UV-assisted degradation of propiconazole in a TiO$_2$ aqueous suspension: identification of transformation products and the reaction pathway using GC/MS

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Photocatalytic degradation of propiconazole, a triazole pesticide, in the presence of titanium dioxide (TiO$_2$) under ultraviolet (UV) illumination was performed in a batch type photocatalytic reactor. A full factorial experimental design technique was used to study the main effects and the interaction effects between operational parameters in the photocatalytic degradation of propiconazole in a batch photo-reactor using the TiO$_2$ aqueous suspension. The effects of catalyst concentration (0.15–0.4 g L$^{-1}$), initial pH (3–9), initial concentration (5–35 mg L$^{-1}$) and light conditions were optimised at a reaction time duration of 90 min by keeping area/volume ratio constant at 0.919 cm$^2$ mL$^{-1}$. Photocatalytic oxidation of propiconazole showed 85% degradation and 76.57% mineralisation under UV light (365 nm/30 W m$^{-2}$) at pH 6.5, initial concentration 25 mg L$^{-1}$ and constant temperature (25 ± 1 °C). The Langmuir–Hinshelwood kinetic model has successfully elucidated the effects of the initial concentration on the degradation of propiconazole and the data obtained are consistent with the available kinetic parameters. The photocatalytic transformation products of propiconazole were identified by using gas chromatography–mass spectrometry (GC/MS). The pathway of degradation obtained from mass spectral analysis shows the breakdown of transformation products into smaller hydrocarbons ($m/z$ 28 and 39).

Keywords: photocatalytic degradation; propiconazole (technical); TiO$_2$; slurry reactor; UV

1. Introduction

Water pollution due to pesticides is a major concern nowadays due to their potential toxicity and bioaccumulation problem. The broad use of pesticides and their resistance to natural degradation, biodegradation, chemical and photochemical degradation under typical environmental conditions has resulted in the direct transformation of these contaminants in natural waters [1, 2]. The continuous addition of pesticides in surface and ground water affects the natural ecosystem and further causes biomagnifications. The extensive use of fungicides may lead to the inadvertent contamination of soil and percolate deeper into the soil and contaminate the groundwater [3]. Among all, triazole fungicides are used worldwide in the agricultural industry. Normally, these fungicides are sprayed directly on plants and crops, and during application, they reach into the soil and water by means of drifting, rain washing and by plant material falling on the ground. Of the triazole family, propiconazole is one of the widely used fungicides in Indian agriculture for controlling caterpillar and scale insects on rice, peanuts, coffee, fruits and maize. World Health Organization has classified propiconazole as a class II toxic compound

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Propiconazole is also known as a demethylation inhibiting fungicide (DMI) due to its deoxyribonucleic acid binding nature [5] in the human body. The environmental fate of the fungicide propiconazole in a rice–paddy soil was determined by using a lysimeter and it was observed that propiconazole can be detected in soil even after 2 years of spraying [3]. Similarly, laboratory degradation studies have been performed on different soil types using two commercial formulations containing either propiconazole alone or a combination of bentazone, dichlorprop and 2-methyl-4-chlorophenoxyacetic acid. It was observed that agricultural soil has the highest persistence for propiconazole, as traces have been found even after 84 days duration of the experiment [6]. The half-life of propiconazole in soil can range from 96 to 575 days depending on the soil type [7]. The photolytic degradation rate of propiconazole in water is as long as 249 days [8], thus there is a strong need for the development of effective techniques for the degradation of such a highly persistent and toxic pesticide in water.

Advanced oxidation processes (AOPs) have been used as emerging wastewater treatment technologies which can effectively handle various hazardous organics in surface and groundwater. They oxidise the organic pollutant into the mineral salt and non-toxic compounds under normal temperature and air pressure [9]. There are two different reaction mechanisms of photocatalysis; (a) generation of OH radicals from the holes present in the valence band and (b) direct oxidation of the compound from valence holes [10]. Thus, the main oxidant behind the degradation of organic compounds is the OH radical. Among AOPs, heterogeneous photocatalysis using TiO$_2$ as a photocatalyst is widely used as the emerging technology these days [11]. The domination of TiO$_2$ in this field can be attributed to its superior photocatalytic oxidation ability and non-photo-corrosive, non-toxic and inexpensive characteristics [12, 13].

The literature survey revealed that not much information is available for the photocatalytic degradation of propiconazole in water. The adsorption of propiconazole in aqueous solution has been studied, using different forms of carbon and about 90% adsorption was achieved at pH 6.5, but the process leads to the transformation of pollutants from one medium to another rather than degradation [14]. Though, degradation of propiconazole in canal water has been reported but without any addition of catalyst and it was concluded that propiconazole does not disperse completely even after 90 days in aqueous systems. Hence, there is strong possibility of leaching down of this fungicide, when applied in the crop, and in turn may contaminate the groundwater [15].

To the best of our knowledge, no such information has been reported on the photocatalytic degradation of propiconazole in aqueous solution. Therefore, the present study was performed to address the extent of its photodegradation by using TiO$_2$ as a catalyst. The objectives of the study were to obtained effective degradation of aqueous solution of fungicide propiconazole in the batch type of reactor under UV light, optimisation of different reaction parameters (by factorial design) such as catalyst loading, pH, different light intensity and on different concentrations of propiconazole, to investigate different transformation products formed during the degradation process and to propose a possible pathway for the degradation of these transformation products, which were analysed by gas chromatography–mass spectroscopy (GC–MS). The experimental study shows that the results presented here provide almost complete degradation of propiconazole through photocatalytic oxidation.

2. Experimental

2.1. Materials

Technical grade insecticide propiconazole (purity 93%) was received from Markfed Agro Chemicals, India. Aeroxide P25 TiO$_2$ (having an anatase to rutile ratio of 70:30%, crystalline
size 32 nm, \( \text{S}_{\text{BET}} 45.7 \, \text{m}^2/\text{g} \), pore volume 0.177 cm\(^3\)/g, average pore size 7.57 nm and porosity 51.5\% \) [16] received as free samples from Evonik, Germany. HCL (LR) and NaOH (essay 97\%) were procured from Sd Fine-Chem Ltd. (Mumbai, India). Ethyl acetate was procured from CDH, India. All chemicals were used as received without any further treatment. Double distilled water was used for preparation of all laboratory solutions. Also, the mineralisation of propiconazole was observed using a chemical oxygen demand (COD) Vario photometer (RD 125), Orbit India.

2.2. Photodegradation studies

The photodegradation study of propiconazole was performed in the hemispherical slurry batch reactor having the total capacity of 1 L (upper diameter 18.8 cm, base diameter 8 cm). For UV light irradiation, the reactor was placed in the UV chamber \([17]\) fitted with 8 blue black UV fluorescent lamps (Philips, 20 W) emitting a predominant wavelength of 365 nm, and an exhaust fan for the controlled temperature (25 ± 1 °C) equilibrium. The reactor was filled with 1 L of 25 mg L\(^{-1}\) of propiconazole solution having an optical density of 0.654 (220 nm) for all experimental studies. The reactor was placed on the digital magnetic stirrer (rpm 1000) for uniform dispersal of the catalyst and on an adjustable stand to work at different light intensities. The pH of the solution was adjusted to the desired value by means of a pH meter (Perfit India) using dilute HCL and NaOH solutions. The light intensity was measured using a Solar Light Co. PMA2100, intentiometer. The effect of varying reaction parameters such as light conditions, catalyst loading, initial concentration, pH and light intensity on the photodegradation of propiconazole has been studied. At varied time intervals, suitable aliquots (3 mL) were withdrawn from the reaction mixture, filtered through 0.22 \( \mu \)m membranes (Millipore) and analysed using a UV-Vis spectrophotometer (model no. 2450).

2.3. GC/MS system

Transformation products of propiconazole were identified using a gas chromatograph. The samples for GC/MS analysis were prepared by extraction of part (3 mL) of irradiated solution (after the removal of TiO\(_2\) particles) with ethyl acetate (3 mL). The extracts were dried in anhydrous sodium sulphate overnight. The percentage recovery of the extracted sample was 86\%. The finished sample was concentrated to 1 mL and then analysed by GC/MS. The GC (MS-Scion-45P) was equipped with a HP-5 MS capillary column. Helium was used as the carrier gas (1 mL min\(^{-1}\)). A split/splitless injector in the splitless mode at 250 °C was used. The transfer line temperature was set at 275 °C and the oven temperature was programmed from 60 °C (5 min hold) to 240 °C at a rate of 50 °C min\(^{-1}\) and then to 295 °C (3 min hold), no hold at 240 and 295 °C. The injected volume was 1 microliter. Chromatographic data were acquired by recording the full scan mass spectra in the \( m/z \) range of 50–500. The identification of transformation products was done by comparing the GC/MS spectra patterns with those of standard mass spectra in the National Institute of Standards and Technology (NIST) library and with ChemSpider.

3. Results and discussion

3.1. Photodegradation reactions

3.1.1. Effect of light conditions

A preliminary experiment was conducted with an initial concentration of 25 mg L\(^{-1}\) and with a photocatalyst loading of 0.25 mg L\(^{-1}\) at pH 6.5. To study the effect of different light conditions,
reactions were carried out under UV only, UV without TiO\textsubscript{2} and no light (dark) conditions with TiO\textsubscript{2}. Degradation was negligible in the presence of a catalyst in the dark. Also, UV light alone did not degrade fungicide in the absence of a catalyst. The degradation of propiconazole solution was irradiated for 90 min under UV light with a known amount of nano TiO\textsubscript{2} catalyst as shown in Figure 1. Degradation was well described by the Langmuir–Hinshelwood (L–H) model and was found to follow pseudo-first order kinetics.

3.2. Factorial design

The experimental work was first carried out using a 2\textsuperscript{4} factorial design in order to examine the main effects and the interactions between catalyst loading, pH, initial concentration and intensity. These two levels (i.e. high and low) were carried out in order to study the 2\textsuperscript{4} factorial experimentations [18]. Positive sign (+) indicated a higher level of variable whereas negative (−) sign indicated a lower level of variables. The effects were designed as in Table 1 which shows the values of the factors selected in this study. The factorial design results in 16 tests with all possible combinations of X\textsubscript{1}, X\textsubscript{2}, X\textsubscript{3} and X\textsubscript{4} as indicated in Table 2.

A first-order model with all possible interactions was chosen to fit the experimental:

\[
Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 \\
+ b_{24}X_2X_4 + b_{34}X_3X_4 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 + b_{134}X_1X_3X_4 + b_{234}X_2X_3X_4 + b_{1234}X_1X_2X_3X_4, \tag{1}
\]

Table 1. Factors and levels used in the 2\textsuperscript{4} factorial design.

| Operating variables       | Code | Low (−1) | High (−1) |
|---------------------------|------|----------|-----------|
| Initial concentration, mgL\textsuperscript{−1} | X\textsubscript{1} | 5         | 35         |
| TiO\textsubscript{2} dose, gL\textsuperscript{−1} | X\textsubscript{2} | 0.15 | 0.4         |
| pH                        | X\textsubscript{3} | 3         | 9          |
| Intensity Wm\textsuperscript{−2}         | X\textsubscript{4} | 20        | 35         |
where Y is the response % photocatalytic degradation efficiency, $X_i$ values ($i = 1$, 2, 3, 4) indicate the corresponding parameter in their coded forms.

Regression analysis was performed to fit the response function (% photocatalytic degradation efficiency) with the experimental data using the obtained regression coefficient, Equation (1) assuming the form.

\[
Y(\%) = 1.5662 + 0.4058X_1 + 175.7752X_2 + 4.0953X_3 + 1.8421X_4 - 6.3749X_1X_2 \\
- 0.1376X_1X_3 - 0.0553X_1X_4 - 20.0948X_2X_3 - 5.1735X_2X_4 - 0.1165X_3X_4 \\
+ 0.7329X_1X_2X_3 + 0.2354X_1X_2X_4 + 0.0069X_1X_3X_4 + 0.7772X_2X_3X_4 \\
- 0.0311X_1X_2X_3X_4
\]  

(2)

Equation (2) shows the effect of individual variables and interactional effects on propiconazole photocatalytic degradation. The positive sign shows that there is a direct relationship between the parameter and the dependent variable. As the coefficient of TiO$_2$ dosage is very high the catalyst dose has a major effect on the degradation. After this, the effect of pH also plays a major role. The effect of the initial concentration and intensity is quite less in comparison to the catalyst loading and pH. Further experiments were planned accordingly to achieve the most optimum process conditions.

### 3.2.1. Effect of catalyst loading

The amount of photocatalyst in the reaction mixture is directly proportional to the rate of photocatalytic oxidation. Different experiments were carried out with TiO$_2$ to assess optimum catalyst dosage by varying the catalyst loading (0.15–0.25 g L$^{-1}$) for degradation of propiconazole (25 mg L$^{-1}$). For different catalyst loading of 0.15, 0.2 and 0.25 g L$^{-1}$, it was observed that degradation increased from 76.77%, 80.06% and 85.39%, respectively, but with a further increase in 0.3 and 0.4 g L$^{-1}$ of catalyst loading there was a gradual decrease (71.8% and 69%, respectively) in the degradation of propiconazole, as shown in Figure 2. The excessive

| Experimental | $X_1$ | $X_2$ | $X_3$ | $X_4$ | Y(%) (experimental) | Y(%) (predicated) | Residue (%) |
|--------------|------|------|------|------|---------------------|-----------------|------------|
| 1            | 1    | 1    | 1    | 1    | 50                  | 50.15           | 0.2954     |
| 2            | 1    | 1    | 1    | -1   | 33                  | 33.09           | 0.2755     |
| 3            | 1    | -1   | 1    | 1    | 47                  | 47.17           | 0.3690     |
| 4            | 1    | -1   | 1    | -1   | 31                  | 31.10           | 0.3416     |
| 5            | 1    | -1   | -1   | 1    | 30                  | 30.05           | 0.1752     |
| 6            | 1    | -1   | -1   | -1   | 21                  | 21.03           | 0.1546     |
| 7            | 1    | 1    | -1   | -1   | 41                  | 41.03           | 0.0854     |
| 8            | 1    | 1    | -1   | -1   | 24                  | 24.02           | 0.0893     |
| 9            | -1   | -1   | 1    | -1   | 48                  | 48.00           | 0.0133     |
| 10           | -1   | -1   | -1   | 1    | 63                  | 63.00           | 0.0749     |
| 11           | -1   | -1   | -1   | -1   | 55                  | 55.01           | 0.0245     |
| 12           | -1   | 1    | -1   | -1   | 61                  | 61.00           | 0.0298     |
| 13           | -1   | 1    | 1    | -1   | 84                  | 84.02           | 0.0254     |
| 14           | -1   | 1    | 1    | -1   | 62                  | 62.01           | 0.0234     |
| 15           | -1   | 1    | -1   | 1    | 68                  | 68.00           | 0.0109     |
| 16           | -1   | -1   | 1    | 1    | 71                  | 71.02           | 0.0349     |

Table 2. Experimental design matrix, experimental results and predicated photocatalytic degradation for propiconazole.
loading of TiO\(_2\) in the solution can tend to increase its agglomeration and results in the blockage of surface light photons which cause decline in the number of active sites [19, 20]. In other words, a decrease in the degradation with an increase in catalyst dosage above the optimum level resulted in decreased light penetration and causes deactivation of activated molecules due to collision with ground state molecules [21]. The aggregation of particles may also decrease the effective surface area of the catalyst for adsorption of a reactant [22].

3.2.2. Effect of pH

The acid–base behaviour of the catalyst surface influences the photocatalytic degradation of propiconazole in aqueous solution [23]. The effect of pH on the photocatalytic degradation of propiconazole was studied in the pH range of 3–8 at a constant initial concentration of 25 mg L\(^{-1}\) and a catalyst dose of 0.25 g L\(^{-1}\) as shown in Table 3. The natural pH of propiconazole solution (6.5) shows maximum degradation as compared to the other pH values. While performing the experiments, pH was measured at regular intervals of time till the end of the reaction. It was observed that the pH of the reaction mixture shows very little variation throughout the reaction irrespective of the initial pH (acidic/basic). However, the rate of degradation was found to be optimum at pH 6.5. The generation of \(^{\bullet}\)OH takes place when hydroxyl ions on the TiO\(_2\) surface and the positive hole react with each other. As the zero point

| pH  | Removal efficiency (%) | Rate constant (min\(^{-1}\)) |
|-----|------------------------|-----------------------------|
| 3   | 50                     | 0.008                       |
| 4   | 59                     | 0.0099                      |
| 5   | 78.5                   | 0.0175                      |
| 6.5 | 85.39                  | 0.02                        |
| 8   | 73.6                   | 0.015                       |
| 9   | 67.6                   | 0.0127                      |

Figure 2. Plot of rate constant versus catalyst loading upon propiconazole degradation (200 mL, 25 mg L\(^{-1}\), pH 6.5, UV 30 W m\(^{-2}\), 1000 rpm).
charge (pHzpc) for titania is around 6.8 i.e. in acidic pH it is positively charged and in alkaline pH it is negatively charged [24]. Thus, it gradually exerted an electrostatic attraction towards the negatively charged compounds [25]. At lower pH (<7) of the medium the positive holes serve as the oxidation sites which lead to the generation of more •OH, resulting in increased degradation rates [26].

3.2.3. Effect of light intensity

The extent of light intensity absorbed is directly related to the degradation efficiency. Therefore, the effect of intensity on the degradation of propiconazole was studied at a constant aperture to volume (A/V) ratio of 0.919 cm$^2$ mL$^{-1}$ and the light intensity was varied by adjusting the distance of the reaction mixture from the UV lamps (15–35 Wm$^{-2}$). It was observed that with the increase in the light intensity from 15 to 35 Wm$^{-2}$, the degradation rate constant also increased from 0.0123 to 0.0228 min$^{-1}$. For a shallow pond batch reactor, the intensity dependence of the reaction rate constant [27] is given by Equation (3).

$$
\frac{k}{k_o} = m \frac{I(\frac{A}{V})^n}{I_o(\frac{A}{V})_o},
$$

where $m$ and $n$ are the empirical constants whose values have been reported by Wyness et al. [27], for some systems and $k_o$ is the reference rate constant corresponding to reference intensity $I_o$. At a constant $A/V$ ratio, Equation (3) can be written as:

$$
\frac{k}{k_o} = m \frac{I^n}{I_o^n}
$$

(4)

Based on the observed data ($K$ vs $I$), the value of $n$ and $m$ are 0.7827 and 0.9621, respectively, (Figure 3). These values are quite similar to the values reported in degradation of 3,4-dichlorophenol in the shallow pond batch reactor [27, 28].

![Figure 3. Rate constant variation with UV intensity (25 mg L$^{-1}$, pH 6.5, 200 mL, TiO$_2$ 0.25 g L$^{-1}$, 1000 rpm).](image-url)
3.2.4. Effect of initial concentration

The initial concentration plays a significant role in determining the rates of most of the photochemical reactions. There was reduction in the rate and the extent of degradation of propiconazole as the initial concentration was increased from 5 to 35 mg L$^{-1}$. The degradation rate for propiconazole in the lower concentrations was the maximum, followed by a slower decrease with the increase in concentration.

The rate of degradation significantly depends on the formation of hydroxyl radicals [29]. With an increase in concentration of pesticide, the screening effect dominates and prevents the penetration of the light to lower depths [30, 31]. Moreover, due to constant catalyst concentration and light irradiation, a lesser number of active catalyst particles are available for the generation of OH radicals at higher initial concentrations, which further decreases the overall rate of degradation. To study the kinetics of degradation of propiconazole, the L–H model was used. The L–H model was originally developed to quantitatively describe gaseous-solid reactions [32], but later on it was used to describe solid–liquid interactions [33]. According to the L–H model, the photocatalytic degradation rate can be expressed as a function of initial concentration [34]

$$r_o = \frac{k_rK C_o}{1 + KC_o},$$  \hspace{1cm} (5)

where $r_o$ is the initial rate of photocatalytic degradation of propiconazole, $k_r$ is the reaction rate constant, $K$ is the equilibrium adsorption constant and $C_o$ the initial concentration, respectively.

The inverse of Equation (5) gives:

$$\frac{1}{r_o} = \frac{1}{k_r} + \frac{1}{k_rK C_o}.$$ \hspace{1cm} (6)

The plot of $1/r_o$ versus $1/C_o$ represented in Figure 4 shows a linear variation, confirming the validity of the Langmuir–Hinshelwood relationship for the initial rates of degradation. The values of $k_r$ and $K$, calculated from the intercept and the slope of the straight line ($R^2 = 0.9981$), were 0.8664 mg L$^{-1}$ min$^{-1}$ and 0.0324 L mg$^{-1}$, respectively.

![Figure 4](image_url)  
Figure 4. Kinetics study of initial concentrations (200 mL, pH 6.5, TiO$_2$ 0.25 g L$^{-1}$, UV 30 W m$^{-2}$, 1000 rpm).
3.3. **Qualitative identification of transformation products**

The photocatalytic degradation reactions of propiconazole were carried out under optimised conditions and transformation products formed during the process were analysed by GC/MS. The chromatogram obtained after 90 min of photocatalytic treatment shows a number of transformation products as given in Table 4. The transformation products formed are identified either by interpretation of their fragment ions in the mass spectra or by comparing the GC/MS spectral patterns with those of standard mass spectra in the NIST library and with ChemSpider. The mass spectra of propiconazole and its transformation products (a–e) are given in Figures 1S and 2S (Supplemental data).

| Sr. No | Transformation products | Chemical structure | R<sub>t</sub> (min) | Molecular weight | Fragment ions (m/z) |
|--------|-------------------------|--------------------|---------------------|------------------|-------------------|
| 1.     | Nitrobenzene            | ![Nitrobenzene](image) | 8.2                 | 123              | 93, 77, 51        |
| 2.     | 2-ethylhexanoic acid    | ![2-ethylhexanoic acid](image) | 9.8                 | 144              | 116.88, 41        |
| 3.     | Benzene,1-methyl-4-nitro| ![Benzene,1-methyl-4-nitro](image) | 11.6                | 137              | 107, 91, 65, 39   |
| 4.     | Benzene-1,3-dinitro     | ![Benzene-1,3-dinitro](image) | 18.4                | 168              | 122, 92, 76, 28   |
| 5.     | Ethyl 5-amino-1-benzyl-3-methyl-1H-pyrazole-4-carboxylate | ![Ethyl 5-amino-1-benzyl-3-methyl-1H-pyrazole-4-carboxylate](image) | 36.1 | 259 | 191, 173, 69, 28 |

Table 4. GC/MS retention times (R<sub>t</sub>) and spectral characteristics of identified transformation products reaction products of the photocatalytic degradation of propiconazole.
Figure 5. MS interpretation of transformation products from (a–e). (b) Proposed degradation pathway of propiconazole with TiO₂.
3.4. Mass spectra analysis

The mass spectral analysis shows the transformation products of propiconazole in Figure 5a. The compound observed at m/z 123, R_t 8.2 min (transformation product a), is nitrobenzene which undergoes fragmentation to form unstable species C_6H_6O at m/z 93, which possibly could be due to the removal of the –NO group. Furthermore, it reduces to the phenyl radical at m/z 77 probably by the removal of the –O group and finally, through ring dissociation, to an open chain hydrocarbon species at m/z 51. The transformation product (b) at m/z 144, R_t 9.8 min is 2-ethylhexanoic acid, might release the –C_2H_4 group to give species at m/z 116. It may further breakdown to butyric acid at m/z 88 and dissociated, by the removal of –CO_2 and H_2O, to species at m/z 41.

Benzene,1-methyl-4-nitro was observed at m/z 137, R_t 11.6 min (transformation product c) and loses the nitro group to give a species at m/z 107, which further reduces to species at m/z 91, 65 and finally to species at m/z 39. The transformation product (d) at m/z 168 appearing at R_t 18.4 is benzene-1,3-dinitro which reduced to 4-nitrophenol feasibly by the loss of the –NO_2 group. It further fragmented to m/z 92 and through ring opening; it dissociates to m/z 76 and 28. The major transformation product (e) was observed at m/z 259, R_t 36.4 min, formed by the breakdown of the C–Cl bond of the parent compound (propiconazole), which dissociates to form species at m/z 191 and 173. After undergoing ring cleavage, the complex breakdown into m/z at 69 and possibly at last converted into simpler molecule ethene at m/z 28. All the transformation products formed are cross checked by the NIST library and with ChemSpider.

3.4.1. Pathway purposed on the basis of transformation-products identified by GC–MS

While performing the photocatalytic experiments, two different pathways of the mechanism of photocatalysis were usually observed; (a) generation of OH radicals from the holes present in
the valence band, (b) direct oxidation of the compound from valence holes. On the basis of the GC/MS analysis of the degraded reaction mixture and the transformation products detected; a possible reaction mechanism (Figure 5b) for the degradation of propiconazole is proposed. Though, the absolute evidence of the pathway was not verified by comparison with authentic standards, we believe that the allocated structures are the best consistent with all data.

This pathway is purely based on the mass spectra analysis, which was carried out after the photocatalytic degradation of propiconazole and its dissociation into various transformation products. Initially, by the breakdown of the C–Cl bond of propiconazole, transformation product ethyl 5-amino-1-benzyl-3-methyl-1 H-pyrazole-4-carboxylate (m/z 259) was detected and a similar fragmentation was observed in cyproconazole photocatalytic degradation [35]. It further undergoes ring breakage to form 2-ethylhexanoic acid (m/z 88) followed probably by reduction to the propargyl radical (m/z 39). The cyclic propagation of the same transformation product (m/z 259) leads to the breakdown into 2-(2-methoxylethyl) isoindolin-1-iminium (m/z 173) [36] which, by the electron transfer and the ring opening, fragmented into prenyl (m/z 69) and into ethene (m/z 28). On the other hand, there is a feasibility of oxidation of the compound at m/z 259, which may breakdown into benzene-1,3-dinitro (m/z 168) followed by the transformation product at m/z 69 [35] and thereafter at m/z 28. The possibility of elimination of the nitro group from the substituent at m/z 168 leads to the formation of species at m/z 92 and finally degraded to ethylene (m/z 28). The formation of benzene, 1-methyl-4-nitro (m/z 137) possibly occurred after the ring cleavage of propiconazole by the attack of the hydroxyl radical, and further the elimination of the nitro group formed into (2-methyl phenyl)oxidanyl (m/z 107). The removal of the –NO₂ group resulted in the formation of furan-2-ethynyl (m/z 92), which further breaks down into ethene (m/z 28) or a propargyl radical (m/z 39). No such complex transformation product has been observed which reflects the parent compound in the pathway chain. All the above formed transformation products have been identified by the NIST library and cross checked by ChemSpider.

4. Mineralisation of propiconazole

The reduction in COD reflects the degree to which an organic species is degraded or mineralised [37]. Therefore, the change in COD was studied for propiconazole under optimised conditions as a function of irradiation time under UV light. Figure 6 shows a change in concentration and
% COD removal as a function of time under optimum conditions. The figure shows that this process is not only degrading the propiconazole but also mineralising the synthetic effluents. Under optimum conditions, fungicides showed 76.57% mineralisation in UV.

5. Conclusion
Photocatalytic degradation of the fungicide propiconazole is possible by using a TiO$_2$ catalyst in suspended aqueous solutions under UV light. The effect of adsorption on the catalyst particles was negligible. The important parameters which affect the removal efficiency of propiconazole such as initial concentration, catalyst loading, pH and intensity were investigated. From the statistical analysis, the most effective parameters in the photocatalytic degradation efficiency were catalyst loading and pH. The results indicate that an optimum concentration of the suspended TiO$_2$ catalyst (0.25 g L$^{-1}$) showed the highest degradation efficiency for 25 mg L$^{-1}$ of propiconazole, at pH 6.5 (natural pH), light intensity 30 Wm$^{-2}$, constant temperature (25 ± 1 °C) and at constant A/V 0.919 cm$^2$ mL$^{-1}$. Under these conditions, 85% of 25 mg L$^{-1}$ substrate was degraded in about 90 min of UV irradiation time. The Langmuir–Hinshelwood kinetic model showed a good agreement for the initial rates of degradation with the appropriate reaction rate constant and the substrate adsorption constant values of 0.8664 mg L$^{-1}$ min$^{-1}$ and 0.0324 L mg$^{-1}$, respectively. COD reduction (nearly 80%) confirms the mineralisation of propiconazole under UV light. Furthermore, it was observed that the GC–MS analysis showed that all the complex molecules were possibly dissociated into the smaller molecules.

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Disclosure statement
No potential conflict of interest was reported by the authors.

Supplemental data
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