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Agricultural residue anion exchanger for removal of dyestuff from wastewater using full factorial design

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Abstract

In this study, Remazol Black B dyestuff removal from wastewater by ion exchange was investigated with in a batch system and 2^3 full factorial design was applied. Anion exchanger resin was prepared from agricultural residue (straw) after reaction with epichlorohydrin and dimethylamine in the presence of pyridine and *N*,*N*-dimethylformamide (EDM method). The effect of individual variables and their interactional effects for dyestuff sorption were determined. From the statistical analysis, the most important parameter which is efficient in dyestuff removal can be obtained to be initial concentration of wastewater, which is followed by initial concentration–initial pH of wastewater. The interaction between initial pH and temperature was the least important factor for dyestuff removal from wastewater. A series of isotherm studies were undertaken, and the data evaluated for compliance with the Langmuir and Freundlich isotherm models.

Keywords: Dyestuff; Agricultural residue anion exchanger; Wastewater; Experimental design

1. Introduction

Many industries, such as textiles, leather, paper, plastics, etc., widely use synthetic dyes in order to colour their final products. Most of the dyes are stable to biological degradation. Colour affects the nature of the water and inhibits sunlight penetration into the stream and reduces photosynthetic action [1]. Major generators of coloured wastewater are textile-finishing operations [2]. Because the textile industry uses large volumes of water in wet processing operations and, thereby, generates substantial quantities of wastewater containing large amounts of dissolved dyestuffs and other products, such as dispersing agents, dyebath carriers, salts, emulsifiers, levelling agents and heavy metals [3].

Reactive dyes are commercially a very important class of textile dyes. The vinyl sulfone and chlorotriazine dyes are the most reactive and versatile of the fibre reactive dyes, which mean that the dye molecules actually react with fabric

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molecules. Reactive dyes bind to the textile fibres such as cotton to through covalent bonds [4,5].

Colour removal from textile effluent is a major environmental problem because of the difficulty of treating such waters by conventional physico-chemical and biological treatment methods. In general, colour can be removed from wastewater by chemical and physical methods including adsorption, ion exchange, membrane-filtration process, coagulation–flocculation, oxidation and electrochemical methods [5]. Adsorption is one of the most effective physical processes for the removal of colour and treatment of textile effluents. The most efficient and commonly used adsorbent is activated carbon, but due to its high price it is not used on a great scale. Several researchers have been studying the use of alternative materials, such as coal, bentonite, clay, cotton waste, rice husk [6,7], calcined alunite [8], perlite [9], sepiolite [10], anion exchange resin [11], agricultural wastes such as coir pith [12], maize cob [13], palm fruit bunch particles [14].

Design of experiments is a powerful technique used for discovering a set of process variables (or factors) which are most important to the process and then determine at what levels these factors must be kept to optimize the process performance. Statistical design of experiments is a quick and cost-effective method to understand and optimize any manufacturing processes [15]. The experiments in which the effects of more than one factor on response are investigated are known as full factorial experiments. In a full factorial experiment, both of the (−1) and (+1) levels of every factor are compared with each other and the effects of each of the factor levels on the response are investigated according to the levels of other factors. Doing so with the factorial planning of the experiments, it was possible to investigate simultaneously the effect of all the variables [16].

In this study, batch sorption tests were performed using anion exchanger resin for dyestuff removal from wastewater. Anion exchanger resin was prepared from agricultural residue (straw) after reaction with epichlorohydrin and *N*,*N*-dimethylformamide (EDM method). The experimental work is carried out using a 2^3 full factorial design in order to examine the effects of main parameters (initial dyestuff concentration, initial pH of wastewater, temperature) and their interactions. The Langmuir and Freundlich isotherm models were tested for their applicability.

2. Experimental

2.1. Materials

Adsorbent: Straw was obtained in Eskişehir, Turkey.

Hydrolysed dye solution: The reactive dyestuff was obtained from Eskişehir Sarar Textile Factory. The commercial name is Remazol Black B. It is an anionic dyestuff and has a vinyl sulfone group. The molecular structure of Black B in non-hydrolyzed form is illustrated in Fig. 1.

2.2. Methods

Preparation of the anion exchange resin: The straw was dried in an oven for 5 h at 40°C and milled (Retch SK100) to a size less than 500 μm. Ten grams of dried straw was reacted with epichlorohydrin (100 mL) in 120 mL of *N*,*N*-dimethylformamide (DMF) at 100°C and stirred

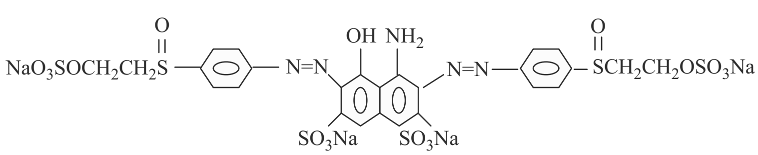

Fig. 1. The molecular structure of Black B in non-hydrolyzed form.

Table 1
Properties of resin adsorbent

Property	Resin adsorbent
BET surface area (m^2/g)	7.12
Adsorption energy (kJ/mol)	17.11
Total pore volume (mL/g)	0.01431
Average pore width (Å)	15

for 1 h. About 40 mL of pyridine was added to the solution to accelerate the rate of wetting and extension of the cellulose polymer. The mixture was stirred for 1 h at 100°C. The reaction product was washed with diluted ethanol at 40°C (ethanol:water = 1:1) in order to remove pyridine salts and epichlorohydrin excess. Amino groups were then introduced into epoxypropyl-by-product after reaction with 50% dimethylamine solution (100 mL) for 3 h at 100°C. The reaction product was again washed with 2 L of 50% ethanol solution, followed by 2 L of NaOH (0.1 M) and 2 L HCl (0.1 M) to remove chemicals and possibly free lignin and extractives. The product was washed with 2 L of distilled water at 50°C, vacuum dried for 24 h at 50°C and used in all experiment [17]. The resin adsorbent employed in the study was analyzed by Quantachrome Autosorb 1-C using a nitrogen adsorption technique and the detailed properties are given in Table 1. The pore size distribution of resin adsorbent is shown in Fig. 2. The pore region of resin adsorbent is displayed in range of 30–360 Å in pore width.

Preparation of the hydrolysed dye solution: In order to work with the dyestuff in the same form as they are found in wastewaters, their preparation follow the typical procedures used in textile dyeing industry.

The appropriate amount of dye (100 mg/L), 30 g/L NaCl, and 1.6 g/L Na_2CO_3 were placed in a beaker and 0.4 mL/L of a 10 M NaOH solution and appropriate volumes of distilled water were added to it. The solution was heated on a stirring plate at 50°C for 1 h. After cooling, pH of the solution was neutralized with 12 M HCl solution, using a pH meter (Inolab). The solution was transferred to a volumetric flask and the volume was completed with distilled water of the same pH [18].

Batch sorption studies: Experiments were conducted in 100 mL Erlenmeyer flasks containing the samples of 0.5 g resin adsorbent with the samples of 50 mL of hydrolysed dye solution. The Erlenmeyer flasks were shaken at 140 rpm

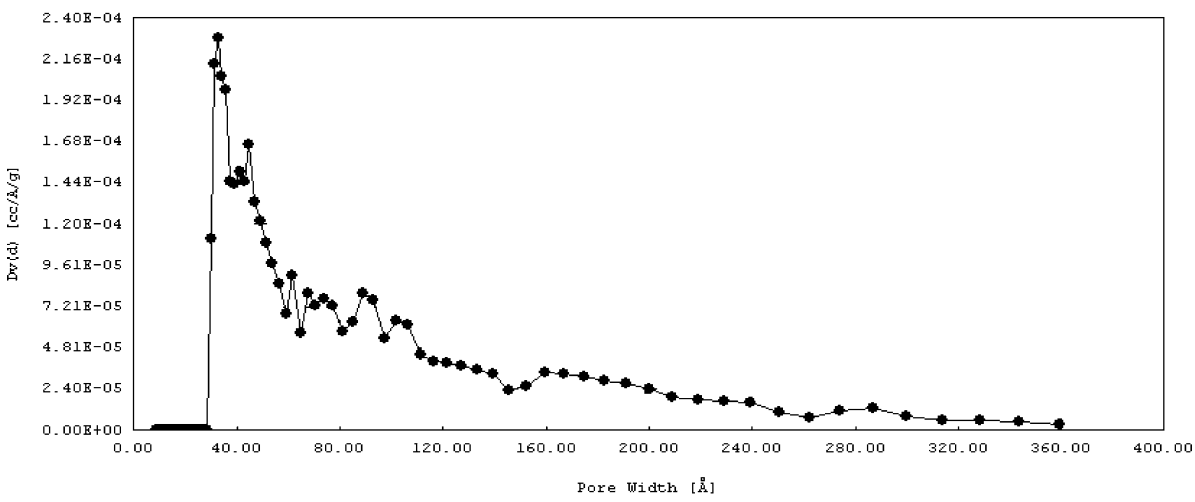

Fig. 2. Pore size distribution of resin adsorbent.

Table 2
Actual and vis-a-vis coded values of parameters

Level of variables	Initial concentration		Initial pH		Temperature	
	Actual (x_1)	Coded (X_1)	Actual (x_2)	Coded (X_2)	Actual (x_3)	Coded (X_3)
First level	30	–	2	–	20	–
Second level	80	+	9	+	50	+

in a temperature-controlled water bath with shaker (Memmert) for 48 h. After sorption, samples were centrifuged and the concentration of dyestuff in the supernatant solution was analysed. All concentrations were measured at 593 nm that corresponds to maximum absorbance, using a spectrophotometer (Shimadzu UV-120-01).

Batch isotherm studies: The samples of 0.5 g of resin adsorbent with the samples of 50 mL of hydrolysed dye solutions having different initial concentration prepared from the stock dye solution were shaken at 140 rpm in a temperature controlled water bath with shaker for 48 h at 20°C. After this period, samples were analysed.

3. Results and discussion

3.1. Statistical analysis

If we call n the number of variables to be tested, in order to measure the effect of all the variables combinations when each variable is tested at a high and a low level, 2^n experiments will be needed [18]. In order to study the variables that define the process, 2^3 factorial experimentations were carried out, in two levels (i.e. high and low). Total sixteen duplicate experiments were done in the factorial design matrix.

In Table 2, x_1, x_2 and x_3 represent the levels of initial concentration, initial pH and temperature, respectively, and X_1, X_2 and X_3 are the corresponding values in coded forms. The experimental matrix along with natural and coded scales is shown in Table 3. The regression equation for the matrix is represented by the following expression [19]:

$$Y_i = b_0 + b_1X_{1i} + b_2X_{2i} + b_3X_{3i} + b_{12}X_{1i}X_{2i} + b_{13}X_{1i}X_{3i} + b_{23}X_{2i}X_{3i} + b_{123}X_{1i}X_{2i}X_{3i} \quad (1)$$

where Y_i is the response (sorbed dyestuff amount), X_{ji} values ($j = 1, 2, 3$; $i = 1, 2, 3,\ldots,16$) indicates

Table 3
Experimental design matrix for dyestuff sorption from hydrolysed dye solution

Run no (i)	Initial concentration		Initial pH		Temperature		Response (Y_i)	
	Actual	Coded (X_1)	Actual	Coded (X_2)	Actual	Coded (X_3)		
1	30	–	2	–	20	–	Y_1	Y_9
2	80	+	2	–	20	–	Y_2	Y_{10}
3	30	–	9	+	20	–	Y_3	Y_{11}
4	80	+	9	+	20	–	Y_4	Y_{12}
5	30	–	2	–	50	+	Y_5	Y_{13}
6	80	+	2	–	50	+	Y_6	Y_{14}
7	30	–	9	+	50	+	Y_7	Y_{15}
8	80	+	9	+	50	+	Y_8	Y_{16}

Table 4
The design matrix and the results for dyestuff sorption from hydrolysed dye solution

Trial	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Y sorbed dyestuff amount (mg/L)	Y sorbed dyestuff amount (mg/L)	Y average sorbed dyestuff amount (mg/L)
1	–	–	–	+	+	+	–	2.584	2.584	2.584
2	+	–	–	–	–	+	+	2.344	2.317	2.330
3	–	+	–	–	+	–	+	1.117	1.117	1.117
4	+	+	–	+	–	–	–	3.117	2.957	3.037
5	–	–	+	+	–	–	+	2.717	2.744	2.730
6	+	–	+	–	+	–	–	3.09	3.09	3.09
7	–	+	+	–	–	+	–	1.517	1.517	1.517
8	+	+	+	+	+	+	+	3.864	4.184	4.024

the corresponding parameter in their coded forms. The coefficient b_0 gives the average value of the results obtained for the sorbed dyestuff amount, the linear coefficients, b_1, b_2 and b_3 show the effect of initial concentration, initial pH and temperature, respectively. Coefficients, $b_{12,}$ b_{13}, b_{23} show the interacting effects of two variables at a time and b_{123} shows the interacting effect of all three variables taken at a time.

The design matrix and the results for dyestuff sorption from hydrolysed dye solution were shown in Table 4. The values of regression coefficients obtained are given in Table 5.

Table 5
Values of model coefficients

Main and interaction coefficients	Values
b_0	2.5537
b_1	0.5666
b_2	–0.13
b_3	0.2866
b_{12}	0.5401
b_{13}	0.15
b_{23}	0.0601
b_{123}	–0.0032

The final regression equation, after putting values of all coefficients, is as follows:

$$Y = 2.5537 + 0.5666X_1 - 0.13X_2 + 0.2866X_3 + 0.5401X_1X_2 + 0.15X_1X_3 + 0.0601X_2X_3 - 0.0032X_1X_2X_3 \quad (2)$$

Eq. (2) shows the effect of individual variables and interactional effects for dyestuff sorption from hydrolysed dye solution. According to this equation, the initial concentration and temperature have a positive effect, while the initial pH has a negative effect on the dyestuff removal in the range of variation of each variable selected for the present study.

In order to determine the importance of each factor, the Fisher's test was employed. The F ratios were computed according to variance analysis of data. F ratios and decisions were given in Table 6. Comparing the calculated F values with Fisher's F values [$F_{0.1}$(1,8)]:3.46; [$F_{0.05}$(1,8):5.32]; [$F_{0.01}$(1,8):11.26] for 90%, 95% and 99% confidence levels (probability levels: $\alpha = 0.1$; $\alpha = 0.05$; $\alpha = 0.01$, respectively), it can be seen that $X_1X_2X_3$ interaction was ineffective at 90% and 95% confidence level moreover X_2X_3 and $X_1X_2X_3$ interactions were ineffective at 99% confidence level for dyestuff sorption from hydrolysed dye

Table 6
Analysis of variance F ratios and decisions

Sources of variation	F ratio	Decision $\alpha = 0.1$	Decision $\alpha = 0.05$	Decision $\alpha = 0.01$
X_1	640.12	Effective	Effective	Effective
X_2	33.69	Effective	Effective	Effective
X_3	163.8	Effective	Effective	Effective
X_1X_2	581.64	Effective	Effective	Effective
X_1X_3	44.86	Effective	Effective	Effective
X_2X_3	7.20	Effective	Effective	Ineffective
$X_1X_2X_3$	0.02	Ineffective	Ineffective	Ineffective

solution. The following final model for sorption of dyestuff was adequate at the 90% and 95% confidence level:

$$Y = 2.5537 + 0.5666X_1 - 0.13X_2 + 0.2866X_3 + 0.5401X_1X_2 + 0.15X_1X_3 + 0.0601X_2X_3 \quad (3)$$

However, at 99% confidence level the equation can be written as the following form:

$$Y = 2.5537 + 0.5666X_1 - 0.13X_2 + 0.2866X_3 + 0.5401X_1X_2 + 0.15X_1X_3 \quad (4)$$

According to the F values the most effective parameter in the sorption process was initial dyestuff concentration, which is followed by the interaction between initial dyestuff concentration and initial pH. The interaction between initial pH and temperature was the least influencing parameter.

3.2. Adsorption isotherms

The Langmuir equation (5) was applied for the sorption equilibrium of resin [20]:

$$1/q_e = 1/Q_o + 1/bQ_oC_e \quad (5)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of dyestuff sorbed at equilibrium (mg/g), Q_o and b are Langmuir constants related to sorption capacity and energy of sorption, respectively.

The Freundlich equation is represented by the equation:

$$\log q_e = \log K + (1/n) \log C_e \quad (6)$$

where K (mg/g)(L/mg)$^{1/n}$ is the Freundlich capacity constant, n is the Freundlich intensity constant, q_e is the amount of dyestuff sorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L).

Experimental data were not fitted to the Langmuir isotherm and not shown. The constants of Langmuir and Freundlich equation were given in Table 7. Negative values for the Langmuir isotherm constants indicate the inadequacy of the isotherm model to explain the sorption process, since these constants are indicative of the surface-binding energy and monolayer coverage [10].

Table 7
Langmuir and Freundlich constants for dyestuff sorption from hydrolysed dye solution

Langmuir isotherm			Freundlich isotherm		
Q_o (mg/g)	b (L/mg)	R^2	K (mg/g)(mg/L)^n	n	R^2
−15.55	−0.128	0.942	2.492	0.948	0.957

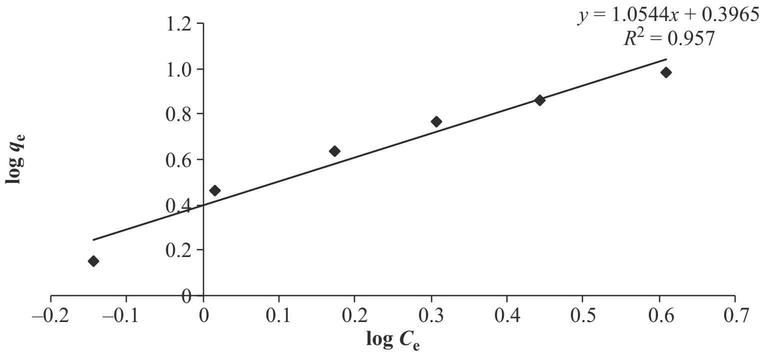

Fig. 3. Freundlich plots for dyestuff sorption from hydrolysed dye solution.

A plot of linear Freundlich equations log q_e vs. log C_e are shown in Fig. 3. The Freundlich model would be applicable for dyestuff sorption from hydrolysed dye solution.

4. Conclusions

Due to the large availability, low cost and biodegradability of agricultural residue (straw), the process of converting agricultural residue into ion exchanger has been investigated for dyestuff sorption from hydrolysed dye solution in this study. Sorption capacity of resin adsorbent was correlated to their mesopore surface area since mesopores (diameter between 20 and 500 Å) are more predominant in this material. From the statistical analysis, it can be concluded that sorption was favoured by increase in initial concentration and temperature and unfavoured by an increase initial pH. The sorption equilibrium data were analysed using Langmuir and Freundlich isotherm models and results have shown that sorption behaviour of Remazol Black B by resin adsorbent could be described by Freundlich model.

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