done by using different common methods like ion exchange, reverse osmosis, chemical oxidation, electro-dialysis, adsorption using activated carbon or activated charcoal etc. But these treatment methods are very costly and require higher energy (Saha and Datta, 2010) to perform. For these reasons, interest has been arisen recently in the investigation of some unconventional methods and materials for removal of dyes from textile effluents which are cheaper and less energy consume process. Adsorption is an alternative and the most effective physical process for the removal of dye of textile effluent. Adsorption is defined as the process where a solute is removed from the liquid phase through the contact with a solid biosorbent which has a affinity for that particular solute from solution (McCabe et al., 2005).

In this present work, rice husk has been used as an efficient biosorbent. Rice husk is an easily available agricultural waste material, and from a literature survey it is revealed that the annual generation of rice husk in India is 18 to 22 million tons. Rice husk is the outer covering of paddy and accounts for 20 – 25% of its weight and is an agricultural byproduct whose major constituents are organic materials and hydrated silicon. The organic materials present in rice husk are cellulose (55 –60 wt% including cellulose and hemicellulose), lignin (22 wt %), crude protein (3%), etc. Carboxyl, hydroxyl and amidogen etc. are some of the functional groups which make the adsorption process possible (Jaman et al., 2009). Hence rice husk is low cost biosorbents and can be easily obtained (Han et al., 2009) for the adsorption.

The presence of safranin causes several acute effects on health (like irritation to mouth, throat and stomach with effects including mucous build up, irritation to the tongue and lips and pains in the stomach, which may lead to nausea, vomiting and diarrhea, irritation to the eyes, with effects including: tearing, pain, stinging and blurred vision, redness and itchiness of skin) (Rejniak and Piotrowska, 1966). Due to its structural stability, safranin is difficult to biodegrade also (Chowdhury et al., 2010; Kumar., 2007).

In the present study, rice husk obtained from the agricultural processing industry was tested as a biosorbent for removal of dyes in a upward packed bed column with a model system of safranin solutions. The solute used in all the experiments was safranin, a basic (cationic) dye.

The aim of the present study was to explore the feasibility of utilizing modified rice husk for the reduction of safranin from wastewater using an upward packed bed column. The effect of factors on biosorption such as the initial dye concentration, flow rate through the husk bed column was investigated at different time intervals. Thomas model, Adams–Bohart model, Yoon–Nelson model and BDST model were used to predict the performance of the experiment. The experimental results were used to develop a model using artificial neural network to decolorization of the dye sample from solution.

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Thomas model

Thomas model is one of the most general and widely used models in the column performance theory. The expression determines the maximum solid phase concentration of the solute on the biosorbent and the rate constant of biosorption for a continuous process using the column experiment. The linearised form of the model is given as (Han et al., 2009):

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_{Th}\,q_0\,m}{Q}-\frac{k_{Th}\,C_0\,V_{eff}}{Q} \quad \text{........ (1)}$$

Where 'K_{Th}' is the Thomas rate constant (mL/mg min), 'q_0' is the equilibrium adsorbate uptake (mg/g) and 'm' is the amount of biosorbent in the column.

The Adams–Bohart model

The Adams–Bohart model describes the initial part of the breakthrough curve. The expression of the model is the given below (Saha et al., 2010):

$$\ln\frac{Ct}{Co}=(K_{AB}Cot-K_{AB}No\frac{Z}{F}) \quad \text{.......... (2)}$$

Where K_{AB} is the kinetic constant (L mg^{-1} min^{-1}), F is the linear velocity calculated by dividing the flow rate by the column section area (cm min^{-1}), Z is the bed depth of column and N_o is the saturation concentration (mg L^{-1}). From this equation, values describing the characteristic operational parameters of the column can be determined from a plot of C_t/C_o against t at a given bed height and flow rate using the non-linear regressive method.

Yoon-Nelson model

Yoon and Nelson model was derived based on the assumption that the rate of decrease in the probability of adsorption for each biosorbate molecule was proportional to the probability of adsorbate biosorption and the probability of adsorbate breakthrough on the biosorbent. The linearised model for a single component system is expressed as (Han et al., 2009):

$$\ln\left(\frac{Ct}{Co-Ct}\right)=K_{YN}t-\tau K_{YN} \quad \text{............ (3)}$$

Where 'K_{YN}' is the rate constant (min^{-1}), 'τ' is the time required for 50% adsorbate breakthrough.

The Bed Depth Service Time (BDST) model

The Bed Depth Service Time model which was a modified form of Bohart-Adams model was used to compare the uptake capacity of the adsorption columns. This model was derived based on the assumption that intra-particle diffusion and external mass transfer resistance were negligible and that the adsorption kinetics was controlled by the surface chemical reaction between solute in the solution and the unused biosorbent. This model also served as a useful tool for comparing the performance of columns operating under different process variables. The BDST model in linear form is expressed as

$$\ln\left(\frac{Co}{Ct}-1\right)=K\left(\frac{Noh}{\mu}-Co\right) \quad \text{........ (4)}$$

Where 'C_o' and 'C_t' are inlet and output concentration respectively, 'k' is the adsorption rate constant (mg min^{-1}), 'N_o' is the adsorption capacity (mg g^{-1}), 'h' is the bed depth (cm) and 't' is the service time to breakthrough (min) (Saha et al., 2010).

Error analysis

A linear regressive method is used to compare the models using experimental data. The statistic is basically the least sum of the squares of the differences between the experimental data and the data obtained by calculating from the models parameters. The values of SS can be obtained as the following formula:

$$SS=\sqrt{\frac{[(C_t/C_0)_c-(C_t/C_0)_e]^2}{n}} \quad \text{........... (5)}$$

where, $(Ct/Co)_c$ is the ratio of effluent and influent safranin concentrations obtained from calculation according to dynamic models, and $(Ct/Co)_e$ is the ratio of effluent and influent safranin concentrations obtained from experiment. If data from the model are similar to the experimental data, SS will be a small number; if they are different, SS will be a large number. In order to confirm the best fit isotherm for the column adsorption system, it is necessary to analyze the data using the values of SS, combined with the values of the determined coefficient (R^2) . Another error analysis method is chi-square (χ^2) analysis method. This analysis in turn evaluates the optimum adsorption isotherm model for dye and the system. Smaller values of chi-square indicate a smaller deviation between models derived data and experimental values and vice versa (Goel et al., 2005; Saha and Datta, 2009)

$$\chi^2=\sum\frac{(q_{exp}-q_{cal})^2}{q_{cal}} \quad \text{..............(6)}$$

Neural network modelling:

An artificial neural network (ANN) is a simplified mathematical and computational model developed by the structure of biological neural networks analysis. The models are usually used to complex relationships between inputs and outputs or to find patterns in data. Neural networks have been trained to perform complex functions in various fields of application for time series forecasting, pattern recognition, identification, classification, speech, vision and control systems. The main advantage of ANN model over traditional methods is that they do not require the complex nature of the underlying process of biosorption (Dutta et al., 2010; Khatee et al., 2011).

A three-layer network with a linear transfer function with back-propagation neural network (3:10:1) was designed in this present study. Most ANN has three layers or more as shown in Figure 1: an input layer, which is used to present data to the model; an output layer, which was used to generate an appropriate result to the given input; and one or more inter-connected layers, which was used to perform as a collection of feature detectors. For developing an ANN model, first proper algorithm and transfer function had to choose. In this study, different algorithms of transfer function 'poslin' for hidden layer and 'purelin' as the output layer transfer functions were used to train the model. MATLAB 7 was used to develop the ANN model. The more the number of neurons, the better was the performance of the neural network in fitting the data. However too many neurons in the hidden layer may result in the over fitting. To find out the optimum number of neuron in the hidden layer was an important work at the time of network development using MATLAB.

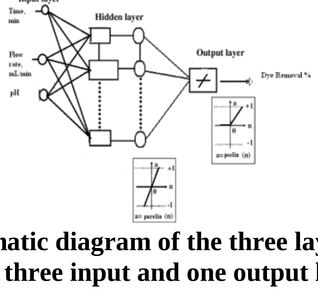

Figure 1. Schematic diagram of the three layers ANN model with three input and one output layer.

Methods

Preparation of rice husk

Rice husk was collected from agricultural industry of nearby areas of Durgapur area, India. It was washed with double distilled water and pretreated with 10% NaOH and at 121^{0}C, 15 Psi for 20-25 min in an autoclave. After pretreatment it was washed with distilled water several times to remove NaOH completely from the rice husk and was dried for 12h at 65 ^{0}C in the oven. The characteristic of ricehusk has been given in the previous work (Chowdhury et al., 2010).

Safranin solution

Stock solution of safranin (1000 mg L^{-1}) was prepared by dissolving safranin powder (Merck, Germany) in distilled water. Experimental safranin solution of different concentrations (100, 250, 350 mg L^{-1}) was prepared by diluting the stock solution using required amount of distilled water using volumetric flasks. The structure and properties of safranine was given in our previous work (Chowdhury et al., 2010).

Methods of adsorption studies

Continuous flow biosorption experiments were performed in a glass column of 1.50 cm internal diameter. Different sets of experiments were conducted with various influent safranin concentrations of 100 mg L^{-1}, 250 mg L^{-1}, 350 mg L^{-1} and at different flow rates (3.0 mL min^{-1}, 4.0 mL min^{-1}, 5.0 mL min^{-1}) separately. Weight of modified biosorbent, i.e. rice husk was kept constant for all the experiment [Figure 2]. The experiments were carried out at room temperature. For varying safranin concentration 5 gm rice husk was packed into a glass column and safranin solution at different concentration was passed individually through the bottom of the column using peristaltic pump in a upward mode. For varying flow rates, concentration of safranin was kept constant at 100 mg L^{-1} with 5 gm rice husk packed in the column. Samples were collected at regular time interval of up-flow direction for all the experiments. The concentration of solution in the effluent was analyzed using a UV/VIS spectrophotometer (Hitachi Brand U-2800) by monitoring the absorbance at a wavelength of 558 nm for safranin.

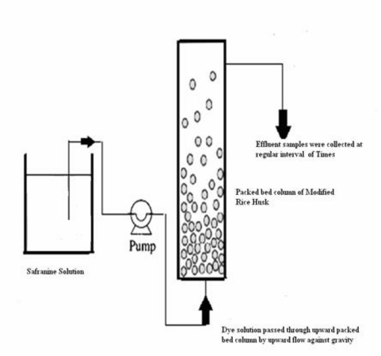

Figure 2: Schematic diagram of the upward packed bed column

Method of ANN analysis:

Optimization of the process parameter was most important step in developing the model using ANN. In the present work, input variables to the feed forward network were as follows: flow rate (mL min^{-1}), decolorization time (min), pH as input variables. The percentage removal of dye was chosen as the experimental responses or output variables for the column or continuous process.

Result and Discussion

Breakthrough curve estimation

Four models: Adams - Bohart, Yoon - Nelson, BDST, and Thomas were applied to the experimental data and their respective parameters were determined using linear regression analysis, to describe the fixed bed column behavior and for scaling up purposes for the industrial applications.

Thomas model

Thomas rate constant K_{TH} and equilibrium adsorbate uptake 'q_o' was calculated by applying Thomas model to column data by Eqn. 1.

Table 1 shows that as the influent concentration increased, equilibrium adsorbate uptake 'q_o' also increased. On the other hand, with increased in flow rate biosorbent bed height increased but there was decreased in equilibrium adsorbate uptake 'q_o'.

This indicates that on increasing safranin concentration, adsorption capacity of rice husk increased while on increasing flow rate of influent safranin, adsorption capacity decreased.

Adams-Bohart model

In Adams-Bohart model the characteristic parameters like, saturation concentration (N_o) and kinetic constant (K_{ab}) was estimated. On application of experimental data, to Eqn. (2) the parameters obtained were listed in Table 2.

On increasing the influent safranin concentration from 100 mg L^{-1} to 350 mg L^{-1}, saturation concentration of safranin increased from 19.3 × 10^3 mg L^{-1} to 22.44 × 10^3 mg L^{-1}. On other hand, with increasing flow rate, saturation concentration of safranin decreased. Maximum saturation concentration was observed at 350 mg L^{-1} safranin concentration with flow rate of 4.0 mL min^{-1}. The regression coefficients for the parameters (R^2) values ranges from 0.619 to 0.963 on increasing the concentration. .

Yoon- Nelson model

The requirement of time for 50% of safranin breakthrough time (τ) could be calculated by Eqn. 3 using linear regression analysis. Values of τ and K_{YN} were listed in Table 3.

It was observed from table 3 that on increasing the initial concentration and flow rate of safranin, time required for 50% biosorbate breakthrough time τ decreased which proved that on increasing safranin concentration, driving force for mass transfer increased, hence less time required for biosorbent bed saturation. At higher flow rates there was more upward flow which had lead to increase in bed height of biosorbent. Due to enhanced rate at higher flow rate, more void spaces created which allowed better mass transfer between dye and biosorbent because of which bed adsorption zone moved fast and bed had taken less time to saturate.

BDST model

The BDST model was based on physically measuring the capacity of bed at different breakthrough values. The model ignores the intraparticle mass transfer resistance and external film resistance such that biosorbate was adsorbed onto the biosorbent surface directly (Han et al. 2009)

From Table 4, it could be seen that on increasing the concentration of safranin from 100 mg L^{-1} to 350 mg L^{-1}, adsorption capacity (N_o) of rice husk increased from 17 × 10^3 mg g^{-1} to 19.9 × 10^3 mg g^{-1} while on increasing the flow rate from 3.0 mL min^{-1} to 5.0 mL min^{-1} there was decreased in adsorption capacity from 18.8 × 10^3 mg g^{-1} to 14.343×10^3 mg g^{-1}. Maximum adsorption capacity was observed at 350 mg L^{-1} safranin concentration with flow rate of 4 mL min^{-1}. R^2 values ranges from 0.821 to 0.991.

Error analysis

SS values were calculated by Eqn. 5 and it was observed that SS values for increasing concentrations of safranin was least for Yoon-Nelson model while Thomas model gave the minimum SS values for different flow rate conditions (Table 5).

χ^2 values were calculated for different models with the help of eqn. 6. Table 6 showed the χ^2 values for different parameters at different conditions. Yoon-Nelson model gave the smaller χ^2

values at different safranin concentrations while at different flow rates BDST and Thomas model showed the minimum χ^2 values which suggested that there was a smaller deviation between models derived data and experimental values and these models could be used for the prediction of breakthrough curves at different time intervals.

Simulation of % removal of adsorption model

Trial and error method was used to find the most suitable network model for the % removal of dye using packed bed column. It was found that 10 – 15 neurons produce the maximum R value (0.988). All the models were tested with 10 neurons. In case of % reduction of dye removal model development, "poslin" transfer function gave the satisfactory results (Figure 3). Levenberg – Marquardt backpropagation algoritm was the most suitable for this model (R = 0.988). Figure 3 showed the most suitable combination model for % removal of dye using rice husk in upward packed bed column model.

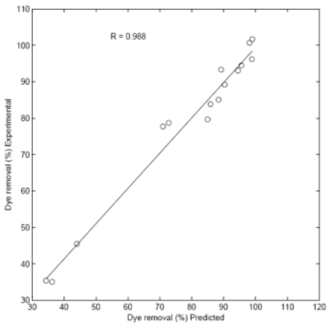

Figure 3: Simulated result vs. experimental result for % removal of dye by ANN model.

Figure 4 compared the simulated result with the experimental results. From Figure 4, it was observed that the simulated result using ANN rep resented the satisfactory result with the experimental value and in all cases the % error between the predicted and experimental values were very low (below 6.5%).

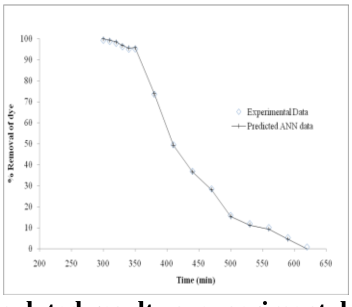

Figure 4. Simulated result vs. experimental result for % removal of dye in respect of time by ANN model.

Conclusions

On the basis of these results obtained in this investigation following conclusions can be drawn:

a. Modified Rice husk can be used as biosorbent to reduce the effects of safranin from solutions using an upward packed column mode.

b. Thomas model and Yoon-Nelson model was found to be best fitted with experimental data at different flow rates and different safranin concentrations respectively.

c. BDST model can also be used for describing initial breakthrough curve for different conditions.

d. The developed ANN model can be used efficiently to predict the % removal of safranin dye at any time using the packed bed column.

References

Kumari K,.; Emilia T A. Biosorption of anionic textile dyes by nonviable biomass of fungi and yeast, Bioresour Technol., 2007, 98: 1704–1710.

Ponnusami V., Gunasekar V., Srivastava S.N., Kinetics of methylene blue removal from aqueous solution using gulmohar (Delonix regia) plant leaf powder: Multivariate regression analysis; J Hazard Mater, 2009, 169: 119-127.

Crini G., Non-conventional low-cost biosorbents for dye removal: A review; Bioresour. Technol. 2006, 97:1061–1085

Saha P., Datta S., Assessment on the Thermodynamics and Kinetic Parameters on Adsorption of Malachite Green using Rice Husk; Inst of Engg J, 2010, 90:11-17.

McCabe W. L., Smith J. C. , Harriott P., Unit Operations of Chemical Engineering,7th ed., International Edition, McGraw-Hill, New York , 2005, 836.

Jaman H, Chakraborty D., Saha P., A Study of the Thermodynamics and Kinetics of Copper Adsorption Using Chemically Modified Rice Husk, Clean 2009, 37:704 – 711

Han R., Ding D., Xu Y , Zou W, Wang Y, Li Y, Zou L., Use of rice husk for the adsorption of congo red from aqueous solution in column mode, Desalination 2009, 245:284–297.

Rejniak L., Piotrowska H., Effect of Malachite Green, Congo Red and Safranin on Cell Division in Gemmae of Allium cepa, Nature 1966, 209: 517 - 518

Chowdhury S, Mishra R, P Kushwaha, P Saha, Removal of safranin from aqueous solutions by NaOH-treated rice husk: thermodynamics, kinetics and isosteric heat of adsorption, Asia-Pac. J. Chem. Eng. 2010, DOI:10.1002/apj.525

Kumar K. V., Pseudo-second order models for the adsorption of safranin onto activated carbon: Comparison of linear and non-linear regression methods, J. Hazard. Mater, 2007, 142: 564–567.

Saha P, Datta S., Sanyal S. K., Application of Natural Clayey Soil as Biosorbent for the Removal of Copper from Wastewater, J Env Engg, 2010, 136 (12):1409 – 1417.

Saha P, Datta S., Assessment on thermodynamics and kinetics parameters on reduction of methylene blue dye using flyash; Desalin. Water Treat. 2009, 12: 219–228

Goel J., Kadirvelu K., Rajagopal C., Garg V.K, Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies; J. Hazard. Mater, 2005, 125: 211–220

Dutta S., Parsons S A, Bhattacharjee C., Bandopadhyay S., Datta S., Development of an artificial neural network model for adsorption and photocatalysis of reactive dye on TiO_2 surface, Expert Syst. Appl., 2010, 37: 8634-8638.

A R Khataee, M Zarei, G. Dehghan, E.Ebadi, M. Pourhassan, Biotreatment of a triphenylmethane dye solution using a Xanthophyta alga: Modeling of key factors by neural network, J. Taiwan Inst Chem Engg, 2011, 42:380-386.

Table 1: Calculated constants for Thomas model

Co (mg L^{-1})	ν (ml min^{-1})	Z (cm)	K_{TH} (ml min^{-1} mg^{-1}) $\times 10^{-4}$	q_o (mg g^{-1}) $\times 10^3$	R^2
350	4	15	0.54	105.9	0.821
250	4	15	1.04	97.69	0.957
100	4	15	1.32	90.4	0.95
100	3	15	1.30	99.75	0.99
100	5	17	1.60	86.12	0.98

Table 2: Adams-Bohart model parameters at various conditions

Co (mg L^{-1})	ν (ml min^{-1})	Z (cm)	K_{ab} (L mg^{-1} min^{-1}) × 10^{-5}	N_o (mg L^{-1}) × 10^3	R^2
350	4	15	5.60	22.438	0.791
250	4	15	3.14	25.900	0.619
100	4	15	9.00	19.270	0.941
100	3	17	13	15.467	0.963
100	5	15	10	19.907	0.945

Table 3: Yoon nelson parameters at different conditions using linear regression analysis

Co (mg L^{-1})	ν (ml min^{-1})	Z (cm)	K_{YN} (min^{-1})	τ	R^2
350	4	15	0.019	360.3	0.821
250	4	15	0.026	457.70	0.944
100	4	15	0.013	1076.20	0.959
100	3	15	0.010	1648.00	0.945
100	5	17	0.013	876.20	0.963

Table 4: The calculated constants for BDST model of adsorption of safranine using linear regression analysis.

Co (mg ml^{-1})	ν (ml min^{-1})	Z (cm)	K_a (mg min^{-1})× 1	N_o (mg g^{-1}) × 10^3	R^2
350	4	15	0.54	19.984	0.821
250	4	15	1.04	18.429	0.957
100	4	15	1.30	17.060	0.959
100	3	15	1.30	18.826	0.991
100	5	17	1.60	14.343	0.985

Table 5: SS values for different models at different conditions

Conditions	THOMAS MODEL	BDST MODEL	YOON-NELSON MODEL	ADAMS-BOHART MODEL
100 mg L^{-1}	0.28	0.283	0.283	0.584
250 mg L^{-1}	0.285	0.285	0.219	0.154
350 mg L^{-1}	0.291	0.291	0.291	0.350
3.2 ml min^{-1}	0.249	0.249	0.508	0.179
4.2 ml min^{-1}	0.283	0.283	0.283	0.584
5.3 ml min^{-1}	0.177	0.217	0.426	0.182