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Mathematical modeling of biosorption of safranin onto rice husk in a packed bed column using artificial neural network analysis

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ABSTRACT

The study was undertaken to find out a suitable low cost, environmental friendly and highly effective biosorbent to remove safranin dye from wastewater. For this a continuous downward packed bed column experiment was carried out by using rice husk as a biosorbent. The effects of the operational parameters like pH, flow rate, time etc were studied in continuous downward column. A feedforward artificial neural network (ANN) model had been proposed to predict the decolorization efficiency of a non-linear behavior of a continuous column operation. The network was trained using different operational parameters and the findings indicated that the developed ANN model provided high performance criteria ($R^2 = 0.99$). The proposed simulated models were estimated the % reduction of dye in respect to time using the packed bed continuous column experiment.

Keywords: Rice husk; Safranin; Packed bed; Biosorption; ANN; Simulation

1. Introduction

Effluents containing safranin are generated from mainly the textiles, printing and dyeing, industries [1–3]. Due to its structural stability, it is very difficult to degrade. It affects on the health like irritation to mouth, throat and stomach, irritation to the tongue and lips and pains in the stomach, which may lead to nausea, vomiting and diarrhea, and irritation to the eyes. The presence of dye increases the chemical and biological oxygen demand, suspended solids and also toxic compounds. The color of it interferes with transmission of light. It has also been reported that safranin is carcinogenic in nature [4–6].

Biosorption technique is quite familiar as the process is very simple as well as the availability of a wide range of adsorbents. It can be defined as the process where a solute molecule is removed from the liquid phase through the contact with solid adsorbent particles which has affinity for that particular solute [7]. Activated carbon, has the property for the biosorption of pollutants from the wastewater [8]. But the main disadvantages of using the activated carbon is the high price of treatment and difficult to regenerate, which increases the cost of wastewater treatment. Thus, there is a demand for other adsorbents, which are less expensive material and does not require any expensive pretreatment step [9–14]. So it is preferable to use low cost adsorbents, such as an industrial waste, natural ores, and agricultural byproducts to remove the pollutants from the wastewater.

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Safranin is cationic dye and is a well-known textile colorant used for dyeing tannin, cotton, bast fibers, wool, silk, leather, and paper. The Chemical Index of safranin is 50,240, molecular formulae: $C_{20}H_{19}ClN_4$ and λ_{max}: 558 nm [15].

Rice husk possesses a granular structure, has chemical stability, high mechanical strength and accounts for about 20% of the whole rice. It consists of about 32% cellulose, 21% hemicelluloses, 21% lignin, 20% silica, and 3% crude protein [16–17]. It also contains abundant floristic fiber, and some functional groups such as carboxyl, hydroxyl and amidogen representing a favorable characteristic of rice husk to be a potential adsorbent material. The characterization study using SEM, FTIR, BET—analysis had been reported earlier [16].

Silica present on the outer surface of rice husks in the form of silicon–cellulose membrane acts as a natural protective layer against termites and other microbial attack on the paddy. The inner surface of rice husk is smooth and as its contain wax and natural fats that provide good shelter for the grain but the presence of these impurities on the inner surfaces of rice husks also affects the biosorption properties of rice husk chemically and physically.

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

Artificial neural network (ANN) is a simple mathematical modeling of neural network for solving the complex problems related to the field of modeling and optimization in order to achieve the high operational performance [18–21]. The functional aspect of it is based on the human brain and their interconnection and interrelation with each other. This modeling process is a new information computing technique inspired by the biological neural processing system. The human brain consists of almost 10 billion of interconnected neurons and each neuron cell receives, process, and transmits the information to the human body. The transmission of information from one neuron to another neuron at synapses is a complex chemical reaction and specific transmitter substances are released through it. In ANN, three functional groups are important: receiving signals from outside, the neurons which process the information and the neurons which generate result. Multilayered perception neural network is the simplest model and normally has three layers: input, output and one or more hidden layer (Fig. 1). Each layer may have one or more numbers of neurons which are interconnected by the parameters. The neurons present in input layer act as a buffer to distribute the input signals to the x_i hidden layer. The neuron in the hidden layer j sums up its signal inputs and computes its output y_j as a function of f of the sum.

$$y_j = f\left(\sum w_{ji} x_j\right) \quad (1)$$

where f is the sigmoid or hyperbolic tangent function.

In this study, feed forward neural network model was employed. Different algorithms of ANN were used to train the model using MATLAB 7 to develop the ANN model.

The ANN model is well presented to fuzzy, noisy and incomplete data and it is also called MIMO algorithm (multiple input, multiple output) that can store a huge amounts of information. The simulated

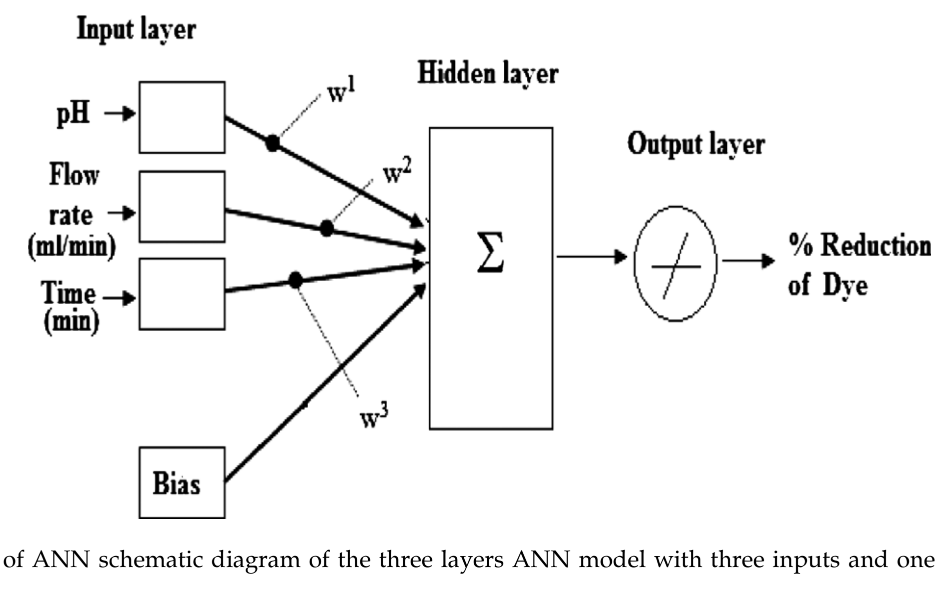

Fig. 1. Structure of ANN schematic diagram of the three layers ANN model with three inputs and one output layer.

models are developed by learning the experimental generated data or using the validated models.

The aim of the present study is to explore the possibility of utilizing rice husk for the adsorptive removal of safranin from wastewater using packed bed column operation. The effect of such factors such as the initial dye concentration, pH of the solution, and bed height on safranin biosorption by husk bed column was investigated. Another aim of this work is to develop of a multilayer neural network model to predict the decolorization of the dye using rice husk. The major important challenge in the modeling of the decolorization is that to study the nonlinear and time varying nature of such processes. Thus an ANN model was applied to predict the performance of the decolorization process. The novelty of the present study lies in the development and application of an ANN-based model to predict the steady state performance of an innovative continuous reactor for the biosorption of safranin dye from the solution.

2. Methods

2.1. Collection and preparation of rice husk

Rice husk was collected from the agricultural industry of Durgapur area, India. It was washed with double distilled water and was dried for 6 h at 60°C using a hot oven. The characterization of the rice husk has been reported elsewhere [16].

2.2. Safranin solution

Stock solution of safranin (1,000 mg/L) was prepared by dissolving required amount of safranin powder in distilled water. Experimental aqueous safranin solution of different concentrations (100, 250, and 500 mg/L) were prepared by diluting the stock solution using required amount of distilled water, while pH was adjusted by using dilute hydrochloric acid (HCl) and sodium hydroxide (NaOH).

2.3. Methods of biosorption studies

Continuous flow biosorption experiments were conducted in a glass column of 3 cm internal diameter. Different sets of experiments were conducted with various influent safranin concentrations, different safranin pH and flow rates. Weight of adsorbent, i.e. rice husk was kept constant (5 g) for all the experiments. The experiments were carried out at room temperature. For varying safranin concentrations, 5 g rice husk was packed into a glass column and aqueous safranin at different concentrations, i.e. 100, 250, and 500 mg/L were passed through the column individually using peristaltic pump. For varying pH, again 5 g rice husk was packed and the aqueous safranin with pH 4, 7 (Standard solution) and 10 was passed through the column using peristaltic pump individually. Again for the different flow rate experiments, 5 g rice husk was packed in a column and aqueous safranin solutions were passed at 3.0, 4.0, and 6.0 mL/min by the help of peristaltic pump. Samples were collected at regular interval down-flow direction for all the experiments. The concentration of solution in the effluent was analyzed using a UV/VIS spectrophotometer (Model: Hitachi Brand U-2800) by monitoring the absorbance at a wavelength of 558 nm.

Data presented in this paper are the average values from two replicates and the standard deviation was within 2%.

A three-layer network with a linear transfer function neural network (3:10:1) was designed in this present study. 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 overfitting [18].

3. Results and discussion

Continuous removal of dye experiments were carried out to study the effects of the operational parameters on the performance of the column reactor.

3.1. Effect of concentration on biosorption using packed bed column

For examining the effect of initial concentrations on safranin biosorption, aqueous solution of safranin at different concentrations (100, 250, and 500 mg/L) was passed through rice husk adsorbent bed separately. From experimental results (Fig. 2), it was observed that with an increase of initial safranin concentration, the breakthrough curves were shifted from right to left indicating that with an increase of initial concentration, safranin removal efficiency of the rice husk decreased. The results showed that breakthrough time decreased at higher concentration of safranin and biosorption capacity of rice husk decreased. So the removal of safranin was more efficient at lower initial concentrations, i.e. 100 mg/L. These results also showed that change of concentration gradient effects breakthrough time, saturation and biosorption efficiency. Moreover, as more biosorption sites were

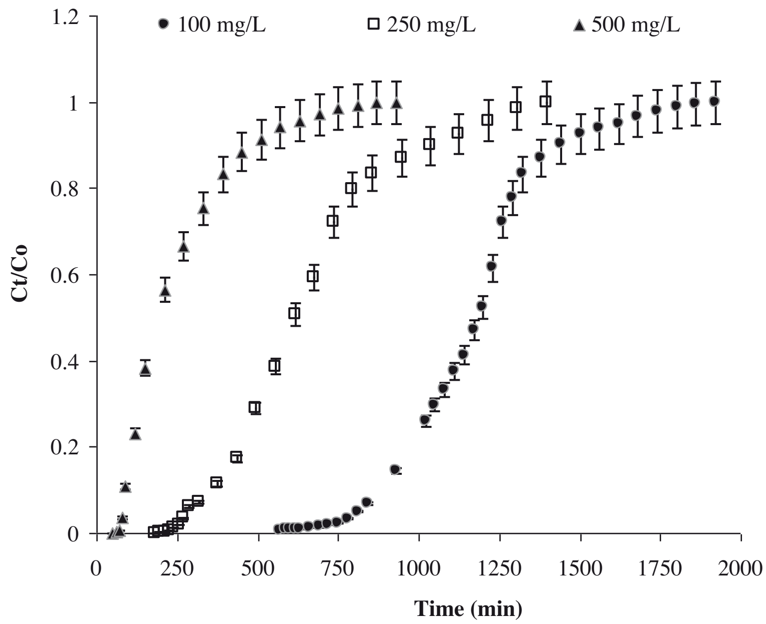

Fig. 2. Effect of concentration on biosorption using packed bed column.

covered at higher safranin concentrations (250 and 500 mg/L), more rice husk got saturated hence breakthrough time was achieved earlier.

3.2. The effect of flow rate on breakthrough curve

It was observed that when the flow rate increased, the breakthrough time decreased, leading to less biosorption efficiency of biosorbent while decreasing the flow rate to lower flow rate, i.e 3.0 mL/min, no distinct changes in removal efficiency were observed (Fig. 3). This was because, at lower rate of influent concentration, safranin had more time to contact with rice husk and therefore resulted in higher removal of safranin. The decreased in breakthrough time with increase in flow rate might be due to the mass transfer phenomenon. At higher flow rate, rate of mass transfer tends to increase. Hence, the amount of dye

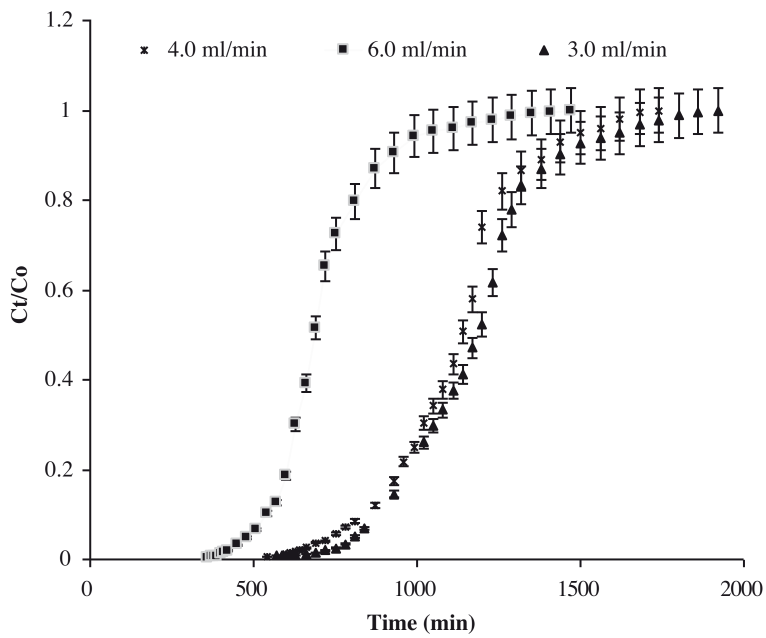

Fig. 3. The effect of flow rate on breakthrough curve.

adsorbed by the adsorbent bed increased with increasing flow rate and mass transfer zone moved fast leading to earlier bed saturation.

3.3. The effect of pH on breakthrough curve

As pH increased to pH 10, breakthrough curves shifted from left to right and there was increase in breakthrough time. At higher pH values, initial breakthrough curve was dispersed and the slope of curve was steeper, while at pH 4 breakthrough curves were sharper. As breakthrough time decreased, adsorbent bed would take less time for saturation and hence less safranin would adsorb (Fig. 4). This showed that biosorption capacity increased at pH 7 which was the standard pH of the safranin solution. Several reasons may be given for this phenomenon. Surface of rice husk may contain a large number of active sites and safranin uptake can be related to active site. Safranin was the cationic dye and at lower pH, hydrogen ions concentrations increased which lead to repulsion between protonated groups of carbon present on rice husk and hydrogen ions in safranin solution, hence it could not able to bind at active sites properly.

3.4. Artificial neural network

A computer programming using MATLAB 7 had been written for training and the testing of the ANN. After a number of training trials, the best neural network model was generated. All algorithms and transfer functions may not be suitable for all processes. To develop the network model, the appropriate training algorithm, transfer function and number of neurons in all layers were very crucial parameters. The maximum number of epochs (training cycles) was chosen by a trial and error approach. Performance goal and minimum performance gradi-

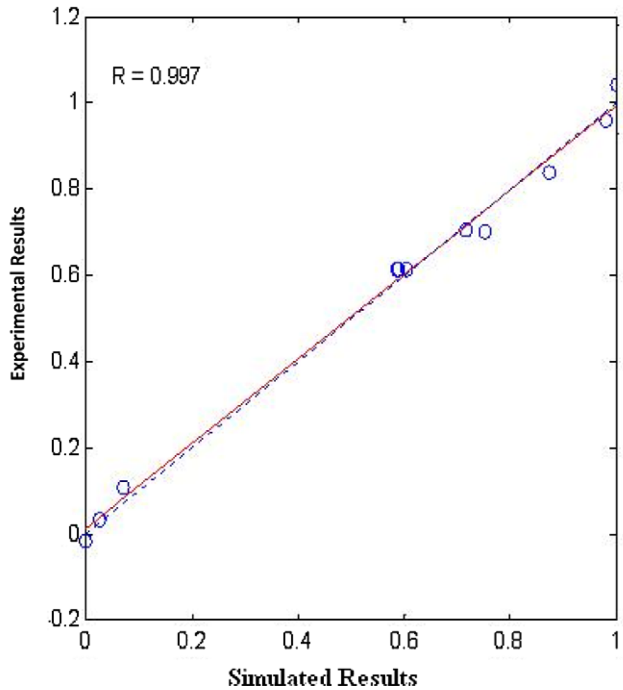

Fig. 5. Comparison of experimental results with simulated results from ANN.

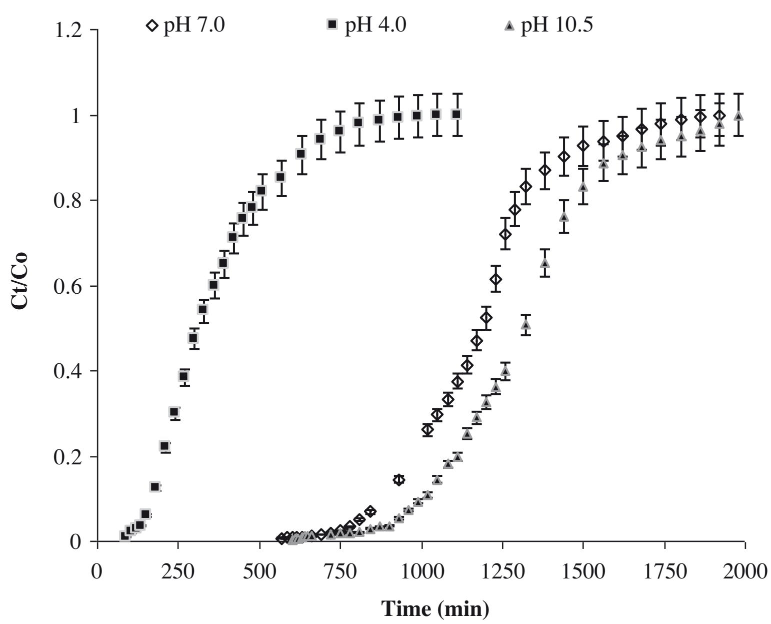

Fig. 4. The effect of pH on breakthrough curve.

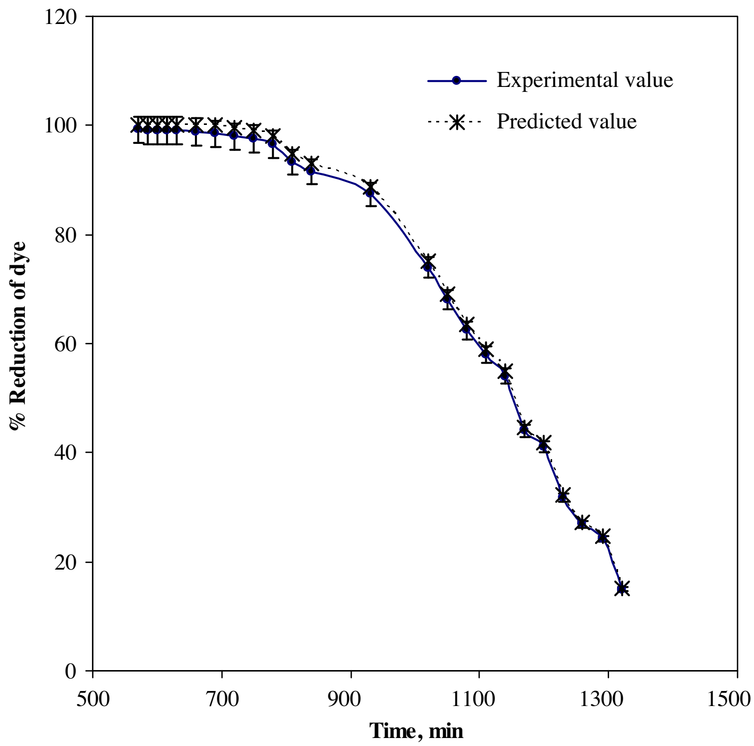

Fig. 6. Simulated results vs. experimental results for the ANN decolorization model using 100 mg/L solution, 10 g or treated rice husk.

ent were set so as to ensure a model with good performance.

After testing, it was observed that 10 neurons produce minimum value of error of the training and validation sets. In the present work, input variables to the feed forward neural network were as follows: pH, flow rate, and time (min). The % removal of dye was chosen the experimental response or output variable. The network, which gave a coefficient of correlation (R) between the model prediction and experimental results near to 1 for training data sets (60), was considered to be suitable and hence selected. The data were normalized and then different algorithms were tested for the decolorization process. Using conjugate gradient backpropagation with Polak-Ribiére update, the values of the correlation coefficient ($R = 0.997$) were observed higher (Fig. 5) than other processes like "Levenberg-Marquardt backpropagation," "scaled conjugate gradient," "resilient backpropagation," and other backpropagation process. Fig. 6 showed a comparison between the calculated and experimental values of the output variables for the test data by using the neural network model. The high correlation coefficient value (0.997) indicated that the neural network reproduced the decolorization in this system within the experimental ranges adopted in the fitting model.

3.5. Validation and simulation of ANN model

Decolorization of dye test was performed at the optimum pH 7 and weight of 10 g for 100 mg/L of safranin dye solution. Fig. 6 compared the simulated result in detail within the experimental results. The agreement between the model predictions and the experimental data was good.

4. Conclusions

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

(a) Rice husk can be used as adsorbent to remove safranin from aqueous solutions.
(b) Biosorption of safranin was dependent on flow rate, inlet concentration, and pH.
(c) The performance of the % removal of dye from solution was successfully predicted by applying a three-layered neural network with 10 neurons in the hidden layer and using the back propagation algorithm.
(d) The proposed model can be used to predict the % reduction of the dye at any time using the packed bed continuous column experiment.

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