Parametric optimization of photocatalytic degradation of catechol in aqueous solutions by response surface methodology

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In this paper, performance of a photocatalytic process for degrading catechol with titanium dioxide and zinc oxide catalysts is described. Response surface methodology (RSM) has been used to plan and analyze the experiments. The factors investigated include catalyst dose, pH and amount of oxidant. The performance of photocatalytic process was investigated in terms of percentage degradation (residual catechol concentration). The experimental results indicated that the proposed mathematical model could adequately describe the performance of the factors being investigated. Further the results showed that catalyst dose and amount of oxidant have significant effect on the degradation process. Photodegradation efficacy was confirmed under optimized conditions. The study was further extended to explore the degradation process under sunlight using titanium dioxide and zinc oxide as photocatalysts.

Keywords: Photocatalysis, Titanium dioxide, Zinc oxide, Response surface methodology, UV light, Catechol

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Pulp and paper industry generates about 175 m³ of wastewater per ton of paper produced¹. A large number of organic and inorganic compounds are introduced during the processing of pulp and paper. Among them, phenol and its derivatives are present extensively in the wastewater of papermaking². These compounds are quite toxic and degrade slowly in the environment³. These substances persist in the environment for a long time and produce number of adverse effects and disorders in human life⁴,⁵. Therefore it becomes imperative to completely degrade these organic compounds. A number of oxidation systems have been reported that can be used for the treatment of wastewater⁶. However most of them have been proved inefficient in the complete degradation of phenol, catechol and their derivatives present in the wastewater. The biological means for degradation of many chlorinated compounds have been a failure because of the fact that these compounds cannot be completely degraded within the stipulated time period⁷,⁸. Moreover the complete degradation of the organics by this technique is very costly and energy consuming. To address these problems, heterogeneous photocatalysis method of wastewater degradation is one of the advanced techniques which may prove useful for the degradation of phenol, catechol and its chloro-derivatives. This system uses the semiconductor powders such as titanium dioxide (TiO₂), zinc oxide (ZnO) and cadmium sulphide (CdS) depending upon the band structure of the photocatalyst and photoactivity of the adsorbate molecule. Basca and Kiwi⁹ have reported the enhancement in the rate of degradation of p-coumaric acid with addition of hydrogen peroxide to photocatalytic system using TiO₂ as catalyst and perchlorate oxidant. The partial degradation of chlorophenols has been also reported by Pandiyan¹⁰. The use of TiO₂ has been recently reported for photocatalyzed mineralization of chlorinated hydrocarbons¹¹,¹².

The photocatalytic process is a complex process, which involves a large number of parameters. Because of large number of parameters, it is very difficult to relate them by a single analytical model. Extensive experimental work is therefore needed to analyze and optimize the process parameters to understand their effect on the process performance. Response surface methodology (RSM) of experimental design is one of the emerging techniques, which helps in carrying out the analysis of experiments with least experimental effort¹³. De Giorgi and Carpignano¹⁴ and Muthukumara et al.¹⁵
have used the design of experiments for discoloration of wastewater. The degradation of cellulose bleaching effluent was also reported by Perez.

In the present paper, an attempt has been made to obtain an optimal setting of process parameters which may yield optimum degradation of the catechol present in the wastewater. Response surface methodology has been used to plan and analyze the experiments. Further, the study is extended to explore the degradation process under sunlight using titanium dioxide and zinc oxide photocatalysts.

**Experimental Procedure**

**Experimental set-up**

The photochemical degradation was carried out in a specially designed reaction vessels in the photoreactor equipped with 4 UV tubes each of 30W (Philips) (Fig. 1). Constant stirring of solution was ensured by using magnetic stirrers and aeration was done with the help of aquarium aerator. The temperature was maintained constant throughout the reaction time by circulating the water in the jacketed wall reactor. For solar experiments, the borosilicate glass reactors of diameter 0.17 m and 800 mL capacity were made with ports at the top for sampling, gas purge and gas outlet. The solar experiments were performed in day time between 10 A.M. to 4 P.M. The spectra were taken with UV-VIS Spectrophotometer (Agilent 8453); pH meter (Thermo Orion 920A) was used to measure the pH of the solution.

**Materials**

Titanium dioxide P-25 (surface area 50 m²/g) was obtained from Degussa and was used as received. ZnO (5 m²/g) was purchased from Merck. Catechol was purchased from Across Organics (99% pure) and used without further purification. Stock solution of catechol (1000 mg/L) was prepared by dissolving catechol in double distilled water. The pH of solutions was adjusted in the range of 3-11 with 1 M HCl or 1 M NaOH, after the addition of oxidant. Sodium hypochlorite (BDH, Merck) having 4% available chlorine was used as an oxidant.

For the degradation experiments, fixed amount of photocatalyst TiO₂ and ZnO was added to 100 mL of catechol solution in each trial. The suspension was subjected to irradiation under UV light and sunlight for a period of 0.5 h and 2.5 h respectively. The aqueous suspension was magnetically stirred. At different time intervals aliquot was taken out with the help of syringe and then filtered through Millipore syringe filter of 0.45 μm. Then absorption spectra were recorded and rate of degradation was observed in terms of change in intensity at λmax of the catechol. The percentage degradation has been calculated as:

Percentage degradation = 100 × (C₀ – C/C₀), where C₀ = initial concentration of catechol, C = concentration of catechol after photoirradiation.

**Process parameters of heterogeneous photocatalytic process**

The process parameters that affect the effectiveness of heterogeneous photocatalytic process can be classified as follows.

(i) Operational parameters: pH, temperature, light intensity, light source (solar/artificial)

(ii) Catalyst parameters: Type, catalyst dose, catalyst doping.

(iii) Oxidant parameters: Type of oxidant, oxidant amount.

(iv) Compound parameters: Nature of pollutant, initial concentration.
The following three independent parameters were chosen for the study

(i) Catalyst dose, A
(ii) pH, B
(iii) Oxidant amount, C

The ranges of these factors were selected on the basis of preliminary experiments. Table 1 gives the levels of various parameters and their designation. The response parameter in the present study was percentage degradation. In each test, the percentage degradation was calculated by change in the concentration of the component.

Response surface methodology

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response. It is a sequential experimentation strategy for empirical model building and optimization. By conducting experiments and applying regression analysis, a model of the response to some independent input variables can be obtained. Based on the model of the response, a near optimal point can then be deduced. RSM is often applied in the characterization and optimization of processes. In RSM, it is possible to represent independent process parameters in quantitative form as:

\[ Y = f(X_1, X_2, X_3, \ldots, X_n) + \epsilon \] … (1)

where, \( Y \) is the response (yield), \( f \) is the response function, \( \epsilon \) is the experimental error, and \( X_1, X_2, X_3, \ldots, X_n \) are independent parameters.

By plotting the expected response of \( Y \), a surface, known as the response surface is obtained. The form of \( f \) is unknown and may be very complicated. Thus, RSM aims at approximating \( f \) by a suitable lower-ordered polynomial in some region of the independent process variables. If the response can be well modeled by a linear function of the independent variables, the function [Eq. (1)] can be written as:

\[ Y = C_0 + \sum_{i=1}^{n} C_i X_i + \sum_{i=1}^{n} d_i X_i^2 + \epsilon \] … (2)

However, if a curvature appears in the system, then a higher order polynomial such as the quadratic model [Eq. (3)] may be used.

\[ Y = C_0 + \sum_{i=1}^{n} C_i X_i + \sum_{i=1}^{n} d_i X_i^2 + \epsilon \] … (3)

The objective of using RSM is not only to investigate the response over the entire factor space, but also to locate the region of interest where the response reaches its optimum or near optimal value. By studying carefully the response surface model, the combination of factors, which gives the best response, can then be established. The response surface method is a sequential process and its procedure can be summarized as shown in Fig. 2.

Process conditions and experimental plan

As already mentioned, three factors are being studied and their low and high levels are given in Table 1. The photocatalytic process was studied with a standard RSM design called central composite design (CCD). Twenty experiments were conducted in duplicate according to the plan mentioned in Table 1. The ‘Design Expert 6.0’ software was used for regression and graphical analysis of the data.

Table 1 — Actual values of the variables for the coded values

<table>
<thead>
<tr>
<th>Variables</th>
<th>Actual values for the coded values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst dose, g/L (X_1)</td>
<td>-1.682  -1.000  0  +1.000  +1.682</td>
</tr>
<tr>
<td>pH (X_2)</td>
<td>0.5  1.0  1.5  2.0  2.5</td>
</tr>
<tr>
<td>Oxidant amount, mL (X_3)</td>
<td>0.2  0.4  0.6  0.8  1.0</td>
</tr>
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</table>
obtained\textsuperscript{18}. The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots\textsuperscript{19}.

**Results and Discussion**

**Degradation of catechol using different photocatalysts**

The photodegradation experiments were carried out by using 1 g/L photocatalyst dose either TiO\textsubscript{2} or ZnO, at natural pH under UV light with 0.5 mL of oxidant. After 60 min, 72 and 61\% degradation was achieved with TiO\textsubscript{2} and ZnO, respectively, as depicted in Fig. 3. Neppolian et al.\textsuperscript{20} also found TiO\textsubscript{2} to be the most effective among different catalysts while studying the photodegradation of three commercial dyes. Recently Evgenidou et al.\textsuperscript{21} investigated the photocatalytic degradation of organophosphorous insecticide, dichlorvos using TiO\textsubscript{2} and ZnO. In their experimental results TiO\textsubscript{2} proved to be more efficient photocatalyst.

**Optimization of process parameters for degradation of catechol**

The results for each trial performed as per the experimental plan are shown in Table 2. These results were input into the Design Expert software for further analysis following the steps outlined in Fig. 2. The results of the quadratic model for percentage degradation in the form of analysis of variance (ANOVA) are given in Table 3. The examination of the fit summary output (Table 3) revealed that the quadratic model is statistically significant for the response and therefore it is used for further analysis.

The value of R\textsuperscript{2} and adjusted R\textsuperscript{2} is close to 1. This means that regression model provides an excellent explanation of the relationship between the independent variables (factors) and the response (percentage degradation). The associated Prob>F value for the model is lower than 0.05 (i.e. \( \alpha = 0.05 \), or 95\% confidence) indicating that the model is considered to be statistically significant\textsuperscript{19}. The lack-of-fit term is not significant.

Further, factor A (catalyst dose), factor B (pH), factor C (oxidant amount), second order term of factor B (pH) and second order effect of C (oxidant amount) have significant effect. The results prove that all the three factors influence the degradation of catechol. The insignificant model terms (not counting those required to support hierarchy) can be removed, it will result in an improved model. The non-significant terms are eliminated by backward elimination process. The ANOVA results for the reduced quadratic model for percentage degradation are shown in Table 4. The reduced model results indicate that the model is significant (R\textsuperscript{2} and adjusted R\textsuperscript{2} are 93 and 91\%, respectively), and lack-of-fit is non-significant (Prob>F value is less than 0.05). Figure 4 displays the normal probability plot of the residuals for percentage degradation. It may be noticed that the

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Catalyst dose (X\textsubscript{1})</th>
<th>pH (X\textsubscript{2})</th>
<th>Oxidant amount (X\textsubscript{3})</th>
<th>Degradation (%)</th>
</tr>
</thead>
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<tr>
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<td>-1(5)</td>
<td>-1(0.4)</td>
<td>32</td>
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<tr>
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<td>-1(5)</td>
<td>-1(0.4)</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>-1(1.0)</td>
<td>+1(9)</td>
<td>-1(0.4)</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>+1(2.0)</td>
<td>+1(9)</td>
<td>-1(0.4)</td>
<td>30</td>
</tr>
<tr>
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<td>+1(0.8)</td>
<td>60</td>
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<td>-1(5)</td>
<td>+1(0.8)</td>
<td>74</td>
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<tr>
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<td>+1(0.8)</td>
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<tr>
<td>8</td>
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<td>+1(9)</td>
<td>+1(0.8)</td>
<td>60</td>
</tr>
<tr>
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<td>0(7)</td>
<td>0(0.6)</td>
<td>35</td>
</tr>
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<td>0(7)</td>
<td>0(0.6)</td>
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<tr>
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<td>0(0.6)</td>
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<tr>
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<tr>
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<td>-1.682(0.26)</td>
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</tr>
<tr>
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<td>0(7)</td>
<td>+1.682(0.94)</td>
<td>80</td>
</tr>
<tr>
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<td>0(7)</td>
<td>0(0.6)</td>
<td>48</td>
</tr>
<tr>
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<td>0(7)</td>
<td>0(0.6)</td>
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<td>19</td>
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<td>0(0.6)</td>
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</tr>
<tr>
<td>20</td>
<td>0(1.5)</td>
<td>0(7)</td>
<td>0(0.6)</td>
<td>42</td>
</tr>
</tbody>
</table>
residuals are falling on a straight line, which means that the errors are normally distributed. Further, each observed value is compared with the predicted value calculated from the model in Fig. 5. It can be seen that the regression model is fairly well fitted with the observed values. After eliminating the non-significant terms, the final response equation for percentage degradation is given as follows:

\[
\text{Percentage degradation} = +45.71 + 8.60A - 6.80B + 10.55C - 6.96B^2 + 7.01C^2
\]

Figure 6 shows the estimated response surface for percentage degradation in relation to the design parameters of catalyst dose and pH. As can be seen from this figure, the percentage degradation tends to increase, considerably with increase in catalyst dose and pH value somewhere at middle of its selected range. Thus, with the increase of catalyst dosage total active surface area increases, hence availability of more active sites on catalyst surface. Increase in percentage degradation by increasing the catalyst dose confirms the result as increase in catalyst provides maximum sites for adsorption and reaction. At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases. This decreased percentage degradation at higher catalyst loading may be due to deactivation of activated...
molecules by collision with ground state molecules. Shielding by TiO$_2$ may also take place [Eq. (4)].

$$\text{TiO}_2^* + \text{TiO}_2 \rightarrow \text{TiO}_2^{\#} + \text{TiO}_2$$ \hspace{1cm} \ldots (4)

where TiO$_2^*$ is the TiO$_2$ with active species adsorbed on its surface and TiO$_2^{\#}$ the deactivated form of TiO$_2$ (ref. 20).

Therefore, an optimum catalyst dose has to be added in order to avoid unnecessary excess catalyst and also to ensure total absorption of light photons for efficient photomineralisation.$^{23}$ The effects of pH and its squared term are significant. The polynomial shows that variable B (pH) and B$^2$ have little negative quadratic influence which indicates that the degradation rate is decreased at very low and high pH. The experimental results reflect that at higher pH, degradation of catechol decreased. Only 20% degradation was observed at pH value of 10 (Table 2). This is also in confirmation to the earlier findings which report a markedly decrease in the percentage of TOC removal with increasing pH in the case of dichlorophenoxyacetic acid.$^{24}$ At pH value of 10, TiO$_2$ is predominantly negatively charged. Most of the hydroxylated aromatic intermediates formed during photocatalysis at basic pH probably exist as anions species and therefore cannot be adsorbed effectively. The maximum adsorption takes place around the pH range of 5-7 (Fig. 6) which is close to the pzc of TiO$_2$ i.e. 6.25. Also from polynomial equations, it can be concluded that variable C and C$^2$ i.e. amount of oxidant has most pronounced positive effect on the degradation of catechol. The presence of hypochlorite oxidant serves as oxygen source and accelerates the degradation process. The associated effects between variables were neglected.

Figure 7 shows the three-dimensional representation of the polynomial for catalyst dose, oxidant amount and the response percentage degradation after 30 min of reaction. It can be seen from this figure that the increase in oxidant amount increases the percentage degradation of catechol. Similar trend was observed for photodegradation of chlorophenols by using UV/TiO$_2$ in presence of inorganic oxidant perchlorate.$^{10}$
Figure 8 represents the effect of pH and oxidant amount on percentage degradation of catechol. It can be concluded that increase in oxidant amount increases the percentage degradation with pH range between 5 to 7.

**Confirmation tests**

Since the response surface equations were derived from quadratic regression fit, confirmation tests must be performed to verify their validity. The independent variable values selected for the confirmation test must lie within the ranges for which the formulae were derived. The four confirmation experiments were performed for percentage degradation. The data from the confirmation runs and their comparisons with the predicted designed for percentage degradation is listed in Table 5. From the analysis of Table 5, it can be observed that the calculated error is small. The error between experimental and predicted values for percentage degradation lies within 1.2 to 7.7%. Obviously, this confirms the excellent reproducibility of the experimental conclusions.

**Photocatalytic degradation of catechol under sunlight**

The photocatalytic experiments were carried out under solar light using TiO₂ and ZnO with sodium hypochlorite as oxidant. The degradation of catechol in solution is initiated by the photoexcitation of the semiconductor, followed by the formation of electron-hole pair on the surface of catalyst when irradiated by the light in the region of absorption charge-transfer bands (Eq. 5).

\[(\text{MO/MO}_2) + h\nu \rightarrow (\text{MO/MO}_2) (e^{-}_\text{CB} + h^+_\text{VB}) \ldots (5)\]

The reactive intermediate which is responsible for the degradation is hydroxyl radical (OH•). It is either formed by the decomposition of water [Eq. (6)] or by reaction of the hole with OH\(^-\) [Eq. (7)].

\[h^+_\text{VB} + \text{H}_2\text{O} \rightarrow H^+ + \cdot\text{OH} \ldots (6)\]

\[h^+_\text{VB} + \text{OH}^- \rightarrow \cdot\text{OH} \ldots (7)\]

Electrons in the conduction band are also responsible for the production of hydroxyl radicals and the species are the primary cause of organic matter mineralization [(Eq. 8)].

\[\cdot\text{OH} + \text{pollutant} \rightarrow \text{degradation of the pollutant} \ldots (8)\]

The experiments were performed by using fixed amount of catechol (100 mg/L) with catalyst dose i.e. 2 g/L (TiO₂ and ZnO) at natural pH (pH 6) and 0.95 mL of NaOCl. The degradation of the catechol was calculated from the absorption spectra plots. The
percentage degradation of catechol using different catalysts is reported in Fig. 9. Photodegradation of catechol in the presence of TiO$_2$ in solar light was 98% and it was observed to be 88% when ZnO was used instead of TiO$_2$ under similar conditions. The results clearly indicate that the degradation occurs at a fast rate in the case of TiO$_2$ as compared to ZnO under solar light also, as was seen under UV irradiation.

**Effect of solar/UV irradiation on the photocatalytic activity**

The photocatalytic degradation of catechol using TiO$_2$ as photocatalyst and solar/UV irradiation as light source has been carried out and the results are presented in Fig. 10. From Fig. 10, it is evident that the complete degradation of catechol is achieved within 45 min under UV irradiation whereas it requires 150 min for the complete removal of catechol under solar irradiation. The difference in the rate of degradation is attributed to difference in the input energy. The energy of UV irradiation is large as compared to band gap energy of the catalysts. Hence, the problem of electron-hole recombination is not fully but largely avoided with UV source.

But in sunlight only 5% of the total radiation possesses the optimum energy for the band gap excitation of electrons$^{25}$. Hence, the percentage degradation is found to be less in solar irradiation of catechol. Although sunlight has only 5% of optimum energy for photocatalytic excitation and ultimately degradation of pollutants, it could be safe and cost effective source. UV source is not only hazardous but also expensive because of large input of electric power to generate UV irradiation. In tropical countries intense sunlight is available throughout the years and, hence, it could be effectively used for photocatalytic degradation of pollutants in wastewater. In case of large surface demanding photocatalytic degradation, sunlight would be the ultimate source. Moreover there is no material deterioration in case that sunlight is used as a radiation source. But UV light source may effect the catalyst decomposition$^{26}$.

**Conclusions**

The following conclusions have been drawn from the study.

(i) Photocatalytic oxidation process using TiO$_2$ as catalyst can efficiently degrade the catechol from aqueous solutions.

(ii) The photocatalytic degradation efficiency is improved when catalyst is combined with oxidant.

(iii) The experimental design has been a valuable methodology to investigate the effect of the selected variables viz. dose of catalyst, pH and amount of oxidant on the photocatalytic degradation of catechol.

(iv) The optimal conditions for the complete degradation of catechol were TiO$_2$-2.0 g/L, pH 6.0, and NaOCl 0.95 mL.

(v) The study reflects that catalyst dose and amount of oxidant have pronounced effect on the degradation of catechol.
(vi) The confirmation tests showed that the error between experimental and predicted values of percentage degradation is within 1.2 and 8%.
(vii) Under sunlight, TiO₂ and ZnO were tested and it was found that the TiO₂ shows excellent performance.

Acknowledgement
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