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Optimising photoelectrocatalytic oxidation of fulvic acid using response surface methodology

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Abstract: In this paper, statistics-based experimental design with response surface methodology (RSM) was employed to investigate the effect of operation conditions on photoelectrocatalytic oxidation of fulvic acid (FA) using a Ti/TiO₂ electrode in a photoreactor. Initially, the Box-Behnken design was employed including the three key variables (initial pH, potassium peroxodisulphate (K₂S₂O₈) and bias potential). Thereafter, the mutual interaction and effects between these parameters and optimum conditions were obtained in greater detail by means of SAS and Matlab software. The results of this investigation reveal that: (1) the regression analysis with R^2 value of 0.9754 shows a close fit between the experimental results and the model predictions; (2) three-dimension response surface plot can provide a good manner for visualizing the parameter interactions; and (3) the optimum pH, K₂S₂O₈ and bias potential is found to be 3.8, 88.40mg/L, 0.88V respectively and the highest FA removal efficiency of 57.1% can be achieved.

Keywords: Optimization; fulvic acid; Ti/TiO₂ electrode; response surface methodology; photoelectrocatalytic oxidation

1. Introduction

Natural organic matter (NOM) with its main components of humic acid (HA) and fulvic acid (FA) can be found most commonly in soil, natural water, and sediments which consisted of a mixture of the decomposition products of plant and animal residues [1,2]. The presence of NOM in raw water could considerably affect the water quality during the water purification process. For example, it is widely accepted that the trihalomethane (THM), one of the disinfection by-products, can be generated from chlorination stage in drinking water treatment when raw water contains NOM [3,4]. In Tianjin, a major city in northern China, it was reported that fulvic acid represents over 70% of NOM in surface waters [5]. Thus, proper control of fulvic acid is a very important issue during the surface water treatment. However, according to the literature, NOM with fulvic acids is difficult to remove by the conventional treatment processes, such as coagulation and sedimentation.

It is noted that photocatalytic (PC) process particularly with TiO₂ as photocatalyst has attracted considerable attention over last decade [6,7]. The appeal of this technology is the prospect of

complete mineralization of the pollutants into harmless compounds to environment in addition to the abundance and relatively low cost, chemical stability and non-toxic nature of the catalyst. However, the practical application of this technology has been limited due to its low PC efficiency and the difficulties of TiO₂ powder separation [8,9]. Thus, an attractive process popularized in the past few years for degrading such organic pollutants is the photoelectrocatalytic (PEC) process that can prevent carrier charge recombination, leading a higher efficiency [10-12]. However, few works have focused on its use for fulvic acid removal from water.

Conventionally, wastewater treatment processes are optimized by using ‘one-at-a-time strategy’ of treatment parameters. Moreover, this approach is time consuming. More importantly the approach ignores the combined interactions between physicochemical parameters [13]. In contrast, statistical experimental design using response surface methodology (RSM) [14] can optimize all the effecting parameters and thus eliminate the limitations of a single factor optimising. The RSM has been widely used in various fields such as in biochemistry [15, 16], in material processing for describing the performance of coated carbide tools [17], and in water treatment for studying the optimization of the coagulation-flocculation process [18]. However, few studies were reported to optimize influencing factors and their interactions to improve FA removal efficiency.

Therefore, an attempt has been made to employ response surface methodology for optimising the key influencing parameters (i.e. initial pH, potassium peroxodisulphate (K₂S₂O₈) and bias potential) of FA photoelectrocatalytic degradation using Ti/TiO₂ as electrodes in a photoreactor.

2. Experimental

2.1. Materials

Fulvic acids were provided by Beijing Chem. Corp with chemical structure to be shown in reference [19]. The concentration of FA used in this experiment was 11.95 mg/L (expressed as TOC). The pH of the FA-rich solutions was adjusted by the addition of either H₂SO₄ or NaOH. All other chemicals were used with GPR grade. The water used for preparation of the FA-rich solutions was produced by Millipore Simplicity 185 ultra-pure water equipment.

2.2. *Ti/TiO₂ electrode preparation*

A Ti sheet (4×5cm, thickness: 140μm) was ultrasonically cleaned in alcohol. The treated Ti and a copper (Cu) plate with same size were submerged in 0.5M H₂SO₄+0.3M H₃PO₄+0.3M H₂O₂+0.03M HF solution and an electrical current was applied between Ti and Cu plate using a DC power supply. The process of anodic oxidation is as follows: (1) the voltage increased to 40V with a rate of 1-3V/min; (2) the voltage was kept at 40V for 30 min; (3) the Ti sheet was picked out and put it into a 0.1 M HF solution. This step aimed to dissolve the fresh titanium oxide on Ti surface and form a smooth surface; repeating step (1) and then keep the voltage at 40V for 25 hours to form TiO₂ film. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis are carried out for Ti/TiO₂ electrode as shown in Fig. 1 & 2. The results clearly show a microporous surface structure and a mixture crystal phase of anatase and rutile.

2.3. *Photoreactor*

The reactor and supplementary equipment are shown in Fig. 3. The main components are the glass reactor, ultraviolet light source, and a potentiostat. The low pressure UV lamp (11W, Philip) emitting a wavelength of predominantly 253.7 nm was suspended vertically inside the quartz glass cylinder in the middle of the reactor. The reactor contained a 200mL sample solution, in which both a Ti/TiO₂ (as anode) and a copper plate (as cathode) were placed in parallel. The photoelectrocatalytic reaction employed a potentiostat (ISO-TECH 1PS 1810H) to connect the two electrodes. Gas was supplied from a porous titanium plate in order to provide dissolved oxygen for photoreaction and to stir the solution. The reaction temperature was maintained at about 20°C with the aid of recirculated cooling water. Additionally, the exterior wall of the reactor was covered with a reflecting aluminum foil to improve the efficiency of UV utilization. All experiments were carried out at fixed irradiation time of 2h.

2.4. *Analytical methods*

SEM (Pholops XL-30 ESEM) was used to analyze the surface morphology and average pore

size. High tension was selected at 20kV. XRD (Rigaku PINT 2200V) was used to determine the crystal phase composition of the Ti/TiO₂ electrode. The pH was measured by using a HACA digital pH-meter (model pHs-3C). The total organic carbon was analyzed using TOC-5000A (Shimadzu, Japan). The TOC removal efficiency (Y) is calculated with Eq. (1)

$$Y(\%) = \frac{TOC_0 - TOC}{TOC_0} \times 100 \quad (1)$$

where TOC_0 is the initial concentration of FA and TOC is the concentration of FA at 2h.

2.5. Response surface methodology

Response surface methodology (RSM) is derived from mathematical and statistical technique. It can be used for studying the effect of several factors at different level and their influence on each other [20]. In the present study, A Box-Behnken design [21] was chosen to evaluate the combined effect of three independent variables, i.e. initial pH, potassium peroxodisulphate (K₂S₂O₈) and bias potential termed as X_1 , X_2 and X_3 , respectively. The minimum and maximum ranges of variables were investigated and the full experimental plan with respect to their values in actual and coded form was listed in Table 1. The coded and actual values of the three independent variables together with the responses are shown in Table 2.

The principle of RSM was described by Khuri and Cornell [22]. An empirical second-order polynomial model for three factors was in the following form:

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

Where Y is the predicted response (FA removal efficiency, %) used as a dependent variable; X_i ($i = 1, 2$ and 3) are the input predictors or controlling variables; and β_0 , β_i ($i = 1, 2, 3$) and β_{ij} ($i = 1, 2, 3; j = 1, 2, 3$) are the model coefficient parameters. The coefficient parameters are estimated by multiple linear regression analysis using the software of Statistical Analysis System (SAS) [23] and response surface contour plots are generated using MATLAB 6.5. SAS is also used to analyze the data collected by performing analysis of variance (ANOVA).

3. Results and discussion

3.1. Model fitting

Table 3 shows the coefficients of the variables in the models and their corresponding R^2 . An empirical relationship between the response and the variables expressed by the following fitting second-order polynomial equation:

$$Y(\%) = 53.24333 - 7.7475X_1 + 1.51625X_2 + 2.04375X_3 - 4.670417X_1^2 - 1.625X_1X_2 - 2.065X_1X_3 - 7.637917X_2^2 + 1.4375X_2X_3 - 13.19792X_3^2 \quad (3)$$

Where Y is the FA removal efficiency in terms of TOC.

Coefficient of determination, R^2 , is defined as the ratio of the explained variation to the total variation and is a measure of the degree of fit [24]. It is also the proportion of the variability in the response variables, which is accounted for by the regression analysis [25]. When R^2 approaches unity, the better the empirical model fits the actual data. The smaller the value of R^2 , the less relevant the dependent variables in the model have in explaining the behavior variation [26,27]. The response surface models developed in this study for predicting the TOC removal efficiency of FA were adequate. Joglekar and May [28] suggested that for a good fit of a model, R^2 should be at least 0.80. The R^2 values for these response variables were higher than 0.80, indicating that the regression models explained the reaction well. The R^2 values were 0.9754 for FA removal.

Table 4 shows the results of RSM model fitting in the form of analysis of variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variances for the purpose of testing hypotheses on the parameters of the model [29]. The ANOVA of this model has demonstrated that the model is highly significant, as is evident from the F ($F_{\text{model}}= 22.06645$) and a very low probability value ($P>F=0.001655$). P value lower than 0.01 indicates that the model is considered to be statistical significant [30].

3.2. Statistical analysis

RSM also gives an insight into the quadratic and interaction effect of the parameters from Table 3. These analyses were done by means of Fisher's ' F ' test and Student ' t ' test. The Student ' t ' test

was used to determine the significance of the regression coefficients of the parameters. The P values are used as a tool to check the significance of each of the interaction among the variables, which in turn may indicate the patterns of the interactions among the variables. In general, the larger the magnitude of t and smaller the value of P , the more significant is the corresponding coefficient term [22]. The parameter estimate and the corresponding P values suggest that, among the test variables, pH value produces the largest effect on TOC removal efficiency.

The coefficient of the quadratic effect of $K_2S_2O_8$ concentration ($P=0.002705$) and bias potential ($P=0.000217$) was slightly significant and other factors were not significant with high P values. The coefficients of the quadratic effects among the variables did not appear to be very significant in comparison to the linear and interaction effects for FA removal efficiency. However, in the interaction effect none of the variables were found significant except between pH and bias potential ($P=0.182059$).

The effect of process conditions on FA removal is shown in Table 2 by the coefficient of the second-order polynomials. To aid visualization and help in identifying the type of interactions between test variables, the response surfaces for FA removal efficiency are shown in Figs. 4-6. Here each plot represents the effect of two variables at their studied range with the other one maintained at its zero level. The shapes of contour plots indicate the nature and extent of the interactions. Prominent interactions are shown by the elliptical nature of the contour plots, while less prominent or negligible interactions would otherwise be shown by the circular nature of the contour plots.

As can be seen in the plots, there is an increase in FA removal with increasing $K_2S_2O_8$ concentration, bias potential and decreasing pH values. However, an increase in both $K_2S_2O_8$ and bias potential beyond the optimum region resulted in a decrease in the expected FA removal.

With decreasing pH values, an increase in FA removal efficiency can be observed. Thus the efficiency of FA removal by photoelectrocatalytic oxidation is influenced by pH below 4; however, it is rapidly decreased with increasing pH in the range of 4-7. This is consistent with the conclusion made by Kim Anderson [31].

At a bias potential lower than critical values, the efficiency of FA removal by oxidation is rapidly increased. As for the enhancement of the degradation efficiency, potential applied across the electrodes exerts its influence in two ways. On the one hand, it accelerates the separation of

electron-hole pairs and produces more oxidative species. This is the central role it plays. On the other hand, the applied positive potential on the working electrodes may enhance the adsorption of FA which increases degradation efficiency to some extent. When the bias potential applied is higher than critical value, FA degradation decreased slightly. This is due to the fact that electrolysis of H_2O_2 becomes the main reaction at electrodes as a higher bias potential applied across the electrodes.

3.3. Optimization of influencing factors

The main objective of the optimization is to determine the optimum values of variables for FA removal efficiency from the model obtained via experiment. In this optimization study, FA removal efficiency is chosen as the objective function. Furthermore, optimum conditions are often calculated in the presence of some constraints which ensure them to be more realistic. If the model used in the optimization study is an empirical basis, high and low levels of the process parameters in the experimental design are considered.

Thus, the optimization problem is defined as:

$$\text{Maximize } Y \quad (4)$$

Constraints on the parameters X_i :

$$-1 < X_i < +1, i=1, \dots, 3 \quad (5)$$

The optimization problem given in Eq. (4) is solved using constrained optimization program supplied in the Matlab optimization toolbox. Maximum FA removal efficiency is 57.06%, whereas maximum values of the process variables in coded values given as follows: $X_1=-0.9012$, $X_2=0.2101$ and $X_3=0.1594$. According to relation between X_i and x_i , the uncoded values of the test variables are shown in Table 5.

3.4. Verification of the results

To confirm the model adequacy for predicting maximum FA removal efficiency, three additional experiments using this optimum operation conditions (Table 5) were performed. The three replicate experiments yielded an average maximum FA removal efficiency 56.26% (Table 6). The good agreement between the predicted and experimental results verified the validity of the

model and reflected the existence of an optimal point. The results derived from this study indicated that the RSM is a powerful tool for optimizing the individual factors.

4. Conclusions

The present study has demonstrated the applicability of the Ti/TiO₂ electrode for fulvic acid degradation. Under optimal values of process parameters (initial pH= 3.8, K₂S₂O₈ = 88.40 mg/L and bias potential= 0.88V), 57.06% removal of FA is obtained. Results from this study show that response surface methodology is one of the suitable methods to optimize the best operating conditions in multi-factor operating environment for the purpose of obtaining maximum FA degradation. In addition, it can be concluded that all the three parameters tested have significant effect on FA removal. The quadratic equation developed in this study shows the presence of a high correlation between observed and predicted values. Interestingly, 3-dimension response surfaces plots can be a good way for visualizing the parameter interaction. Overall, statistical approach has been testified to be a powerful tool in studying photoelectrocatalytic oxidation process.

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Tables

Table 1 Level and code of variables for RSM^a

Variables	Symbols		Levels		
	Uncoded	Coded	-1	0	1
pH	x_1	X_1	3.5	6.5	9.5
K ₂ S ₂ O ₈ (mg/L)	x_2	X_2	40	80	120
Bias potential (V)	x_3	X_3	0.3	0.8	1.3

^a Code level limits based on preliminary investigations and also to reflect what is done in practice. ($X_1=(x_1-6.5)/3$, $X_2=(x_2-80)/40$, $X_3=(x_3-0.8)/0.5$)

Table 2 The design of RSM and its actual and predicted values

Run	X_1	X_2	X_3	FA removal (%)	
				Experimental	Predicated
1	-1	-1	0	46.34	45.54125
2	-1	1	0	50.76	51.82375
3	1	-1	0	34.36	33.29625
4	1	1	-1	32.28	18.46458
5	0	-1	1	31.24	31.49749
6	0	-1	-1	28.68	30.28499
7	0	1	1	33.26	37.40499
8	0	1	-1	36.45	30.44249
9	-1	0	1	37.26	47.23124
10	1	0	-1	25.63	27.64874
11	-1	0	-1	49.25	39.01374
12	1	0	1	29.36	27.60624
13	0	0	0	53.26	53.24333
14	0	0	0	53.22	53.24333
15	0	0	0	53.25	53.24333

Table 3 Coefficient of regression and t checking

Variable	Standard deviation	t	$P>t$	Co-efficient
X_1	0.942638	-8.21896	0.000434	-7.7475
X_2	0.942638	1.608518	0.168634	1.51625
X_3	0.942638	2.168118	0.082338	2.04375
X_1X_1	1.387525	-3.366	0.019977	-4.670417
X_1X_2	1.333091	-1.21897	0.277221	-1.625
X_1X_3	1.333091	-1.54903	0.182059	-2.065
X_2X_2	1.387525	5.5047	0.002705	-7.637917
X_2X_3	1.333091	1.078321	0.330141	1.4375
X_3X_3	1.387525	9.51184	0.000217	-13.19792

$R^2=97.54\%$; Adj $R^2=93.12\%$

Table 4 Analysis of variance (ANOVA) for the RSM model

Source	Degree of freedom (DF)	Sum of squares (SS)	Mean squares (MS)	$F_{statistics}$	$P>F$
Model	9	1411.74	156.86	22.06645	0.001655
Linear	3	531.9975	531.9975	74.83933	0.251406
Square	3	939.0851	939.0851	132.1068	0.022899
Interaction	3	35.88503	35.88503	5.048165	0.789421
Error	5	35.54264	7.108528		
Total	14	1447.282			

Table 5 Optimum value of the process parameter for maximum efficiency

Parameter	Optimum value
Y (removal efficiency, %)	57.06
X_1 (pH)	3.80
X_2 ($K_2S_2O_8$, mg/L)	88.40
X_3 (Bias potential, V)	0.88

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

	FA removal efficiency (%)
Predicated	57.06
Experimental	56.26

Figure Captions

Fig.1: The SEM image of the surface of Ti/TiO₂ film

Fig.2: X-ray diffraction Spectra for Ti/TiO₂ electrode

Fig.3: Schematic representation of the photoelectrocatalytic reactor

Fig.4: X_1 , X_2 surface and X_1 , X_2 contour of predicted Y ($X_3=0.8V$)

Fig.5: X_1 , X_3 surface and X_1 , X_3 contour of predicted Y ($X_2=80mg/L$)

Fig.6: X_2 , X_3 surface and X_2 , X_3 contour of predicted Y ($X_1=6.5$)

Figures

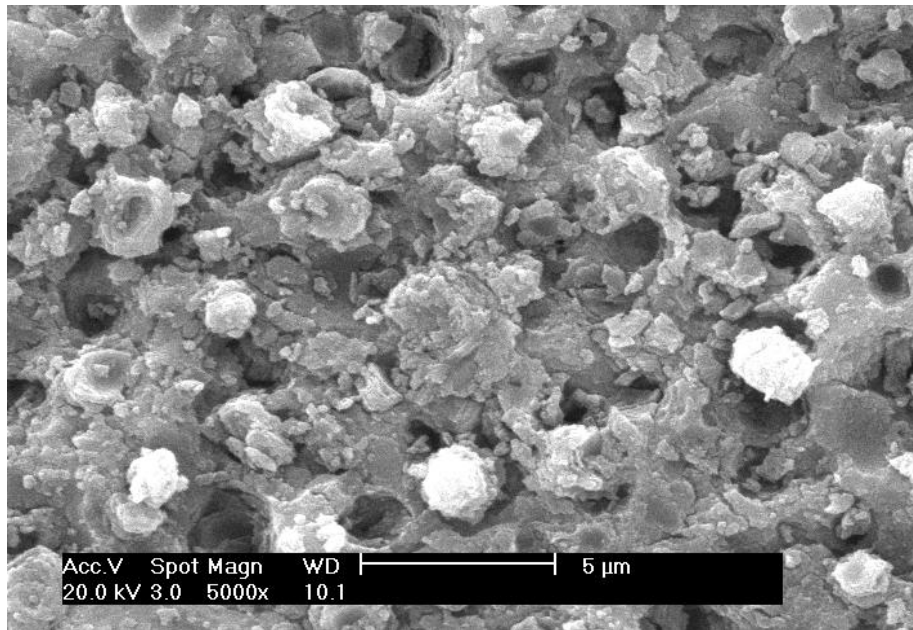


Fig.1. The SEM image of the surface of Ti/TiO₂ film

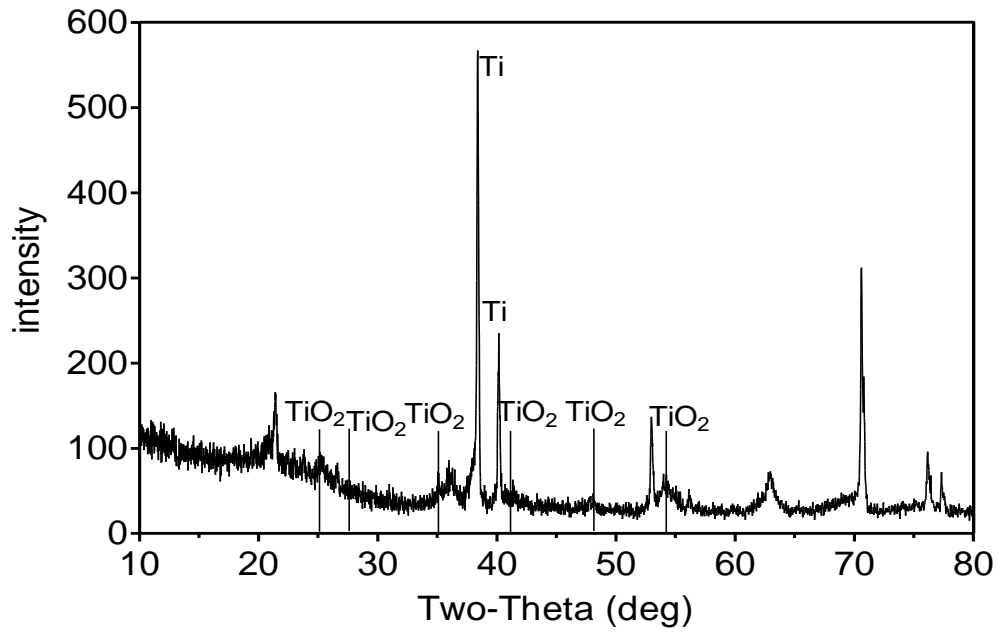


Fig.2. X-ray diffraction Spectra for Ti/TiO₂ electrode

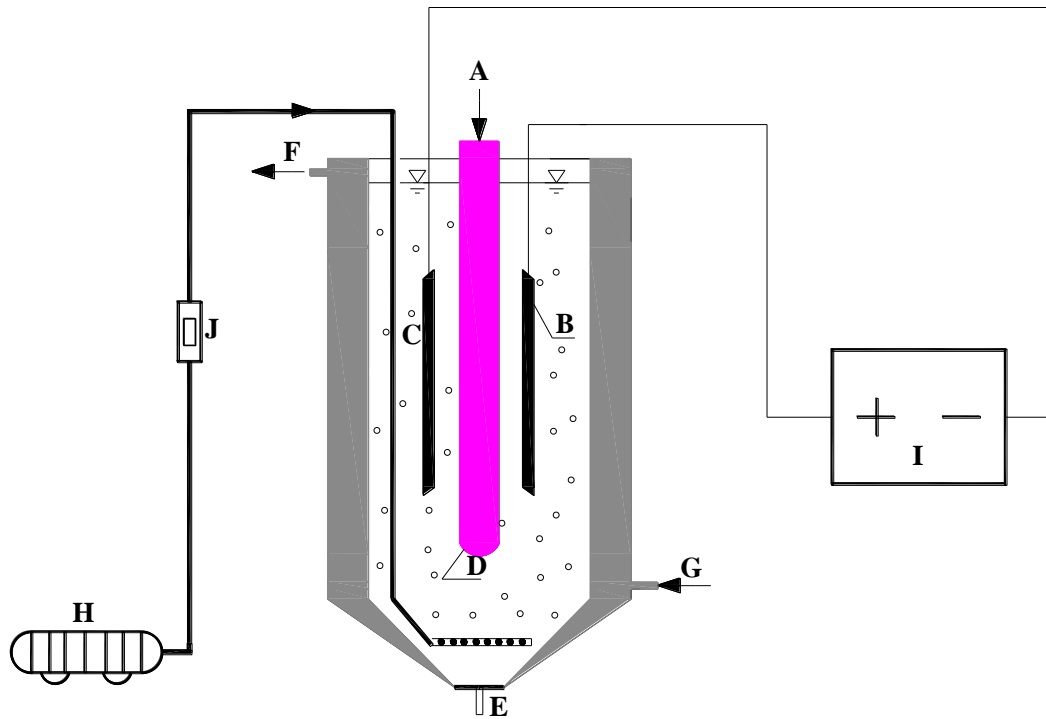


Fig.3. Schematic representation of the photoelectrocatalytic reactor

A: UV lamp B: Ti/TiO₂ electrode C: Cu electrode D: Quartz sleeve E: sampling F: outlet of cooling water G: inlet of cooling water H: air compressor I: potentiostat J: air flow meter

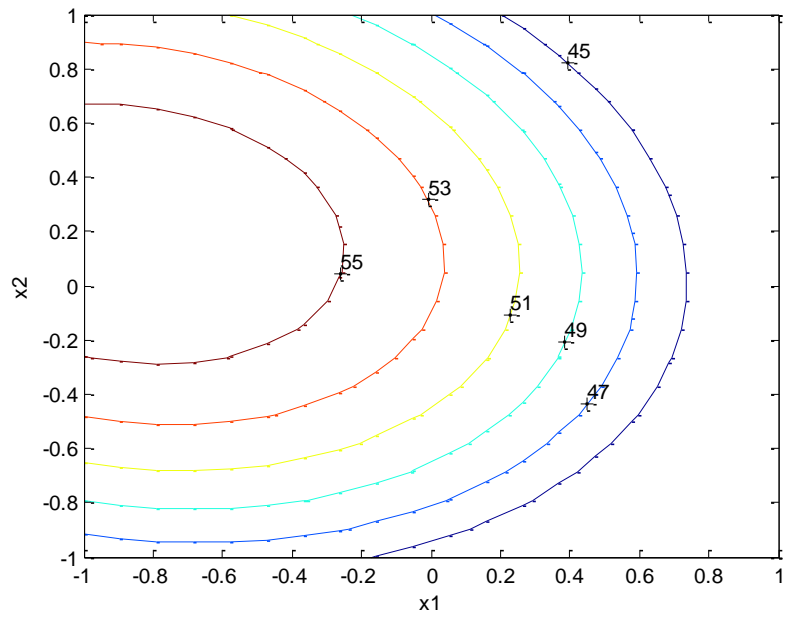
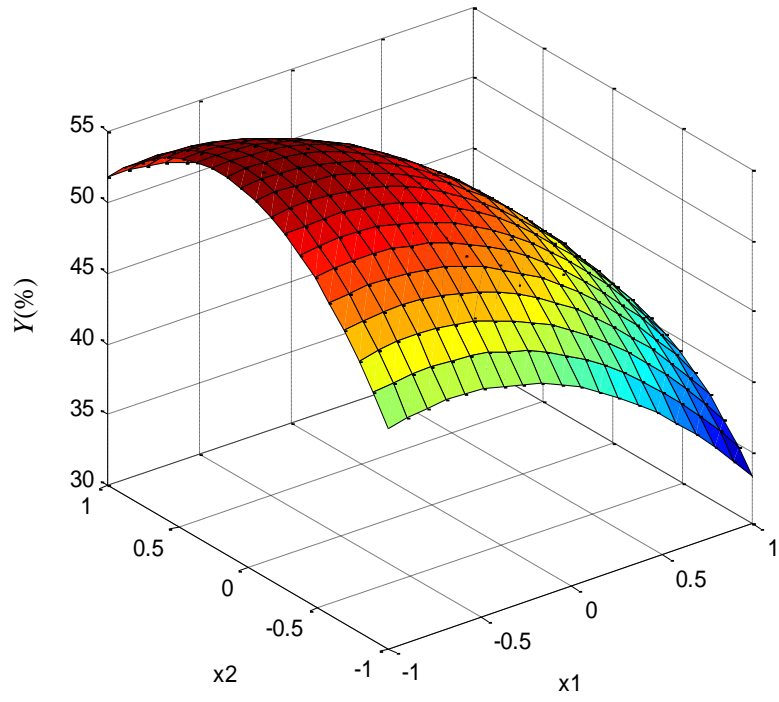


Fig.4. X_1 , X_2 surface and X_1 , X_2 contour of predicted Y ($X_3=0.8V$)

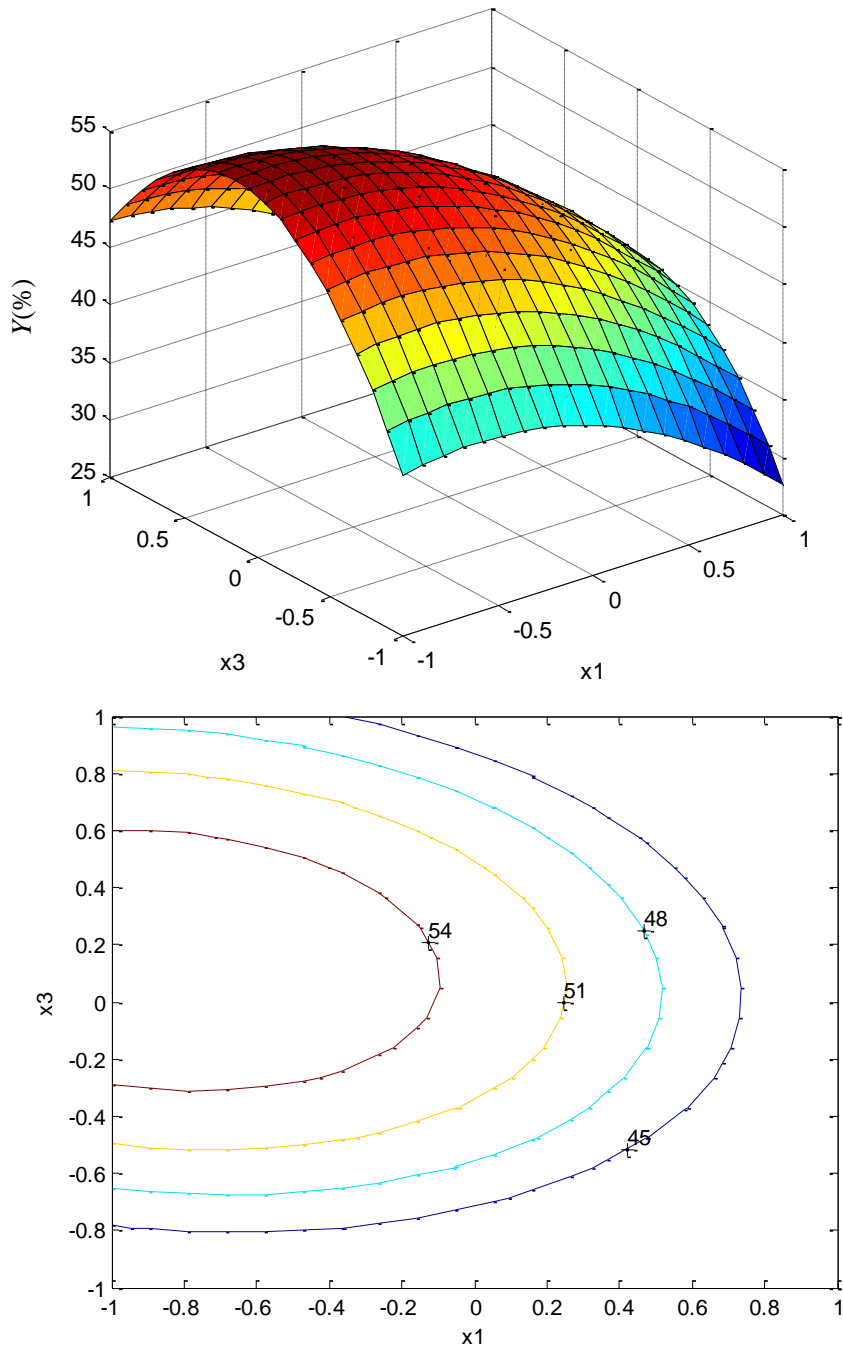


Fig.5. X_1, X_3 surface and X_1, X_3 contour of predicted Y ($X_2=80\text{mg/L}$)

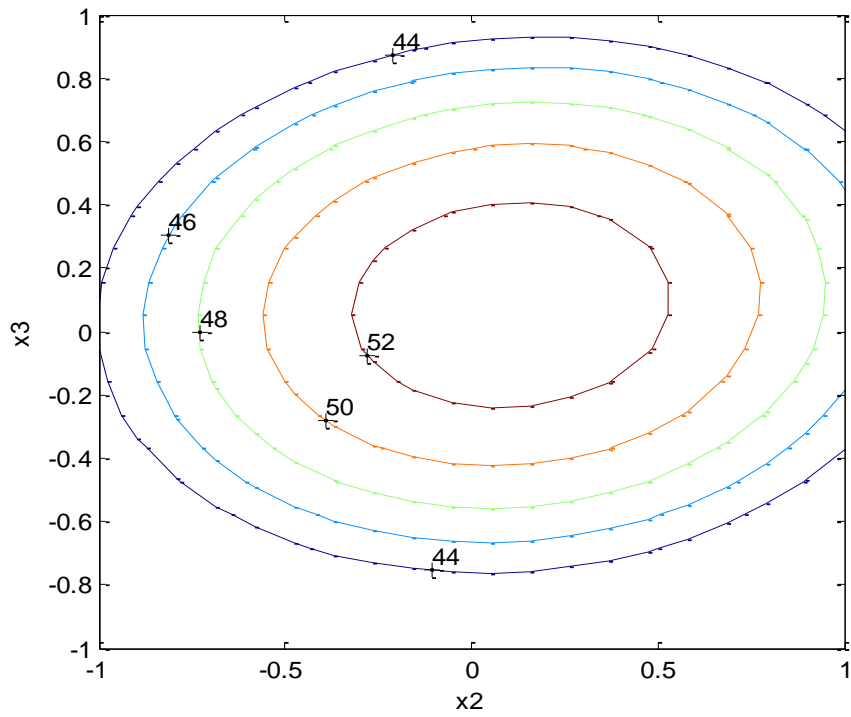
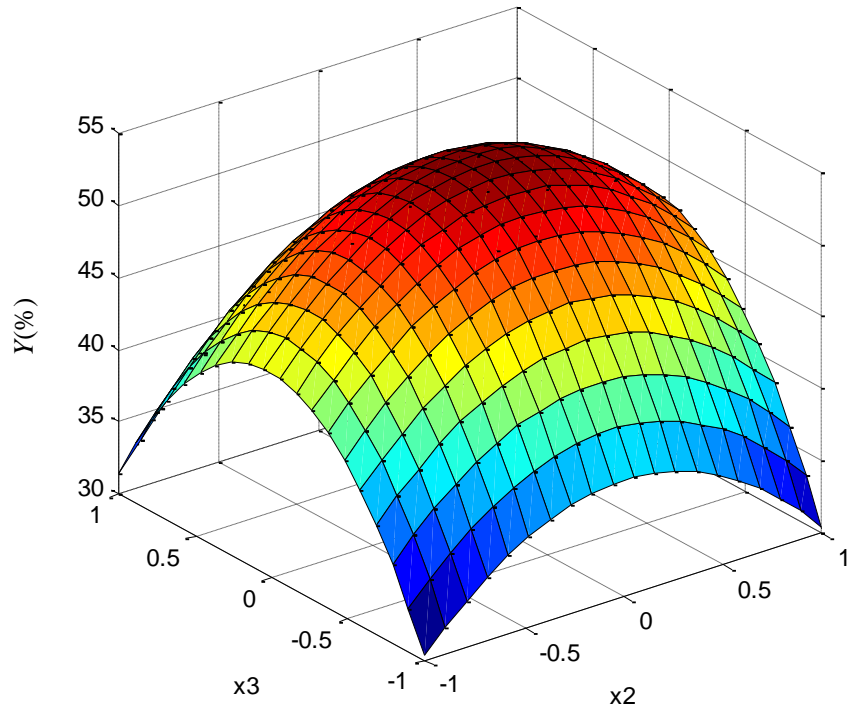


Fig.6. X_2 , X_3 surface and X_2 , X_3 contour of predicted Y ($X_1=6.5$)