

## Statistical optimization of process conditions for photocatalytic degradation of phenol with immobilization of nano TiO<sub>2</sub> on perlite granules

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**Abstract**—Response surface methodology (RSM) using D-optimal design was applied to optimization of photocatalytic degradation of phenol by new composite nano-catalyst (TiO<sub>2</sub>/Pelite). Effects of seven factors (initial pH, initial phenol concentration, reaction temperature, UV irradiation time, UV light intensity, catalyst calcination temperature, and dosage of TiO<sub>2</sub>/perlite) on phenol conversion efficiency were studied and optimized by using the statistical software MODDE 8.02. On statistical analysis of the results from the experimental studies, the optimum process conditions were as follows: initial pH, 10.7; initial phenol concentration, 0.5 mM; reaction temperature, 27 °C; UV irradiation time, 6.5 h; UV light intensity, 250 W; catalyst calcination temperature, 600 °C; and TiO<sub>2</sub>/perlite dosage, 6 g/L. Analysis of variance (ANOVA) showed a high coefficient of determination ( $R^2$ ) of 91.8%.

Key words: Photocatalyst, Phenol, TiO<sub>2</sub>, Pelite, Experimental Design

### INTRODUCTION

More than 1000 compounds that are included in various lists of hazardous substances identified by the U.S. Environmental Protection Agency (EPA) have been tested by photocatalytic technology. The most-studied compounds are phenol derivatives, dye compounds as a class, pesticides and herbicides as a class, oxides of nitrogen and chlorinated solvents. Phenol and phenolic substances are used as raw materials in petrochemical, chemical and pharmaceutical industries. The photocatalytic, photoelectrochemical and photosonochemical of phenol degradation have been reported by several research groups [1-3]. Many photocatalytic techniques were reported for phenol destruction in aqueous solutions, for example, novel silica gel supported TiO<sub>2</sub> [4], TiO<sub>2</sub> particulate film on indium tin oxide coated glass [5], nafion-coated TiO<sub>2</sub> [6], multi-walled carbon nanotubes (MWNT)-TiO<sub>2</sub> composite catalyst [7], oxidation by H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub> [8] and TiO<sub>2</sub> fiber [9]. Also, most experimental work on aqueous systems has been performed using the photocatalyst in the form of fine particles suspended in the liquid phase. In a waste treatment application it would be simpler if the catalyst were immobilized in the photoreactor, so the material would not have to be done with immobilized catalysts. Titanium dioxide has been affixed to a variety of surfaces.

In a previous work, degradation of phenol was studied by immobilization of TiO<sub>2</sub> nano-particles on perlite as a new composite nano-catalyst [10]. However, reaction conditions and catalyst preparation variables have significant influence on achieving effective performance. According to the literature, no experimental research exists on the determination of the optimum conditions for photocatalytic

degradation rate by TiO<sub>2</sub> on perlite.

The optimization procedures are usually based on univariate approaches which facilitate the interpretation of the results obtained, but interactions between variables are not taken into consideration. Consequently, a wrong maximum may be attained, leading to the use of certain conditions in which the combination of the variables is not that which provides the best analytical response [11].

To establish better conditions by relating all the factors considered, numerous experiments have to be carried out with all the possible parameter combinations, which is not practical [12]. The design of experiments (DOE) is one approach, by taking a large number of variables. Thus, it is the aim of the present study to determine the optimum process conditions by using statistical DOE technique. One of the most used multivariate tools is the D-optimal design. The proposed method facilitates a systematic mathematical approach to understand the phenol degradation process and the optimization of near optimum design parameters, only with a few well-defined experimental sets [13]. In this approach the main effects of the variables and their interactions are estimated. This is one of the greatest advantages of multivariate optimization compared to univariate optimization [13]. Another advantage is that the number of experiments is considerably reduced. However, if the number of variables to be optimized becomes large, this will increase the number of experiments. Therefore, the selection of the most important process parameters is very essential. These parameters which would control the degradation rate of the target compound are initial pH, initial pollutant concentration, reaction temperature, UV irradiation time, UV light intensity, calcination temperature, and TiO<sub>2</sub>/perlite dosage. It has been demonstrated that catalyst dosage, initial concentration of pollutant, UV light intensity, temperature, and pH of the solution are the main parameters affecting the phenol degradation rate [14].

The main objective of this research was to determine the opti-

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imum experimental conditions of the photocatalytic degradation of phenol by  $\text{TiO}_2$ /Perlite catalyst. Since the aim of the successful degradation was to find the suitable condition where maximum phenol degradation is achieved, practical strategies were needed to design the degradation process. A practical approach favors the predictive design of degradation process using this technique and minimizes the necessary time for the design of degradation process.

## EXPERIMENTAL

### 1. Materials

Titanium dioxide P-25 was supplied by Degussa Company (Degussa AG, Germany). Nitric acid, phenol, hydrochloric acid, sodium hydroxide, ethanol were purchased from Merck (KgaA, Darmstadt, Germany). The water employed in catalyst preparation was deionized and the desired solutions of phenol concentration were prepared in distilled water. All the other chemicals used were of analytical grade.

### 2. Procedure & Instrumentation

Experiments were carried out in a photochemical reactor made of Pyrex glass. In all experiments the solution was aerated to provide the dissolved oxygen required for the reactions, agitation and removal of heat of reaction away from reactor. Also, the UV radiation source with various values of intensity was installed 15 cm above the catalyst surface. The lamp was continuously cooled by compressed air to keep the temperature down and protect the lamp from overheating. To minimize the loss of light irradiation and to improve utilization of reflected and deflected light, a hexagonal aluminum box surrounded the photoreactor and the UV lamp. Schematic diagram of experimental setup was shown in Fig. 1.

Perlite granules were coated with  $\text{TiO}_2$  particles (Anatase/Rutile: 80/20, particle size around: 22 nm, surface area:  $55 \text{ m}^2/\text{g}$ ), and used as a photocatalyst. Perlite is a volcanic glass able to expand 4-20 times of its original volume upon heating, resulting in flakes with porosity greater than 95% [15]. The pieces of this material can easily float on water surface due to its extremely low density, even after being coated with  $\text{TiO}_2$  particles, without being precipitated or suspended. It means that when  $\text{TiO}_2$  coated pieces of perlite, usually available in the form of granules, are used as photocatalysts floating on top of the polluted water solution, they can be in direct contact with the polluted solution and the radiation source simultaneously, and it can be located above the solution. This also eliminates the need to use pumping to put the catalyst into contact with the solution, and no filtration is required either. The main chemical compo-

nents of perlite have been reported to be  $\text{SiO}_2$  (~67 mol%),  $\text{Al}_2\text{O}_3$  (~13 mol%),  $\text{Na}_2\text{O}$  (~6 mol%),  $\text{K}_2\text{O}$  (~5 mol%),  $\text{CaO}$  (>1 mol%), and others (<1 mol%) [15,16].

To coat supports with titanium dioxide, 0.5 g of titanium dioxide powder is added to 18 mL ethanol as the base medium of the slurry in which the titania powder can be properly dispersed. At the second step, 1.5 mL of dilute nitric acid with a pH of 3.5 is added to slurry in order to provide the proper acidity in the slurry, which is necessary for the titania powder to be adequately dispersed. The slurry is sonicated for 5 min to separate the flocculated titania powders and obtain more uniform slurry. After the slurry is prepared and ready, 1 g of perlite granules (which are previously washed in deionized water assisted by air bubbling) is added to the slurry. In the final stage of coating process, the perlite granules which have adsorbed enough titania slurry are filtered from the slurry and calcined at  $450^\circ\text{C}$  for 30 min. When coating process is completed and perlite granules are cooled enough, they are once again washed in deionized water assisted by air bubbling in a vessel for a few minutes in order to remove the titania which are not attached properly to the perlite granules. Details of catalyst preparation method were described earlier [10].

For each experiment, 250 mL solution of phenol with different concentrations and various amounts of catalyst in a desired temperature was filled into the reactor. The pH was adjusted by adding a dilute aqueous solution of NaOH and HCl. At specific times samples were withdrawn from the reactor and centrifuged to remove  $\text{TiO}_2$  particles before the analysis. However, the catalyst coating on the perlite, at the end of reaction time 5% of initial  $\text{TiO}_2$  was washed out, which means that the coating process needs improvement. The clean transparent solution was analyzed by UV-vis spectroscopy (UV-2100 spectrophotometer, UNICO, USA). The absorbance at wave length between 270-290 nm was followed to determine the phenol concentration [17]. Complementary analysis of the application, such as TOC and COD, is recommended.

### 3. Statistical Analysis

Experimental design is the way to conduct and plan experiments in order to extract the maximum amount of information from the collected data in the presence of noise in the fewest numbers of experimental runs [13]. The basic idea is to vary all relevant factors simultaneously over a set of planned experiments, and then connect the results by means of a mathematical model. This model is then used for interpretation, predictions and optimization. Due to the complex dependence of the factors involved, D-optimal design and response surface methodology (RSM) were employed to determine the optimal process conditions for the conversion of phenol by photocatalytic reaction and better evaluate the interaction among the factors. The Influence of the different factors affecting the conversion of phenol like UV light intensity, initial pH, calcination temperature, substrate concentration, UV irradiation time, catalyst dosage, and reaction temperature was studied using experimental design techniques, according to Myers and Montgomery [13], with the assistance of the commercial statistical software MODDE 8.02 from Umetric (Umeå, Sweden). After fitting the data obtained for each parameter with the above experimental design to full second-order models, analysis of variance (ANOVA) for the models was performed and the models' significance was examined (Myers et al., 2002). RSM is an effective technique for optimization of complicated systems, which enables the evaluation of effects of multiple

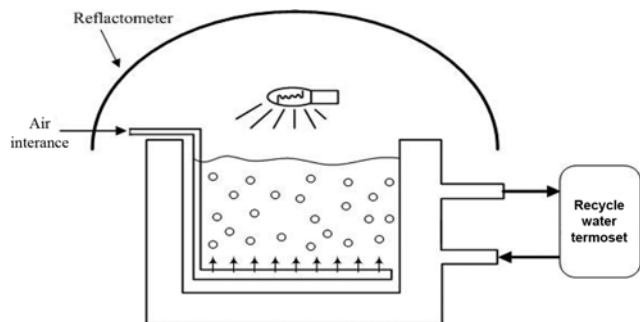


Fig. 1. Simplified schematic diagram of experimental setup.

**Table 1. Process parameters and assigned levels**

Symbol	Variables	Level		
		Low (-1)	Middle (0)	High (+1)
A	UV light intensity (W)	125	---	250
B	Initial pH	2	7	12
C	Calcination temperature (°C)	300	450	600
D	Substrate concentration (mM)	0.5	1	1.5
E	UV irradiation time (hr)	1	4	7
F	TiO <sub>2</sub> dosage (g/L)	6	11	16
G	Reaction temperature (°C)	20	40	60

parameters, alone or in combination with response variables [13].

A total of 37 experiments including five center points were generated and analyzed by the DOE. Parameter ranges were adjusted based on primary investigations on a single factor.

## RESULTS AND DISCUSSION

In the development of a degradation process, the number of the necessary empirical experiments to determine the process conditions can be reduced by using a practical approach that exploits the known effects of system parameters on the degradation behavior of phenol [13]. To analyze the effect of changes in parameters involved and to model the dimensional accuracy for various degradation conditions and to better evaluate the interaction between the parameters, the D-optimal design and response surface methodology was implemented. The adequacy of the model is also tested by the method of analysis of variance (ANOVA) and additional degradation experiments [13]. The levels of parameters are shown in Table 1, while the detailed experimental designs with coded and actual values of parameters are shown in Table 2. In our experimental design, we use the UV intensity at 2 level and other parameters in 3 levels. It's due to the availability of UV intensity (125 and 250 W). This type of design is one of standard experimental design [13].

### 1. Optimization of Process

A statistical model for an optimized phenol degradation employing the significant variables was determined by the response surface regression procedure. The model based on response surface methodology predicted with good accuracy the optimal conditions for phenol degradation by photocatalytic process. Besides showing the optimum conditions for degradation, the model describes an interesting interaction between the variables. These interactions cause the optimal level of one variable to change in response to change in the other variables. This interaction is substantial and it might have complicated the optimization if it had been conducted using the "one variable at a time" approach.

After fitting the data obtained for each parameter with the above experimental design to full second-order model (models containing all two parameter interactions), analysis of variance (ANOVA) for the models was performed and the models significance was examined by Fisher's statistical test (F-test) by testing for significant differences between sources of variation in experimental results, i.e., the significance of the regression (SOR), the lack of fit (LOF), and the coefficient of multiple determination ( $R^2$ ) [13]. Since the

**Table 2. D-optimal experimental design in coded and obtained experimental phenol conversion**

Run No.	Experimental Factors							Exp. results
	A	B	C	D	E	F	G	
1	125	12	300	0.5	1	6	20	8.80
2	125	2	600	0.5	1	6	20	2.16
3	125	12	600	1.5	1	6	20	64.07
4	125	2	300	0.5	7	6	20	42.50
5	125	12	300	1.5	7	6	20	42.95
6	125	2	600	1.5	7	6	20	16.10
7	125	2	300	1.5	1	16	20	14.33
8	125	12	600	0.5	7	16	20	36.24
9	125	2	300	1.5	1	6	60	15.24
10	125	12	300	0.5	7	6	60	87.50
11	125	2	600	0.5	7	6	60	99.65
12	125	12	600	1.5	7	6	60	24.67
13	125	2	300	0.5	1	16	60	12.05
14	125	12	600	0.5	1	16	60	29.98
15	125	12	300	1.5	1	16	60	53.70
16	125	2	600	1.5	1	16	60	29.53
17	125	2	300	1.5	7	16	60	77.83
18	250	2	300	0.5	1	6	20	4.42
19	250	12	300	1.5	1	6	20	38.81
20	250	2	600	1.5	1	6	20	4.07
21	250	12	600	0.5	7	6	20	99.86
22	250	12	600	0.5	1	16	20	31.50
23	250	12	300	0.5	7	16	20	98.82
24	250	2	600	0.5	7	16	20	47.26
25	250	2	300	1.5	7	16	20	40.49
26	250	12	600	1.5	7	16	20	71.44
27	250	12	300	0.5	1	6	60	16.18
28	250	2	600	0.5	1	6	60	36.44
29	250	12	600	1.5	1	6	60	71.81
30	250	2	300	0.5	7	6	60	92.20
31	250	12	300	1.5	7	6	60	60.06
32	250	2	600	1.5	7	6	60	92.51
33	250	2	300	1.5	1	16	60	25.8
34	250	12	600	0.5	7	16	60	98.95
35	250	7	450	1.0	4	11	40	85.57
36	250	7	450	1.0	4	11	40	83.50
37	250	7	450	1.0	4	11	40	88.80

full second-order models (models containing all two parameter interactions) were not accepted by the required tests, they were improved by elimination of the models' terms until the determined conditions were fulfilled. The regression coefficients of the proposed accuracy final models and their P-values (probability of error), which are used to determine the significance, are shown in Table 3. For each elimination, the significance of model term of the model was F-tested according to the following expression:

$$F = [SS_{diff}/(p-g)]/[SS_e/(n-p)] \quad (1)$$

where  $SS_e$  refers to the sum of squares of residuals in the reduced model and  $SS_{diff}$  refers to the difference between the sum of squares

**Table 3. Coefficients and P-values of the factors for linear, quadratic and interaction effects**

Conversion	Coefficient	P
Constant	79.5148	1.92e-008
A	6.97916	0.00906
B	9.84204	0.00085
C	2.94604	0.24512
D	-2.66118	0.29786
E	19.8093	1.21e-007
F	-1.0685	0.67388
G	8.44848	0.00171
G <sup>2</sup>	-30.2544	0.00149
AB	3.59259	0.13858
AC	2.63225	0.27048
AE	4.2497	0.09633
BE	-5.98095	0.01546
BG	-7.31286	0.00433
CE	-3.67597	0.11660
CF	-6.25366	0.02110
DE	-9.22547	0.00081
DF	3.53147	0.17026
DG	-2.11774	0.36079
EG	3.34506	0.16784

of residuals in the complete and reduced models. The letters n, p, and g refer to the total number of experiments, the number of parameters in complete model, and the number of parameters in the reduced model, respectively. If F-significance was lower than 95% the reduced model was accepted. Otherwise, the discarded parameters with the highest significance were added until the condition was fulfilled. If one of these conditions was not satisfied, the model was accepted when  $R^2 > 0.95$ , which means that more than 95% of the data is explained by the model [13]. The regression coefficients of the proposed accuracy final model and their p-values (probability of error), which are used to determine the significance level, are shown in Table 3. Analysis of variance of the final model resulted in coefficients of determination and adjusted coefficients of determination for phenol degradation of 0.918 and 0.823, indicating the adequacy of fit of the model with p-value 0.000. This indicates that the model could explain 91.8% of the variability in the response. Because  $R^2$  increases as the model terms (variables) are added to the model, adjusted  $R^2$  could be used to check the amount of reduction in the variability of responses by using the regressor variables in the model. In general, the adjusted  $R^2$  will not increase with the addition of variables. In fact, if unnecessary terms are added, the value of  $R^2_{adj}$  will often decrease. In this case  $R^2$  and  $R^2_{adj}$  are relatively close to each other, which indicates that all the used terms in the model are necessary for building the correct model [18]. As a function of these results, the analysis of variance (ANOVA) was performed considering all the significant effects in Table 4.

The p-value for the lack of fit of the model indicates that the probability of error for the lack of fit was high and the model represents the actual relationships of parameters well within the range selected. The comparison between experimental results and their predictions is shown in Fig. 2. It can be seen that the model can predict the re-

**Table 4. Analysis of variance (ANOVA)**

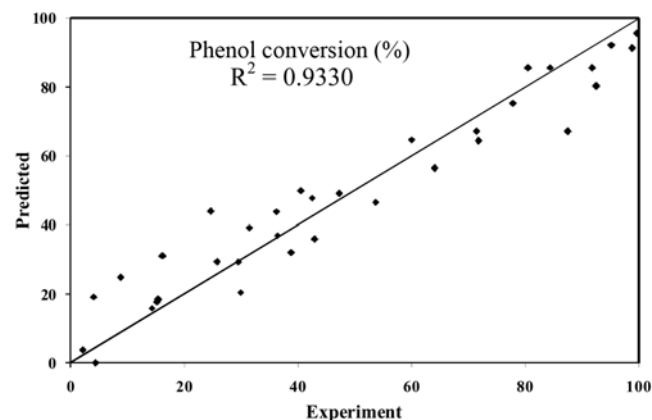
Conversion	DF <sup>a</sup>	SS <sup>b</sup>	MS <sup>c</sup>	F	P
Regression	19	33605.9	1768.73	9.7876	0.000
Lack of fit	15	3006.19	200.413	6.083	0.150
Residual	17	3072.08	180.711		
Total	37	130136	3517.2		

$R^2=91.8\%$ ,  $R^2(\text{adj})=82.3\%$

<sup>a</sup>SS, sum of squares

<sup>b</sup>DF, degree of freedom

<sup>c</sup>MS, mean square

**Fig. 2. Predicted vs. experiment phenol conversion.**

sults well in the selected variables range. In few points the deviation is relatively higher, but the model can predict the conversion in most range of the variables. Also, the practical conversion is maximum 100%. But the calculated response may be exceeding from 100%. This result is due to the nature of the model. From a physical viewpoint it means that the response is at maximum level.

It was observed that UV irradiation time ( $p < 0.0000$ ) very high significantly and initial pH ( $p < 0.001$ ) and reaction temperature ( $p < 0.002$ ) high significantly affected degradation. Also UV light intensity significantly ( $p < 0.01$ ) affects the response. In addition, substrate concentration affected interactively with UV irradiation time ( $p < 0.001$ ), and initial pH affected interactively with reaction temperature ( $p < 0.005$ ). UV irradiation time and initial pH had the most significant effects on phenol degradation, respectively. They gave positive signals on the response. Substrate concentration and  $\text{TiO}_2$ /perlite dosage gave negative signals on phenol degradation. Interactions of the initial pH with reaction temperature and UV irradiation time had negative effect on the response, which means that initial pH increases with simultaneous increase in reaction temperature or UV irradiation results in lower phenol degradation. Also, the interaction of substrate concentration with UV irradiation time gave negative signal on response, which means that decreasing of substrate concentration with simultaneous increase in UV irradiation time increases phenol degradation. Because at the higher substrate concentration, the increased amount of reactant molecules may also occupy and/or block all the active catalyst sites present on the surface of the photocatalyst and lead to decrease in degradation rate. The second-order term of reaction temperature also had high sig-

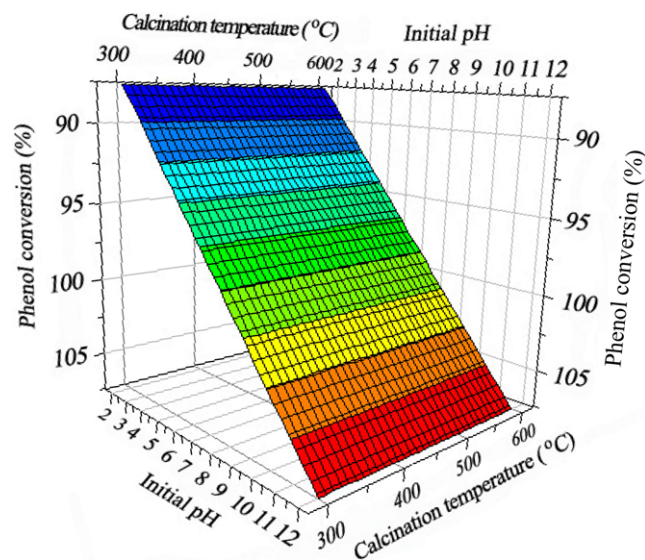
**Table 5. The optimum process conditions on the degradation of phenol by TiO<sub>2</sub>/Perlite catalyst**

Variables	Value
UV light intensity (W)	250
Initial pH	10.7
Calcination temperature (°C)	600
Substrate concentration (mM)	0.5
UV irradiation time (hr)	6.5
TiO <sub>2</sub> dosage (g/L)	6
Reaction temperature (°C)	27
Predicted conversion (%)	99.47
Experimental conversion (%)	97.30 <sup>a</sup>
R <sup>2</sup> =91.8%	

<sup>a</sup>Average of 3 replications

nificant effect on phenol degradation. The quadratic sign of reaction temperature is negative; hence, it represents some form of maximum (or approach to it) in the selected parameters ranges.

The calculated optimum process conditions are given in Table 5 by taking the models into account. These conditions were established with effective parameters obtained by variance analysis conducted at a 92% confidence level. For the examination of accuracy of predicted optimum condition, the degradation was carried out three times and the average value of 97.3% of the experimental phenol conversion was obtained. It can be seen that the experimental conversion results confirm the accuracy of optimization results with 3.4% of absolute average deviation. Also, the optimum condition obtained in this paper is a global optimum. If we fixed some of the



**Fig. 3.** 3D graph shows the effect of the initial pH (B) and calcination temperature (C) on phenol concentration response. The color change from blue to red corresponds to increase in responses. This figure is plotted by considering other variables at center points (Reaction temperature=40 °C, TiO<sub>2</sub> dosage=11 g/L, Substrate concentration=1.0 mM, Calcination temperature=450 °C, Initial pH=7, and UV irradiation time=4 hr).

variables (like calcination temperature) in one level, we could not obtain a global optimum.

## 2. Effect of Initial pH

Fig. 3 shows that the solution pH plays an important role in the photocatalytic process of various pollutants [18,19]. The pH of the suspension was adjusted to a different value by the addition of diluted solutions of HCl and NaOH before irradiation. Photodegradation efficiency of phenol was increased with increasing pH in the range of 2-12.

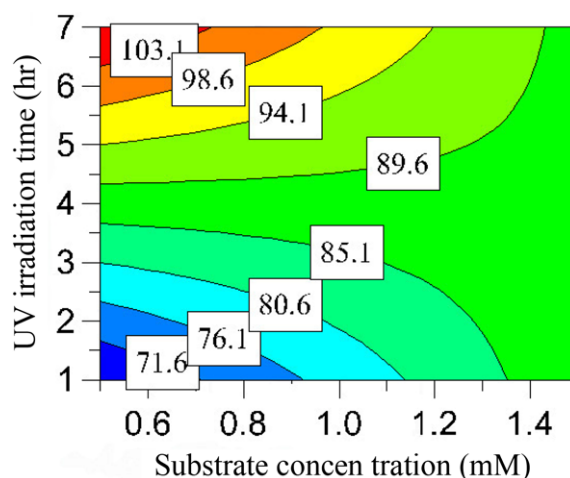
The point of zero charge (PZC) of the TiO<sub>2</sub> (Degussa P-25) is at pH~6.25. Therefore, in lower level of PZC, TiO<sub>2</sub> surface is positively charged by means of adsorbed H<sup>+</sup> ions and negatively charged by means of adsorbed OH<sup>-</sup> ions specifically. Consequently, TiO<sub>2</sub> takes advantage of its ability to generate hydroxyl radicals by oxidation of adsorbed OH<sup>-</sup> or H<sub>2</sub>O molecules on to surface upon irradiation with light of enough energy [20] as indicated in Eqs. (2) and (3). The Positive-hole (h<sup>+</sup><sub>vb</sub>) of titanium dioxide which absorbs UV radiation breaks the water molecule to form hydrogen gas and hydroxyl radical (Eq. (2)) or creating of OH<sup>•</sup> from adsorbed OH<sup>-</sup> (Eq. (3)). Therefore, the presence of large amounts of OH<sup>-</sup> ions on the TiO<sub>2</sub> surface favors the formation of OH<sup>•</sup> [21].



The interpretation of pH effect on the photocatalytic process is a very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals that formed during the reaction process. The ionization state of the photocatalyst surface can be protonated and deprotonated under acidic and alkaline conditions, respectively, as shown in Eqs. (2) and (3).

## 3. Effect of Substrate Concentration

In this set of experiments, the influence of substrate concentration (0.5 to 1.5 mM), on the degradation rate of phenol was investigated. It can be seen that the conversion is constant with the increase of concentration in the selected range (Fig. 4).



**Fig. 4.** Contour plot of the phenol concentration response: UV irradiation time (E) vs. substrate concentration (D). The color change from blue to red corresponds to increase in responses. This figure is plotted by considering other variables at center points.



The constant rate of degradation with increasing pollutant concentration could be explained as follows: increasing phenol concentration generates high concentration of intermediate products, which may adsorb on the surface of the catalyst, and even a slow diffusion of the intermediate products from the catalyst may be expected which deactivates or blocks the catalytic sites of the photocatalyst. Consequently, a constant degradation rate was observed. On the other hand, the generation and migration of the photogenerated electron-hole pair, and the reaction between photogenerated hole (or hydroxyl radical) and organic compound are two processes that occur in series. Therefore, each step may become rate determining for the overall process [14].

#### 4. Effect of $\text{TiO}_2$ /Perlite Dosage

In the slurry photocatalytic process, initial reaction rate is affected directly by catalyst dosage [22]. The optimal  $\text{TiO}_2$  dosage was reported in an extensive range from 0.15 to 8 g/L for different geometry and working conditions of the photoreactor. For  $\text{TiO}_2$  (Degussa P25), optimal concentration has a wide range from 0.15 to 2.5 g/L; therefore, no general conclusion has been made [14]. Photocatalyst dosage in the range of 6–16 g/L was selected. Each 11 gr of perlite adsorb 1 g  $\text{TiO}_2$ , so the  $\text{TiO}_2$  concentration range is 0.545–1.45 g/L. Obviously, this range is in optimal range that was reported.

The increase in catalyst dosage can lead to the two opposite effects. The total active site increases with increasing catalyst dosage but the UV light penetration due to increased scattering effect decreases. Due to these effects, conversion (%) does not change with increasing  $\text{TiO}_2$  concentration in the selected range (Fig. 5).

#### 5. Effect of UV Light Intensity

The UV illumination source used for the experiments was two medium-pressure mercury lamps (Osram), one 125 W and the other 250 W. Fig. 6 shows that the photodegradation efficiency increased

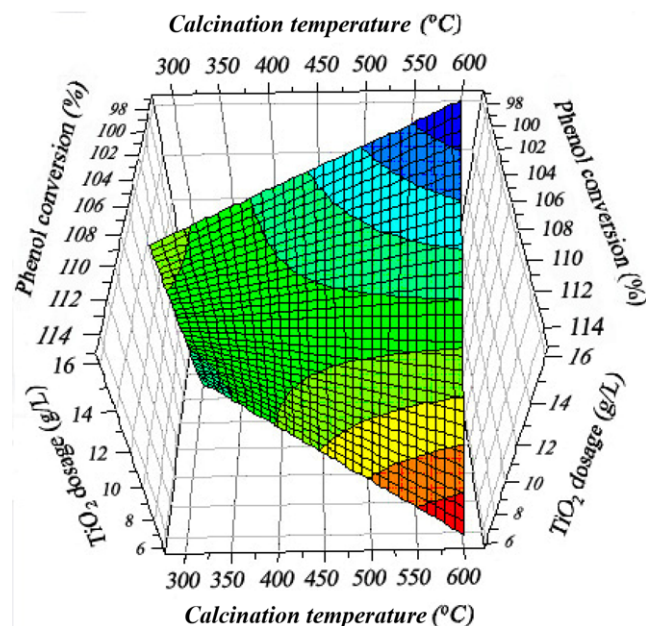


Fig. 5. 3D graph shows the effect of the  $\text{TiO}_2$ /Perlite dosage (F) and calcination temperature (C) on phenol concentration response. The color change from blue to red corresponds to increase in responses. This figure is plotted by considering other variables at center points.

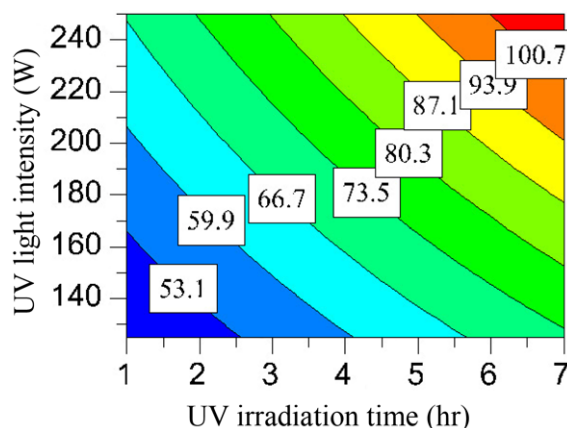


Fig. 6. Contour plot of the phenol concentration response: UV light intensity (A) vs. UV irradiation time (E). The color change from blue to red corresponds to increase in responses. This figure is plotted by considering other variables at center points.

with the increasing UV lamps power from 125 to 250 W. Lee et al. [23] reported that the rate of photon of energy increased linearly as the UV intensity increased. It means that the electron-hole generation process was positively affected by rate of photon irradiation. Consequently, the rate of reaction closer to semiconductor surface improves; thus, phenol conversion increases.

#### 6. Effect of Calcination Temperature

The effect of calcination temperature, in the range of 350 °C to 600 °C, on phenol conversion is shown in Fig. 7. Due to low mechanical strength of  $\text{TiO}_2$  coated perlite, the catalysts must be calcined at high temperature. Calcination can lead to changes in the crystal sized surface area, pore size, and  $\text{TiO}_2$  structure. The effects of calcination temperature were studied by Hosseini et al. [10]. The SEM images of perlite surface confirm the high porosity of perlite granules as a good support for titanium dioxide. The effect of calcination temperature in the case of  $\text{TiO}_2$ /perlite composite shows that it is calcined at 450 °C; the  $\text{TiO}_2$  grain size became larger than 350 °C

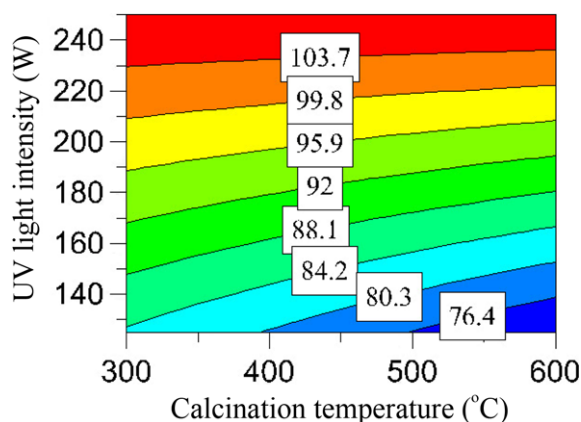


Fig. 7. Contour plot of the phenol concentration response: UV light intensity (A) vs. calcination temperature (C). The color change from blue to red corresponds to increase in responses. This figure is plotted by considering other variables at center points.

calcination process. Also, quality of coatings from the structural point of view, i.e., whether or not the P-25 crystals have undergone noticeable changes in structural properties such as rutile to anatase phase ratio and crystallite size during the immobilization process was assessed by analyzing XRD patterns. In the XRD pattern obtained, for the sample coated on perlite as a disorder in the form of an arc-shaped base line can be observed which shows that some of the material present in the sample is amorphous. Noting that this sample was ground without separating the perlite support itself, the amorphous portion of the sample can be attributed to the perlite [10]. According to the literature [24,25], it is difficult to estimate the separate contribution of each of them. In this study, no change was observed in conversion at different calcination temperatures.

The nature of the photocatalyst determines the rate and efficiency of the process. The P25 consists of mixed phase of TiO<sub>2</sub>, Anatase and Rutile. The Anatase form of titanium dioxide has the desirable properties of being chemically stable, readily available, and active as a catalyst for the oxidation process. Rutile has a smaller band gap, 3.0 eV, but only a few reports observe photocatalytic activity for this form. Rutile form is less effective than the oxidation of most organic compounds. According to the literature [26], Anatase-Rutile phase transformation took place at temperature between 600 and 800 °C.

Mills and Morris [27] reported that no loss in catalyst surface area was observed when powdered P25 was calcined at a temperature lower than 600 °C, while the phase transition from Anatase to Rutile occurred at a temperature above 600 °C. The result indicates that catalyst activity was not affected by the phase transfer and changing of the surface area in the studied range (Fig. 7). These results were similar to that presented by Fernandes et al. [28], who reported all TiO<sub>2</sub> samples calcined between 200 and 500 °C presented similar

phenol degradation percentages. Calcination temperature had no effect on the activity of the powdered P25 catalyst at a high temperature [14].

### 7. Effect of Reaction Temperature

The influence of the temperature, in the range of 20 to 60 °C, on the photodegradation efficiency of phenol was investigated. Fig. 8 reveals that the photodegradation efficiency increased with increasing the temperature up to 40 °C and decreases afterwards. According to the Arrhenius equation, the rate of degradation was increased with increasing temperature. But for temperatures above 40 °C there is a significant decrease in oxygen solubility in water. As a result of these two effects, the rate of reaction decreases.

The presence of an electron acceptor is necessary to remove the photogenerated electrons for continuation of the photocatalyst oxidation of organic compounds. Otherwise, the accumulated photons in the catalyst particle will recombine with holes, which are the initiators of the photocatalytic reaction. The commonly used electron acceptor is oxygen as it is easily available, soluble under most conditions and non-toxic to the environment. Wag et al. [29] observed that the photocatalytic activity was completely suppressed in the absence of oxygen which has a profound effect on the rate of photocatalyzed decomposition of organic compounds. Alberici and Jardim [30] found that the decomposition of phenol non-aerated solutions containing TiO<sub>2</sub> was much slower compared with aerated ones. Sclafani et al. [31] found that the concentration decay of phenol was much faster when oxygen was bubbled through the solution containing Anatase TiO<sub>2</sub> instead of He. The e<sup>-</sup> is picked up by oxygen according to Eq. (4):



It has been suggested that hydroxyl radicals (OH<sup>•</sup>) and superoxide radical anions (O<sub>2</sub><sup>•-</sup>) are the primary oxidizing species in the photocatalyst oxidation process [32]. Chatterjee et al. [22] reported similar results earlier.

### 8. Effect of UV Irradiation Time

Increasing UV irradiation time will result in increasing the conversion percentage (Fig. 4 and Fig. 6) due to the increase in the electron-hole generation. Also, according to Eqs. (2) and (3), hydroxyl radical and superoxide radical formation increased as a result of phenol conversion increasing.

## CONCLUSION

The work presented here provides support for the degradation of phenol as a model for environmental contaminant. The experimental design used allows rigorous analysis of the factors influencing phenol degradation in a photocatalytic process. The optimum process conditions obtained through a statistical method D-optimal was successfully determined to maximize the phenol degradation. The model predicted that UV irradiation time, initial pH, UV light intensity and reaction temperature had significant effects on photocatalytic phenol degradation. Such an approach is extremely useful for defining optimal condition for photocatalytic process in general.

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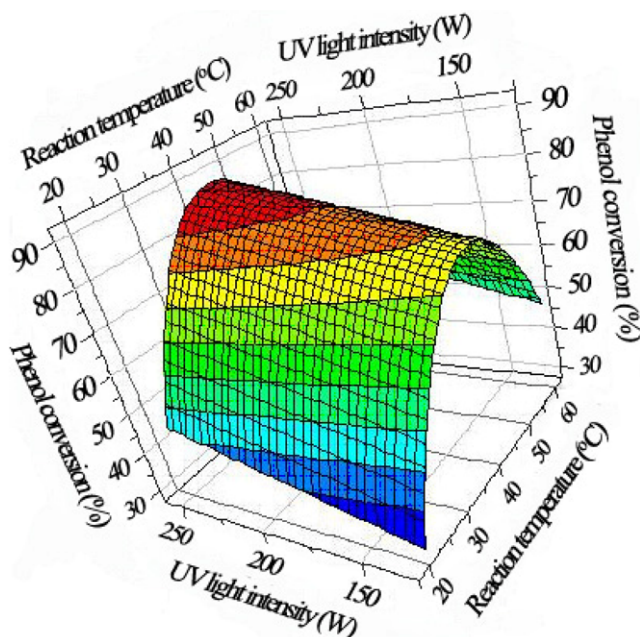


Fig. 8. 3D graph shows the effect of the reaction temperature (G) and UV light intensity (A) on phenol concentration response. The color change from blue to red corresponds to increase in responses. This figure is plotted by considering other variables at center points.

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