International journal of scientific and technical research in engineering (IJSTRE)
www.ijstre.com Volume 1 Issue 3 ǁ June 2016

Experimental Design for Removal of Acid Orange 7 Dye from Aqueous Solution Using the Exchange Resin Amberlite FPA-98 as an Efficient Adsorbent in Fixed Bed Reactor Using Box–Behnken Design and Full Factorial Design

S. Akazdam[1]*, M. Chafi[1], L. Sebbahi[1], R. Benchekroune[1], B. Gourich[1],
N. Barka[2],M.Essahli[3], O. Cherkaoui[4]

[1] *Laboratory of Engineering, Processes and Environment (LEPE) High School of Technology University Hassan II of Casablanca Morocco .*
[2]*The University Hassan 1, Laboratoire des Sciences des Matériaux, des Milieux et de la Modélisation(LS3M), BP.145, 25000 Khouribga, Morocco.*
[3]*The University Hassan 1, Laboratory of Applied Chemistry and Environment, Faculty of Science and Technology, BP 577, Settat, Morocco.*
[4]*Laboratoire traitement des eaux usées ESITH, casablanca, Morocco.*
* *E-mail : said.akazdam@gmail.com*

Abstract—*In the present study, application of Amberlite FPA-98 was investigated for the removal of Acide Orange 7 from aqueous solution using the continuous method and was optimized using Box–Behnken design (BBD) and full factorial design (FFD). Fixed bed adsorption has become a frequently used in wastewater treatment processes. In this work, the intention of the study was to explore the efficacy and feasibility for azo dye, Acid Orange 7 (AO7) adsorption onto fixed bed column of Amberlite FPA-98. The effect of operating parameters such as flow rate, initial dye concentration, and bed height was modeled by response surface methodology (RSM). This study compares Box–Behnken design (BBD) and full factorial design (FFD) utility for modeling and optimization by response surface methodology. The precision of the equation obtained by RSM was confirmed by the analysis of variance (ANOVA)and calculation of correlation coefficient relating the predicted and the experimental values of adsorption efficiency. The results revealed a good agreement between the predicted values, as obtained by full factorial design (FFD) and the experimental values for AO7 (R2 = 0.987) . 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 were (R2 = 0.959). The application of response surface methodology in order to optimize using Box–Behnken design (BBD) and full factorial design (FFD). The research on modeling adsorption by RSM has been highly developed and The Amberlite 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, Amberlite, RSM, BBD, FFD, optimization, modelling.*

I. 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 environment. 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 tonnes 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. Acid Orange 7 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. When Acid Orange 7 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 Acid Orange 7 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 Acid Orange 7 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 Acid Orange 7 concentration [8].

Because a number of exchange resins have been used quite efficiently for the removal of specific organic compounds [9], this study investigates the adsorption characteristics of Acid Orange 7 dye on the strongly basic polyacrylic anion exchanger Amberlite FPA-98 of macroporous structure. The present work deals with the estimation of the adsorption properties of Amberlite FPA-98 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 Amberlite FPA-98 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 acide dye, Acide Orange 7 (AO7), as the adsorbate. The Amberlite FPA-98 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 adsorber does not run under equilibrium conditions and the effect of flow condition (hydrodynamics) at any cross-section in the column affects the flow behaviour 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 ion exchange bed or removal of toxic organic compounds by carbon adsorption [14].

In this study, the amberlite has been tested for removal of aqueous solutions. In this paper, amberlite 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 amberlite 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.

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 an 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 amberlite 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 and full factorial design (FFD) [20].

Conclusions as a result, the adsorptions of dyes onto AC were commonly investigated using traditional methods, but the AO7 adsorptions based onto amberlite FPA 98 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 amberlite FPA 98 have been investigated in continuous 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. [21].

II. MATERIAL AND METHODS

A. Porous Polymers (Resin Adsorbent) :Amberlite FPA 98

There are two main criteria for the choice of adsorbent: The maximum adsorption capacity (q_m): solute concentration transmitted in the solid phase, must be maximized. The adsorption kinetics: the adsorption must take place rapidly. Exchange resins, strongly basic anionic ion (85% adsorbent and 15% anion exchange), the principle is to exchange certain ions, or all with active groups on the resins. Resins, which are in the form of beads or powder form are thus able to exchange mobile ions with ions of the same sign, contained in a solution with which they are contacted. Strongly basic anionic resins bind the strong and weak acid anions in a pH range between 1 and 12. This type of resin is regenerated with sodium hydroxide solution and in the form of grains aspheric 0.5 to 1.5 mm in diameter, with specific surface areas of up to 750 m^2/g. Amberlite FPA98 is unique, food-grade acrylic macroporous strong base anion resin. This use of ion exchange technology based discoloration was more effective and more economical. The application of these adsorbents AMBERLITE FPA98 Cl mainly develop in water treatment in the domain refining of sugar as adsorbents dyes capturing and purification of pharmaceuticals and The guard beds for precious chromatography media [22].

B. Adsorbate Preparation

The dye chosen in this study is the Acide Orange 7, also called Acide 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 Table I; 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].

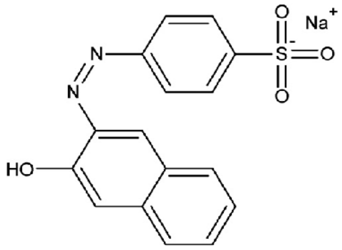

Fig. 1 Molecular structure of Acide Orange 7

TABLE I : MAIN CHARACTERISTICS OF THE BASIC DYE ACIDE ORANGE II

Dye	Acide 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

III. SORPTION EXPERIMENTS IN FIXED-BED TECHNIQUE

A. 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 Amberlite FPA-98 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 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 [24].

The schematic diagram of fixed bed column used in adsorption study is shown in Fig. 2. The experimental detail is given in Table II. Briefly, the experiment was carried out by passing through column (packed with 21 g of Amberlite FPA-98) with controlled flow rate .

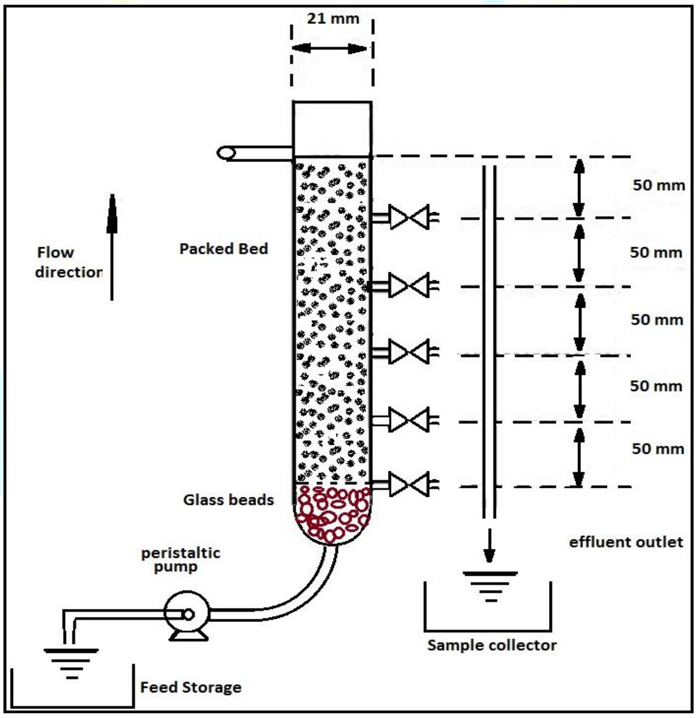

Fig. 2 Schematic diagram of fixed bed column used in adsorption study of AO7 onto Amberlite FPA 98.

TABLE II
EXPERIMENTAL DETAILS FOR COLUMN ADSORPTION OF AO7 ONTO AMB FPA 98

EFFECT OF 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

B. Removal efficiency

The dye removal percentage using Amberlite FPA98 adsorbent was calculated from:

$$Re(\%) = 100 \text{ x } (C_0 - C_e)/C_0 \qquad (1)$$

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).

C. 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. [25].In this study, response surface methodology was applied to optimize the adsorption of Acide orange 7 by AmberliteFPA98 . Experiments were performed using Box– Behnken design (BBD) and full factorial design (FFD). 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 Statgraphics Software [26].

D. 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 (X_1), bed height (X_2) and flow rate (X_3) 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 III). The parameters (X_i) were coded as x_i via Eq. (2):

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

where X_0 and dX are the values of X_i 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:

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

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 (b_1,b_2, b_3) are linear effect, quadratic effect (b_{11}, b_{22}, b_{33}) and interactions (b_{12}, b_{23}, b_{13}) effects, respectively; x_i and x_j 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 (R^2) between predicted and experimental points [27].

Nonlinear X^2 analysis is a useful method, which can compare the experimental and model predicted data. And it is estimated using the following equation:

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

whereY_{exp}. (%) and Y_{pred}. (%) are the adsorption removal of AO7 onto Amberlite FPA 98 by experiment determined and model predicted.

E. 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 X_1–X_3, respectively. The dye concentration (X_1) range of 10–50 mg/ L, flow rate (X_2) range of 2–6 ml/min, bed height (X_3) of 5–20 cm were chosen as given in Table III.

TABLE III : 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

F. 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 IV (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–Behnken design (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 (X_1), flow rate (X_2) and bed height (X_3) 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 adsorption capacity were taken as a response (Y). The matrix design is shown in Table IV. On the basis of BBD three the most significant parameters were chosen for further investigation (modeling and optimization by RSM).

TABLE IV : BOX–BEHNKEN DESIGN MATRIX WITH CODED AND UNCODED VALUES OF THE INDEPENDENT VARIABLES INFLUENCING ADSORPTION OF AO7 BY AMBERLITE WITH EXPERIMENTAL AND PREDICTED VALUES OF THE RESPONSE.

	Coded values (uncoded values)			Removal dye Y [(%)]	
Experimental run No.	X_1 [ppm]	X_2 [cm]	X_3 [ml/min]	Experimental values	Predicted responses
1	0 (30)	-1 (5)	-1 (2)	50	53,2375
2	0 (30)	-1 (5)	1 (6)	66	64,7375
3	1 (50)	0 (10)	1 (6)	69	70,0125
4	-1 (10)	-1 (5)	0 (4)	48,9	46,675
5	-1 (10)	0 (10)	-1 (2)	52	50,9875
6	0 (30)	1 (15)	-1 (2)	58	59,2625
7	1 (50)	1 (15)	-1 (2)	38	34,5125
8	0 (30)	1 (15)	1 (6)	79	75,7625
9	-1 (10)	0 (10)	1 (6)	40	43,4875
10	1 (50)	1 (15)	0 (2)	58	60,225
11	1 (50)	-1 (5)	0 (2)	49	49,25
12	-1 (10)	1 (15)	0 (2)	53	52,75
13	0 (30)	0 (10)	0 (2)	58	57
14	0 (30)	0 (10)	0 (2)	57	57
15	0 (30)	0 (10)	0 (2)	56	57

G. Full factorial design

Factorial designs allow the simultaneous study of the effects that several factors may have on the optimization of a particular process. It determines which factors have the important effects on the response as well as how the effect of one factor varies with the level of the other factors. The effects are the differential quantities expressing how a response changes as the levels of one or more factors are changed. Also, factorial designs allow measuring the interaction between each different group of factors. The interactions are the driving force in many optimizations of the processes. Without the use of factorial experiments, some important interactions may remain undetected, and the overall optimization may not be attained. One of the simplest types of factorial designs used in experimental work is one having two levels (2^k). In a 2^k factorial design experiment, each factor may be assigned two levels: low (-1) and high (+1). If k factors are considered, then 2^k measurements are required to perform a factorial design analysis [28]. In this investigation, three operating factors were chosen as independent variables, namely: initial AO7 dye concentration (X_1), flow rate (X_2) and bed height (X_3) was used to predict the removal of dye . The natural values of each factor and their respective levels are presented in Table V.

TABLE V : THE EXPERIMENTAL RANGES AND LEVELS OF INDEPENDENT VARIABLES.

Levels	$[AO7]_0$ (mg/L)	Qv (mL/min)	H (cm)
-1	10	2	5
+1	50	6	20

The selection of levels of different factors is carried out on the basis of the preliminary trials and previous publishing result: Initial dye concentration $[AO7]_0$ ranging from 10 to 50 mg/L, flow rate from 2 to 6 mL/min and bed height from 5 to 20 cm . The design performed according to Table VI was composed of 2^3 factorial designs.

TABLE VI : 2^3 FULL FACTORIAL DESIGN. FULL FACTORIAL DESIGN WITH CODED AND UNCODED VALUES OF THE INDEPENDENT VARIABLES AND EXPERIMENTAL AND PREDICTED VALUES OF THE RESPONSE.

	Coded values (uncoded values)			Removal dye Y [(%)]	
run No.	X_1 [ppm]	X_2 [ml/min]	X_3 (cm)	Experimental values	Predicted responses
1	-1 (10)	-1 (2)	-1 (5)	55	54,625
2	1 (50)	-1 (2)	1 (20)	57	56,625
3	-1 (10)	-1 (2)	1 (20)	52	52,375
4	1 (50)	1 (6)	-1 (5)	56	55,625
5	1 (50)	1 (6)	1 (20)	50	50,375
6	1 (50)	-1 (2)	-1 (5)	62	62,375
7	-1 (10)	1 (6)	1 (20)	53	52,625
8	-1 (10)	1 (6)	-1 (5)	54	54,375

The experimental data are analyzed by full factorial design to fit the following first order polynomial equation (Eq. (5)).

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 + e \qquad (5)$$

Where Y the estimated removal of dye ; b_0 is the value of fitted response at the centre point of design; b_j and b_{ji} are the linear and interaction terms, respectively [29].When the response data are obtained from the test work, a regression analysis is carried out to determine the coefficients of the response model (b_1; b_2; . . . b_n), as well as their standard errors and their significance. In addition to the constant (b_0) and error (e) terms, the response model incorporates .Linear terms in each of the variables (x_1; x_2; . . . ; x_n). First-order interaction terms for each paired combination (x_1x_2; x_1x_3; . . . ; $x_{n-i}\,x_n$)

H. 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.

IV. RESULTS and discussion

A. 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 AMB FPA 98 , 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 Figs.3. Fig. 3 shows that the removal efficiency increases with increasing AO7 dye concentration, flow rate or bed height. Consequently, we note high AO7 removal efficiencies at high flow rate and bed height.

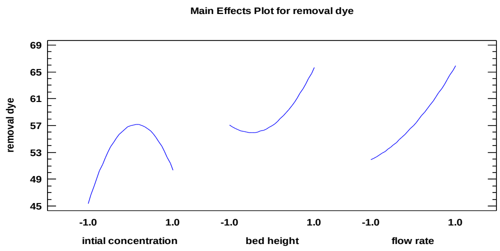

Fig. 3. Main effects plot of parameters for AO7 removal efficiency.

Table VII 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. (6) . 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 VII THE EXPERIMENTAL DATA FOR AO7 REMOVAL EFFICIENCY IN SOLUTION ACCORDING TO BBDESIGN.

	Removal dye Y [(%)]	
Experimental run No.	Experimental values	Predicted responses
1	50	53,2375
2	66	64,7375
3	69	70,0125
4	48,9	46,675
5	52	50,9875
6	58	59,2625
7	38	34,5125
8	79	75,7625
9	40	43,4875
10	58	60,225
11	49	49,25

12	53	52,75
13	58	57
14	57	57
15	56	57

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 Tables VIII for the removal of AO7. It is observed that the coefficients for the linear effect of the factors flow rate and bed height (P =0.0191and p=0.0025) for the responses are significant except AO7 dye concentration (P = 0.1008) for removal of dye is slightly less significant.
However, for the removal efficiency of AO7, the interaction effect of the variables dye concentration and flow rate is found highly significant p=0.0017 exempt the interaction between dye concentration and bed height (P = 0.5194) . Consequently, the best fitting response function , for the AO7 removal efficiency model are then conveniently written as follows:

$$Y = 57{,}0 + 2{,}5125.x_1 + 4{,}2625.x_2 + 7{,}0.x_3 - 9{,}1375.x_1^2 + 1{,}225.x_1.x_2 + 10{,}75.x_1.x_3 + 4{,}3625.x_2^2 + 1{,}25.x_2.x_3 + 1{,}8875.x_3^2 \qquad (6)$$

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.

TABLE VIII 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	50,5012	1	50,5012	4,04	0,1008
B:bed height	145,351	1	145,351	11,62	0,0191
C:flow rate	392,0	1	392,0	31,33	0,0025
AA	308,285	1	308,285	24,64	0,0042
AB	6,0025	1	6,0025	0,48	0,5194
AC	462,25	1	462,25	36,95	0,0017
BB	70,2698	1	70,2698	5,62	0,0640
BC	6,25	1	6,25	0,50	0,5113
CC	13,1544	1	13,1544	1,05	0,3522
Total error	62,5525	5	12,5105		
Total (corr.)	1547,04	14			

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, 4 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level. The R-Squared statistic indicates that the model as fitted explains 95,9566% 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 88,6785%. Further, the ANOVA for AO7 removal efficiency in solution indicates that the second-order polynomial model Eqs. (6) is highly significant and adequate to represent the actual relationship between the response and variables, with very a high value of coefficient of determination (R^2 = 0.959566 for AO7 removal efficiency in solution. This implies that 95.95% of sample variation for AO7 removal efficiency in solution is explained by the model.

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 VIII), the $F_{statistics}$ 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 $F_{statistics}$ 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 (Figs. 4 and 5) is given.

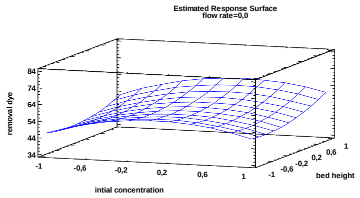

Fig. 4. Response surface plot of AO7 removal efficiency .

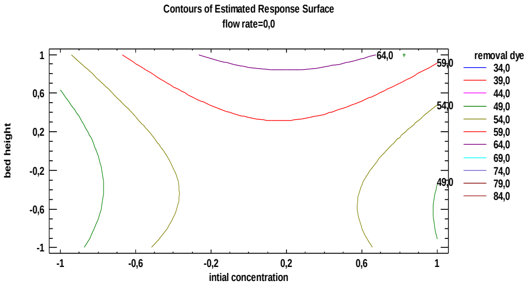

Fig. 5. Contour plot of estimated response surface of AO7 removal efficiency.

Thus, the surface and contour plots for AO7 removal efficiency in Fig. 7 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 is between 10 and 15 cm and remains unchanged.
The bed height increases and initial concentration is between 10 and 20 PPM and remains stable.

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.

B. Full factorial design

The model equation for adsorption of AO7 by amberlite in fixed bed was obtained after performing eight experiments and discarding the insignificant effect (b12) is as follows using some statistical tests . Table IX shows the experimental results of removal efficiency of AO7 in the solution for the 8 experiments.

TABLE IX THE EXPERIMENTAL DATA FOR AO7 REMOVAL EFFICIENCY IN SOLUTION ACCORDING TO FF DESIGN.

	Removal dye Y [(%)]	
run No.	Experimental values	Predicted responses
1	55	54,625
2	57	56,625
3	52	52,375
4	56	55,625

5	50	50,375
6	62	62,375
7	53	52,625
8	54	54,375

$$Y=54,875 + 1,375.x_1 - 1,625.x_2 - 1,875.x_3 - 1,625.x_1.x_2 - 0,875.x_1.x_3 + 0,125.x_2.x_3 \qquad (7)$$

The model's coefficients were estimated by standard lest square regression techniques using an EXCEL software. A good adjustment of the (Eq. (7)) to the experimental data was verified through the high correlation coefficient value obtained R2 = 0.987 (Fig. 2). The (Fig. 2) shows the absence of a trend, indicating that the mathematical model is adequate and that there is no inconsistency between the experimental and calculated values of the response.

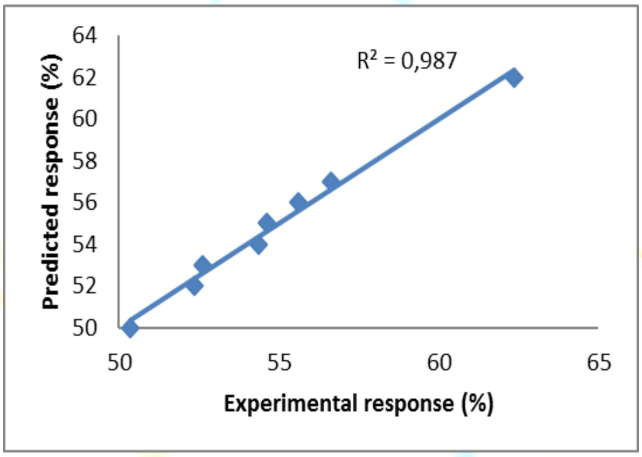

Fig.6. Analysis of quality of model by comparison of experimental and predicted responses.

fig.6 shows that the difference between the measured and the predicted values do not exceed 1%. Therefore, all those results indicate that the model can adequately represent the data. Initial AO7 concentration $[AO7]_0$ (x_1) has the strongest effect on the response since coefficient of x_1 (b1 = +1,375) is large than the coefficients of the other investigated factors, the positive sign indicate that there is a direct relation between Initial AO7concentration $[AO7]_0$ and response . According the regression equation, flow rate (x_2) and bed height (x_3) have a negative effect on the response (b_2 = -1,625 and b_3 = - 1,875) respectively which have been explained by reduction in residence time. The significance interactions found by the design of experiments are between flow rate-bed height (x_2x_3) with effect (b_{23}= +0,125).

The main effects of each of the parameter on AO7 removal efficiency is given in Figs.7. Fig. 7 shows that the removal efficiency increases with increasing AO7 dye concentration and decreases with increasing flow rate or bed height. Consequently, we note high AO7 removal efficiencies at high AO7 dye concentration and low the both of flow rate and bed height

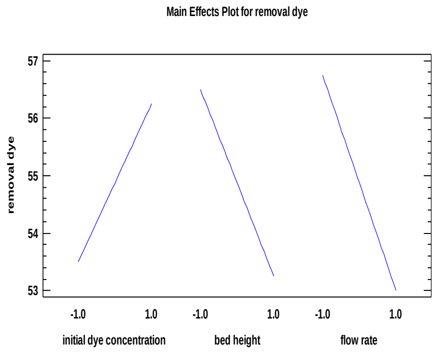

Fig. 7. Main effects plot of parameters for AO7 removal efficiency.

Results of analysis of variance were summarized in Table X. They indicated that the three regressions, F and P values for the linear and interaction effects of the parameter were significant at the probability level of 95 % to 99 %.

TABLE X ANALYSIS OF VARIANCE FOR REMOVAL DYE

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
A:initial dye concentration	15,125	1	15,125	13,44	0,1695
B:bed height	21,125	1	21,125	18,78	0,1444
C:flow rate	28,125	1	28,125	25,00	0,1257
AB	21,125	1	21,125	18,78	0,1444
AC	6,125	1	6,125	5,44	0,2578
BC	0,125	1	0,125	0,11	0,7952
Total error	1,125	1	1,125		
Total (corr.)	92,875	7			

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, 0 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level. The R-Squared statistic indicates that the model as fitted explains 98,7887% 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 91,5209%.

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 dye of AO7 (Figs. 8 and 9) is given.

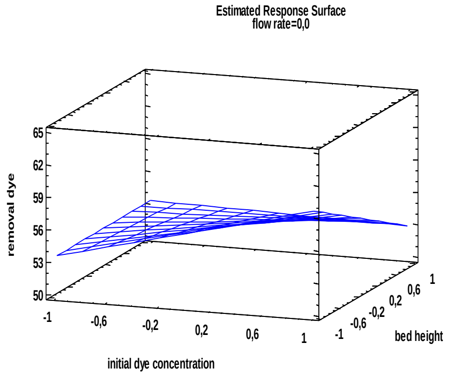

Fig. 8. Response surface plot of AO7 removal efficiency .

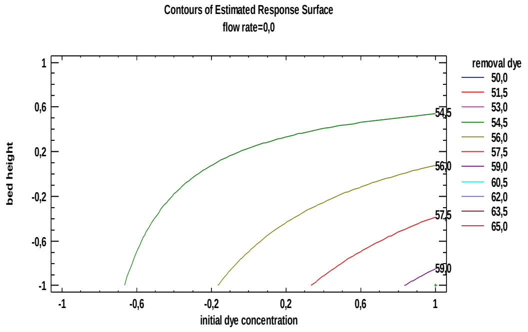

Fig. 9. Contour plot of estimated response surface of AO7 removal efficiency.

Thus, the surface and contour plots for AO7 removal efficiency in Fig. 9 shows the interaction effect of bed height and initial dye 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 cases: The initial concentration increase and the bed height decrease simultaneously. The initial concentration increases and the BED HEIGHT is between 5 and 10 cm and remains unchanged.

The bed height decreases and initial concentration is between 40 and 50 ppm and remains stable.

The geometrical representation of the response removal dye, when The bed height decreases 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 low bed height of column. The lowest value of the bed height which gives maximum of AO7 removal is 5cm.

V. CONCLUSION

The present study clearly demonstrated the applicability of adsorption process using the fixed bed for AO7 removal. This study clearly showed that RSM is one of the suitable methods to optimize the best operating conditions to maximize the AO7 removal. BB and FF design is successfully employed for experimental design and analysis of results. The Amberlite FPA 98 , 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 amberlite FPA 98 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 amberlite. 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.

REFERENCES

[1] S.M. Chin, E. Park, M. Kim, J.S. Jurng, Photo catalytic degradation of methylene blue with TiO2 nano particles prepared by a thermal decomposition process, Powder Technol. 201 (2010) 171–176.

[2] A. Lo´ pez, D. Acosta, A.I. Martı´nez, J. Santiago, Nano structured low crystallized titanium dioxide thin films with good photo catalytic activity, Powder Technol. 202 (2010) 111–117.

[3] A. Fujishima, X. Zhang, D.A. Tyrk, TiO2 photocatalysisandrelated surface phenomena, Surf. Sci. Rep. 63 (2008) 515–582.

[4] S. Sato, S. Oimatsu, R. Takahashi, T. Sodesawa, F. Nozaki,Pore size regulation of TiO2 by use of a complex of titaniumtetraisopropoxide and stearic acid, Chem. Commun. (1997)2219–2220.

[5] M. Addamo, V. Augugliaro, A. Di Paola, E. Garcı´a-Lo´ pez, V.Loddo, G. Marcı‘, R. Molinari, L. Palmisano, M. Schiavello,Preparation, characterization, and photoactivity of polycrystalline nanostructured TiO2 catalysts, J. Phys. Chem. B 108 (2004) 3303–3310.

[6] Z. Zhang, C.C. Wang, R. Zakaria, J.Y. Ying, Role of particlesize in nanocrystalline TiO2-based photocatalysts, J. Phys.Chem. B 102 (1998) 10871–10878.

[7] H. Gerischer, A. Heller, The role of oxygen in photooxidationoforganic molecules on semiconductor particles, J. Phys. Chem. 95(2004) 5261–5267.

[8] G. Rothenberger, J. Moser, M. Gratzel, N. Serpone, D.K. Sharma, Charge carrier trapping and recombination dynamics in small semiconductor particles, J. Am. Chem. Soc. 107 (1985)8054–8059.

[9] L. Zang, W.Macyk, . Lange, et al, Visible-light detoxificationand charge generation by transition metal chloride modifiedtitania, Chem. Eur. J. 6 (2000) 379–384.

[10] A. Dawson, P.V. Kamat, Semiconductor-metal nano composites. Photo induced fusion and photo catalysis of goldcappedTiO2 (TiO2/Gold) nanoparticles, J. Phys. Chem. B 105(2001) 960–966.

[11] M.S. Lee, S.S. Hong, M. Mohseni, Synthesis of photo catalyticnano sized TiO2–Ag particles with sol–gel method usingreduction agent, J. Mol. Catal. A Chem. 242 (2005) 135–140.

[12] V. Rupa, D. Manikandan, D. Divakar, T. Sivakumar, Effect ofdeposition of Ag on TiO2 nano particles on the photo degradation of reactive yellow-17, J. Hazard. Mater. 147 (2007) 906–913.

[13] S.X. Liu, Z.P. Qu, X.W. Han, C.L. Sun, A mechanism for enhanced photo catalytic activity of silver-loaded titanium dioxide, Catal. Today 93 (2004) 877–884.

[14] A. Danion, C. Bordes, J. Disdier, J.V. Gauvrit, C. Guillard, P.Lantri, et al, Optimization of a single TiO2-coated optical fiberreactor using experimental design, J. Photochem. Photobiol.AChem. 168 (2004) 161–167.

[15] J. Fernandez, J. Kiwi, J. Baeza, J. Freer, C. Lizama, H.D. Mansilla, Orange II photo catalysis on immobilized TiO2: effectof the pH and H2O2, Appl. Catal. B Environ. 48 (2004) 205–211.

[16] A.M. Amat, A. Arques, S.H. Bossmann, A. Braun, S. Gob,M.A. Miranda, et al, Oxidative degradation of 2,4-xylidine byphotosensitization with 2,4,6-triphenilpyrilium: homogeneousand heterogeneous catalysis, Chemosphere 57 (2004)1123–1130.

[17] C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, Optimized photodegradation of reactive Blue 19 on TiO2 and ZNO suspensions, Catal. Today 76 (2002) 235–246.

[18] L.C. Chen, Effect of factors and interacted factors on the optimal decolorisation process of methyl orange by ozone, Water Res. 34 (2000) 947–982.

[19] A. Gursesa, M. Yalcina, C. Dograb, Electrocoagulation of somereactive dyes: statistical investigation of some electrochemicalvariables, Waste Manage. 22 (2000) 491–494.

[20] Joseph Goldstein, Scanning Electron Microscopy and X-RayMicroanalysis, Springer. ISBN 978-0-306-47292-3, Retrieved 26May 2012.

[21] Jump up Joseph Goldstein Scanning Electron Microscopy andX-Ray Microanalysis, Springer. ISBN 978-0-306-47292-3, Retrieved 26 May 2012.

[22] John Coates, Interpretation of Infrared Spectra, APracticalApproach. Encyclopedia of Analytical Chemistry, John Wiley &Sons Ltd., Chichester, 2000.

[23] N. Daneshvar, S. Aber, M. Seyeddorraji, A. Khataee, M. Rasoulifard, Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystallineZnO powders under irradiation of UV-C light, Sep. Purif. Technol. 58 (2000) 91–98.

[24] C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, Optimized photodegradation of Reactive Blue 19 on TiO2 and ZnO suspensions, Catal. Today 76 (2002) 235–246.

[25] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M.Palanichamy, V. Murugesan, Solar photocatalyticdegradationofazo dye: comparison of photocatalytic efficiency of ZnO andTiO2, Solar Energy Mater. Solar C 77 (2003) 65–82.

[26] J.R. Guimara˜ es, M.G. Maniero, R. Nogueira de Arau´ jo, Acomparative study on the degradation of RB-19 dye in anaqueous medium by advanced oxidation processes, J. Environ.Manage. 110 (2012) 33–39.

[27] H. Shu, M. Chang, H. Fan, Effects of gap size and UV dosageondecolorisation of C.I. Acid Blue 113 wastewater in the UV/H2O2 process, J. Hazard. Mater. 118 (2005) 205–211.

[28] M. Muruganandham, M. Swaminathan, Solar photocatalyticdegradation of a reactive azo dye in TiO2-suspension, Sol.Energy Mater. Sol. Cells 81 (4) (2004) 439–457.

[29] E. Kusvuran, O. Gulnaz, S. Irmak, O.M. Atanur, H.I. Yavuz,O. Erbatur, Comparison of several advanced oxidation processes for the decolorisation of Reactive Red 120 azo dye in aqueous solution, J. Hazard. Mater. 109 (2004) 85–93.

[30] W.Z. Tang, H. An, UV/TiO2 photocatalytic oxidation of commercial dyes in aqueous solutions, Chemosphere 31 (1995)4157–4170.