



Research Article

## Photocatalytic Degradation of Imidacloprid in Water Using TiO<sub>2</sub>, ZnO and Modified TiO<sub>2</sub>: Kinetics, Mineralization and Process Optimization

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**Abstract:** The present study investigated the photocatalytic degradation of imidacloprid in aqueous media using TiO<sub>2</sub>, ZnO and modified TiO<sub>2</sub> as semiconductor photocatalysts. Photocatalytic experiments were carried out in a controlled batch reactor, and the effects of catalyst dosage, initial imidacloprid concentration, solution pH, light intensity, temperature and hydrogen peroxide dose were systematically evaluated. Residual imidacloprid was quantified by HPLC-DAD, while total organic carbon analysis was used to assess mineralization. The degradation kinetics were interpreted using an apparent pseudo-first-order model, and scavenger experiments were conducted to examine the contribution of hydroxyl radicals, superoxide-related species and photogenerated holes. Among the tested catalysts, modified TiO<sub>2</sub> showed the highest photocatalytic performance, achieving 97.62 ± 0.19% imidacloprid degradation after 120 min, with an apparent rate constant of 0.031 min<sup>-1</sup> and a half-life of 22.36 min. The most favourable responses were observed at approximately 1.00 g L<sup>-1</sup> catalyst loading, pH 7, 30 °C, full reference light intensity and 10 mM H<sub>2</sub>O<sub>2</sub>. TOC removal reached 77.74 ± 0.14% after 120 min, indicating that parent-compound degradation proceeded faster than complete mineralization. Scavenger studies suggested that hydroxyl radicals played a major role, while superoxide-related species and photogenerated holes also contributed. Modified TiO<sub>2</sub> retained approximately 90.6% of its initial activity after five reuse cycles. Overall, modified TiO<sub>2</sub> demonstrated promising potential for the photocatalytic removal of imidacloprid from aqueous systems.

**Keywords:** Imidacloprid; Photocatalytic degradation; TiO<sub>2</sub>; ZnO; Modified TiO<sub>2</sub>; HPLC-DAD; Mineralization; Reactive oxygen species.

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**Conflict of interest:** None

## Introduction

Imidacloprid is a widely used neonicotinoid pesticide whose residues can enter aquatic environments through agricultural runoff, leaching, spray drift and improper disposal. Its occurrence in water has created concern because pesticide residues may persist long enough to affect aquatic systems and may not be completely eliminated by conventional treatment processes. Therefore, the development of efficient treatment methods for the removal and degradation of imidacloprid from contaminated water is important from both environmental and water-quality perspectives [1].

Among advanced treatment approaches, heterogeneous semiconductor photocatalysis has attracted considerable attention because it can promote the oxidative degradation of organic contaminants under irradiation. In this process, irradiation of a semiconductor photocatalyst generates electron-hole pairs, which subsequently participate in the formation of reactive oxygen species. These reactive species can attack pesticide molecules and convert them into progressively oxidized products. In the present work,  $\text{TiO}_2$ ,  $\text{ZnO}$  and modified  $\text{TiO}_2$  were selected as photocatalysts for the degradation of imidacloprid in aqueous media. The experimental design integrates catalyst characterization, controlled batch photocatalysis, process optimization, HPLC-based determination of residual imidacloprid, total organic carbon analysis, kinetic modelling, reactive-species probing and catalyst-reuse assessment [2].

Titanium dioxide and zinc oxide were used as pristine semiconductor photocatalysts, while modified  $\text{TiO}_2$  was included as a comparative material intended to improve photocatalytic performance. The modified  $\text{TiO}_2$  was prepared by a sol-gel route using titanium(IV) isopropoxide and urea, followed by aging, drying and calcination. The actual phase composition, surface bonding environment and optical behaviour of the modified photocatalyst were intended to be established through XRD, FTIR and UV-Vis diffuse-reflectance spectroscopy rather than assumed solely from the preparation method [3-4].

The efficiency of photocatalytic degradation depends strongly on operating conditions. Catalyst dosage affects the number of available active sites, although excessive solids can increase scattering, shielding and aggregation. Initial pollutant concentration influences competition for reactive sites and photon penetration. Solution pH can modify semiconductor surface charge, pollutant behaviour and radical chemistry, while light intensity affects the generation of photogenerated charge carriers. Temperature can influence diffusion, adsorption-desorption behaviour and oxygen solubility. Hydrogen peroxide can also enhance reactive oxygen species generation at suitable concentrations, although excessive addition may reduce net efficiency by scavenging hydroxyl radicals. For these reasons, the present study systematically evaluated catalyst dosage, initial imidacloprid concentration, pH, light intensity, temperature and  $\text{H}_2\text{O}_2$  dose [5].

Accurate assessment of pesticide treatment requires measurement of both parent-compound disappearance and mineralization. In the present investigation, HPLC-DAD was used as the principal quantitative method for determining residual imidacloprid after photocatalytic treatment. A reversed-phase C18 column was employed, with acetonitrile:water (30:70, v/v) as the mobile phase, a flow rate of  $1.0 \text{ mL min}^{-1}$  and detection at 270 nm. Total organic carbon analysis was additionally used to determine the extent of mineralization and to distinguish disappearance of the parent compound from complete oxidation of organic carbon [6-7].

Kinetic analysis was also incorporated to describe the degradation behaviour of imidacloprid. Time-course data were evaluated using kinetic representations, with particular emphasis on an apparent pseudo-first-order relationship. The apparent rate constant, half-life and regression behaviour were used to compare photocatalytic performance under matched experimental conditions [8].

To obtain further mechanistic information, reactive oxygen species were investigated using selective scavenger experiments. Isopropanol, *p*-benzoquinone and EDTA were used to probe the involvement of hydroxyl radicals, superoxide radicals and photogenerated holes, respectively. In addition, the optimized photocatalyst system was evaluated over five consecutive reuse cycles to assess activity retention and operational stability [9].

Accordingly, the present study was undertaken to investigate the photocatalytic degradation of imidacloprid in water using  $\text{TiO}_2$ , ZnO and modified  $\text{TiO}_2$ . The work aimed to compare catalyst performance, optimize the major operating conditions, evaluate degradation kinetics and mineralization, examine the contribution of reactive oxygen species and assess photocatalyst reusability. This integrated approach provides a systematic basis for evaluating semiconductor photocatalysis as a potential treatment strategy for imidacloprid-contaminated aqueous systems [10-11].

## Materials and Methods

### Experimental Design

The study was designed to evaluate the photocatalytic degradation of imidacloprid in aqueous media using  $\text{TiO}_2$ , ZnO and modified  $\text{TiO}_2$  as semiconductor photocatalysts. The experimental programme included photocatalyst characterization, controlled batch photocatalysis, optimization of operational parameters, chromatographic determination of residual imidacloprid, total organic carbon assessment, kinetic modelling, reactive oxygen species studies and catalyst-reuse evaluation. The principal variables investigated were catalyst dosage, initial imidacloprid concentration, solution pH, irradiation time, light intensity, temperature and hydrogen peroxide dose [12].

A one-variable-at-a-time optimization strategy was combined with replicate time-course experiments. All photocatalytic experiments were performed in triplicate ( $n = 3$ ). Unless otherwise specified, the reference conditions were an initial imidacloprid concentration of  $20 \text{ mg L}^{-1}$ , catalyst loading of  $0.75 \text{ g L}^{-1}$ , pH 7.0, temperature of  $30 \pm 1^\circ\text{C}$  and full reference light intensity. Samples were collected at 0, 15, 30, 45, 60, 90 and 120 min. Dark adsorption and photolysis controls were included to distinguish photocatalytic degradation from adsorption and direct photolysis [13].

### Chemicals and Reagents

Analytical-grade imidacloprid was used as the target pesticide. Titanium dioxide and zinc oxide of photocatalytic/nanoparticle grade were used as pristine semiconductor photocatalysts. Titanium(IV) isopropoxide (TTIP), urea, absolute ethanol, nitric acid and deionized water were used for the preparation of modified  $\text{TiO}_2$ . HPLC-grade acetonitrile and methanol, ultrapure water, orthophosphoric acid/formic acid, hydrogen peroxide (30% w/w), sodium hydroxide and hydrochloric acid were used as required. Isopropanol (IPA), *p*-benzoquinone (BQ) and disodium EDTA were used as scavengers for hydroxyl radicals, superoxide radicals and photogenerated holes, respectively. All aqueous solutions were prepared using Type-I water with a resistivity of approximately  $18.2 \text{ M}\Omega \text{ cm}$  [14].

### Preparation of Imidacloprid Stock and Working Solutions

A primary stock solution of imidacloprid was prepared at a concentration of  $1000 \text{ mg L}^{-1}$  using a water/methanol mixture as required for complete dissolution. Working solutions in the range of  $5\text{--}40 \text{ mg L}^{-1}$  were prepared by volumetric dilution with deionized water. The organic-solvent fraction was maintained as low and as constant as practicable during comparative experiments. Fresh working solutions were prepared for each experimental block and protected from direct light before use.

The initial solution pH was adjusted using dilute HCl or NaOH and measured with a calibrated digital pH meter. pH adjustment was performed before photocatalyst addition. Buffers were not used during the

main photocatalytic runs because buffer anions may compete with reactive oxygen species or modify catalyst surface chemistry [15].

#### **Preparation of Photocatalysts**

Commercial TiO<sub>2</sub> and ZnO were used as baseline photocatalysts. Before use, the powders were dried at 105 °C, cooled in a desiccator and stored in amber glass containers. Catalyst suspensions were freshly prepared in the imidacloprid solution immediately before dark equilibration.

Modified TiO<sub>2</sub> was prepared using a sol-gel procedure. Briefly, 20 mL of TTIP was dissolved in 80 mL of absolute ethanol under continuous magnetic stirring. Urea was separately dissolved in 20 mL of deionized water to obtain an approximate nominal N/Ti molar ratio of 0.10. The aqueous urea solution was added dropwise to the TTIP solution under vigorous stirring. Dilute nitric acid was used to maintain the hydrolysis mixture at approximately pH 2–3. The resulting sol was stirred for 2 h, aged for 24 h, dried at 80 °C and gently ground. The dried gel was calcined at 450 °C for 3 h using a heating rate of 5 °C min<sup>-1</sup> [16].

#### **Photocatalyst Characterization**

TiO<sub>2</sub>, ZnO and modified TiO<sub>2</sub> were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and UV-Visible diffuse-reflectance spectroscopy (UV-Vis DRS). These techniques were used to assess crystalline phase, crystallite-size characteristics, surface bonding and functional groups, and optical absorption behaviour.

XRD measurements were performed using Cu K $\alpha$  radiation over a 2 $\theta$  range of 10–80° with a step size of 0.02°. Average crystallite size was estimated using the Scherrer equation:  $D = K\lambda / (\beta \cos \theta)$ , where D is the crystallite size, K is the shape factor (0.9),  $\lambda$  is the X-ray wavelength,  $\beta$  is the full width at half maximum, and  $\theta$  is the Bragg angle. FTIR spectra were recorded over 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> using 32 scans. UV-Vis diffuse-reflectance spectra were recorded from 200 to 800 nm, and optical band-gap values were estimated using the Kubelka–Munk transformation and an appropriate Tauc plot [17].

#### **Photocatalytic Reactor and Irradiation System**

Photocatalytic experiments were conducted in a jacketed borosilicate-glass batch photoreactor with a working volume of 100 mL. A 200 W tungsten lamp was positioned above the reactor at a fixed geometry. The reaction suspension was continuously stirred using a magnetic stirrer to minimize catalyst settling and external mass-transfer limitations. The reactor jacket was connected to a circulating-water system to maintain the reaction temperature at 30  $\pm$  1 °C under reference conditions. The lamp-to-liquid distance was maintained constant throughout comparative experiments. Relative irradiance was varied to 25, 50, 75 and 100% during light-intensity experiments [18].

#### **Photocatalytic Degradation Procedure**

For each experiment, 100 mL of imidacloprid working solution was transferred to the reactor and the required amount of photocatalyst was added. The suspension was stirred in darkness for 30 min to establish adsorption-desorption equilibrium. A time-zero sample was then collected and the lamp was switched on to initiate photocatalysis. Aliquots were withdrawn at predetermined time intervals and immediately separated from the catalyst by centrifugation followed by filtration through a 0.22  $\mu$ m membrane filter before instrumental analysis.

The standard reference condition consisted of 20 mg L<sup>-1</sup> imidacloprid, 0.75 g L<sup>-1</sup> photocatalyst, pH 7, 30 °C and full reference irradiation. All experiments were conducted as independent triplicate reactor runs [19].

#### **Control Experiments**

Dark adsorption was assessed during the 30 min pre-irradiation period. Separate control experiments included: imidacloprid under light without catalyst, imidacloprid with catalyst in darkness, catalyst plus

light, H<sub>2</sub>O<sub>2</sub> plus light without catalyst and catalyst + H<sub>2</sub>O<sub>2</sub> + light. These controls enabled separation of direct photolysis, adsorption, peroxide-assisted oxidation and photocatalytic effects [20].

#### Optimization of Operational Parameters

The effects of major operating variables were investigated independently. Catalyst loading was varied at 0.25, 0.50, 0.75, 1.00 and 1.25 g L<sup>-1</sup>. Initial imidacloprid concentration was varied at 5, 10, 20, 30 and 40 mg L<sup>-1</sup>. Solution pH was evaluated at pH 3, 5, 7, 9 and 11. Relative light intensity was varied at 25, 50, 75 and 100% of the reference irradiance. Temperature was studied at 20, 25, 30, 35 and 40 °C, and H<sub>2</sub>O<sub>2</sub> concentration was investigated at 0, 2.5, 5, 10 and 20 mM. Unless the relevant factor was intentionally varied, all other experimental conditions were maintained at their reference levels [21].

#### UV-Visible Spectrophotometric Screening

UV-Visible spectroscopy was used as a rapid screening method for spectral changes and preliminary monitoring of imidacloprid degradation where a suitable absorption band was present. Spectra were recorded in quartz cuvettes over approximately 200–500 nm against reagent blanks. Quantitative interpretation was based primarily on chromatographic determination because degradation products may overlap with the UV absorbance of the parent compound [22].

#### HPLC-DAD Determination of Imidacloprid

HPLC-DAD was used as the principal quantitative method for determining residual imidacloprid following photocatalytic treatment. Analysis was performed using an Agilent 1260 Infinity II HPLC system equipped with a diode-array detector and a reversed-phase C18 column (150 × 4.6 mm, 5 μm) maintained at 30 °C. The mobile phase consisted of acetonitrile:water (30:70, v/v) at a flow rate of 1.0 mL min<sup>-1</sup>. Detection was carried out at 270 nm with an injection volume of 20 μL.

Calibration standards covering the relevant analytical range were prepared separately from the experimental samples. A minimum of five concentration levels was used. Calibration acceptance was based on linear response across the working range and examination of residuals. Solvent blanks, filter blanks, quality-control standards and matrix-free standards were included to monitor contamination, carryover and analytical consistency [23].

#### Calculation of Photocatalytic Degradation

Residual imidacloprid concentration was calculated from the corresponding HPLC calibration function. Percentage degradation at irradiation time *t* was calculated as: Degradation (%) = [(C<sub>0</sub> – C<sub>t</sub>)/C<sub>0</sub>] × 100, where C<sub>0</sub> is the concentration measured at the beginning of irradiation after dark equilibration and C<sub>t</sub> is the concentration at irradiation time *t*. Using the post-equilibration value as C<sub>0</sub> prevented adsorption loss from being incorrectly included as photocatalytic degradation [24].

#### Total Organic Carbon and Mineralization

Mineralization was assessed through total organic carbon analysis. TOC removal was calculated using: TOC removal (%) = [(TOC<sub>0</sub> – TOC<sub>t</sub>)/TOC<sub>0</sub>] × 100. TOC measurements were obtained at 0, 30, 60, 90 and 120 min to compare mineralization with disappearance of the parent imidacloprid compound [25].

#### Kinetic Analysis

Time-course data were evaluated using zero-order, first-order and pseudo-first-order representations. For dilute heterogeneous photocatalytic systems, the principal kinetic relationship was expressed as  $\ln(C_0/C_t) = k_{app} t$ , where *k<sub>app</sub>* is the apparent pseudo-first-order rate constant. The corresponding half-life was calculated as  $t_{1/2} = \ln(2)/k_{app}$ . The apparent rate constant was obtained from the slope of the linear regression of  $\ln(C_0/C_t)$  against irradiation time. Model adequacy was assessed using the coefficient of determination, residual behaviour and reproducibility among replicate experiments [26].

### Reactive Oxygen Species and Scavenger Studies

Reactive-species involvement was investigated using scavenger experiments. Isopropanol was used as a hydroxyl-radical scavenger, p-benzoquinone as a superoxide-radical scavenger and EDTA as a photogenerated-hole scavenger. Each experiment was compared with a no-scavenger photocatalytic control under identical conditions. A reduction in degradation in the presence of a scavenger was interpreted as evidence for involvement of the corresponding reactive species, while acknowledging that scavenger selectivity is not absolute [27].

### Catalyst Reusability

The optimized photocatalyst system was evaluated over five consecutive reaction cycles. After each cycle, the catalyst was recovered by centrifugation, washed repeatedly with deionized water followed by a small volume of ethanol, dried at approximately 80 °C and reused under the same experimental conditions. Activity retention was calculated as: Activity retention (%) = [Degradation in cycle n / Degradation in cycle 1] × 100. Where sufficient recovered catalyst was available, post-use XRD and/or FTIR analysis was included to assess major structural changes, surface fouling or agglomeration [28].

### Quality Assurance and Quality Control

Quality-assurance procedures were applied throughout sample preparation, photocatalytic treatment and instrumental analysis. Appropriate volumetric glassware was used for standards and dilutions, balances and pH meters were checked before use, and temperature was monitored throughout the experiments. Analytical runs included solvent blanks, calibration standards, continuing calibration checks and replicate quality-control samples. Membrane filters were pre-rinsed where appropriate, and filter blanks were examined to minimize possible analyte loss or contamination. Independent reactor runs were considered true experimental replicates, whereas repeat HPLC injections were treated only as instrumental precision checks [29].

### Statistical Analysis

Experimental data were summarized as mean ± standard deviation. For optimization studies involving one independent factor, one-way analysis of variance was specified when distributional and variance assumptions were satisfied. Where appropriate, robust or non-parametric alternatives were considered. Dunnett-type post-hoc comparisons were used when treatments were compared with a designated control, while Tukey-type comparisons were applicable for all-pair comparisons. Statistical significance was assessed at  $\alpha = 0.05$ . Time-course and kinetic datasets were analyzed primarily using regression, with apparent rate constants, half-lives and goodness-of-fit statistics reported for the photocatalyst systems [30].

## Results and Discussion

The photocatalytic degradation of imidacloprid was evaluated using TiO<sub>2</sub>, ZnO and modified TiO<sub>2</sub> under controlled batch conditions. The experimental programme included time-dependent degradation, kinetic modelling, optimization of operating variables, mineralization assessment, reactive-species probing and catalyst-reuse studies. All experiments were conducted as independent triplicate reactor runs under the reference condition of 20 mg L<sup>-1</sup> imidacloprid, 0.75 g L<sup>-1</sup> catalyst, pH 7, 30 °C and full reference irradiation, with sampling up to 120 min.

### Comparative Photocatalytic Degradation and Kinetic Behaviour

Imidacloprid degradation increased progressively with irradiation time for all three photocatalysts. Modified TiO<sub>2</sub> showed the highest degradation efficiency, followed by pristine TiO<sub>2</sub> and ZnO. At 90 min, degradation reached 94.02 ± 0.40% with modified TiO<sub>2</sub>, compared with 88.69 ± 0.93% for TiO<sub>2</sub> and 84.61 ±

0.34% for ZnO. At 120 min, the corresponding degradation values increased to  $97.62 \pm 0.19\%$ ,  $94.37 \pm 0.34\%$  and  $91.91 \pm 0.29\%$ , respectively.

**Table 1:** Comparative degradation and pseudo-first-order kinetic parameters of imidacloprid

| Photocatalyst             | Degradation at 90 min (%) | Degradation at 120 min (%) | $k_{app}$ ( $\text{min}^{-1}$ ) | $t_{1/2}$ (min) | $R^2$  |
|---------------------------|---------------------------|----------------------------|---------------------------------|-----------------|--------|
| TiO <sub>2</sub>          | $88.69 \pm 0.93$          | $94.37 \pm 0.34$           | 0.024                           | 28.88           | 0.9867 |
| ZnO                       | $84.61 \pm 0.34$          | $91.91 \pm 0.29$           | 0.021                           | 33.01           | 0.9883 |
| Modified TiO <sub>2</sub> | $94.02 \pm 0.40$          | $97.62 \pm 0.19$           | 0.031                           | 22.36           | 0.9873 |

The apparent pseudo-first-order rate constant was highest for modified TiO<sub>2</sub> at  $0.031 \text{ min}^{-1}$ , followed by TiO<sub>2</sub> at  $0.024 \text{ min}^{-1}$  and ZnO at  $0.021 \text{ min}^{-1}$ . The corresponding half-life was lowest for modified TiO<sub>2</sub>, indicating the most rapid disappearance of imidacloprid under the experimental conditions. The high  $R^2$  values for all three catalysts indicate a good fit to the apparent pseudo-first-order kinetic model. The rapid decrease in parent imidacloprid concentration is consistent with the expected behaviour of semiconductor-mediated photocatalysis. The better performance of modified TiO<sub>2</sub> may reflect more effective utilization of incident light or photogenerated charge carriers. However, the supplied characterization dataset does not contain measured XRD, FTIR or optical values sufficient to establish the structural or electronic origin of this improvement. Therefore, the present interpretation should remain limited to experimentally observed photocatalytic performance.

#### Effect of Catalyst Dosage

The influence of modified TiO<sub>2</sub> loading on imidacloprid degradation was evaluated between 0.25 and  $1.25 \text{ g L}^{-1}$ .

**Table 2:** Effect of catalyst dosage on imidacloprid degradation at 90 min

| Catalyst dosage ( $\text{g L}^{-1}$ ) | Degradation (%)  |
|---------------------------------------|------------------|
| 0.25                                  | $69.41 \pm 1.28$ |
| 0.50                                  | $79.41 \pm 0.70$ |
| 0.75                                  | $89.30 \pm 1.18$ |
| 1.00                                  | $89.44 \pm 0.49$ |
| 1.25                                  | $87.35 \pm 1.84$ |

Increasing catalyst loading from 0.25 to  $1.00 \text{ g L}^{-1}$  progressively improved imidacloprid degradation, with the highest value of  $89.44 \pm 0.49\%$  observed at  $1.00 \text{ g L}^{-1}$ . A slight decline to  $87.35 \pm 1.84\%$  occurred at  $1.25 \text{ g L}^{-1}$ . The initial increase in removal can be attributed to the greater availability of active catalyst surface and enhanced photon capture. At excessive catalyst loading, however, greater turbidity, light scattering, shielding and particle agglomeration may reduce the effective illuminated surface. Thus, approximately  $1.00 \text{ g L}^{-1}$  represented the most favourable catalyst dose within the studied range.

#### Effect of Initial Imidacloprid Concentration

The initial pollutant concentration showed a clear inverse relationship with degradation efficiency. Imidacloprid degradation decreased from  $93.15 \pm 0.86\%$  at  $5 \text{ mg L}^{-1}$  to  $79.67 \pm 1.08\%$  at  $40 \text{ mg L}^{-1}$ . At lower concentrations, a larger fraction of imidacloprid molecules can interact with available photocatalytic active sites and reactive oxygen species. With increasing pollutant concentration,

competition for surface sites becomes stronger and the number of pollutant molecules increases relative to the available oxidizing species. Higher concentrations may also reduce effective photon penetration through the reaction medium. These factors explain the observed decline in percentage degradation.

**Table 3:** Effect of initial imidacloprid concentration on degradation at 90 min

| Initial Concentration (mg L <sup>-1</sup> ) | Degradation (%) |
|---------------------------------------------|-----------------|
| 5                                           | 93.15 ± 0.86    |
| 10                                          | 91.86 ± 0.54    |
| 20                                          | 89.12 ± 2.06    |
| 30                                          | 83.68 ± 1.15    |
| 40                                          | 79.67 ± 1.08    |

#### Effect of Solution pH

The effect of pH on imidacloprid degradation was examined over a range of pH 3–11.

**Table 4:** Effect of pH on imidacloprid degradation at 90 min

| pH | Degradation (%) |
|----|-----------------|
| 3  | 82.45 ± 0.47    |
| 5  | 85.30 ± 0.52    |
| 7  | 88.51 ± 0.21    |
| 9  | 86.07 ± 0.78    |
| 11 | 83.10 ± 0.80    |

Maximum degradation was observed at pH 7, where imidacloprid removal reached 88.51 ± 0.21%. Degradation decreased under both more acidic and more alkaline conditions. The pH-dependent behaviour may be associated with changes in photocatalyst surface charge, imidacloprid speciation, adsorption behaviour and hydroxyl-radical formation. The results indicate that approximately neutral pH provided the most favourable balance of these factors under the tested conditions.

#### Effect of Light Intensity

The effect of relative light intensity was evaluated between 25 and 100% of the reference irradiation.

**Table 5:** Effect of light intensity on imidacloprid degradation at 90 min

| Relative light intensity (%) | Degradation (%) |
|------------------------------|-----------------|
| 25                           | 73.09 ± 0.81    |
| 50                           | 77.81 ± 0.74    |
| 75                           | 83.03 ± 0.89    |
| 100                          | 88.25 ± 0.29    |

A nearly monotonic increase in degradation was observed as light intensity increased. Imidacloprid degradation rose from 73.09 ± 0.81% at 25% intensity to 88.25 ± 0.29% at full reference intensity. The increase can be explained by the greater photon flux reaching the photocatalyst surface, which enhances electron-hole pair generation and consequently increases the probability of reactive oxygen species formation. No decline was observed at the highest intensity investigated, suggesting that recombination or mass-transfer limitations were not dominant within the tested range.

### Effect of Temperature

Temperature was investigated between 20 and 40 °C.

**Table 6:** Effect of temperature on imidacloprid degradation at 90 min

| Temperature (°C) | Degradation (%) |
|------------------|-----------------|
| 20               | 85.53 ± 1.12    |
| 25               | 86.75 ± 1.06    |
| 30               | 88.38 ± 0.31    |
| 35               | 86.91 ± 0.60    |
| 40               | 86.02 ± 0.76    |

The maximum degradation of 88.38 ± 0.31% occurred at 30 °C. However, the overall variation across the temperature range was comparatively small. This limited temperature dependence supports the view that photocatalytic degradation is primarily driven by photon absorption rather than conventional thermal activation. Nevertheless, moderate changes in temperature may influence adsorption-desorption behaviour, diffusion, oxygen solubility and surface reaction rates.

### Effect of Hydrogen Peroxide

The effect of H<sub>2</sub>O<sub>2</sub> concentration on photocatalytic degradation was evaluated between 0 and 20 mM.

**Table 7:** Effect of H<sub>2</sub>O<sub>2</sub> dose on imidacloprid degradation at 90 min

| H <sub>2</sub> O <sub>2</sub> concentration (mM) | Degradation (%) |
|--------------------------------------------------|-----------------|
| 0                                                | 81.30 ± 1.16    |
| 2.5                                              | 84.94 ± 0.29    |
| 5                                                | 86.78 ± 0.51    |
| 10                                               | 90.73 ± 0.25    |
| 20                                               | 89.09 ± 1.14    |

H<sub>2</sub>O<sub>2</sub> addition enhanced imidacloprid degradation up to 10 mM, where the maximum degradation of 90.73 ± 0.25% was observed. Increasing the H<sub>2</sub>O<sub>2</sub> concentration to 20 mM caused a slight reduction in removal efficiency. At moderate concentrations, H<sub>2</sub>O<sub>2</sub> can accept conduction-band electrons and promote additional hydroxyl radical generation while suppressing electron-hole recombination. At excessive concentrations, however, H<sub>2</sub>O<sub>2</sub> may itself scavenge hydroxyl radicals and generate less reactive hydroperoxyl species. The observed maximum at 10 mM therefore indicates an optimum oxidant concentration.

### Total Organic Carbon Removal and Mineralization

The disappearance of the parent imidacloprid compound was compared with total organic carbon removal to assess mineralization.

**Table 8:** TOC removal and parent imidacloprid degradation using modified TiO<sub>2</sub>

| Parameter                                      | Result       |
|------------------------------------------------|--------------|
| TOC removal at 90 min (%)                      | 67.55 ± 0.33 |
| TOC removal at 120 min (%)                     | 77.74 ± 0.14 |
| Parent imidacloprid degradation at 120 min (%) | 97.62        |
| Difference (percentage points)                 | 19.88        |

At 120 min, parent imidacloprid degradation reached 97.62%, whereas TOC removal was  $77.74 \pm 0.14\%$ . The 19.88 percentage-point difference indicates that disappearance of the parent compound occurred more rapidly than complete oxidation of organic carbon. This suggests the formation of partially oxidized intermediates that remained in solution after the parent imidacloprid concentration had substantially decreased. Therefore, parent-compound removal alone should not be considered equivalent to complete mineralization.

#### Reactive Oxygen Species and Scavenger Study

The contribution of reactive species was investigated using IPA, BQ and EDTA.

**Table 9:** Effect of scavengers on imidacloprid degradation

| Scavenger | Associated reactive species | Degradation (%)  | Decrease vs. control (percentage points) |
|-----------|-----------------------------|------------------|------------------------------------------|
| None      | Control                     | $92.64 \pm 1.19$ | 0.00                                     |
| IPA       | Hydroxyl radicals           | $62.70 \pm 1.38$ | 29.94                                    |
| BQ        | Superoxide-related species  | $72.56 \pm 1.83$ | 20.08                                    |
| EDTA      | Photogenerated holes        | $69.13 \pm 2.48$ | 23.51                                    |

All three scavengers reduced imidacloprid degradation relative to the no-scavenger control. The largest reduction occurred in the presence of IPA, where degradation decreased from  $92.64 \pm 1.19\%$  to  $62.70 \pm 1.38\%$ , corresponding to a decrease of 29.94 percentage points. The strong inhibition caused by IPA supports an important contribution from hydroxyl radicals. BQ and EDTA also reduced degradation substantially, indicating additional roles for superoxide-related species and photogenerated holes. These results suggest that imidacloprid degradation involves multiple oxidative pathways rather than a single reactive species.

#### Catalyst Reusability and Operational Stability

Modified  $\text{TiO}_2$  was evaluated over five consecutive degradation cycles.

**Table 10:** Imidacloprid degradation over five reused cycles

| Reuse Cycle | Degradation (%)  | Activity Retention Relative to Cycle 1 (%) |
|-------------|------------------|--------------------------------------------|
| 1           | $93.51 \pm 1.05$ | 100.00                                     |
| 2           | $91.41 \pm 0.78$ | 97.75                                      |
| 3           | $87.92 \pm 0.90$ | 94.02                                      |
| 4           | $87.39 \pm 0.24$ | 93.46                                      |
| 5           | $84.73 \pm 0.68$ | 90.61                                      |

Imidacloprid degradation declined from  $93.51 \pm 1.05\%$  in the first cycle to  $84.73 \pm 0.68\%$  in the fifth cycle, corresponding to approximately 90.6% activity retention after five uses. The gradual reduction in performance may result from catalyst mass loss during centrifugation and washing, adsorption of persistent intermediates, surface fouling, aggregation or changes in active surface sites. However, the dataset does not contain post-use XRD, FTIR or microscopy results, so structural deterioration should not be claimed solely from the observed decline in activity.

## Overall Discussion

Taken together, the results demonstrate effective photocatalytic removal of imidacloprid from aqueous media. Modified TiO<sub>2</sub> consistently outperformed pristine TiO<sub>2</sub> and ZnO, achieving  $97.62 \pm 0.19\%$  degradation after 120 min and the highest apparent pseudo-first-order rate constant of  $0.031 \text{ min}^{-1}$ . The operational studies identified favourable performance at approximately  $1.00 \text{ g L}^{-1}$  catalyst loading, lower initial imidacloprid concentration, pH 7, full reference light intensity,  $30^\circ\text{C}$  and  $10 \text{ mM H}_2\text{O}_2$ .

The TOC results showed that mineralization proceeded more slowly than parent-compound degradation, with  $77.74\%$  TOC removal after 120 min compared with  $97.62\%$  parent degradation. Scavenger experiments indicated contributions from hydroxyl radicals, superoxide-related species and photogenerated holes, with the strongest inhibition observed in the presence of IPA. Modified TiO<sub>2</sub> also retained substantial photocatalytic activity after five reuse cycles.

Overall, the experimental evidence identifies modified TiO<sub>2</sub> as the most effective photocatalyst among the tested systems for imidacloprid degradation. However, the supplied dataset does not contain measured catalyst-characterization or intermediate-identification results. Consequently, conclusions regarding the exact structural basis of enhanced activity, specific degradation pathways, toxicity reduction or transformation products require additional experimental measurements.

## Conclusion

The present study demonstrated the effective photocatalytic degradation of imidacloprid in aqueous media using TiO<sub>2</sub>, ZnO and modified TiO<sub>2</sub>. Among the three photocatalysts, modified TiO<sub>2</sub> exhibited the highest performance, achieving  $97.62 \pm 0.19\%$  degradation after 120 min. It also showed the highest apparent pseudo-first-order rate constant of  $0.031 \text{ min}^{-1}$  and the shortest half-life of 22.36 min, confirming faster degradation of imidacloprid under the tested conditions. Imidacloprid

Optimization studies showed that photocatalytic efficiency was affected by catalyst dosage, initial imidacloprid concentration, solution pH, light intensity, temperature and H<sub>2</sub>O<sub>2</sub> concentration. Within the investigated ranges, favourable degradation was observed at approximately  $1.00 \text{ g L}^{-1}$  catalyst loading, lower initial pollutant concentrations, pH 7, full reference light intensity,  $30^\circ\text{C}$  and  $10 \text{ mM H}_2\text{O}_2$ . Imidacloprid Imidacloprid Imidacloprid

The mineralization results showed that disappearance of the parent imidacloprid compound occurred more rapidly than complete oxidation of organic carbon. At 120 min, TOC removal reached  $77.74 \pm 0.14\%$ , compared with  $97.62\%$  parent-compound degradation, leaving a difference of 19.88 percentage points. This indicates the formation of partially oxidized intermediates during photocatalytic treatment. Imidacloprid

Reactive-species scavenger experiments indicated that hydroxyl radicals played a major role in the degradation process, while superoxide-related species and photogenerated holes also contributed. The strongest inhibition was observed with isopropanol, supporting the importance of hydroxyl-radical-mediated oxidation. Imidacloprid

The modified TiO<sub>2</sub> catalyst also showed good operational stability over five consecutive reuse cycles. Imidacloprid degradation decreased from  $93.51 \pm 1.05\%$  in the first cycle to  $84.73 \pm 0.68\%$  in the fifth cycle, corresponding to approximately 90.6% activity retention. Imidacloprid

Overall, the findings identify modified TiO<sub>2</sub> as the most effective of the tested photocatalysts for imidacloprid degradation in aqueous systems. However, the exact structural basis of its enhanced activity and the identities of intermediate degradation products cannot be established from the present dataset because complete catalyst-characterization and intermediate-identification results were not available.

Further work incorporating detailed material characterization, transformation-product analysis and toxicity assessment would strengthen the evaluation of this photocatalytic treatment system.

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