ADSORPTION EFFICIENCY FOR THE REMOVAL CONGO RED BY SEAFOOD SHELL USING ANN

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ABSTRACT

In this study, batch adsorption studies were performed for the removal of congo red using seafood sheel. To this purpose was examined varying parameters such as contact time, adsorbent dosage and initial dye concentration. The equilibrium adsorption data were analyzed by Langmuir, Freundlich and Temkin adsorption isotherm models. The experimental data were used to construct an artificial neural network (ANN) model to predict removal of congo red by seafood shell. A three-layer ANN, an input layer with four neurons, a hidden layer with 12 neurons, and an output layer with one neuron is constructed. Different training algorithms were tested on the model to obtain the proper weights and bias values for ANN model. The results show that seafood shell is an efficient sorbent for congo red dye and ANN network, which is easy to implement and is able to model the batch experimental system.

Keywords: Seafood shell, adsorption, congo red, ANN

1. Introduction

Discharge of wastewater into natural streams and rivers from the industries using dyes can color large water bodies, which not only affects aesthetic merit but also reduces light penetration and photosynthesis. Conventional wastewater treatment plants are not suited to remove the dyes due to their non-biodegradable features (Alpat *et al*., 2008; Han, *et al*., 2009; Lian *et al*., 2009; Gong etal., 2009; Jirekar *et al*., 2014). Adsorption is the most popular method for wastewater treatment due to its easy and inexpensive operation, but there are certain problems using activated carbon as adsorbents due to the high cost of use and regeneration. ANN has been widely applied for the modeling and optimization of separation processes related to the extraction of various compounds from different liquid and solid phases (Marchitan *et al*, 2010). The ability of an ANN to learn and generalize the behavior of any complex and non-linear process makes it a powerful modeling tool. The main advantage of ANN models over traditional methods is that they do not require the complex nature of the underlying process. This modelling tool is newly grown and has not been used yet to model the adsorption of congo red by sea food shell. In the present study, we investigated the adsorption of congo red dye on sea food shell. The effects of adsorption time, adsorbent amount, initial dye concentrations on the adsorption were examined. Langmuir, Freundlich and Temkin isotherms were applied to fit the experimental data. Also in this work, experimental data were modeled by ANN to predict removal of dye ions.

2. Materials and methods

2.1. Materials

The sea food shell samples were collected from a popular restaurant in Galicia (Spain). They were repeatedly washed several times with tap water to remove fresh remmants attached to the shell and then were dried in oven at 375 K for 12 h. The shells were crushed and powdered to small grains. The shell partcile size used in the experimental studies were selected 0.177-0.105 mm. The resulting shell powders were finally dried at 103 ^oC for 24 h, and then stored in the desiccator. The X-ray difraction of the seafood shell sample is given Figure1.

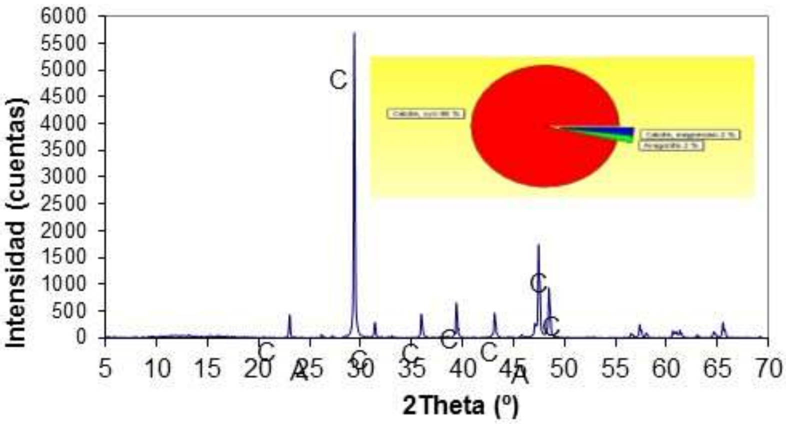

Figure1: X-Ray Difraction of seafood shell sample

2.2. Experimental Study

The stock solution of 1000 mg/L was prepared by dissolving accurately weighed amounts of congo red in separate 1000 mL deionized water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary. Adsorption experiments were performed by shaking 0.2 - 2 g of sea food shell samples in a 50 mL of aqueous solutions of congo red. The adsorption experiments were performed for initial congo red concentrations of 5, 10, 15, 20, 25, 30, 35, 40, 50, and 60 mg/L. The contact time ranges between 5-300 min. The solutions were stirred at 200 rpm for 2 h at 25^{o}C. The concentration of congo red in each aqueous solution was measured on UV/Vis Spectrophotometer by measuring absorbance at λ_{max} of 500 nm.

2.3. Modelling approach

Considering then on linear nature of there alword problems a dynamic recurrent ANN methodology is also considered. The NARX neural network is a dynamic recurrent network that encloses several layers with feedback connections (Chen *et al*., 1990). The reason for choosing a NARX network is that it converges much faster and generalizes better than other network and it is a powerful modelling and validation tool (Çoruh *et al*., 2014).

2.3.1. The NARX model

A NARX network output during training can be mathematically expressed by Eq. (2).

$$y(t) = f(u(t-n_u),...,u(t-1),u(t),y(t-n_y),...,y(t-1) \qquad (2)$$

where *f* is a nonlinear function describing the system behavior (obtained via ANNs), *u(t)* and *y(t)* represent input and output of the network at time *t*, n_u and n_y are the input and output order. While training, the network output is regressed on the actual target values since they are available. These actual target values are feedback to the network during the training process. This essentially renders better training and learning and the network behaves as a feedforward network that is always stable. In an otherwords, when the function *f* can be approximated by a Multilayer Perceptron, there sulting system is called a NARX network (Chen *et al*., 1990; ramesh etal., 1996). In this study, a three-layer NARX network is used to predict the adsorption efficiency. The network, an input layer including recurrent unit with 3 neurons (concantration, adsorbent dosage, time), hidden unit with 10 neurons and an output layer with 1 neurons (removeal), is established.

3. Results and discussion

3.1. Effect of contact time on dye removal

Figure 2 shows the effect of contact time on the removal of congo red dye using sea foo shell. The contact time ranges between 5-240 min. The results showed that the adsorption of congo red dye increases with time rapidly and saturation in about 120 min.

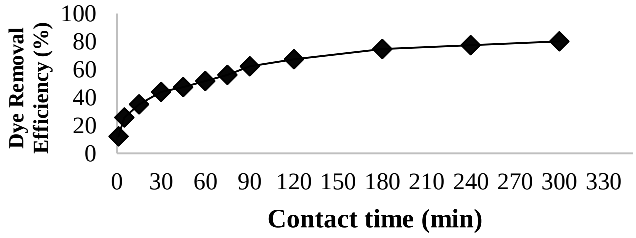

Figure 2: Effect of contact time on congo red adsorption (T: 25ºC, C_o: 20 mg/l, dosage: 20 g/L)

3.2. Effect of sea food shell dosages on dye removal

Figure 3 shows the effect of the amount of sea foos shell dosage on the congo red removal.. The removal efficiencies for 4g/L of sea food shell samples were found to be 13.80 %, but as the sea food shell dosages were increased to 40 g/L, removal efficiencies were found to be 81.45 %. These results showed that removal efficiency increased with increasing dosages of the sea food shell. This may be due to increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent (Maghri *et al*., 2012).

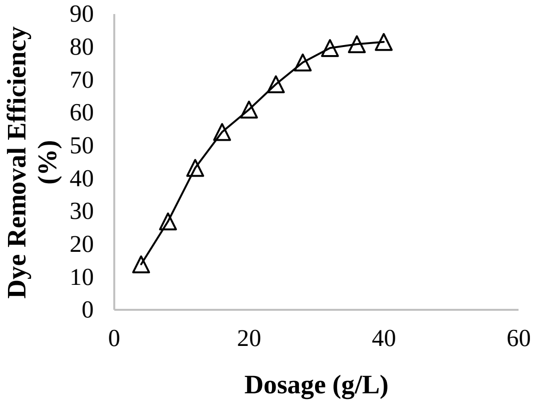

Figure 3: Effect of sea food shell dosages on congo red adsorption (C_o : 20 mg/L, time: 2h)

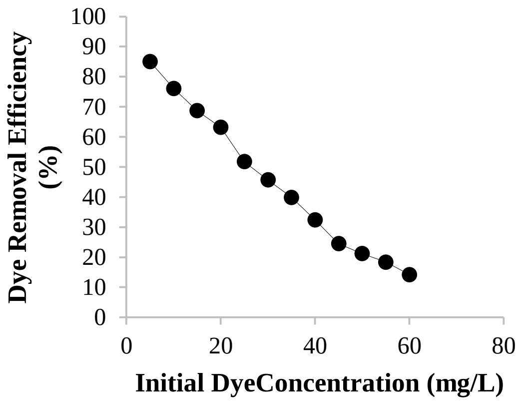

Figure 4: Effect of initial dye concentration on congo red adsorption (Dosage: 20 g/L, time:2h)

3.3. Effect of initial concentration on dye removal

The effect of initial congo red concentration in the range of 5- 60 mg/L on the adsorption was investigated under the specified conditions. Figure 4 shows the adsorption of congo red dye on sea food shell as an initial dye concentration. As it can be seen from Figure 4, increasing the dye concentration led to an decrease in the congo red adsorption by sea food shell.

3.4. Adsorption isotherms models

Several isotherm equations are available. In this research, in order to determine the mechanism of crystal violet adsorption on fly ash the experimental data was applied to the Langmuir, Freundlich and Temkin isotherm equations (Li, 2006; Lin, 2008).

A comparison of coefficient of determination for the Langmuir, Freundlich and Temkin isotherms was given Table 1. The coefficient of determination for the Langmuir isotherm was greater than Freundlich and Temkin isotherms. The values R^2 are calculated to be 0.9858, 0.6758 and 0.6873 for Langmuir, Freundlich and Temkin isotherms, respectively. This suggests that some heterogeneity in the surface or pores of the seafood shell will play a role in dye adsorption. Consequently, the Langmuir isotherm was the most suitable model for the sorption system of congo removal on seafood shell.

Table 1: The parameters for Langmuir, Freundlich and Temkin isotherms

Materials	Langmuir constants			Freundlich constants			Temkin constants		
	q_m (mg/g)	K_L (l/mg)	R^2	K_F (mg/g)	$1/n$ (g/l)	R^2	A (l/g)	B (j/mol)	R^2
Seafood shell	0.54	0.417	0.9858	3.27	0.244	0.6758	21.11	0.102	0.6873

3.5. Modeling with NARX neural network

It can be seen in the literature (Lin *et al*., 1996) that there are several modified NARX neural network models and architectures being used in engineering applications to model or approximate properties. It has been demonstrated that they are well suited for modeling nonlinear systems such as wastewater treatment plants (Su and McAvoy, 1991). In this study a 3 × 10 × 1 NARX neural network with tangent sigmoid transfer function (tan sig) at hidden layer were used. Practically, the typical performance function MSE is used in network training.

$$\mathrm{MSE} = \frac{1}{N}\sum_{i=1}^{N}(t_i - y_i)^2 \tag{3}$$

The network training function updates the weight and bias values according to Back-probagation (BP) algorithm used together with gradient decent momentum (GDM) optimization. It minimizes a combination of squared errors and weights and, then determines the correct combination so as to produce a network which generalizes well. The training parameters and training validation sets used in this paper are listed in Table 2 and Table 3, respectively. Fig. 5 represents the training performance of the network.

Table 2: The NARX Network Training Parameters

Parameter	**Value**
Number of input nodes	3
Delta max	50
Number of output node	1
Learning rule	BP-GDM
Number of epochs	100
Error goal	0.001
Mu	0.00001

Table 3: The range of the data used for NARX Network

Parameter	**Training Data**		**Validation Data**		**Testing Data**	
	Min	**Max**	**Min**	**Max**	**Min**	**Max**
Consantration (mg/L)	5	60	5	60	5	45
Time (sec.)	1	300	1	300	5	180
Adsorbent dosage (g/L)	4	40	4	40	12	40
Removal efficiency (%)	12	86	12	86	24	85

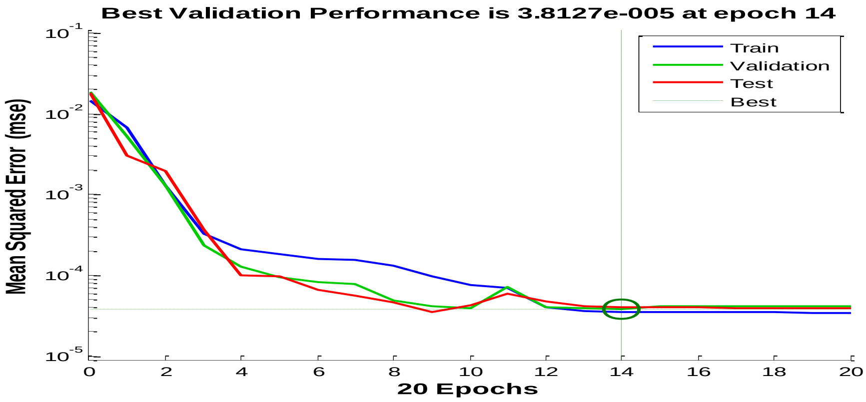

Figure 5: The training performance of the network.

4. Conclusions

From the results of congo red dye adsorption on seafood shell under our experimental conditions, the following conclusions can be obtained:

- Increasing initial congo red dye ions concentration increases significantly the equilibrium adsorption uptake of seafood shell sample. At higher initial concentration, the mass transfer driving force is larger, and hence, this results in more adsorption of dye ions.
- Contact time is very important parameter. It is show that adsorption of the dye is rapid in the beginning and then it becomes constant.
- Langmuir, Freundlich and Temkin isotherm models were applied to the equilibrium data. The adsorption isotherms of dye adsorption on seafood shell can be described well by the Langmuir model.
- ANN is used some experimental data to predict the response of the experiments at new similar conditions for the problem of the removal of dye ions.
- The present study indicate that seafood shell were excellent low-cost adsorbents for the removal of dye congo red for industrial effluents treatment.

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