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استفاده از روش طراحی آزمایش رویه‌ی پاسخ جهت بهینه‌سازی تأثیر پارامترها بر تخریب کاتالیستی ٤-کلرو-٢ نیترو فنل

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The Response Surface Methodology to Optimize the Catalytic Degradation of 4-Chloro 2-Nitro Phenol

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چکیده
تخریب ترکیب آروماتیک ۴_کلرو ۲_نیتروفنل با استفاده از نانوذرات تیتانیم دی اکسید به عنوان کاتالیزور تحت فرایند کوپل‌شده ازوناسیون سونولیزی انجام گرفت. سپس از روش طراحی آزمایش رویه‌ی پاسخ جهت بهینه‌سازی تأثیر پارامترها بر تخریب ۴_کلرو ۲_نیتروفنل استفاده شد. برای بررسی تأثیر شرایط عملیاتی در تخریب آلاینده چهار متغیر مستقل انتخاب شد که عبارتند از: غلظت اولیه ۴_کلرو ۲_نیتروفنل ، مقدار ازون ورودی، غلظت تیتانیم دی اکسید و قدرت فرایند التراسونیک. سپس برای بررسی اثرات عوامل اصلی و متقابل در تخریب از جدول آنالیز واریانس استفاده شد. تجزیه تحلیل نتایج آنالیز واریانس نشان داد که مدل از نظر آماری قابل قبول است و مشاهده شد که پیشنهادات روش رویه‌ی پاسخ با نتایج تجربی موافق است.

واژه‌های کلیدی
روش طراحی آزمایش رویه پاسخ؛ فرایند کوپل شده ازوناسیون سونولیزی؛ تخریب کاتالیستی ۴-کلرو-۲ نیترو فنل.

Abstract
The catalytic degradation of 4-chloro 2-nitro phenol aromatic compound has been studied with coupled ozone-sonolysis method. The response surface methodology was used to optimize the influence of operation parameters on the catalytic degradation of 4-chloro 2-nitro phenol. In order to evaluate the influence of operation conditions in the degradation of 4-Chloro 2-Nitro Phenol, four independent variable chosen: 4-Chloro 2-Nitro Phenol concentration, mass flow rate of O_3, TiO_2 concentration and ultra sonic power. Analysis of variance was employed to consider main factors effects and interactive effects in the optimization of catalytic degradation of of 4-Chloro 2-Nitro Phenol. Analysis of variance results present that the model is statistically significant. The response surface methodology predictions were in agreement with the experimental values.

Keywords
Response Surface Methodology; Coupled Ozone-Sonolysis Method; Catalytic Degradation of 4-Chloro 2-Nitro Phenol.

1. INTRODUCTION

Phenol has been considered as a priority contaminant and found in wastewaters and industrials effluents. Phenol derivatives have been known as a persistent chemical in the environment. Different methods have been developed to remove Phenol derivatives from wastewaters and industrials effluents. Conventional methods have suffered from some disadvantages such as long reaction time, low efficiency and high cost. Recently, the advanced oxidation processes (AOP_S) are used to depredate phenol compounds, which have more chemical stable structures in the environments.

Advanced oxidation processes are based on that to produce hydroxyl radicals or other intermediates, which be able to oxidize toxic and non-biodegradable compounds. The advanced oxidation processes are widely used to treatment wastewaters such as ozonation, UV, Fenton process, hydrogen peroxide and TiO_2 catalysts [1-8]. Recently, many tries have been done to

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substitute more effective way such as Response Surface Methodology (RSM) for One-factor-at-atime method. This method has been established based on analysis, statistical explanation, and experimental design is a good strategy to determine the optimal condition in multiple variables systems [9-12]. In addition, the above three-stage procedure is typically operated in an iterative manner, where the information attained from previous iterations is utilized to guide the search for better response variables. RSM is particularly applicable to problems where the understanding of the process mechanism is limited and/or is difficult to be represented by the first principles mathematical model. Depending on specific objectives in practice, these RSM techniques differ in the experimental design procedure, the choice of empirical models, and the mathematical formulation of the optimization problem. In this study, the response surface methodology (RSM) was used to optimize the catalytic degradation of 4-chloro 2-nitro phenol aromatic compound by coupled ozone sonolysis method.

2. EXPERIMENTAL

2.1. Experiment Process

All experimental were conducted in a 250 ml glass reactor (6). Ozone gas was generated from the ozone generator (1) with a flow meter (2) for measuring gas mass flow rate. Samples withdrawal at different interval to measure 4-chloro 2-nitro phenol residual by UV spectrometer. Coupled Ozone-Sonolysis Method was used to catalytic degradation as shown in Fig. 1.

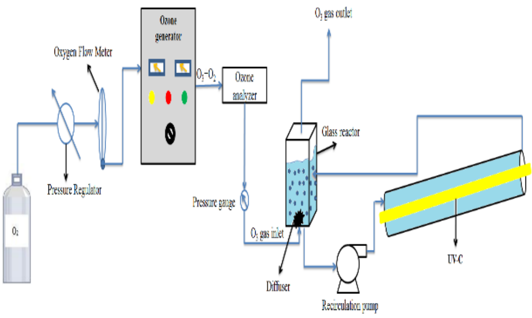

Fig. 1. Schematic diagram of experiment system.

2.2. Design of Experiments

In this study, the response surface methodology was used to optimize the catalytic degradation of 4-chloro 2-nitro phenol coupled with the factorial Experimental Design of central composite design (CCD). In order to evaluate the influence of operation conditions in the degradation of 4-Chloro 2-Nitro Phenol, four independent variable chosen: 4-Chloro 2-Nitro Phenol concentration (X_1), mass flow rate of O_3 (X_2), TiO_2 concentration (X_3) and ultra sonic power (X_4) as presented Table 1. Miniclip softwares and detailed menus on quality control issues and its extremely high outputs have made this software a lot in the field of quality control. According to the central composite design with Minitab17 31 experiments are designed for 4 independent variables as shown in Table 2. The independent and dependent variable are correlated by a second order polynomial equation. Where Y is response, k is the number of factors, β_o off set term and β_i, β_{ii} and β_{ij} are the first- order, second - order and interaction effects respectively.

$$Y= \beta_o + \sum^{k}_{i=1} \beta_i X_i + \sum^{k}_{i=1} \beta_i X_i^2 + \sum^{k}_{1\leq i\leq j} \beta_{ij} X_i X_j$$

Table 1. Independent Variables for Response Surface Methodology.

Variables	Factor	Range and Level				
		-2	-1	0	+1	+2
X_1	$[CNPH]_o$ (mg/L)	70	80	90	100	110
X_2	O_3 (mg/h)	5	10	15	20	25
X_3	TiO_2 (mg/L)	50	100	150	200	250
X_4	SU (W)	100	200	300	400	500

Table 2. Designed Experiments for Degradation of 4-Chloro 2-Nitro Phenol.

RUN	$[CNPH]_o$ (mg/L)	O_3 (L/min)	TiO_2 (mg/L)	SU (W)
1	80	10	100	200
2	100	10	100	200
3	80	20	100	200
4	100	20	100	200
5	80	10	200	200
6	100	10	200	200
7	80	20	200	200
8	100	20	200	200
9	80	10	100	400
10	100	10	100	400
11	80	20	100	400
12	100	20	100	400
13	80	10	200	400
14	100	10	200	400
15	80	20	200	400
16	100	20	200	400
17	70	15	150	300
18	110	15	150	300
19	90	5	150	300
20	90	25	150	300
22	90	15	50	300
22	90	15	250	300
23	90	5	150	100
24	90	15	150	500
25	90	15	150	300
26	90	15	150	300
27	90	15	150	300
28	90	15	150	300
29	90	15	150	300
30	90	15	150	300
31	90	15	150	300

3. RESULT AND DISCUSSION

3.1. XRD of nano-TiO_2

The phase analysis and structure of as-prepared TiO_2 was investigated using XRD pattern and the results are presented in Fig. 2. XRD patterns exhibited strong diffraction peaks at 24° and 52° indicating TiO_2 in the anatase phase. All peaks are in good agreement with the standard spectrum (JCPDS no.: 84-1286).

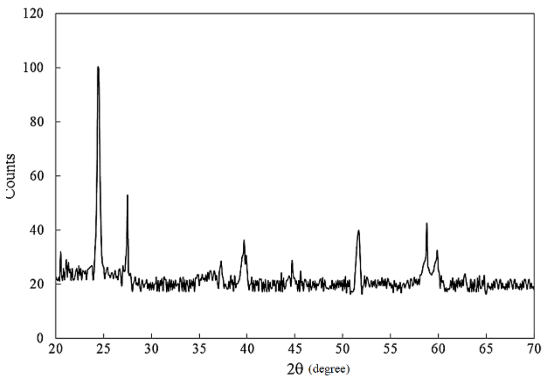

Fig. 2. XRD pattern of TiO_2.

3.2. FT-IR spectrum of nano- TiO_2

Fig. 3 shows the FTIR spectra of as prepared TiO_2 sample. The peaks at 3400 and 1650 cm^{-1} in the spectra are due to the stretching and bending vibration of the -OH group. In the spectrum of pure TiO_2, the peaks at 550 cm-1 show stretching vibration of Ti-O and peaks at 1450 cm^{-1} shows stretching vibrations of Ti-O-Ti.

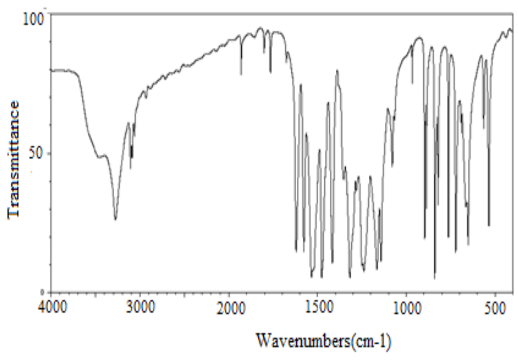

Fig. 3. FT-IR spectrum of TiO_2.

3. 3. Optimization function

The second order polynomial equation shows the relation between the depended variable and in-depended variables.

Absorbance% = $- 27.856 + 1.553X_1 + 1.913X_2 + 0.290X_3 + 0.0855X_4 + 0.0311X_1 X_2 + 2.70625E-004\ X_1 X_3 + 1.99031E-003\ X_1 X_4 - 9.57625E-003\ X_2 X_3 - 5.15812E-003 X_2 X_4 - 2.72187E-004\ X_3 X_4 - 0.021662X_1^2 - 1.29792E-003\ X_2^2 + 2.84021E-004\ X_3^2 - 9.54948E-005\ X_4^2$

3. 4. Analysis of Variance

Analysis of variance (ANOVA) for second order polynomial expression employed in the optimization of catalytic degradation of of 4-Chloro 2-Nitro Phenol as results shown in Table 3. 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 purpose of testing hypotheses on the parameters of the model. The Fisher's F-test was used to verify the statistical significance of the model. The results show that at 99% confidence level the lack of fit is not statistically significant. The Fisher's F values present that the model is significant for the catalytic degradation. P value equal and less than 0.001are significant, while as values greater than 0.01 are not significant. Based on analysis of variance (ANOVA) results the coefficient of determination (R^2= 96.14%) is statistically significant as shown in Fig. 4.

Table 3. Analysis of Variance for Degradation of 4-Chloro 2-Nitro Phenol.

Source	dF	Sum of Square	Mean Square	F-Value	P-Value
X_1	1	334.2	344.2	652.92	0.001
X_2	1	2153.4	2153.42	569.36	0.001
X_3	1	74.523	74.5	314.29	0.000
X_4	1	658.2	685.23	452.14	0.000
$X_1 X_2$	1	45.12	45.2	12.72	0.001
$X_1 X_3$	1	0.89	0.85	0.25	0.536
$X_1 X_4$	1	652.63	652.65	34.96	0.000
$X_2 X_3$	1	963.11	963.2	41.7	0.000
$X_2 X_4$	1	89.39	89.42	96.78	0.000
X_3X_4	1	79.65	79.6	9.12	0.000
X_1^2	1	965.478	965.4	11.93	0.000
X_2^2	1	7.6	7.65	9.45	0.396
X_3^2	1	23.85	23.9	75.3	0.213
X_4^2	1	63.14	63.1	14.45	0.000
Error	38	125.15	6.7		
Total	52				
R^2	96.14%				

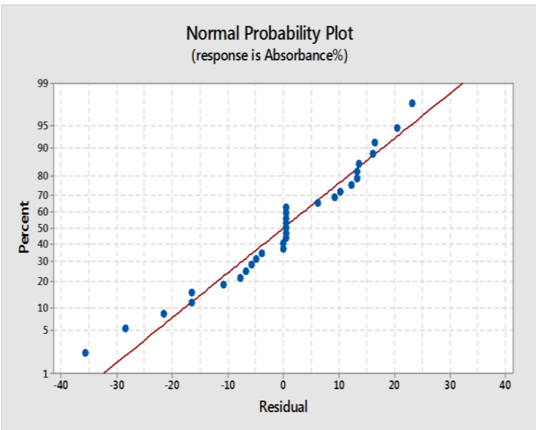

Fig.4. the model equation and experimental values.

3. 5. Interactive Effects of Independent Variables on the the Degradation of 4-Chloro 2-Nitro Phenol

Fig. 5 shows the 3D plot of the effect of O_3 flow rate and ultra sonic power on the catalytic Degradation of 4-Chloro 2-Nitro Phenol. The results present that by increasing the O_3 flow rate and ultra sonic power the catalytic Degradation of 4-Chloro 2-Nitro Phenol was also increased.

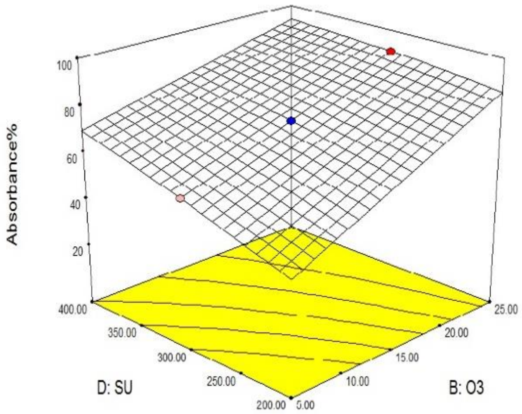

Fig. 5. Interactive Effects between O_3 flow rate and ultra sonic power.

The effect of CNPH concentration at TiO_2 constant concentration was considered. By incrasing CNPH concetration the efficincy of degration was decased as shown in Fig. 6. While by incrasing O_3 flow rate the efficincy of degradation was incrased.

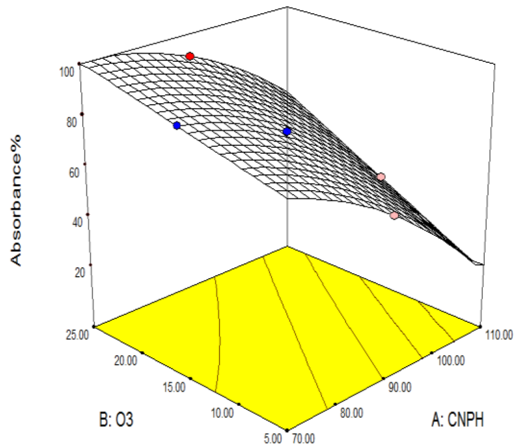

Fig. 6. Interactive Effects between O_3 flow rate and CNPH.

Fig.7 presents the 3D plot of the Interactive Effects between O_3 flow rate and TiO_2 concentration on the catalytic Degradation of 4-Chloro 2-Nitro Phenol. The results present that by increasing the O_3 flow rate and TiO_2 concentration the catalytic degradation of 4-Chloro 2-Nitro Phenol was also increased.

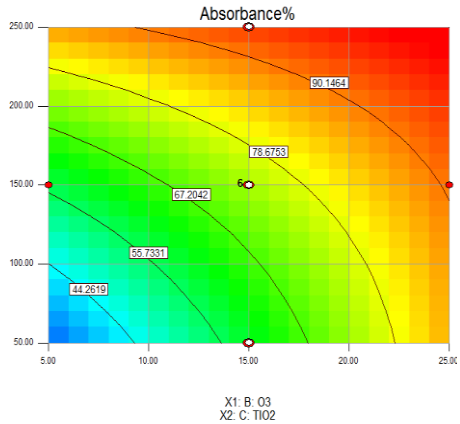

Fig. 7. Interactive Effects between O_3 flow rate and TiO_2 concentration.

3. 6. Model optimization

The model was used to predicate the maximum degradation efficiency to achieve highest treatment performance. The optimum predicted values for independent variables are presented at the Table 4. The model predictions were in agreement with the experimental values. According to Table 4, when our initial concentrations were 90 mg / L, the ozone input was 15 L/min, the catalyst is 150 mg/L, and the ultrasonic power of 300 W is the highest, we will have the most elimination.

Table 4. Degradation efficiency at Optimum Value.

Variables	Optimum Predicted Value
$[CNPH]_o$ (mg/L) (X_1)	90
O_3 (L/min) (X_2)	15
TiO_2 (mg/L) (X_3)	150
SU (W) (X_4)	300
Degradation efficiency %	99.2

4. CONCLUSIONS

In this study, degradation of 4-chloro-2-nitrophenol has been study by experimental design method.

The obtained results of the RSM model, the linearity of the normal distribution curve and the randomness of the remaining values indicates the suitability of the model**.**The results of the analysis table of variance showed that the most effective parameters on the percentage of pollutants removal are respectively**:** Initial concentration, O_3 (Input Ozone), Catalytic value, The power of the ultrasonic process**.** Also, according to the two-dimensional and three-dimensional diagrams obtained from the software, we found that increasing the amount of input ozone, Catalytic value, and the power of ultrasonic process have an incremental effect on the degradation of the pollutant**.** Also increasing the initial concentration has a decreasing effect on the degradation of 4-chloro-2-nitro phenol.

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