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Decolourization of Acid Orange 7 Dye from Aqueous Solution by Adsorption on NaOH Treated Eggshells in Continuous Fixed Bed Reactor Application using Response Surface Methodology: Optimization by Box–Behnken Design.

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Abstract

NaOH Treated Eggshells (TES) was investigated for the removal of Acid Orange 7 (AO7) from aqueous solution using the continuous method was modeled by response surface methodology (RSM) and was optimized using Box–Behnken design (BBD). Fixed bed adsorption has become a frequently used in wastewater treatment processes. Various low cost adsorbents have been studied for their applicability in treatment of different types of effluents. In this work, the intention of the study was to explore the efficacy and feasibility for azo dye, AO7 adsorption onto fixed bed column of TES. The effect of operating parameters such as flow rate, initial dye concentration, and bed height were exploited in this study. The studies confirmed that the breakthrough curves were dependent on flow rate, initial dye concentration solution of AO7 and bed depth. The precision of the equation obtained by Box–Behnken design (BBD) utility for modeling and optimization by response surface methodology RSM was confirmed by the analysis of variance (ANOVA) and calculation of correlation coefficient relating the predicted and the experimental values of removal of dye. The results revealed a good agreement between the predicted values, as obtained by the model, and the experimental values for AO7. The optimum conditions proposed by Box–Behnken design (BBD) to reach the maximum dye removal through adsorption process. Under the optimum conditions, the removal efficiency of AO7 was 89.89%.The application of response surface methodology in order to optimize using Box–Behnken design (BBD). The research on modeling adsorption by RSM has been highly developed and The TES was shown to be suitable adsorbent for adsorption of AO7 using fixed-bed adsorption column.

Keywords: *Adsorption, acid orange 7, bed depth, fixed-bed column, wastewater, dye Removal, TES, RSM, BBD, optimization, modeling.*

1. Introduction

Textile industry is very greedy in water and thus, [1] generates an important quantity of effluents highly charged with pollutants which constitute a serious threat for the environment. Consequently, these effluents require a preliminary treatment in order to decrease their polluting load before being rejected into the natural environnement. It is considered that the textile industry is responsible for 15% to 20% of the global water pollution [2]. Among the discharged pollutants, organic dyes of are not only responsible for an esthetic pollution of water, but also count among the most toxic compounds, even at low concentration[3]. Today, about 10,000 different dyes are produced worldwide, for a global production of 7.105 tons per year. Dye effluents discharged from the dyestuff manufacturing, dyeing, printing and textile industries represent a serious problem all over the world. They contain different types of synthetic dyes which are known to be a major source of environmental pollution in terms of both the volume of dye discharged and the effluent composition [4]. Most of these dyes are toxic, mutagenic and carcinogenic [5]. From an environmental point of view, the removal of synthetic dyes is of great concern. Natural colorants have been used since prehistoric times. In 1856, Perkin's discovery of mauve marked the start of the modern synthetic dye industry. In the last 145 years, several million different colored compounds have been synthesized, with ca. 15,000 colorants over time, produced on a commercial scale. The annual worldwide production of dyes is approximated at 800,000 tones and about 50% of these are azo dyes [6].Anionic azo dyes contain many compounds from the most varied classes of dyes, which exhibit characteristic differences in structure (e.g. azoic, antraquinone, triphenylmethane, and nitro dyes) possessing water-solubilizing, ionic substituents as a common feature. AO7 has been reported to induce bladder tumors. It can also easily undergo enzymatic breakdown along with reduction and cleavage to give aromatic amines, which, upon exposure, can cause methemoglobinemia. The intermediate amines thus formed also tend to oxidize the heme iron of hemoglobin from Fe(II) to Fe(III) and block oxygen binding, resulting in some characteristic symptoms such as cyanosis of lip and nose, weakness, and dizziness. When AO7 enters the human body through ingestion, it is considered genotoxic; however, if some impurities, such as aromatic amines, are present, it shows mutagenic activity. Due to large amounts of AO7 consumption, it is essential to have a proper method to remove this dye from wastewater in order to avoid potential threat for the environment. As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, also AO7 does not decompose biologically, and resists to light irradiation and chemical oxidation. In general, chemical and physical discoloration methods have been used for dye removal from wastewaters [7] such as coagulation and flocculation processes which are largely used for wastewater treatment in the textile industries. However application of these methods is somewhat restricted due to some limitations such as operational costs, formation of hazardous by-products, intensive energy requirement and limited adaptability to a wide range of effluents and these processes are not always effective for dye removal. Moreover, they can sometimes generate secondary pollution due to the excessive use of chemical reagents. However, the adsorption of this dye on efficient solid supports is considered as a simple and economical method for its removal from water and wastewater providing sludge-free cleaning operations and many studies have been conducted to find suitable adsorbents to reduce AO7 concentration [8]. Because a number of bioadsorbent have been used quite efficiently for the removal of specific organic compounds [9], this study investigates the adsorption characteristics of AO7 dye on the TES. The present work deals with the estimation of the adsorption properties of TES that constitutes a possible source of adsorbent that could be used for the removal of dyes from textile wastewater and, more generally, in industrial wastewater . The focus of the present study was to assess the potentiality of TES as an adsorbent for the dye AO7 from aqueous solution as an ideal alternative to the current expensive methods of removing dyes from wastewater using the treatment of a synthetic textile effluent containing an acid dye,AO7, as the adsorbate. The TES will be, first, characterized in terms of chemical composition, structure and texture [10].

Adsorption studies were carried out under various parameters such as flow rate, initial dye concentration, and bed height. The continuous adsorption in fixed-bed column is often desired from industrial point of view. It is simple to operate and can be scaled-up from a laboratory process [11]. A continuous packed bed adsorbed does not run under equilibrium conditions and the effect of flow condition (hydrodynamics) at any cross-section in the column affects the flow behavior downstream. Breakthrough determines bed height and the operating life span of the bed and regeneration times [12]. Adsorption in fixed-bed columns using activated carbon has been widely used in industrial processes for the removal of contaminants from aqueous textile industry effluents, since it does not require the addition of chemical compounds in the separation process [13]. Adsorption in a fixed bed column can be used continuously under high effluent flow rates and it has been used in many pollution control processes such as removal of ions by an adsorbent bed or removal of toxic organic compounds by carbon adsorption [14]. In this study, the TES has been tested for removal of aqueous solutions. In this paper, TES is used to remove azo dye (AO7) from aqueous solution through column studies. The objective of this study was to investigate the adsorption potential of AO7 onto TES fixed-bed. The important design parameters such as inlet concentration of dye solution, fluid flow rate and column bed height [15] were investigated using a laboratory scale fixed-bed column. The breakthrough curves for the adsorption of AO7 were analyzed at different flow rates, bed heights, and initial concentrations. In application of adsorption process on an industrial scale, it is crucial to improve process efficiency, reduce operational cost and time to minimum and take into account the most important factors, what can be achieved by applying the optimization techniques such as response surface methodology (RSM). Determining the effect of a single factor on the efficiency of the process is relatively simple. It is definitely more of a challenge to assess the effect of several parameters at once. Response surface methodology based on experimental data makes easier to plan the entire modeling process by reducing the number of experiments to the necessary minimum, and allows a mathematical equation to fit the experimental results, which is required for the process optimization [16]. In general, RSM is a mathematical technique applied in the progression of an appropriate functional relationship between the response and the related input variables. The structure of this relationship is unknown, but can be approximated by low-order polynomials (the most common are first and second-degree polynomial models). This methodology helps to determine the most important parameters and its main, quadratic effect or interactions which influence the response. RSM has been extensively used as an optimization, prediction and interpretation technique for factorial designs [17]. RSM is a useful tool for the modeling and analysis of systems in which response of interest depends on several factors and the relationship between independent and dependent variables in a system is unknown. RSM modeling has been successfully applied for biosorption in the past few years. RSM was selected as an effective statistical and mathematical approach in order to recognize the efficiency of an experimental system [18]. Various parameters were simultaneously appraised using RSM with a minimum number of experiments. Therefore, a study conducted by RSM can reduce the cost, decrease process variability and need less time in comparison to the conventional one-factor-at-a-time statistical strategy [19]. The present study investigates the application of response surface methodology approaches to predict adsorption capacity of TES for the removal of AO7 from aqueous solution. The effect of various operational parameters, including the initial dye concentration, flow rate, and bed height on the adsorption of AO7 were examined and modeled by response surface methodology RSM. The Box–Behnken design BBD and the full factorial design FFD with structure optimized by RSM models were compared in terms of predictability and accuracy of fit, taking into account their implementations and limitations. Optimization of BBD by response surface method is completely novel approach of RSM approximation application in chemical processes. The main objectives of this work are to investigate the individual and the interactive effects of three operating parameters, mainly: initial dye concentration, flow rate, and bed height on the adsorption of AO7 in a fixed bed reactor by using a BBD [20]. Conclusions as a

result, the adsorptions of dyes onto AC were commonly investigated using traditional methods, but the AO7 adsorptions based onto TES have not been studied. Moreover, Box-Behnken design (BBD) is rarely used for the AO7 removal from aqueous solution. Then in the text, the adsorptions of dye onto TES have been investigated in batch systems. The main effects and interaction effects between process variables on the dye adsorptions were analyzed based on the BBD. Their maximum adsorption capacities have been optimized using RSM method. In addition, their adsorption isotherm and kinetics were also discussed [21].

2. Materials and methods

2.1. Adsorbent: Preparation and Characterization of Eggshell Powder

Eggshell, were collected from houses and local restaurants. To remove impurity and adhering dirt, it were first washed several times in tap water, and then boiled in distilled water. The washed materials were then dried at 100°C for 24 h in the dry oven. The dried eggshells were crushed and sieve to recover the particle size powders between 0.250 and 0.711 mm. Finally, the sieved material was treated with sodium hydroxide NaOH 2N for 2 h in a flask heated with reflux, and then the sample was washed until neutralization and dried in the oven at 100°C for 24 h. To remove moisture before each use, we put the resulting adsorbent TES in a dryer. Fourier Transform Infrared (FTIR) analysis was applied to determine the surface functional groups, using FTIR spectrophotometer (SCO TECH SP-FTIR-1). The spectra were recorded from 4000 to 400 cm^{-1} [22] and was characterized X ray diffraction (DRX).

2.1. Adsorbate Preparation

The dye chosen in this study is the AO7, also called Acid Orange II (Sigma-Aldrich), belonging to the family of the anionic dyes. It is representative of a textile type of pollution. Its main features are represented in Table1; its structural formula is shown in **Figure** 1. Stock solutions were prepared by dissolving requisite quantity of dye without further purification in distilled water, and the concentrations used were obtained by dilution of the stock solution. The pH was adjusted to a given value by addition of HCl (1N) or NaOH (1N) [23].

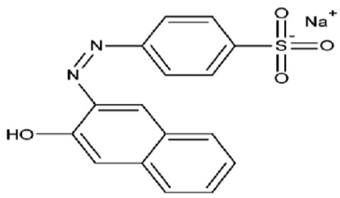

Figure. 1 Molecular structure of Acid Orange 7

TABLE **1: main** characteristics of the basic dye acid orange ii

Dye	Acid Orange 7
Molecular formula	C16H11N2NaO4S
Molecular weight [g/mol]	350.33
Molecular volume (Å/molecule)	231.95
Molecular surface area (Å/molecule)	279.02
Width (Å)	7.3
Length (Å)	13.6
Depth (Å)	2.3
λ (nm)	485
pKa	pK1 11.4; pK2 1.0

3.1 sorption experiments in fixed-bed technique

3.1. Experimental Procedures

The fixed bed experiments were carried out in a glass column of 2 cm internal diameter, 30 cm of the length height and three sampling points at 5 cm intervals. A known quantity of the prepared activated carbon TES was packed in the column to yield the desired bed height of the adsorbent 50, 100 and 150 mm (equivalent to 3.5, 7 and 10, 5 g of activated carbon) with a layer of glass wool at the bottom. Distilled water was passed through the column in order to remove impurities from the adsorbent. Three flow rates (2, 4 and 6 mL/min) were pumped to the top of the packed column by using peristaltic pump (name) with different initial dye concentrations (5, 30, 50, 80 mg/L). The samples of AO7 solutions at the outlet of the column were taken at regular time intervals and the concentration of dye was measured using an UV–visible spectrophotometer (Neptune Chemical Pump) at wavelength of 485 nm. Fixed bed studies were terminated when the column reached exhaustion. The experiments were carried out at temperature of 301 K (28 ±1 ◦C) without any pH adjustment [24]. The schematic diagram of fixed bed column used in adsorption study is shown in **Figure**. 2. The experimental detail is given in Table2. Briefly, the experiment was carried out by passing through column (packed with 21 g of TES) with controlled flow rate and pH. The pH of influent was maintained by 1.0 N HCl or 1.0 N NaOH during experiments.

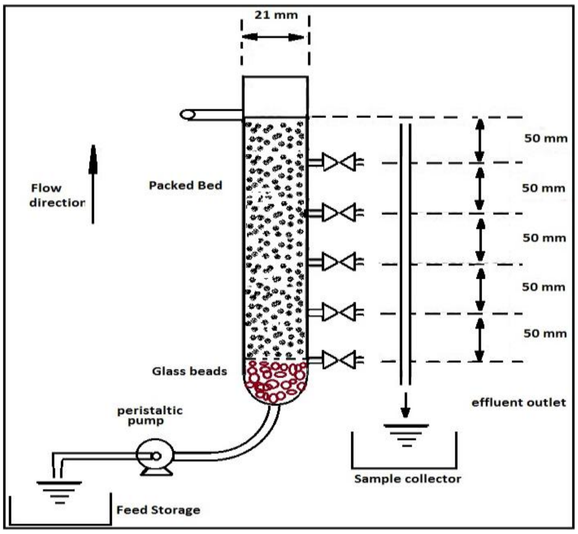

Figure. 2 Schematic diagram of fixed bed column used in adsorption study of AO7 onto TES.

TABLE **2:** experimental details for column adsorption of ao7 onto tes

SYSTEM	Flow rate(mL/min)	[AO7](ppm)	Bed height(cm)
Flow rate	2, 4 and 6	30	15
Initial Concentration	15	10, 30 and 50	15
Bed height	15	30	5, 10 and 15

3.2. Analysis of Fixed-Bed Column Data

For good design of fixed bed system, it is important to predict the breakthrough curve for effluent parameters. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption fixed-bed column. The breakthrough curves show the loading behavior of dye to be removed from solution in a fixed-bed column. It is usually expressed in terms of adsorbed dye concentration (Cad), inlet AO7 concentration (C0), outletAO7 concentration (Ct) or normalized concentration defined as the ratio of outlet AO7 concentration to inlet AO7 concentration (Ct/C0) as a function of time for a given bed height [25]. To design a column adsorption process, it is necessary to predict the breakthrough curve or concentration-like profile and adsorption capacity of the adsorbent for the selected adsorbate under the given set of operating conditions. It is also important for determining maximum sorption column capacity, a significant parameter for any sorption system.

3.3. Removal efficiency

The dye removal percentage using TES adsorbent was calculated from:

$$Re(\%) = 100 \times (C_0 - C_e)/C_0 \qquad (1)$$

Where C_0 is the initial concentration of dye in solution (mg/L), and C_e is the final dye concentration in aqueous solution after phase separation (mg/L).

3.4. Response surface methodology

Response surface methodology is an experimental technique used for predicting and modeling complicated relation between independent factors and one or more responses. In this study, response surface methodology was applied to optimize the adsorption of Acid orange 7 by TES. Experiments were performed using Box– Behnken design (BBD). The second-order polynomial equation extended with additional cubic effects was employed as an objective function. The second order model is usually sufficient for the modeling and optimization on the basis of designs, however third order and higher effects are sometimes important, especially in order to achieve better fit and insignificant lack-of-fit. For instance, Box–Behnken design was created to estimate the second-order model, however there may be situations in which non- random portion of this model provides an inadequate representation of the true mean response, an indication of lack-of-fit of the second- order model. Thus, in this study some third order model terms were added to the second order polynomial equation. Accuracy of model fitting was evaluated by means of ANOVA. All calculations were performed in Stat graphics [26].

3.5. Box–Behnken design

In this study, the BBD design methodology was employed to optimize the operational variables and was used to predict impacts of respective parameters on the adsorption process. Among many factors affecting the adsorption process, three process variables , i.e. initial AO7 dye concentration (X1), bed height (X2) and flow rate (X3) were selected and were considered as independent variables and the removal of dye (Y) as a response was defined and modeled. BBD contains set of 15 experiment runs whose values of each factor with three levels (low, medium, high), being is coded to standard values (-1, 0,+1) in the appropriate range and levels of parameters were listed in (Table 3).

The parameters (Xi) were coded as xi via Eq. (2):

$$x_i = \frac{(X_i - X_0)}{\delta X} \qquad (2)$$

where X0 and dX are the values of Xi at the center point and step change, respectively . The second-order polynomial response equation was used to probe the interaction between the dependent and independent variables. The removal (%) of dye is selected as the response for the combination of independent variables, Subsequently experimental data was fitted to the second order polynomial model extended with additional cubic interaction effects (Eq. (3)) using the least square procedure as follows:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{22}x_2^2 + b_{23}x_2x_3 + b_{33}x_3^2 + e \quad (3)$$

where y is the predicted response associated with each factor level combination; The coefficients in the equation represent: the intercept (b_0) is constant, the main (b1,b2, b3) are linear effect, quadratic effect (b11, b22, b33) and interactions (b12, b23, b13) effects, respectively; xi and xj are the coded values of independent variables; and e is the residual error. Validation of the model fit and significance analysis of variables were performed using analysis of variance (ANOVA). The results were analyzed by analysis of variance (ANOVA) and a calculation correlation coefficient (R2) between predicted and experimental points [27]. Nonlinear x2 analysis is a useful method, which can compare the experimental and model predicted data. And it is estimated using the following equation:

$$X^2 = \frac{\sum (Y_{exp} - Y_{pred})}{Y_{pred}} \quad (4)$$

Where Y_{exp}. (%) and Y_{pred}. (%) are the adsorption removal of AO7 onto TES by experiment determined and model predicted.

3.6. Model validation and optimization

Validation set was employed to explore the predication performance of the developed model. Moreover, the optimization process variables were obtained for the AO7system based on the D-optimality index in the Stat graphics software. The least square method was used to calculate the model coefficients through Eq. (3) using the Stat graphics software (version 4.2). To evaluate the statistical significance, ANOVA analysis (R^2, adjusted R^2, F-test and t-test), normal plots and residuals analysis were employed. The significance of the regression coefficients was appraised by the F and Student’s t tests at the confidence level of 95%.

3.7. Experimental design

To determine the optimal conditions for the main parameters, a Box–Behnkendesign (BBD) was applied. For the adsorption process, significant variables, such as the initial dye concentration, flow rate, and bed height were regarded as the independent variables and designated as X1–X3, respectively. The dye concentration (X1) range of 10–50 mg/ L, flow rate (X2) range of 2–6 ml/min, bed height (X3) of 5–20 cm were chosen as given in Table 3.

TABLE **3:** independent process variables and their experimental levels used for box–behneken design (bbd) .

Variables, unit	Factors	Levels		
	X	-1	0	+1
Initial dye concentrations of AO7 (mg/L)	X_1	10	30	50
bed height (cm)	X_2	5	10	15
flow rate (ml/min)	X_3	2	4	6

3.8. Selection of the significant parameters

The Box–Behnken design consists of 15 experimental points. The experimental conditions and the adsorption capacity obtained for each point set by the Box– Behnken design are shown in Table 3 (1–11), together with the three central point repetitions (12–15). The relationship between responses and processed variables was examined for the response approximation function (Y) using Eq. (1), following by the statistical analysis of the model obtained.

The most significant process variables were identified by Box–Behnkendesign (BBD) experimental design. The advantage of this design is its ability to investigate of a large number of factors in a relatively low number of experimental runs. In this study 15 run BB design with 3 factors, including AO7 dye concentration (X1), flow rate (X2) and bed height (X3) was considered. Each independent variable was tested at two levels, high and low, which were -1 and +1, respectively. All experiments were conducted in duplicate and the average values of removal dye were taken as a response (Y). The matrix design is shown in Table 4. On the basis of BBD three the most significant parameters were chosen for further investigation (modeling and optimization by RSM).

TABLE **4:** box–behnken design matrix with coded and uncoded values of the independent variables influencing adsorption of ao7 by tes with experimental and predicted values of the response.

	Coded values (uncoded values)			Removal dye Y [(%)]	
Experimental run No.	X1 [ppm]	X2 [cm]	X3 [ml/min]	Experimental values	Predicted responses
1	1 (50)	0 (10)	-1 (2)	56	56,950034
2	0 (30)	0 (10)	0 (2)	54,2	54,2667
3	0 (30)	0 (10)	0 (2)	54,3	54,2667
4	0 (30)	-1 (5)	1 (6)	52	52,700037
5	0 (30)	-1 (5)	-1 (2)	51,6	51,400037
6	-1 (10)	0 (10)	1 (6)	56	55,050034
7	0 (30)	1 (15)	1 (6)	51,8	52,000037
8	1 (50)	0 (10)	1 (6)	54,8	54,850034
9	-1 (10)	1 (15)	0 (2)	50,2	50,950037
10	1 (50)	1 (15)	0 (2)	55	54,750037
11	-1 (10)	-1 (5)	0 (4)	52	52,250037
12	-1 (10)	0 (10)	-1 (2)	53	52,950034
13	0 (30)	1 (15)	-1 (2)	54	53,300037
14	0 (30)	0 (10)	0 (2)	54,3	54,2667
15	1 (50)	-1 (5)	0 (2)	53	52,250037

3.9. Analysis of variance (ANOVA)

ANOVA expounds every variation in the statistically obtained model and importance of each model parameters. The significance of the model was evaluated by F-test for a confidence level of 95% as well as lack-of-fit test. In general, the greater the F-value and the smaller the p-value, the more significant is a model. Moreover, effects and their importance in the model were investigated adapting t-test and p-value. Usually, the larger the t-value and lower

probability p-value ($p < 95\%$), the model parameter is considered as significant [30].The sum of squares, degree of freedom and mean squares were also determined for the model and error.

4. Results and Discussions

4.1 FTIR and DRX Spectral Analysis

Analysis of FT-IR spectrum of TES biosorbent in the range of 400 – 4000 cm-1 as shown in **Figure**.3 shows some bands at 3520 cm-1 that are assigned to –OH stretching mode vibrations due to inter-and intra-molecular hydrogen bonding of polymeric compounds. The peak at 1638cm-1 is due to asymmetric stretching vibrations of C=O and the peak observed at 1525cm-1 can be assigned to aromatic compound group and the stretching and folding of carbonate group has been assigned to peaks at 1500 cm-1 and 865 cm-1.The X-ray diffraction of our biosorbent is shown in **Figure**.4.The **Figure** shows a main peak appeared at 2Theta = 30. In addition, this spectrum shows several other small peaks at 2Theta = 22.78, 35.88, 40.28, 48, 49, 54.78, 62.58, 50.858, 57.488, 60.748 and 62. This spectrum confirms the presence of calcite.

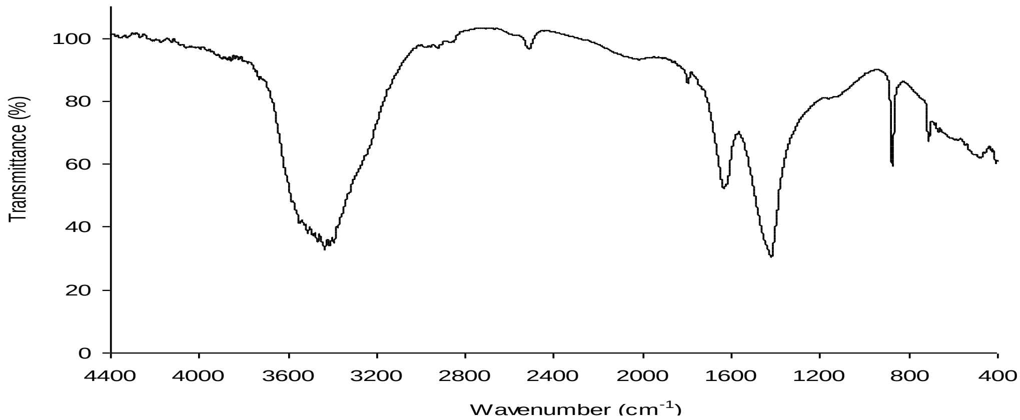

Figure.3. FTIR spectra of TES

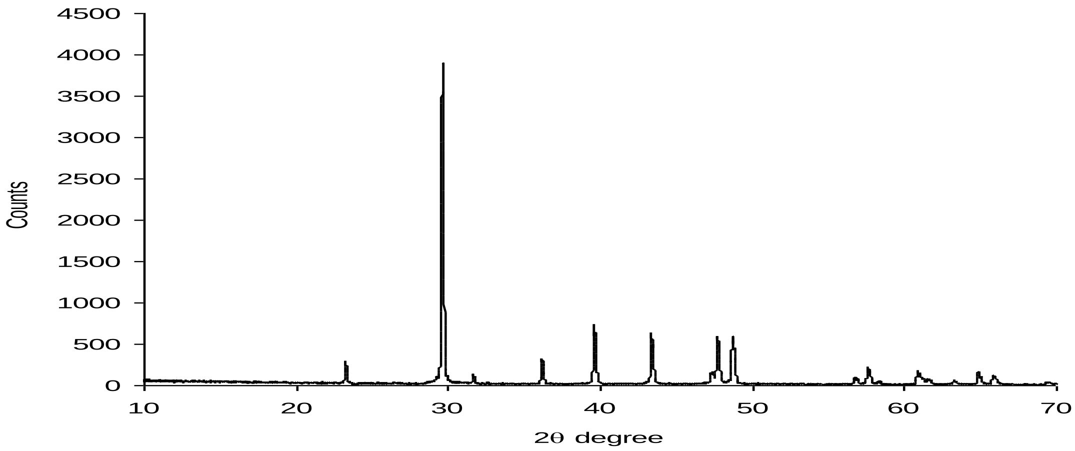

Figure.4 X-ray diffraction pattern of TES

4.2. Breakthrough curves for AO7 adsorption column by TES

A. Effect of Initial Dye Concentration

The variable effect of inlet AO7 concentration from 5 to 80 mg/L on the adsorption of AO7 in the TES containing column was studied at 10 cm constant adsorbent bed height, 4 mL/min solution flow rate, 7.04 constant AO7 solution pH and 301 K temperature. The breakthrough curves for all initial concentrations were drawn between the time and

Ct/C0 as shown in **Figure**. 5. It is observed that the break point time decreased with increased initial AO7 concentration from 5 to 80 mg/L. On increasing the initial ion concentration, the breakthrough curves became steeper and breakthrough volume decreased because of the lower mass-transfer system from the bulk solution to the adsorbent surface. It is illustrated that the breakthrough time slightly decreased with increasing inlet AO7 concentration. At lower inlet AO7 concentrations, breakthrough curves were dispersed and breakthrough occurred slower. As influent concentration increased, sharper breakthrough curves were obtained. This can be explained by the fact that a lower concentration gradient caused a slower transport due to a decrease in the diffusion coefficient or mass transfer coefficient. The larger the inlet concentration, the steeper is the slope of breakthrough curve and smaller is the breakthrough time. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time, or in other words, the diffusion process is concentration dependent. The adsorption capacity was expected to increase with increasing the inlet concentration because a high concentration difference provides a high driving force for the adsorption process. The breakdown time and exhaust time were increasing with decreasing initial dye concentration. The breakthrough and the exhausting times for different dye concentrations of 5, 30, 50 and 80 ppm were deceased as 48, 38, 30, and 15 min and 160, 140, 130, and 80 min, respectively. This is due to the TES getting saturated more quickly at higher initial reactive dye concentrations. Thus, breakthrough and the exhausting times for the higher influent concentration were less or earlier than those for the lower influent concentration.

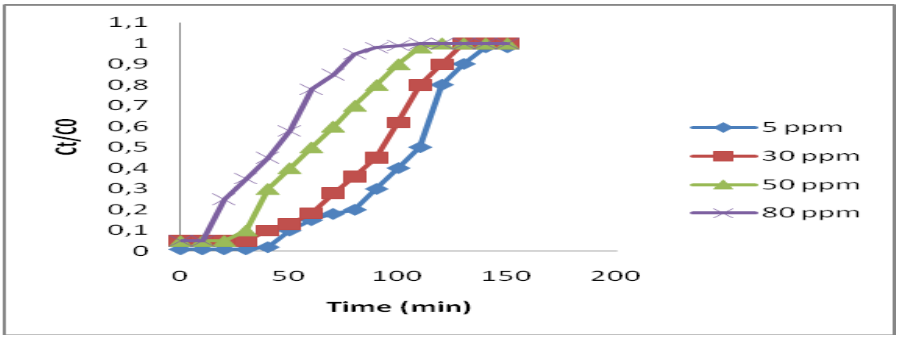

Figure. 5 Breakthrough curves for AO7 adsorption column by TES at different initial AO7 concentrations

B. Effect of the Solution Flow Rate

The effect of the flow rate on the adsorption of AO7 using the TES was investigated by varying the flow rate (2, 4 and 6 mL/min) using 30 mg/L initial AO7 concentration, 10 cm bed height, pH 7.04 at 301 K., as shown by the breakthrough curve in **Figure**. 6. **Figure**. 6 show that the breakthrough curve occurred faster at higher flow rate. This is because the lower residence time of the influent in the column, thus reducing the contact time between AO7 and the TES. It was shown that breakthrough generally occurred faster with higher flow rate. Breakthrough time reaching saturation was increased significantly with a decreased in the flow rate. When at a low rate of inlet AO7 had more time to contact with TES that resulted in higher removal of AO7 ions in column. The variation in the slope of the breakthrough curve and adsorption capacity may be explained on the basis of mass transfer fundamentals. The reason is that at higher flow rate the rate of mass transfer gets increased, i.e. the amount of dye adsorbed onto unit bed height (mass transfer zone) gets increased with increasing flow rate leading to faster saturation at higher flow rate. At a higher flow rate, the adsorption capacity was lower due to insufficient residence time of the solute in the column and diffusion of the solute into the pores of the adsorbent, and therefore, the solute left the column before equilibrium occurred. The column adsorption experiment was carried out at different flow rates of 2, 4and 6 mL/min using initial AO7 concentration of 30 ppm and bed height of 10 cm at neutral pH. The resulting breakthrough graph is mentioned

in **Figure**. 6, in which breakthrough occurred faster with higher flow rate of 6 mL/min. And breakthrough curve of the lower flow rate of 2 mL/min tended to be more gradual, meaning that the column was difficult to be completely exhausted. Increasing the flow rate in the TES bed caused a decrease in AO7 removal efficiency. This is attributed to the fact that low contact time between the adsorbate and adsorbent reduces the adsorption efficiency in the TES bed. In addition, at higher flow rates, the movement of adsorption zone along the bed is faster reducing the time for adsorption of dye on the TES bed.

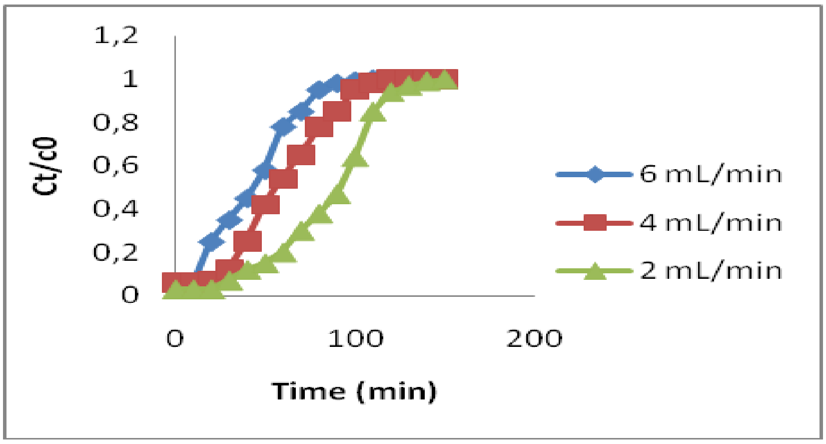

Figure. 6 Breakthrough curves of the effect of flow rate on AO7adsorption onto TES column

C .Effect of Activated Carbon Bed Height

The fixed bed study was carried out at different bed height of 5, 10 and 15 cm (3.5, 7 and 10.5 g) with influent AO7 concentration of 30 mg/L, 4 mL/min flow rate, and pH 7.04 and at 301 K. **Figure**. 7 shows that the breakthrough time decreased with increasing the bed height and increasing by the way the number of sorption sites and the residence time of the AO7 in the column, thus increasing the removal efficiency of AO7 in the fixed bed system.

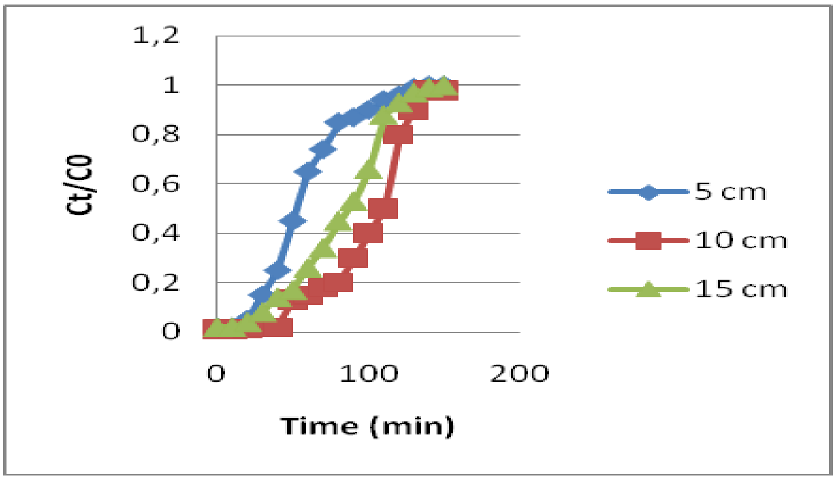

Figure. 7 Breakthrough curves for AO7 adsorption by TES at different bed heights

Figure.7 shows the breakthrough curve obtained for AO7 adsorption on the TES. From **Figure**. 7 both the breakthrough and time increased with increasing the bed height. When the bed height increases, AO7 had more time to be in contact with TES that results in higher removal efficiency of AO7 in the column. So, the higher bed column results in a decrease in the solute concentration in the effluent at the same time. The slope of breakthrough curve decreased with increasing bed height, which resulted in a broadened mass transfer zone. A high adsorption capacity

was observed at the highest bed height due to an increase in the surface area of adsorbent, which provided more binding sites for the adsorption. The effect of bed height for adsorption of AO7 dye onto TES bed at heights of 5, 10 and 15 cm at influent concentration 30 ppm and flow rate 4 mL/min is shown in **Figure**.5. This indicates that breakthrough time and the exhausting time were increased from 30 to 120 and 10 to 105 min, respectively, when the bed height passed from 5 to 15 cm. The throughput volume of dye solution was increased with the increase in bed height due to the increase in surface area of adsorbent providing by the way, *more* binding sites for the adsorption and more number of sorption sites in general.

4.3. Box–Behnken

Response surface methodology (RSM) is more advantageous than the traditional single parameter optimization because it can save time, space and raw material. In experimental design, a Box– Behnken design (BBD) is a type of RSM, and it is used for optimizing the important process variables. The most important parameters, which affect the efficiency of adsorption of AO7 onto TES , are AO7 dye concentration, flow rate and bed height of the solution in a continuous fixed bed. In order to study the combined effect of these factors, experiments are performed for different combinations of the physical parameters using statistically designed experiments. The initial dye concentration range studied is between 10 and 50 ppm. The flow rate is between 2 and 6 ml/min. The bed height is varied between 5 and 20 cm . The main effects of each of the parameter on AO7 removal efficiency is given in **Figure**s.8. **Figure**. 8 shows that the removal efficiency increases with increasing AO7 dye concentration and bed height and with decreasing flow rate. Consequently, we note high AO7 removal efficiencies at high initial dye concentration.

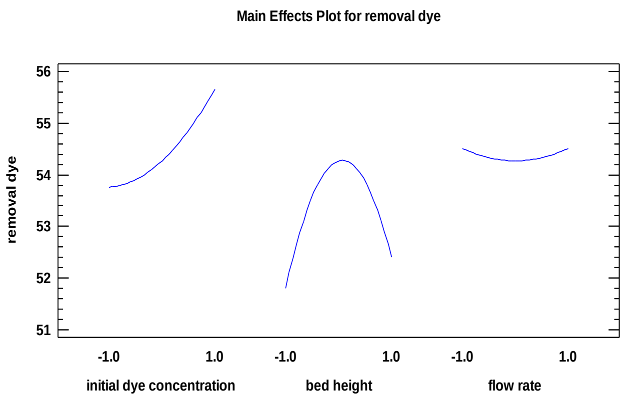

Figure.8. Main effects plot of parameters for AO7 removal efficiency.

Table 5 shows the experimental results of removal of AO7 in the solution for the 15 experiments. Using the experimental results, the regression model equations (second-order polynomial) relating the response is developed and is given in Eqs. (5) . Apart from the linear effect of the parameter for the response, the RSM also gives an insight into the quadratic and interaction effect of the parameters. These analyses are done by means of Fisher's 'F' test and Student 't' test. The Fisher's 'F' test is used to determine the significance of each of the interaction among the variables, which in turns may indicate the patterns of the interactions among the variables.

Table 5: the experimental data for ao7 removal efficiency in solution according to design.

	Removal dye Y [(%)]	
Experimental run No.	Experimental values	Predicted responses
1	56	56,950034
2	54,2	54,2667
3	54,3	54,2667
4	52	52,700037
5	51,6	51,400037
6	56	55,050034
7	51,8	52,000037
8	54,8	54,850034
9	50,2	50,950037
10	55	54,750037
11	52	52,250037
12	53	52,950034
13	54	53,300037
14	54,3	54,2667
15	53	52,250037

In general, the larger the magnitude of F, the smaller the value of P, the more significant is the corresponding coefficient term. The regression coefficient, F and P values for all the linear, quadratic and interaction effects of the parameter are given in Table 6 for the removal of AO7. It is observed that the coefficients for the linear effect of the factors initial dye concentration (p=0.0316) for the response is significant except flow rate and bed height (P =1.000 and p=0.3932) for removal of dye is slightly less significant. However, for the removal efficiency of AO7, the interaction effect of the variables dye concentration and bed height is found highly significant p=0.007 exempt the interaction between dye concentration and flow rate (P = 0.0688). Consequently, the best fitting response function, for the AO7 removal efficiency model are then conveniently written as follows:

$$Y = 54{,}2667 + 0{,}95.x_1 + 0{,}3.x_2 + 0{,}0.x_3 + 0{,}441667.x_1^2 + 0{,}95.x_1.x_2 - 1{,}05.x_1.x_3 - 2{,}15833.x_2^2 - 0{,}65.x_2.x_3 + 0{,}241667.x_3^2 \quad (5)$$

Where Y (%) is the removal dye of AO7, and x_1, x_2 and x_3 are the AO7 dye concentration, flow rate and bed height respectively. The ANOVA Table partitions the variability in removal dye into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 3 effects have P-values less than 0, 05, indicating that they are significantly different from zero at the 95, 0% confidence levels. The R-Squared statistic indicates that the model as fitted explains 89, 8965% of the variability in removal dye. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 71, 7102 %. Further, the ANOVA for AO7 removal efficiency in solution indicates that the second-order polynomial model Eqs. (5) Is highly significant and adequate to represent the actual relationship between the response and variables, with very a high value of coefficient of

determination (R2 = 0.8989for AO7 removal efficiency in solution. This implies that 89.89% of sample variation for AO7 removal efficiency in solution is explained by the model.

Table **6:** analysis of variance and corresponding f and p values for ao7 removal efficiency.

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
A:intial concentration	7,22	1	7,22	8,75	0,0316
B:bed height	0,72	1	0,72	0,87	0,3932
C:flow rate	0,0	1	0,0	0,00	1,0000
AA	0,720256	1	0,720256	0,87	0,3931
AB	3,61	1	3,61	4,37	0,007
AC	4,41	1	4,41	5,34	0,0688
BB	17,2003	1	17,2003	20,84	0,0060
BC	1,69	1	1,69	2,05	0,2118
CC	0,215641	1	0,215641	0,26	0,6310
Total error	4,12667	5	0,825333		
Total (corr.)	40,844	14			

The statistical significance of the ratio of mean square variation due to regression and mean square residual error is tested using ANOVA. ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the model. According to the ANOVA (Table 6), the Statistics values for all regression are higher. The large value of F indicates that most of the variation in the response can be explained by the regression equation. The associated P value is used to estimate whether Statistics is large enough to indicate statistical significance. The ANOVA Table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct. The 3D response surface and 2D contour plot are generally the graphical representation of the regression equation. We will use it to search the optimal values of the process parameters. Then, the response surface plots and contour plots to estimate the removal efficiency (**Figure**s. 9 and 10) is given. Thus, the surface and contour plots for AO7 removal efficiency in **Figure**. 8 shows the interaction effect of bed height and initial concentration .The response surface of mutual interactions between the variables is found to be elliptical and the maximum AO7 removal efficiency is obtained in the following cases: The bed height and initial concentration increase simultaneously. The initial concentration increases and the bed height are between 10 and 15 cm and remain unchanged. The bed height increases and initial concentration is between 10 and 20 ppm and remains Table. The geometrical representation of the response removal dye , when the bed height and initial concentration increases the removal dye increases. We also note that, the influence of flow rate is not significant. Then, to have a good removal dye it is beneficial to work with high bed height of column. The highest value of the bed height which gives maximum of AO7 removal is 15 cm.

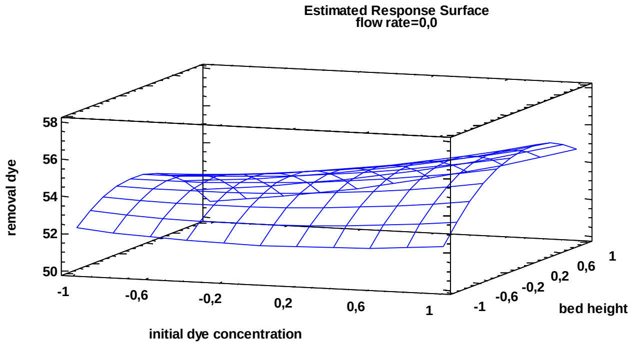

Figure. 9. Response surface plot of AO7 removal efficiency.

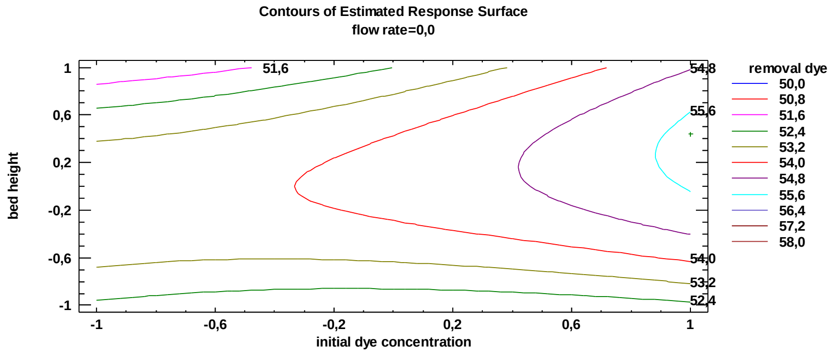

Figure. 10. Contour plot of estimated response surface of AO7 removal efficiency.

5. Conclusion

The present study clearly demonstrated the applicability of adsorption process using the fixed bed for AO7 removal. The breakthrough curve (Ct/C0 vs. time) for various parameters of flow rate, initial AO7 concentration and bed height was plotted. The breakthrough time and exhaust time were increased with increasing flow rate, and bed height and decreasing initial AO7 concentration. This study clearly showed that RSM is one of the suitable methods to optimize the best operating conditions to maximize the AO7 removal. BB design is successfully employed for experimental design and analysis of results. The TES, which was used without further purification for the removals of AO7 from aqueous solution because it leans, close to practical purposes. The process variables of removal of dye by TES have been optimized based on RSM method and the individual and interaction effects of the process variables were investigated. The results indicated that all the three process variables have a direct relationship for the removal AO7 dye onto TES. Satisfactory empirical model equations are developed for the removal of AO7 in solution using RSM to optimize the parameters. Graphical response surface and contour plot is used to locate the optimum point.

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