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<b>Authors(s)</b>	Fu, J.F., Zhao, Y.Q., Xue, X.D., Li, W.C., Babatunde, A.O.
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# Multivariate-parameter optimization of acid blue-7 wastewater treatment by Ti/TiO<sub>2</sub> photoelectrocatalysis via Box-Behnken design

J.F. Fu<sup>a,b\*</sup>, Y.Q. Zhao<sup>b</sup>, X.D. Xue<sup>c</sup>, W.C. Li<sup>b</sup>, A.O. Babatunde<sup>b</sup>

<sup>a</sup>*School of Energy and Environment, Southeast University, 210096, Nanjing, P.R. China*

<sup>b</sup>*Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering, University College Dublin, Newstead, Belfield, Dublin4, Ireland*

<sup>c</sup>*Environmental Institute, Zhejiang University of Science & Technology, Hangzhou 310012, P.R. China*

**Abstract:** The aim of this study is to obtain optimal decolourization conditions for Acid blue-7 (AB7) wastewater treatment by Ti/TiO<sub>2</sub> photoelectrocatalysis using response surface methodology (RSM). On the basis of a three-variable Box-Behnken design (BBD), RSM was used to determine the effect of pH values (ranged from 3.2 to 6), light intensity (ranged from 10 to 20 ×10<sup>2</sup> μW/cm<sup>2</sup>) and bias potential (ranged from 0.1 to 1.1V) on the levels of response, i.e. decolourization efficiency. By applying the quadratic regression analysis, the equations describing the behaviors of the response as simultaneous functions of the selected independent variables were developed. Accordingly, the optimal conditions were determined as pH of 3.41, light intensity of 16.02×10<sup>2</sup> μW/cm<sup>2</sup> and bias potential of 0.68V. Decolourization efficiency of 90.13%, obtained experimentally under such optimal conditions was highly agreed with that of 90.44%, estimated by the equations.

*Keywords:* Acid blue-7; Box-Behnken design (BBD); Optimization; Response surface methodology (RSM); Ti/TiO<sub>2</sub> electrode

## 1. Introduction

During dye production and textile manufacturing processes a large amount of wastewater containing dyestuffs with intensive color and toxicity can be produced and consequently introduced into aquatic systems. Because of the nature of synthetic dyes, conventional biological treatment methods appear ineffective for decoloring such wastewaters. Alternatively, dyes are usually removed by adsorption and/or coagulation in conventional industrial wastewater treatment. However, these methods merely transfer dyes from the liquid to the solid phase, causing secondary pollution and requiring further treatment [1-5].

The strong potential of advanced oxidation processes (AOPs) for dye wastewater treatment is universally recognized. Many oxidation processes, such as  $\text{TiO}_2/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{UV}$ , photo-Fenton and ozone ( $\text{O}_3$ ,  $\text{O}_3/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ ) etc. are currently employed by many investigators [6-9]. Among these, an attractive process popularized in the past few years for degrading organic pollutants is the photoelectrocatalytic (PEC) process. The method consists on applying a biasing potential into the photocatalytic process. In this system, a biasing potential is applied across a photoanode on which the catalyst is supported. This configuration allows for a more effective separation of photogenerated charge carriers ( $e^-$  and  $h^+$  generated on the electrode surface due irradiation of UV light lower than 380 nm) thereby increasing the lifetime of these electron-hole pairs [10-12]. Many literatures have reported that the photo-anodes were prepared by coating  $\text{TiO}_2$  on a conducting material. But the weakness of such photoanode is the poor mass transition of electron mass transfer between  $\text{TiO}_2$  films and supporting carriers. Recently, our research group successfully prepared an  $\text{Ti}/\text{TiO}_2$  photoelectrode by anodising a  $\text{TiO}_2$  film on titanium (Ti) for PEC degradation of fulvic acid [13]. This electrode had a large surface area and its microporous surface structure achieved an excellent adsorption of pollutants. Some investigators have also studied the influencing parameters on PEC oxidation including pH, bias potential and electrolyte etc [14-15].

In assessing the effect of parameters on treatment results, response surface

methodology (RSM) is a well known efficient experimentation technique and has been applied in a wide range of fields such as drug and food industry, chemical and biological processes etc., for the purpose of either producing high quality products or operating the process in a more economical manner and ensuring the process in a more stable and reliable way [16,17]. RSM is a multivariate technique that mathematically fits the experimental domain studied in the theoretical design through a response function [18]. The two most common designs commonly used in RSM are central composite design (CCD) and Box-Behnken design (BBD). BBD is considered as an efficient option in RSM and an ideal alternative to CCD [19].

RSM has been assisted by the developments in the field of computer software, such as SAS, Minitab, and Design-Expert etc. Generally, the RSM usually contains five steps [20]: (i) defining the independent input variables and desired responses with the design constrains while adopting experimental design, (ii) performing the regression analysis with the quadratic model of response surface, (iii) calculating the statistical analysis of variance (ANOVA) for the independent input variables and to find which parameter significantly affects the desired response, (iv) obtaining the optimal influencing parameters with the design constrains, (v) conducting confirmation experiment and verify the optimal parameters.

Literature survey has shown that RSM has been successfully applied to different oxidation processes to optimize the experimental design. Its application includes TiO<sub>2</sub>-coated/UV oxidation [21,22], TiO<sub>2</sub> slurry/UV oxidation [23,24], O<sub>3</sub> oxidation [25] and electrochemical oxidation [26]. However, the application in Ti/TiO<sub>2</sub> photoelectrocatalysis for Acid blue-7 (AB7) decolourization is not yet reported.

Therefore, the aim of this work is to optimize the influencing factors on photoelectrocatalytic oxidation for AB7 decolouring. A laboratory scale photoelectrocatalytic reactor was employed for an artificial AB7 wastewater treatment. A BBD was selected to study simultaneously the effects of three influencing variables (pH, light intensity and bias potential) on the response (decolourization efficiency). RSM was used to determine the optimal condition and an empirical model correlating the decolourization efficiency to the three variables was then developed.

## 2. Experimental

### 2.1. Materials

AB7 ( $C_{37}H_{36}N_2NaO_6S_2$ ) was obtained from Tianjin Chemical Reagent Co., China. Its general molecular structure is shown in Fig. 1. All other chemicals used to prepare the artificial wastewater were used with GPR grade. The water used for making the AB7-enriched solution (20mg/L) was produced by Millipore Simplicity 185 ultra-pure water equipment. The pH of the solutions was adjusted by the addition of either  $H_2SO_4$  or  $NaOH$ . Ti/TiO<sub>2</sub> electrode was prepared in our previously work [13].

### 2.2. PEC reactor

The PEC oxidation experiment was accomplished in a photo-reactor system, as shown schematically in Fig. 2, which was composed of a quartz glass reactor, ultraviolet light source (11W, 253.7 nm, Philip), and a potentiostat (Jiangsu Electroanalytical Co., China). The lamp was positioned vertically in a double-welled U-tube outside the reactor surrounded by circulating water to decrease the heating effect of the lamp. The Ti/TiO<sub>2</sub> anode and Cu cathode were placed in parallel and a saturated calomel electrode (SCE) served as the reference electrode. Gas was supplied from a porous titanium plate in order to provide dissolved oxygen for photoreaction and to stir the solution. Batch operation of the PEC reactor was applied and the irradiation time of 1h was employed.

### 2.3. Analytical methods

The concentration of the AB7 in filtrate was determined on a UV-Vis Spectrophotometer (Cary100, Varian, USA) at  $\lambda_{max} = 640$  nm. The decolourization efficiency of AB7 was calculated with the following equation:

$$Y(\%) = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (1)$$

where  $C_0$  is the initial concentration of AB7 and  $C$  is the concentration of AB7 at 1h. The pH was measured by using a HACA digital pH-meter (model pHs-3C). The light intensity was monitored by UV-A irradiation equipment (Beijing Photoelectroanalytical Co., China). The relationships between distance ( $Z$ ) and light intensity are shown in Table. 1.

#### 2.4. RSM-BBD

The optimization experimental design was done using RSM-BBD according to Myers and Montgomery [27]. As shown in Fig. 3, this rotatable experimental plan consisted of 15 runs. For three variables and two levels (low (-1) and high (+1)), the total number of experiments was 15, as shown in Table 2 and 3.

#### 2.5. Statistical analysis

The experimental data (Table 3) were analyzed by the response surface regression (RSREG) procedure to fit the following second-order polynomial model:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{ii} X_i^2 \quad (2)$$

Where  $Y$  is response (decolourization efficiency, %);  $\beta_0$ ,  $\beta_i$  ( $i = 1, 2, 3$ ) and  $\beta_{ij}$  ( $i = 1, 2, 3; j = 1, 2, 3$ ) are the model coefficient and  $X_i$  and  $X_j$  the coded independent variables.

Statistical Analysis System (SAS) was the computer program used for performing the analysis of variance (ANOVA) and response surface studies. All three-dimensional response surface graphs and two-dimensional contour plots were generated using STATISTICA software (Release 5.1, Statsoft, USA).

### 3. Results and discussion

#### 3.1. Model build-up and ANOVA analysis

The RSREG procedure for SAS was employed to fit the second-order polynomial

Eq. (2) to the experimental data, represented as decolourization efficiency in Table 3. From the SAS output of RSREG, the second-order polynomial equation is given below:

$$Y = +86.84333 - 7.7475X_1 + 1.47875X_2 + 2.08125X_3 - 4.957917X_1^2 - 1.625X_1X_2 - 0.065X_1X_3 - 7.350417X_2^2 + 0.8625X_2X_3 - 12.91042X_3^2 \quad (3)$$

where  $Y$  is the decolourization efficiency of AB7;  $X_1$ ,  $X_2$  and  $X_3$  are the coded values of the operational variables pH, light intensity and bias potential, respectively.

The analysis of variance (ANOVA) from Table 4 indicated that the second-order polynomial model (Eq. (3)) was statistically significant and adequate to represent the actual relationship between the response (decolourization efficiency) and the significant variables, with very small  $P$  value (0.0001) and satisfactory coefficient of determination ( $R^2 = 0.9759$ ). Furthermore, absolute average deviation (AAD) between the predicted and observed data is very small (ADD=1.774) [28]. So,  $R^2$  and AAD values for the three models indicate that the model equations are adequate to describe the experimental designs. Fig. 4 shows the predicted values versus the experimental values for decolourization efficiency. As can be seen, the predicted values obtained were quite close to the experimental values, indicating that the model developed was successful in capturing the correlation between the influencing parameters to the decolourization efficiency of AB7.

### 3.2. Effects of parameters

For decolourization efficiency, pH of solution was found to have the greatest effect on the response, with the highest  $F$  value (Table 4) of 70.8775, while both the bias potential and the light intensity exhibited less effect regarding the decolourization efficiency. More importantly, according to Table 4, the interaction effects between the variables appeared insignificant due to the larger values of  $P$ . Figs. 5-7 showed the three-dimensional response surfaces which were generated to show the effects of the

influencing variables on the decolourization efficiency ( $Y$ ). These graphs represent the effect of two variables at their studied range with the third one maintained at its zero level.

The colour removal efficiency of AB7 was found to increase with decreased pH and increased light intensity and bias potential. The highest yield was obtained when all the three variables were at the maximum point within the range studied.

As seen from Fig. 5-6, with decreasing pH values, an increase in decolourization efficiency can be observed. Thus decolourization efficiency by PEC oxidation is influenced by pH below 4; however, it is rapidly decreased with increasing pH in the range of 4-7 due to the fact that this dye will be easily adsorbed onto the surface of electrode under the acid conditions. This result was consistent with observations made by other investigators [29] for PEC degradation of humic acid and our previous work for PEC degradation of fulvic acid [13].

In PEC, bias potential is an important factor that influences PEC efficiency. As seen from Fig. 6-7, the decolourization efficiency of AB7 by PEC oxidation is rapidly increased with bias potential lower than critical values. This result was similar to that reported by Leng et al. [30]. Therefore, it is reasonable to believe that PEC oxidation accelerated the separation of electron-hole pairs and produces more oxidative species. As anodic potential increased, a large amount of photoelectrons passed through the Ti/TiO<sub>2</sub> electrode. When the transportation and creation of photoelectrons reached equilibrium, photocurrent was saturated. So the colour removal efficiency decreased slightly.

It is seen also from Fig. 6-7 that the decolourization efficiency increased with light intensity up to a point, beyond which no further increases were observed. It is possible that the Ti/TiO<sub>2</sub> surface was fully utilized at critical value and the excitation of electron-hole pair by UV irradiation was a maximum at that point. If this is the case, further increases in light intensity would have no additional effect on the colour removal of AB7.

In addition to the effect of each of the variables such as pH, light intensity and bias potential on the removal of dye individually, it is also important to explore the



integrated effect of these variables. Based on  $F$  values in Table 4, the integrated effect between pH and bias potential seems most important compared with other integration of pH and light intensity or light intensity and bias potential.

### *3.3. Optimum condition and verification*

Under the help of using numerical technique with the software MATHEMATICS (v5.2, Wolfram Research, Inc.), the accurate optimal values of the variables were obtained. Table 5 summarizes the optimal levels of the variables (in both coded and real values) for decolourization efficiency of AB7. The predicted data of responses in each setting of variables are also presented.

Verification experiments were conducted under optimum operational conditions (pH 3.4, light intensity  $16.02 \times 10^2 \mu\text{W}/\text{cm}^2$  and bias potential 0.68V). The three replicate experiments yielded an average maximum AB7 removal efficiency of 90.13% (Table 6). The good agreement between the predicted and experimental results verified the validity of the model and existence of an optimal point. This indicated that the RSM was a powerful tool for determining the exact optimal values of the individual factors.

## **4. Conclusions**

A Box-Behnken design was adopted to study the effects of three influencing factors, which were pH, light intensity and bias potential, on the decolourization efficiency of AB7 by Ti/TiO<sub>2</sub> photoelectrocatalytic oxidation. A mathematical model was developed to correlate the influencing parameters to the colour removal efficiency. Through ANOVA analysis, pH was found to have the most significant effects on decolourization efficiency, compared to light intensity and bias potential. Process optimization was carried out and the optimal values of pH (3.4), light intensity ( $16.02 \times 10^2 \mu\text{W}/\text{cm}^2$ ) and bias potential (0.68V) were thus determined. Under such optimal condition, AB7 removal of 90.13% can be achieved, suggesting that the

Ti/TiO<sub>2</sub> photoelectrocatalytic oxidation is a promising technology for AB7 removal from aqueous solutions. Additionally, experimental values of AB7 removal were found to agree satisfactory with the predicted values.

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## Tables

**Table 1.** Relation between light intensity and vertical distance of lamp with Ti/TiO<sub>2</sub> electrode surface Z

Z (cm)	Light intensity ( $\times 10^2 \mu\text{W}/\text{cm}^2$ )
21	20.11
27	12.80
35	10.54
46	5.02

**Table 2.** Factors and levels in the three factor three-level RSM design

Variables	Symbols		Levels		
	Uncoded	Coded <sup>a</sup>	-1	0	1
pH	x <sub>1</sub>	X <sub>1</sub>	3.2	4.6	6
Light intensity ( $\times 10^2 \mu\text{W}/\text{cm}^2$ )	x <sub>2</sub>	X <sub>2</sub>	10	15	20
Bias potential (V)	x <sub>3</sub>	X <sub>3</sub>	0.1	0.6	1.1

<sup>a</sup> Code level limits based on preliminary investigations and also to reflect what is done in practice.  
( $X_1=(x_1-4.6)/1.4$ ,  $X_2=(x_2-15)/5$ ,  $X_3=(x_3-0.6)/0.5$ )

**Table 3.** The design of RSM and its actual and predicted values

Run	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	Decolourization efficiency (%)	
				Experimental	Predicted
1	-1	-1	0	79.94	79.18
2	-1	1	0	84.36	85.39
3	1	-1	0	67.96	66.93
4	1	1	0	65.88	66.64
5	0	-1	-1	64.84	63.88
6	0	-1	1	63.58	66.32
7	0	1	-1	67.86	65.12
8	0	1	1	70.05	71.00
9	-1	0	-1	70.86	74.58
10	1	0	-1	59.23	59.21
11	-1	0	1	82.85	78.87
12	1	0	1	62.96	63.24
13	0	0	0	86.86	86.84
14	0	0	0	86.82	86.84
15	0	0	0	86.85	86.84

**Table 4.** ANOVA table for the RSM model

Source	DF	SS	MS	$F_{\text{statistics}}$	$P$
X <sub>1</sub>	1	480.1901	480.1901	70.8775	0.0004
X <sub>2</sub>	1	17.4936	17.4936	2.5821	0.1690
X <sub>3</sub>	1	34.6528	34.6528	5.1149	0.0732
X <sub>1</sub> <sup>2</sup>	1	90.7604	90.7604	13.3965	0.0146
X <sub>1</sub> X <sub>2</sub>	1	10.5625	10.5625	1.5591	0.2671
X <sub>1</sub> X <sub>3</sub>	1	17.0569	17.0569	2.5177	0.1734
X <sub>2</sub> <sup>2</sup>	1	199.4903	199.4903	29.4454	0.0029
X <sub>2</sub> X <sub>3</sub>	1	2.9756	2.9756	0.4392	0.5368
X <sub>3</sub> <sup>2</sup>	1	615.4296	615.4296	90.8393	0.0002
Model	9	1374.489	152.721	22.5421	0.0016
Error	5	33.8746	6.7749		
Total	14	1408.364			

DF: degrees of freedom of variance source; SS: sum of squares; MS: mean of squares (=SS/DF);  $F$ :  $F$ -value of variance source =MS/MS<sub>res</sub>;  $P$ : probability of error to be significant. The numbers indicated as subscript of  $F$  are degrees of freedom of variance source (i.e. regression, lack of fit) and degree of freedom of error, respectively.  $R^2 = 0.9759$  and  $R^2 \text{ adj} = 0.9327$ , where  $R^2 = 1 - (\text{SS}_{\text{reg}}/\text{SST})$  and  $R^2 \text{ adj} = [1 - ((n - 1)/(n - p))](1 - R^2)$  (here,  $n$  is the number of experiments and  $p$  is the number of variables in model).

**Table 5.** Optimum value of the process parameter for maximum efficiency

Parameter	Optimum value	
	Coded values	Real values
Y (Decolourization efficiency, %)	90.44	90.44
X <sub>1</sub> (pH)	-0.8470	3.41
X <sub>2</sub> (Light intensity, $\times 10^2 \mu\text{W}/\text{cm}^2$ )	0.2033	16.02
X <sub>3</sub> (Bias potential, V)	0.1551	0.68

**Table 6.** Predicted and experimental value for the responses at optimum conditions

pH	Light intensity ( $\times 10^2 \mu\text{W}/\text{cm}^2$ )	Bias potential (V)	Decolourization efficiency (%)	
			Predicted	Experimental
3.41	16.02	0.68	90.44	90.13

## Figure Captions

Fig. 1: General formula and molecular structure of acid blue 7 dye

Fig. 2: Schematic representation of the PEC reactor

Fig. 3. Schematic diagram of BBD as a function of  $X_1$ ,  $X_2$  and  $X_3$

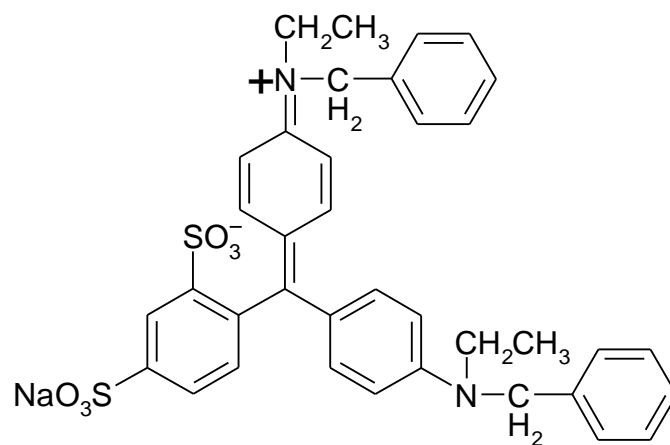
Fig. 4. Comparison between the experimental values and the predicted values of RSM model

Fig. 5. pH, light intensity surface and pH, light intensity contour of predicted  $Y$

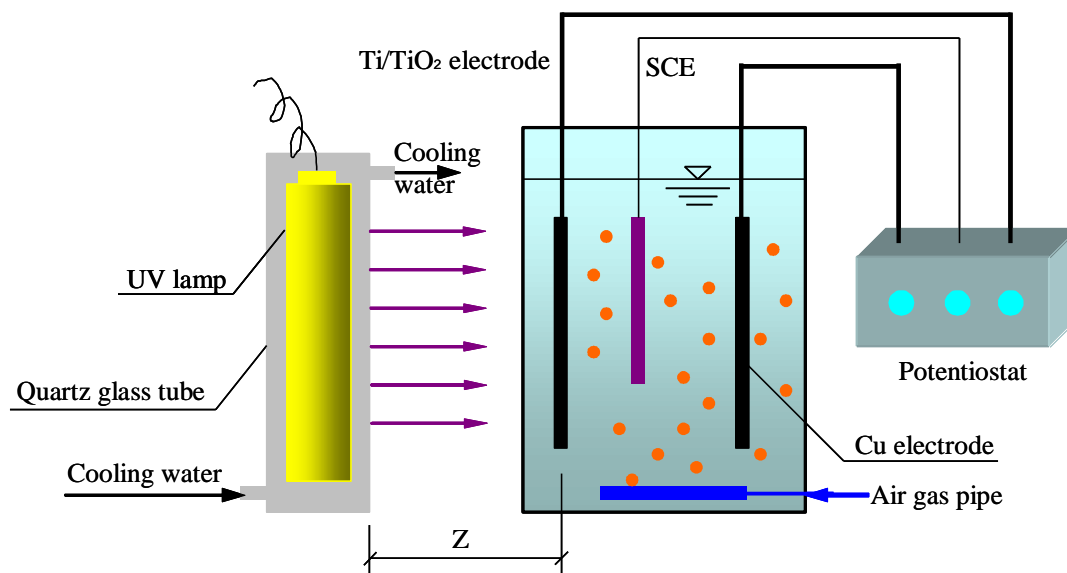
Fig. 6. pH, bias potential surface and pH, bias potential contour of predicted  $Y$

Fig. 7. Light intensity, bias potential surface and light intensity, bias potential contour of predicted  $Y$

## Figures

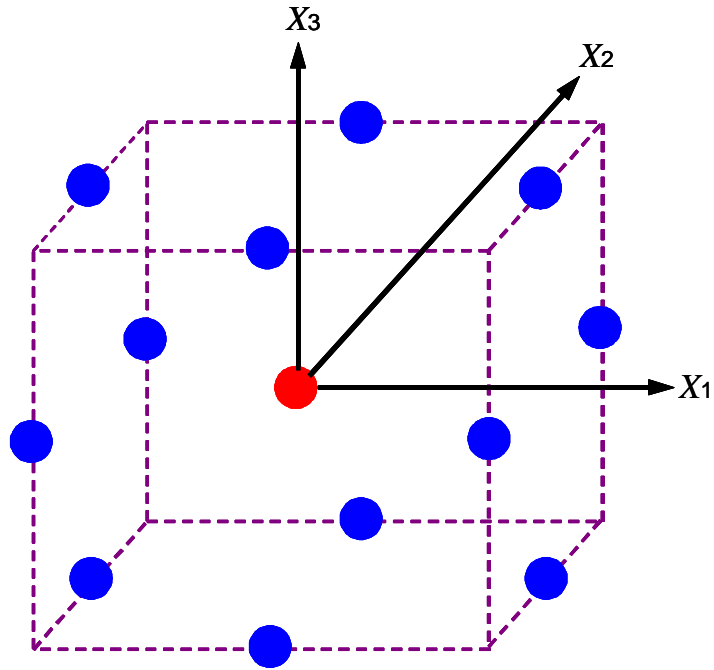


**Fig. 1.** General molecular structure of acid blue-7 dye

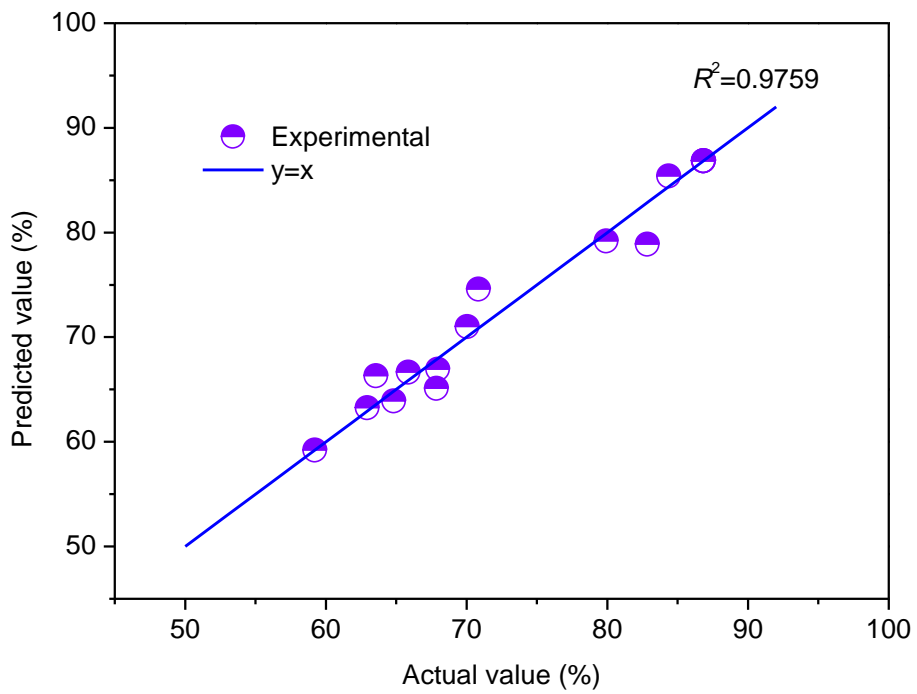


**Fig. 2.** Schematic diagram of photoelectrocatalytic reactor

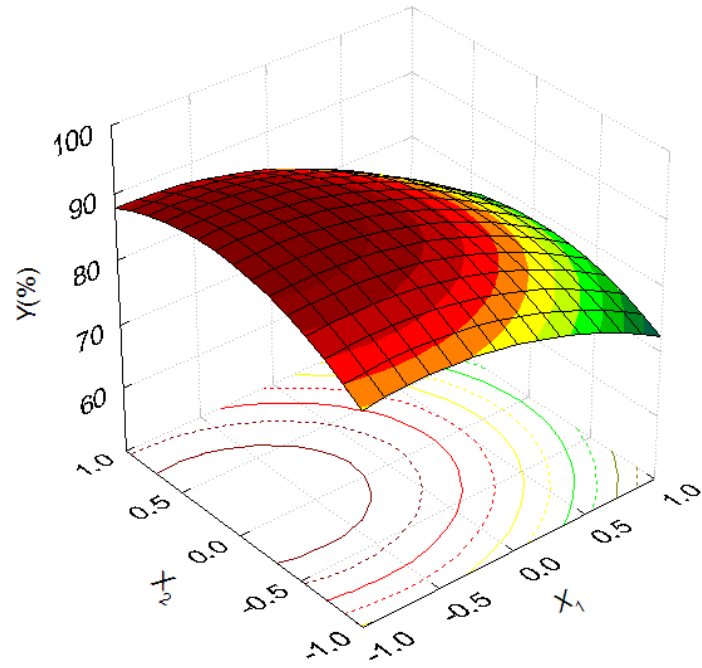




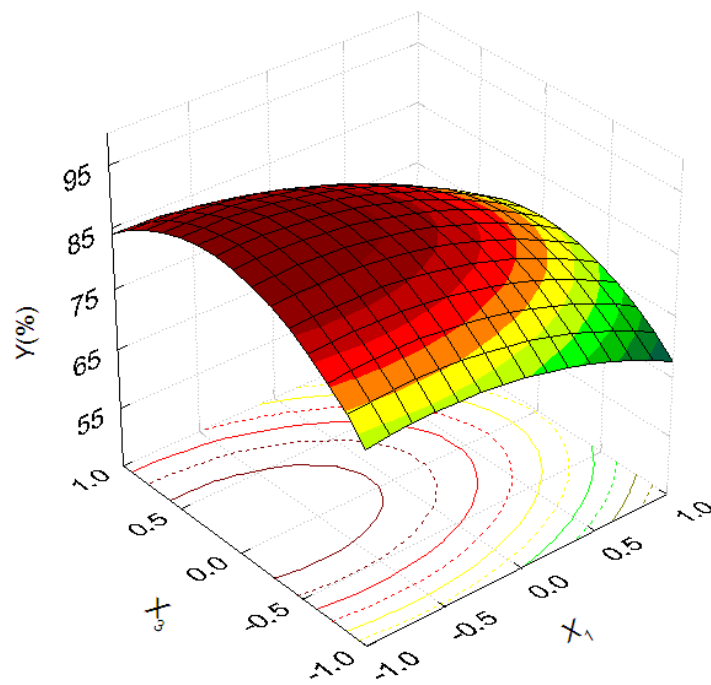
**Fig. 3.** Schematic diagram of BBD as a function of  $X_1$ ,  $X_2$  and  $X_3$



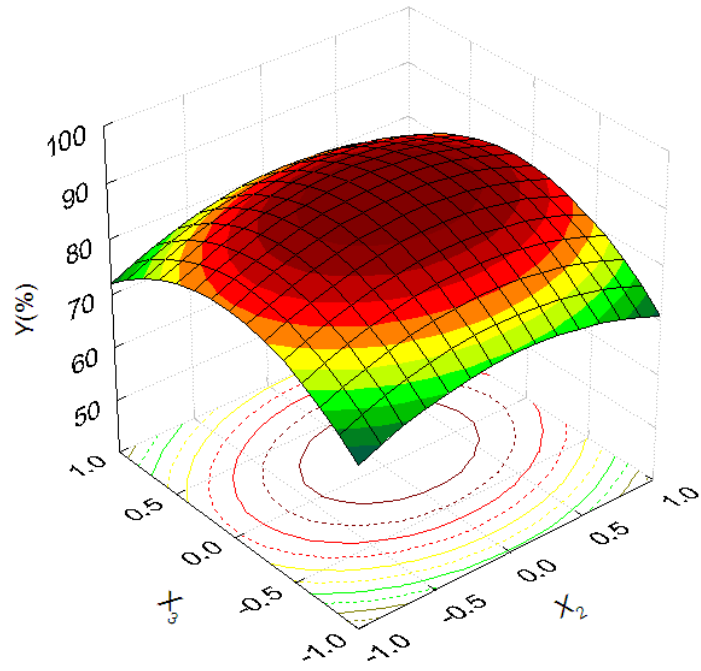
**Fig. 4.** Comparison between the experimental values and the predicted values of RSM model



**Fig. 5.** pH, light intensity surface and pH, light intensity contour of predicted  $Y$



**Fig. 6.** pH, bias potential surface and pH, bias potential contour of predicted  $Y$



**Fig. 7.** Light intensity, bias potential surface and light intensity, bias potential contour of predicted  $Y$