



OPEN N-doped TiO₂/prosopis juliflora biochar nanocomposites for removal of ciprofloxacin from pharmaceutical industrial wastewater

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The contamination of aquatic ecosystems by pharmaceutical residues, particularly ciprofloxacin (CIX), can pose severe environmental and public health risks. This study aimed to optimize the photodegradation of CIX from pharmaceutical industrial wastewater using N-doped TiO₂/Biochar Nanocomposites. A novel N-doped TiO₂/BC nanocomposite was synthesized via sol–gel techniques and evaluated under UV and sunlight irradiation. Kinetic degradation parameters were optimized using Response Surface Methodology (RSM) with a Central Composite Design (CCD). The optimized conditions included a contact time of 72 min, a pH of 6.9, a nanocomposite dosage of 2 g/L, and an initial CIX concentration of 50 mg/L. Maximum degradation efficiencies of 98.9% and 96.9% were achieved under UV and visible light, respectively. The statistical evaluation confirmed the model's validity and adequacy, with a high *F*-value (86,345) and significant model terms ($p < 0.0001$). Additionally, the lack-of-fit test yielded a non-significant value ($p = 0.93$), indicating an excellent fit of the model to the data. The determination coefficients (R^2 0.98, adjusted $R^2 = 0.93$, and predicted $R^2 = 0.96$) further supported the model's robustness and predictive accuracy. The optimized parameters were applied to real pharmaceutical wastewater, achieving degradation efficiencies of 86.9% and 84.3% for UV and sunlight, respectively. These findings highlight the potential of N-doped TiO₂/BC nanocomposites for efficient CIX degradation and pharmaceutical pollutant removal by modifying the limitations of pristine TiO₂. Further, it solves scaling up the process and optimizes photocatalyst selection, stability, and reusability for practical environmental applications.

Keywords Efficiency, Industrial effluent, Micropollutants, Pharmaceutical, Pollution, Water treatment

Pharmaceutical residues in aquatic environments pose a significant threat to ecological balance and public health, making it a complicated and pressing issue. One common broad-spectrum antibiotic that is important to the aquatic environment is ciprofloxacin (CIX)¹. Releasing pharmaceutical residues into water streams at various concentrations poses a significant environmental challenge². This reflects the transformative effects of modern pharmaceutical practices in aquatic environments. The rapidly increasing demand for pharmaceuticals also increases the discharge of effluent residues into water bodies from different sources^{3–5}. The effluent residues are not easily degradable, which significantly impacts water quality, ecological dynamics, and human health⁶. The persistence of pharmaceutical residues enhances their accumulation potential in the food chain, which can affect terrestrial ecosystems^{7,8}. This will present a potential threat to aquatic life and human health. Because of its broad-spectrum antimicrobial qualities, CIX is a well-known example of a pharmaceutical residue and is frequently used in health facilities, agricultural, and veterinary settings. As a result, proactive and effective strategies are essential to mitigate pharmaceutical residues and prevent negative effects on the environment and

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human health^{9,10}. CIX is highly effective against bacterial infections due to its complex chemical structure. But it doesn't fully break down during wastewater treatment. This leads to the development of antibiotic-resistant bacteria in water bodies^{10,11}. This antibiotic's resilience to conventional treatment methods allows it to enter aquatic ecosystems through treated effluents. It remains persistent in these marine ecosystems, which might potentially pose environmental and human health risks¹². Conventional wastewater treatment methods are effective for many pollutants but struggle to remove persistent pharmaceutical residues. These chemicals are hard to break down because of their complex structures and resist breakdown by microorganisms^{12,13}. Moreover, various advanced technologies such as adsorption have been employed to address emerging micropollutants, including pharmaceutical residues. However, the utilization of these technologies has drawbacks due to the generation of concentrated by-products. These by-products (pollutants bound to the adsorbent) require further treatment and special disposal techniques^{14,15}. As a result, it is essential to investigate alternative efficient technologies to address the challenges posed by such emerging organic pollutants, including pharmaceutical residues, as a first-line¹⁶.

As a result of the search for viable and sustainable solutions, photocatalytic degradation has emerged as a promising method for treating organic pollutants¹⁷. To produce reactive oxygen species (ROS) that are responsible for the degradation of organic pollutants from wastewater including pharmaceutical residues, with the action of light energy using semiconductor photocatalysts, such as titanium dioxide (TiO₂) and/or zinc oxide (ZnO), into less hazardous by-products like carbon dioxide, water, and other inorganic salts^{18,19}. Photocatalysis is effective because it can break down complex organic compounds into environmentally safe materials²⁰. Photocatalytic degradation of CIX has shown promising results in laboratory settings. However, the practical applications require a thorough understanding of the interaction between various influencing factors²¹. It is influenced by many interdependent factors, including type of photocatalyst, photocatalyst material, target pollutant in wastewater, pH, strength of irradiation intensity, and contact time²². Understanding the interactions among these factors is crucial for enhancing the overall efficiency of the photocatalytic degradation process^{18,23}. Lack of clear understanding of how the mentioned factors influence the photocatalytic degradation of CIX and its application to real wastewater was a gap to be searched. While individual factors have been studied, there is a notable lack of comprehensive investigations considering the combined impact of multiple parameters simultaneously²⁴. Therefore, a more comprehensive approach was needed to develop robust and universally applicable strategies. These helped to optimize the photocatalytic degradation process and its application in real-world scenarios. Hence, the study aimed to thoroughly investigate the need to enhance the degradation of CIX residues in pharmaceutical wastewater through photocatalysis. By employing advanced full factorial experimental design and response surface methodology (RSM), the research was intended to enhance the overall efficiency of the photocatalytic degradation process. Identification of key factors affecting efficiency and looking for optimal conditions for maximum removal was conducted in the study. The factorial experimental design offers a structured method to explore the effects of multiple factors on a given response simultaneously²⁵. This approach enables researchers to identify critical parameters and their optimal levels. Hence, the enhanced efficiency of CIX degradation in wastewater provided insights into the intricate relationships between different factors to scale up environmental sustainability^{26,27}.

The selection of a photocatalyst is of paramount importance in the photocatalytic degradation process and warrants extensive investigation within a factorial experimental design framework. With a multitude of photocatalysts with distinct properties, systematic evaluation is essential to determine the most suitable candidate for CIX degradation^{28,29}. By examining the individual and interactive effects of various photocatalyst types, concentrations, and combinations, researchers can enhance the likelihood of identifying the most effective configuration³⁰. Similarly, the concentration of CIX in the water matrix significantly influences the kinetics of photocatalytic degradation³¹. Exploring different concentration levels within a factorial experimental design framework allows the identification of optimal ranges that balance effective degradation with practical applications. Understanding the impact of CIX concentration is crucial, as different levels can lead to saturation effects or underutilization of the photocatalyst. Some scholars studied how to scale up the degradation efficiency of CIX under synthetic conditions. Even though its application in real pharmaceutical industry wastewater is left as a main gap³². Therefore, the complex behavior of CIX in aquatic environments underscores the need for optimized and scalable remediation strategies in real pharmaceutical wastewater. While photocatalytic degradation shows promise for removing CIX from wastewater, key gaps remain. The combined effects of multiple influencing factors on degradation efficiency are not well understood³³. Most studies focus on controlled laboratory conditions, with limited application to real pharmaceutical wastewater. Additionally, scaling up the process and optimizing photocatalyst selection, stability, and reusability require further investigation. Addressing these gaps through advanced experimental design will enhance the practical implementation of photocatalysis for effective pharmaceutical wastewater treatment. Our work addresses these gaps through integrated approaches that can significantly tackle emerging micropollutants, for more effective applications of N-doped TiO₂/BC nanocomposites in environmental remediation.

Methods and materials

Chemicals

The chemicals and reagents utilized for this research are all laboratory-grade and used without any modifications. For synthesizing TiO₂, Titanium Isopropoxide (TTIP) with a purity of 27.8–28.6% was used as a source and obtained from SISCO Research Laboratory PVT. Ltd in New Mumbai, India. Additionally, for nanocomposite preparation, absolute ethanol (99.98%) purity was obtained from local suppliers in Addis Ababa, Ethiopia, while HPLC grade Isopropanol was obtained from SISCO Research Laboratory PVT. Ltd in Maharashtra. We purchased 99.9% purity nitrogen gas from Chora Gas and Chemical Products Factory. Titan Biotech LTD was the supplier of the 99.8% pure laboratory-grade urea. Sigma Aldrich provided the tert-butyl alcohol ((CH₃)₃COH,

99.5%), 1, 4-benzoquinone ($C_6H_4O_2$, 99%), and Ethiopian Pharmaceutical Manufacturing S.C. provided the 99.98% pure CIX utilized in Rajasthan, India. Prosopis Juliflora (PJ) plant, a known invasive weed found in rural areas Afar Regional State of Ethiopia, is used as a source of BC in this investigation³⁴. The plant material was chopped into pieces that were between 2 and 5 cm in diameter, and it was then allowed to dry for 15 days in the sunlight. After that, the material size reduction was conducted using a hammer mill, and to get uniform calcination, it was standardized by using a 60-mesh size laboratory sieve. The detailed characterization of the BC has been previously documented in our earlier publication^{35,36}.

Synthesis of N-doped TiO_2 /BC nanocomposite

The nanocomposite N-doped TiO_2 /BC was synthesized using a sol-gel method, as detailed procedure depicted in Fig. 1. The process was undertaken by mixing a 1:1 ratio of isopropanol and absolute ethanol with a volume of 100 mL in a 250 mL borosilicate beaker was stirred on a magnetic stirrer for 30 min, and then adding 10 mL of TTIP with gentle stirring for another 30 min without supplying heat. Calculated ratios of BC to TiO_2 were added to the solution and stirred for an additional 30 min on the magnetic stirrer. Then, the solution was transferred to a hotplate and stirred at a temperature of 80 °C for 120 min until a greyish-thick gel was formed and could be visually seen. After forming on a hotplate, the thick gel was dried for a day at 105 °C in an oven. A mortar was used to crush the dried sample, and it was then calcined in a muffle furnace at 600 °C for two hrs at heating rates of 10 °C per minute while nitrogen gas flowed over it to protect oxygen, facilitating the ash formation³⁷. The core of this research lies in the material optimization, where various TiO_2 /BC nanocomposite samples were prepared by fixing the TTIP volume ratios and adjusting the BC mass ratio from 1:9 to 1:1. The obtained samples denoted TiO_2 /BC_{1:9}, TiO_2 /BC_{2:8}, TiO_2 /BC_{3:7}, TiO_2 /BC_{4:6}, and TiO_2 /BC_{5:5}. Furthermore, when N-doped was prepared, a similar method with TiO_2 /BC composite adding TiO_2 to urea with ratio of 1:5 in the first phase of stirring on magnetic stirrer before adding BC into the solution³⁸. A pure TiO_2 sample was also prepared using similar synthesis strategies and used as a control without combining BC. Finally, the synthesized photocatalyst (Nitrogen-doped titanium dioxide nanocomposite with biochar) is denoted as N-doped TiO_2 /BC_x, where x is the ratio of TiO_2 : BC. Through a series of characterizations, the optimized material was thoroughly evaluated and selected based on its performance. All the synthesizing procedures were taken under the flow of pure N 99.9% purity) to protect against the interference of oxygen. This chosen N-doped TiO_2 /BC nanocomposite was then utilized for its intended applications, demonstrating its effectiveness and suitability for the desired processes.

Characterization of N-doped TiO_2 /BC nanocomposites

The surface area of the synthesized nanocomposite (N-doped TiO_2 /BC) was analyzed using a variety of advanced techniques. The Horriba SA9603 USA instrument was employed to evaluate the nanocomposite's surface area. Scanning electron microscopy (SEM) combined with an energy-dispersive X-ray (EDX) analyzer running at 30 kV (Hitachi, Japan) was used to evaluate the chemical composition and surface morphology in detail³⁹. Fourier-transform infrared spectroscopy (FTIR) was used to analyze the possible existing functional groups in the nanocomposite material. A Perkin Elmer instrument (Annapolis, MD, USA) was used to capture spectra in

Synthesis process, characterization, and application of N-doped TiO_2 /BC Nanocomposite

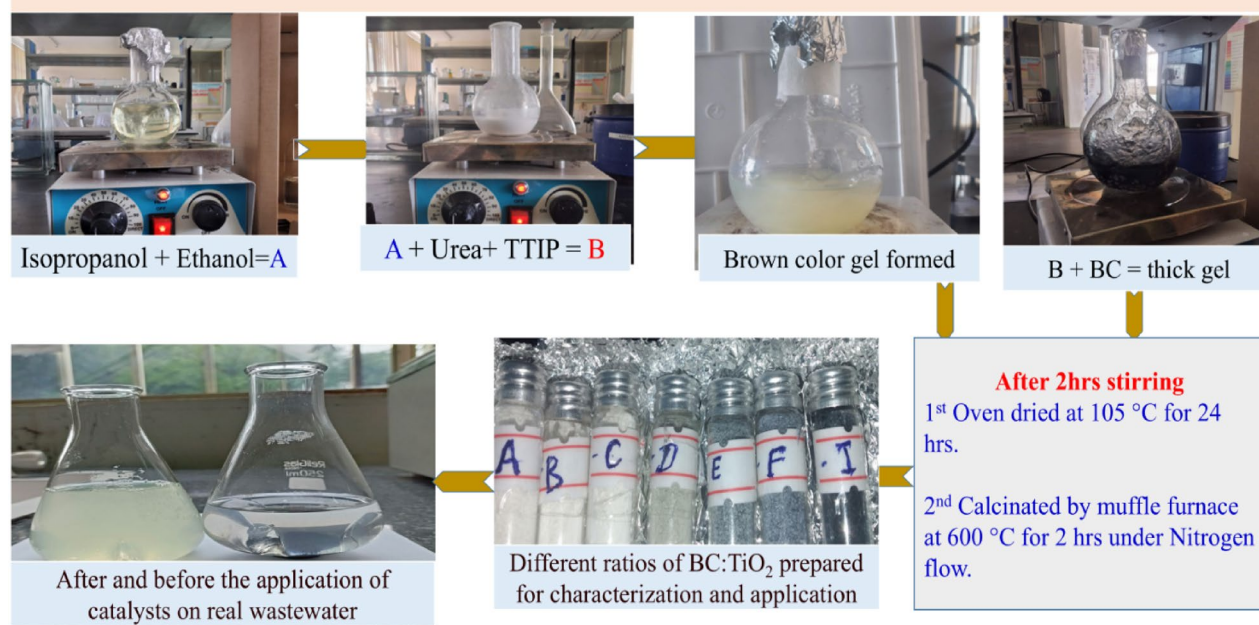


Fig. 1. The schematic diagram for synthesizing N-doped TiO_2 /BC nanocomposite photocatalyst.

transmission mode throughout a wavelength range of 4000–400 cm^{-1} . A Rigaku Smart Lab SE X-ray equipment (Japan) was used for X-ray diffraction (XRD) investigation to look into the material's changes in crystal structure. The samples were created by raising them on carbon tape and applying a small layer of gold before imaging. To identify the working pH for target pollutants, the point of zero charge (pH_{pzc}) was determined using the salt addition method, where pH changes were monitored to identify this parameter³⁶. Through these comprehensive analyses, an in-depth understanding of the structural and textural characteristics of the synthesized N-doped TiO_2/BC nanocomposites was achieved.

Photocatalytic degradation

Pure CIX in the form of powder obtained from Ethiopian Pharmaceutical Manufacturing Industry plc, and a standard solution of 50 mg/L was prepared by dissolving 50 mg of CIX in 1 L of deionized water, and then the desired solutions were prepared through dilution. The photocatalytic degradation of CIX was investigated using N-doped TiO_2/BC nanocomposites under various experimental conditions. The reactor, irradiated with 19 W UV light and shielded from visible light interaction, was stirred continuously, and samples were collected at regular intervals to determine the residual CIX concentration using UV–Vis spectrophotometry. The effect of temperature was investigated from room temperature to ~ 25 to 50°C ⁴⁰, while the pH effect between (3–11) was studied by adjusting the pH with 0.1 M HCl and 0.1 M NaOH, and degradation efficiency was investigated with a fixed catalyst dose⁴¹. The effect of CIX concentration (5–65 mg/L) was investigated using different concentrations, by maintaining a fixed catalyst dose in each case, and catalyst loading was tested by varying N-doped TiO_2/BC nanocomposite (0.5–3 g/L). Contact time (30–120 min) was investigated, adjusting other parameters to their optimum results⁴². All experiments were conducted with continuous stirring under UV light irradiation, ensuring consistent mixing and the degradation progress was monitored via UV–Vis spectrophotometry⁴³. After conducting all procedures, samples for analysis were taken at regular intervals during the degradation experiments, and the concentration of CIX was determined using UV–Vis spectrophotometry, and/or LC–MS. The percentage degradation of CIX was calculated by comparing the initial concentration with the concentration at each time interval according to Eq. 1⁴⁴.

$$\text{Degradation of CIX (\%)} = \frac{(C_o - C_t)}{C_o} * 100 \quad (1)$$

where C_o represents the initial concentration and C_t represents the final concentration of CIX.

Finally, to evaluate the effectiveness of the optimized parameters derived from the RSM model, the optimal conditions were applied to real wastewater samples to assess their practical applicability. This involved duplicating the conditions identified as optimal during the RSM analysis, such as catalyst concentration, pH, contact time, and CIX concentration, on actual wastewater containing CIX and other potential contaminants. The photocatalytic degradation efficiency under these conditions was then measured and compared to the results obtained with synthetic solutions of CIX. This comparison enabled an assessment of how real-world complexities, such as the presence of competing substances, organic matter, or varying ionic strengths, influence the performance of the optimized N-doped TiO_2/BC nanocomposite. The findings provided valuable insights into the adaptability and strength of the optimized parameters for environmental applicability.

Assumptions and modifications

During the RSM model for effective degradation, the following assumptions and modifications were made to ensure accurate statistical modeling and response prediction:

Assumptions

1. The response (degradation efficiency, Central composite design (CCD), and Total Organic Carbon (TOC) removal) follows a continuous and smooth surface, allowing polynomial regression fitting.
2. The selected independent variables (catalyst dose, reaction time, pH) do not significantly interact with unaccounted external factors.
3. No Significant Lack of Fit: The experimental data sufficiently fits the chosen polynomial model (linear, quadratic, or interaction terms).
4. Normally Distributed Errors: The residuals in the model follow a normal distribution, satisfying ANOVA assumptions.

Modifications

Factor level adjustments: Some factor ranges were adjusted based on preliminary experiments to ensure meaningful responses.

Removal of insignificant terms: Higher-order or interaction terms with negligible influence (p -value > 0.05) were eliminated for model simplification.

Transformation of response variable: If necessary, transformations (e.g., logarithmic or square root) were applied to meet normality assumptions.

Optimization constraints: The RSM optimization was conducted with practical constraints, ensuring that the suggested conditions are experimentally feasible.

These assumptions and modifications were incorporated to improve the reliability of the RSM-CCD model in predicting optimal conditions for pollutant degradation.

Optimization for photodegradation

A thorough investigation of intensive data analysis approaches was used to identify the intricate relationships driving the photocatalytic degradation process in the N-doped TiO₂/BC nanocomposites. As shown in Table 1, the data collected from degradation trials were statistically examined using a Factorial Experimental Design, which allowed for the simultaneous modification of several parameters, including pH, catalyst dosage, agitation period, and beginning CIX concentration. This method makes it possible to evaluate both individual components and their interactions. To describe the intricate interactions between components and the response variable in this example, the efficiency of CIX degradation, a CCD was used after the factorial design. The RSM-derived mathematical model is a useful optimization tool that directs the process of determining the ideal conditions for optimum decreasing efficiency⁴⁵. The model's dependability was verified by further validation tests carried out under the anticipated ideal circumstances, and the results are shown in Eq. 2¹⁴. Using N-doped TiO₂/BC nanocomposites, sensitivity analysis was also carried out to identify the most important variables in the photocatalytic degradation of CIX residues. The goal of this thorough data analysis approach is to help build an effective and optimized photocatalytic degradation strategy for the treatment of pharmaceutical wastewater by offering a solid grasp of the critical parameters influencing the degradation process.

$$Y = \beta_o + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} * \sum_{j=2}^k \beta_{ij} X_i X_j + e_i$$

where Y represents the dependent variable, which is the degradation efficiency. X_i and X_j denote the encoded independent variables. The coefficients β_o, β_i, β_{ii}, and β_{ij} stand for the linear, second-order, and interaction parameters in the regression model, respectively. K is the count of parameters involved, and e_i signifies the error term.

Reusability test

The N-doped TiO₂/BC nanocomposite was investigated for reusability in the photodegradation process of 50 mg/L CIX solution under UV irradiation 19 W/m² across five consecutive reaction cycles. After each reaction cycle, filtration was employed, and the collected nanoparticles were reused with deionized water. Subsequently, to finalize the degradation process of the contaminant, under consistent initial CIX, the rinsed photocatalyst with deionized water was subjected to oven-drying at 80 °C for 2 h, and similar procedures were applied to all steps⁴⁶.

Results and discussion
Characterisation of actual wastewater

The real wastewater was characterized to assess its impact on photocatalysis, including COD, TOC, ionic strength, and organic pollutant concentration (LC-MS). The initial COD was 2498 mg/L, which significantly reduced to 197.3 mg/L post-treatment, indicating effective organic degradation. Similarly, TOC decreased from 1050 to 155 mg/L, demonstrating substantial mineralization. The LC-MS analysis further confirmed pollutant removal, with an initial concentration of 109 mg/L reducing to 17.2 mg/L after treatment with a removal efficiency of 84.4%. These results align with previous studies highlighting the role of ionic strength in influencing photocatalytic efficiency. As reported in our earlier publication³⁶ Increased ionic strength can hinder charge transfer and radical generation, potentially slowing degradation rates. Despite these challenges, the system exhibited high degradation efficiency, suggesting that the applied photocatalytic process effectively overcame inhibitory factors.

Characterization of N-doped TiO₂/BC nanocomposite

XRD analysis

As shown in Fig. 2, the XRD analysis, refined using Rietveld refinement, confirms that the synthesized photocatalyst consists of 87% anatase and 13% rutile. The anatase crystalline structure before treatment is characterized by prominent diffraction peaks at 25.3° (101), 37.8° (004), and 48.0° (200)⁴⁷. A slight shift at 48.0° (200) is observed after photocatalytic treatment, which may indicate minor structural adjustments due to reaction dynamics. The composite retains a high degree of crystallinity throughout the treatment process, as evidenced by the stability of the diffraction peaks. A modest decrease in peak intensity following treatment suggests some surface modifications but no significant structural degradation. The presence of 13% rutile contributes to enhanced charge separation, promoting improved photocatalytic performance through anatase-rutile heterojunction interactions. Furthermore, the absence of significant peak shifts confirms that nitrogen

Levels	Factors	Levels		
		Low (− 1)	Medium (0)	High (+ 1)
1	Time (A)	30	75	120
2	pH (B)	3	7	11
3	Dose (C)	0.5	1.75	3
4	Initial Con. (D)	5	35	65

Table 1. Factors and levels used in factorial design.

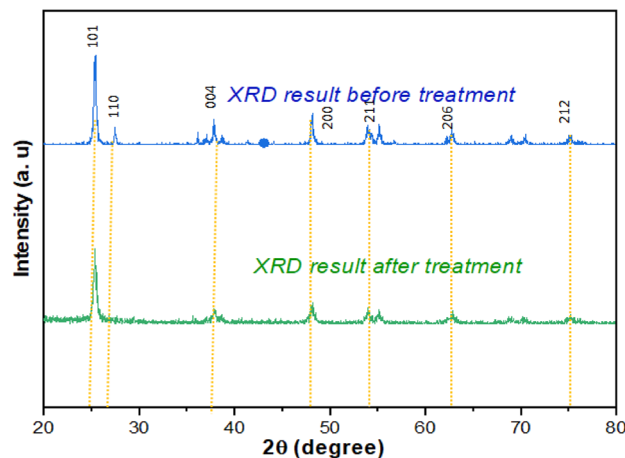


Fig. 2. XRD results of N-doped TiO₂/BC nanocomposite after and before treatment.

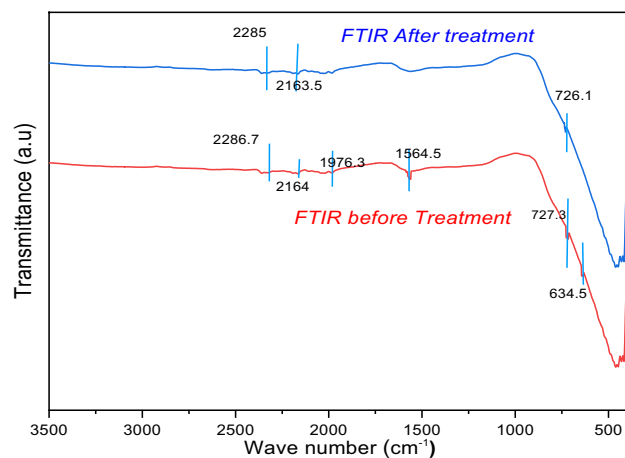


Fig. 3. FTIR results of N-TiO₂/BC nanocomposite before and after treatment.

dopants remain well-integrated within the TiO₂ lattice, experiencing minimal leaching or structural alteration under photocatalytic conditions⁴⁸. This structural durability reinforces the reusability and stability of the N-doped TiO₂/BC nanocomposite, making it a reliable material for sustained photocatalytic applications.

FTIR analysis

According to the FTIR characterization data, the N-doped TiO₂/BC nanocomposite has significant functional groups such as C–O, N–H, Ti–O–Ti, N–Ti–O, Ti–C, and C=O. The observed functional groups determine the composite's structural stability and photocatalytic activity. The N-doped TiO₂/BC nanocomposite shows a notable degree of structural retention when compared before and after photocatalytic treatment (Fig. 3). The composite stays mostly constant throughout the process, as evidenced by the key characteristic peaks showing very slight variations. Following treatment, the positions of certain peaks at 2286.24 cm^{−1}, 2164.34 cm^{−1}, 1895.84 cm^{−1}, 1248 cm^{−1}, 1091 cm^{−1}, 860 cm^{−1}, and 432.42 cm^{−1} show only minor changes, indicating that the main structural bonds in the composite matrix are stable and only slightly change during the photocatalytic cycles. Peaks at 2286.24 cm^{−1}⁴⁹ and 2164.34 cm^{−1} may be indicative of N-related functions, which are essential for modifying photocatalyst band gaps^{50,51}. These peaks' longevity indicates that there is no discernible N leaching or degradation and that the N dopants in the TiO₂ structure remain robust under the treatment conditions. This stability supports the structural integrity of the composite and is consistent with the XRD results, which showed that the TiO₂ anatase phase peaks changed little before and after treatment⁵². The existence of oxygenated functionalities involved in photocatalytic processes is shown by the peaks at 1248 cm^{−1} and 1091 cm^{−1}, which are linked to the C–O and C=O groups from the BC component. The modest peak shifts seen after treatment imply that these groups may have interacted with reactive species produced during⁵³. Despite photocatalysis, their persistence indicates that the BC is still structurally stable in the composite. The TiO₂ crystallinity retention seen in the XRD data is further supported by a 432.42 cm^{−1} peak, which corresponds to Ti–O–Ti stretching. Furthermore, the additional peaks at 3234.8 cm^{−1} and 1649.2 cm^{−1}, show the production of surface hydroxyl groups during photocatalysis, indicating increased photocatalytic efficiency without appreciable structural

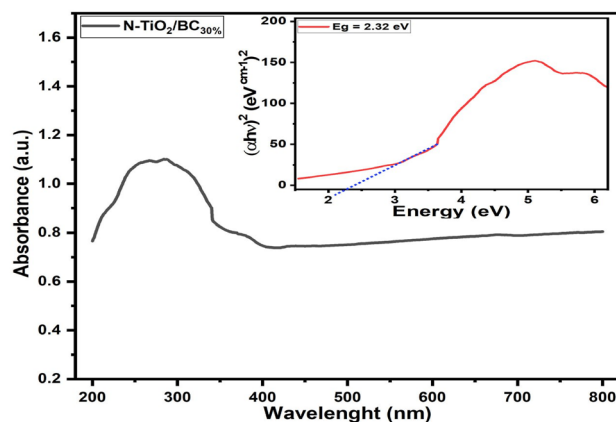


Fig. 4. Band gap modification of N-doped TiO₂/BC nanocomposite from its original material.

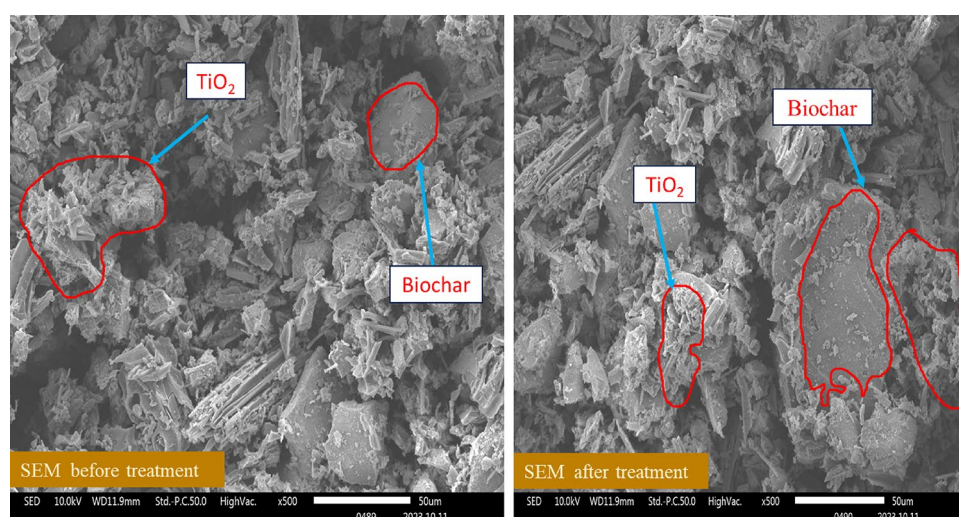


Fig. 5. SEM images of N-doped TiO₂/BC nanocomposite before and after treatment.

degradation. In conclusion, the N-doped TiO₂/BC nanocomposite's strong stability is confirmed by the FTIR and XRD data.

DRS analysis

As shown in Fig. 4, the N-doped TiO₂/BC nanocomposite's DRS analysis shows a notable band gap reduction from 3.2 eV bare TiO₂ to 2.23 eV. This reduction increases the material's photocatalytic potential in a wider range of light circumstances by moving the absorption edge into the visible light area. The main cause of the band gap shrinking is the introduction of intermediate gap states by nitrogen and carbon doping, which enables the composite to absorb photons with lower energies. Because of this structural change, the composite is more responsive to visible light, which is a desirable property for photocatalytic applications⁵⁴. Furthermore, BC contributes by serving as an electron sink, which lowers electron–hole recombination and preserves a high photocatalytic efficiency. According to XRD and FTIR data, which show structural stability and efficient N incorporation, the combined effect of N doping and BC integration enhances light absorption and increases the material's activity to visible light⁵⁵. Because of these changes, the N-doped TiO₂/BC nanocomposite is especially well-suited for environmental uses like wastewater treatment, where its increased light absorption promotes the breakdown of pollutants in both artificial and natural light.

SEM analysis

As shown in Fig. 5, the SEM images of the N-doped TiO₂/BC nanocomposite show a well-developed, porous morphology with a consistent distribution of TiO₂ nanoparticles within the BC surface. Because the BC offers high-surface-area support, TiO₂ nanoparticles may disperse efficiently, increasing light exposure and photocatalytic activity. According to the SEM micrographs, the TiO₂ particles are mostly in the nanoscale range and interact closely with the BC matrix, which is a necessary characteristic for effective charge transfer and decreased electron–hole recombination. According to the DRS results, this porous, structured surface enhances

active sites for pollutant adsorption and permits more light penetration into the composite, which is especially advantageous for photocatalytic applications under both UV and visible light. After photocatalytic cycles, the nanocomposite retains its structural integrity with no aggregation or separation of TiO_2 nanoparticles from the BC matrix, according to post-treatment SEM analysis⁵⁶. The XRD and FTIR results, which show that the N-doped TiO_2/BC nanocomposite maintains its crystalline and functional properties even after exposure to contaminants, are consistent with this stability. In addition to supporting recurrent usage in photocatalytic applications, the steady shape and distribution of TiO_2 on BC also imply that the nanocomposite is robust under actual wastewater conditions⁵⁷. The N-doped TiO_2/BC nanocomposite's potential as a dependable material for long-term pollutant degradation in environmental remediation initiatives is confirmed by its endurance as well as the improved light absorption qualities brought about by the narrowed band gap.

Effect of the operating parameters

Effect of CIX concentration

The concentration of CIX in pharmaceutical industry wastewater typically exceeds levels found in other sources. To optimize the degradation potentials of the prepared nanocomposite, the concentration of CIX was varied from 5 to 65 mg/L, and an increase from 5 to 35 mg/L showed a high degradation efficiency of ~98.6% was achieved. However, as concentrations of CIX increase to 65 mg/L, degradation efficiency decreases to 86.2% as depicted in Fig. 6. This decrease in efficiency with higher CIX concentrations can be attributed to the saturation of active sites on the catalyst within the nanocomposite. At lower concentrations of CIX, the catalyst's active sites are sufficiently available to generate necessary radicals for degradation. Conversely, at higher concentrations of CIX, these active sites become occupied by CIX molecules, hindering the formation of OH radicals essential for degradation. Coincidentally, the degradation efficiency decreases. Higher removal observed at lower CIX concentrations can be attributed to the elevated reaction kinetics. These findings align with similar observations reported by Alam et al., who also investigate the effects of differing CIX concentrations⁵⁸.

Impact of pH

Between pH 3 and 11, the impact of pH on CIX breakdown efficiency was investigated. The surface distributions, absorption capacity, disassociations, and oxidative potentials of the catalytic valence band of the nanocomposites are all impacted by changes in pH. CIX molecules have a positive charge in acidic environments, which are usually found in wastewater from the pharmaceutical industry, whereas the surfaces of nanocomposite materials have a negative charge. As a result, positively charged CIX molecules are drawn to the negatively charged surfaces of nanocomposite photocatalysts by electrostatic attraction⁵⁹. The ensuing photocatalytic degradation process is accelerated by these adsorptions, which improve contact between CIX and the photocatalyst. Electron transfer processes take place as soon as CIX sticks to the photocatalyst surface. Positively charged CIX molecules are reduced by electrons produced in the conduction band. Degradation pathways could be started if this electron transfer breaks chemical bonds inside CIX molecules. Furthermore, CIX and the photocatalyst interact to produce ROS like OH, which are extremely reactive substances that can oxidize organic pollutants like CIX and cause a decline similar to⁶⁰. Conversely, electrostatic repulsion forces reduce degradation effectiveness in alkaline circumstances ($\text{pH} > 8$), where the photocatalyst is negatively charged and the CIX molecules are neutral or negatively charged⁶¹. Overall, positively charged CIX and negatively charged N-doped TiO_2/BC nanocomposite photocatalysts interact more effectively due to electrostatic interactions, which facilitate effective CIX photocatalytic degradation in wastewater treatment.

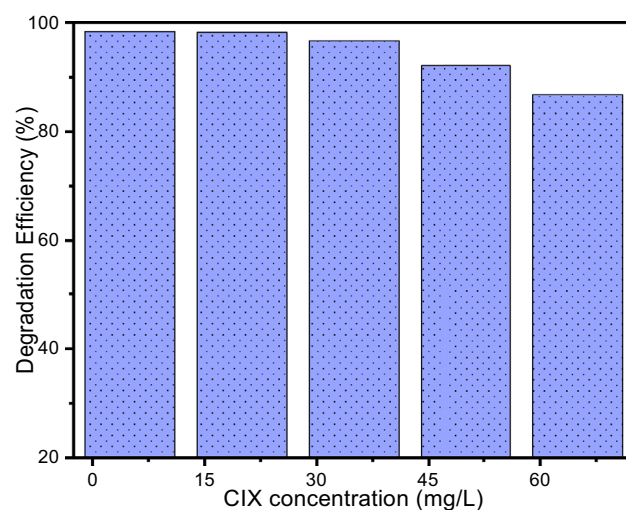


Fig. 6. Effect of initial concentration of CIX on degradation efficiency.

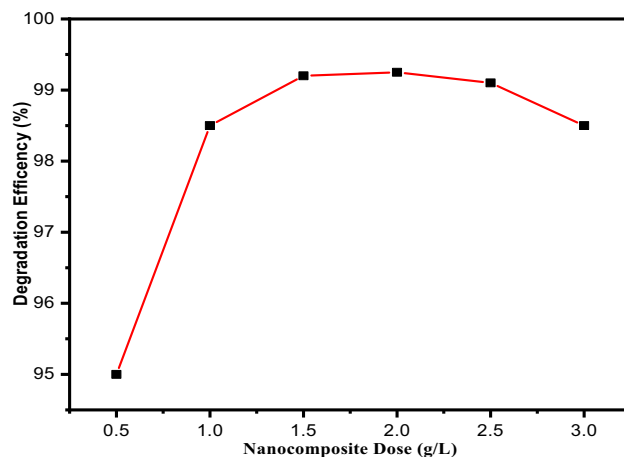


Fig. 7. Effect of nanocomposite dosage on photocatalytic degradation of CIX.

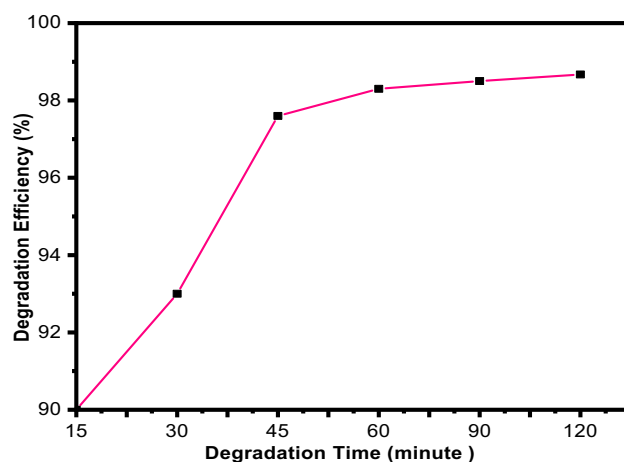


Fig. 8. Effect of agitation time on photocatalytic degradation of CIX.

Effects of catalyst loading

The synthesized N-doped TiO_2/BC nanocomposite has been used as a catalyst for CIX degradation based on its ability to absorb UV and natural sunlight compared with its bare TiO_2 . Nanocomposite shows lower degradation efficiency on a low dose of 0.5 g/L, (95.3%), and the result shows increased efficiency at a rising concentration up to 2 g/L to 99.2%. This could occur because, at a lower concentration, there were low active sites that absorb the target pollutant, but when concentration increases, there would be highly active sites that absorb more light than scattered sites that generate important radicals as depicted in Fig. 7. But when the concentration of nanocomposite increases to 3 g/L the degradation efficiency starts to decrease (98.5%), this may happen because of the sheltering of light sources that can reduce the activation of the nanocomposite. Therefore, optimizing catalyst doses in nanocomposites helps reduce the appropriate amount of used cost of utilized nanocomposites as well for photocatalytic degradation of CIX. Even though the degraded efficiency upscaled with dosage concentration, kinetic results showed a high value at 1.5 g/L.

Effect of time

Figure 8 illustrates how the CIX degradation increased noticeably over time. At 15 min, a comparatively low degradation efficiency of 75% was noted; this early phase most likely corresponds to the times when the photocatalyst surface is saturated with CIX molecules and ROS production starts. The degrading efficiency increased dramatically to 92% as the treatment time was extended to 40 min. The increased availability of ROS, including OH radicals, which actively degrade the CIX molecules, is the cause of this rise. More interaction between the CIX molecules and the reactive radicals produced on the photocatalyst surface is made possible by the longer contact duration. Degradation efficiency increased to 97.23% when the treatment period was further extended to 60 min. At this point, there is a significant increase in the reaction between CIX and the current radicals. More CIX molecules will experience photocatalytic reactions as a result of the extended exposure period, producing intermediate byproducts that will subsequently decompose into smaller, less dangerous chemicals. The removal efficiency was 98.2% at the 120 min CIX observation time. This high efficiency suggests that

photocatalytic degradation affected almost all of the CIX molecules in the solution. Even the most recapitulated molecules will have enough time to interact with the ROS and degrade thanks to the longer duration. These findings demonstrate how crucial time is to the photocatalytic degradation process. The data clearly shows a positive relationship between degrading efficiency and longer time. Over time, the combined consequences of overtime, and greater overall degradation are caused by the cumulative effects of ongoing ROS production and interaction with amoxicillin molecules. Additionally, the total efficiency is increased by the creation of intermediates during the degradation process, which may also be susceptible to further breakdown. Longer treatment periods guarantee that these intermediates are further broken down into simpler, non-toxic end products rather than building up. The study concludes by showing that the photocatalytic degradation of CIX is greatly enhanced by extending the treatment duration from 15 to 120 min. The results highlight how crucial it is to maximize treatment duration to attain maximal degradation efficiency, which enhances the efficacy of photocatalytic processes in the treatment of pharmaceutical wastewater. The identification of intermediate byproducts produced during the degradation process and an investigation of their effects on the environment should be the main goals of future research.

Model fitting and statistical analysis

Where the photocatalytic degradation of CIX occurred, the RSM was used for model fitting and statistical analysis. As shown in Table 2, the experimental setup consists of four variables and six central points, for a total of 30 runs. The adequacy of quadratic modeling was evaluated using analysis variance (ANOVA). Table 3 summarizes the findings, which showed that the input response variables had significant parameters (p -value < 0.05). Indicating the statistical significance of the model parameter, the calculated F -values (86,875.85) showed model significance with a corresponding p -value (< 0.0001). Strong model fit to the data was indicated by a high R^2 value of 0.97, which was backed by a lower probability of less than 0.05. Furthermore, the model's goodness of fit is further confirmed by the R^2 adjusting value of 0.962. The model's validity was validated by the lack of significance in the p -values for lack of fit (0.93), which exceeded the significance threshold of 0.05. Table 2 displays the findings from the four-factor CCD studies on CIX degradations. Expert software-generated

Run	Factors				Response	
	Time (A) (min)	pH (B)	Dose (C) (g/L)	Initial con. (D) (mg/L)	Degradation efficiency %	Predicted value
1	40	9	2	50	96.97	97.18
2	90	9	2	20	93.25	94.45
3	65	7	1.5	35	99.40	99.60
4	40	5	2	50	87.45	87.71
5	40	5	1	50	80.46	81.05
6	65	11	1.5	35	85.86	86.07
7	65	7	1.5	35	99.45	99.10
8	40	9	1	50	91.25	91.94
9	40	5	1	20	89.50	89.53
10	90	9	1	50	93.69	93.50
11	15	7	1.5	35	95.28	96.51
12	65	7	1.5	5	99.0	99.93
13	90	9	1	20	96.25	96.07
14	65	7	2.5	35	98.98	99.60
15	65	7	0.5	35	95.03	94.16
16	90	5	2	20	87.19	88.19
17	65	7	1.5	35	99.51	99.60
18	65	7	1.5	35	99.52	99.60
19	90	5	1	20	89.00	88.39
20	115	7	1.5	35	94.89	95.38
21	65	7	1.5	35	99.49	99.60
22	90	5	1	50	84.85	84.61
23	40	5	2	20	90.10	90.87
24	65	7	1.5	35	99.50	99.60
25	40	9	2	20	98.02	99.13
26	40	9	1	20	98.68	99.21
27	90	5	2	50	89.46	89.72
28	65	7	1.5	65	93.78	94.19
29	65	3	1.5	35	69.03	68.93
30	90	9	2	50	97.12	97.18

Table 2. Steps of the experimental design using CCD response surface methodology of four factors.

Source	Sum of squares	df	Mean square	F-value	P-value	
Model	1404.44	14	100.32	86,875.85	<0.0001	Significant
A-time	0.2426	1	0.2426	210.10	<0.0001	
B-pH	424.03	1	424.03	3.672E+05	<0.0001	
C-dose	23.57	1	23.57	20,411.22	<0.0001	
D-initial concentration	40.51	1	40.51	35,078.26	<0.0001	
AB	3.62	1	3.62	3133.39	<0.0001	
AC	5.54	1	5.54	4798.65	<0.0001	
AD	24.00	1	24.00	20,786.63	<0.0001	
BC	1.50	1	1.50	1303.28	<0.0001	
BD	2.57	1	2.57	2227.12	<0.0001	
CD	41.03	1	41.03	35,531.27	<0.0001	
A ²	33.39	1	33.39	28,918.23	<0.0001	
B ²	833.83	1	833.83	7.221E+05	<0.0001	
C ²	10.65	1	10.65	9219.70	<0.0001	
D ²	16.56	1	16.56	14,341.49	<0.0001	
Residual	0.0173	15	0.0012			
Lack of fit	0.0070	10	0.0007	0.3375	0.9323	Not significant
Pure error	0.0103	5	0.0021			
Cor total	1404.45	29				

Statistical fit summary of degradation					
Source	SD	R ²	Adjusted R ²	Predicted R ²	Press
Linear	1.39	0.874	0.8544	0.8257	67.53
2FI	1.44	0.8987	0.8454	0.7626	92.00
Quadratic	0.9867	0.9767	0.9623	0.9271	83.11

Table 3. Results of the analysis of variance for the degradation of CIX via photocatalytic reaction.

regression equations and quadratic models were used to examine this experiment. The link between the coding and actual factors for CIX degradation (%) in both coding and correct forms is shown by this equation.

$$\begin{aligned} \text{CIX degradation efficiency (\%)} = & 99.48 - 0.10A + 0.42B + 0.99C - 1.30D \\ & - 0.30AB - 0.58AC + 1.22AD - 0.30BC + 0.40BD + 1.60CD \quad (3) \\ & - 1.10A^2 - 5.51B^2 - 0.62C^2 - 0.77D^2 \end{aligned}$$

where A, B, C, and D are the coded symbols for the agitation time, pH, catalyst dose, and initial concentration of CIX, respectively.

Additionally, residual analysis, which includes the predicted versus actual plot and the normal probability plot of residuals, was used to assess the model's relevance and suitability for the degradation of CIX in the N-doped TiO₂/BC nanocomposite. To determine if the residuals had a normal distribution, the normal probability plot of residuals was utilized. As anticipated in Fig. 9, the plot's straight-line pattern shows that the residuals are normally distributed, confirming the model's presumptions and the accuracy of the findings. By contrasting the expected values with the actual experimental values, the predicted vs actual plot was also utilized to assess the prediction accuracy of the model. The model predictions and the observed data closely match, as shown by the close alignment along the diagonal line in this plot. When taken as a whole, these studies show that the model fits the experimental data well and meets the assumptions required for reliable RSM predictions.

The analysis of DFFITS against RUN in the N-doped TiO₂/BC nanocomposite showed that the majority of points were clustered inside the prescribed boundary, indicating that the majority of model runs fell within an acceptable range. However, a small number of runs were seen beyond this limit, suggesting a greater possible impact on the model. Consequently, as shown in Fig. 10, this pattern highlights the model's overall stability while pointing out certain runs that might affect its consistency and dependability. These observations are crucial for assessing the impact of specific data points on the overall performance of the model.

As indicated in Fig. 11, a great removal efficacy of 99.2% was attained in the RSM process optimization under particular conditions. The following were found to be the ideal settings for this process: agitation time: 72 min, pH level: 6.9, nanocomposite dosage: 2 g/L, and CIX concentration: 50 mg/L. These results demonstrate how well RSM works to optimize complicated processes by systematically adjusting several parameters to find the ideal circumstances for peak performance⁶². Enhancing the effectiveness of contaminant removal requires a thorough understanding of the interactions between many variables, which is made possible by the use of RSM.

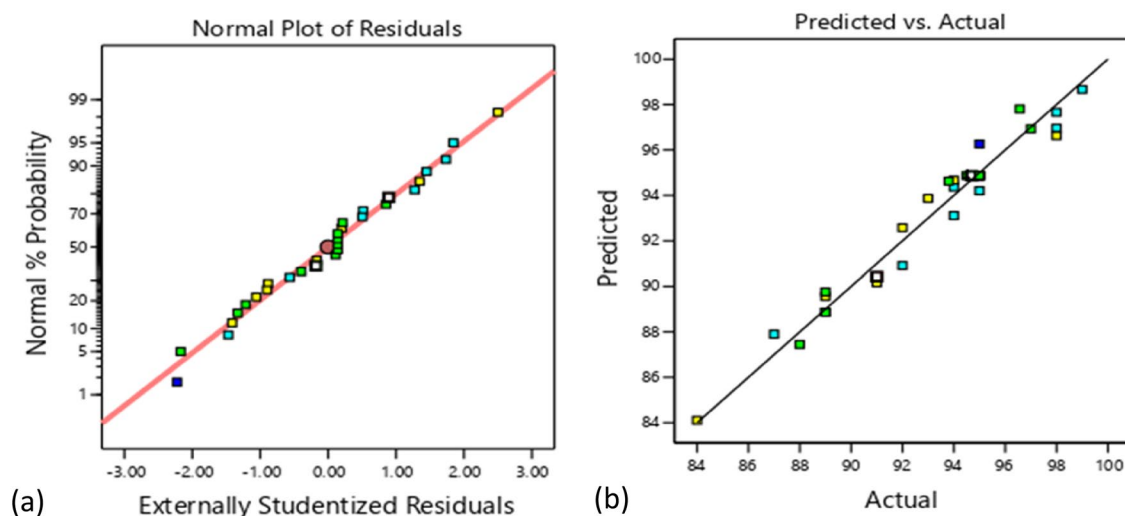


Fig. 9. Normal plot of residual (a) and actual versus predicted value (b).

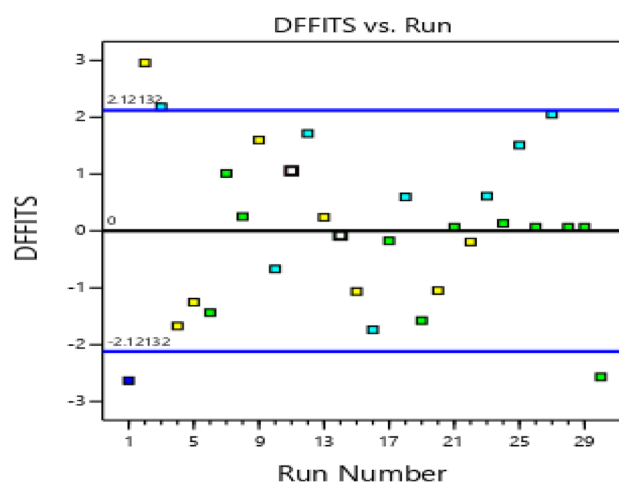


Fig. 10. Graphic representation of DFFITS versus run.

The interaction effects of parameters

Effects of contact time and pH

The degradation of CIX residues was investigated by examining the combined effects of contact time and pH using 3D and 2D response surface methodologies. Figure 12 illustrates the 3D surface and contour responses. The study focused on the interaction between solution pH and contact time on the degradation efficiency of CIX residue. Experiments were conducted under specific conditions: a catalyst dose of 1.5 g/L, and an initial CIX concentration of 35 mg/L, using a magnetic stirrer as a mixer. The results indicated that the pH of the solution significantly influences the photocatalytic degradation of CIX. Increasing the pH from 5 to 8 enhanced the degradation efficiency, with particularly notable improvements around the neutral conditions. The effect of pH on CIX degradation can be attributed to the properties of both the catalyst and the CIX at various pH levels. At a pH closer to neutral, the zwitterionic nature of CIX allows for effective interaction with the catalyst, while at a slightly alkaline pH, CIX might be more anionic, facilitating better adsorption on the positively charged catalyst⁶³. The degradation efficiency peaked at a contact time of 40–90 min and a pH of 5–7, the degradation efficiency fell between 69 and 99.5%, and it showed a slight decrease in removal efficiency with the increments of pH to alkaline. Achieving a high degradation efficiency at a contact time of 90 min and pH of ~7 indicates that the system works at around neutral pH, and the positive interaction between contact time and pH was evident, validating the findings predicted by the quadratic regression model.

Effect of dose and pH

Crucial elements in photocatalytic systems are highlighted by the chemistry between adsorbent dosage and solution pH on the degradation efficiency of CIX. Figure 13a and b show the contour map and 3D response surface. According to research, the circumstances for optimal contaminant degradation can be optimized by

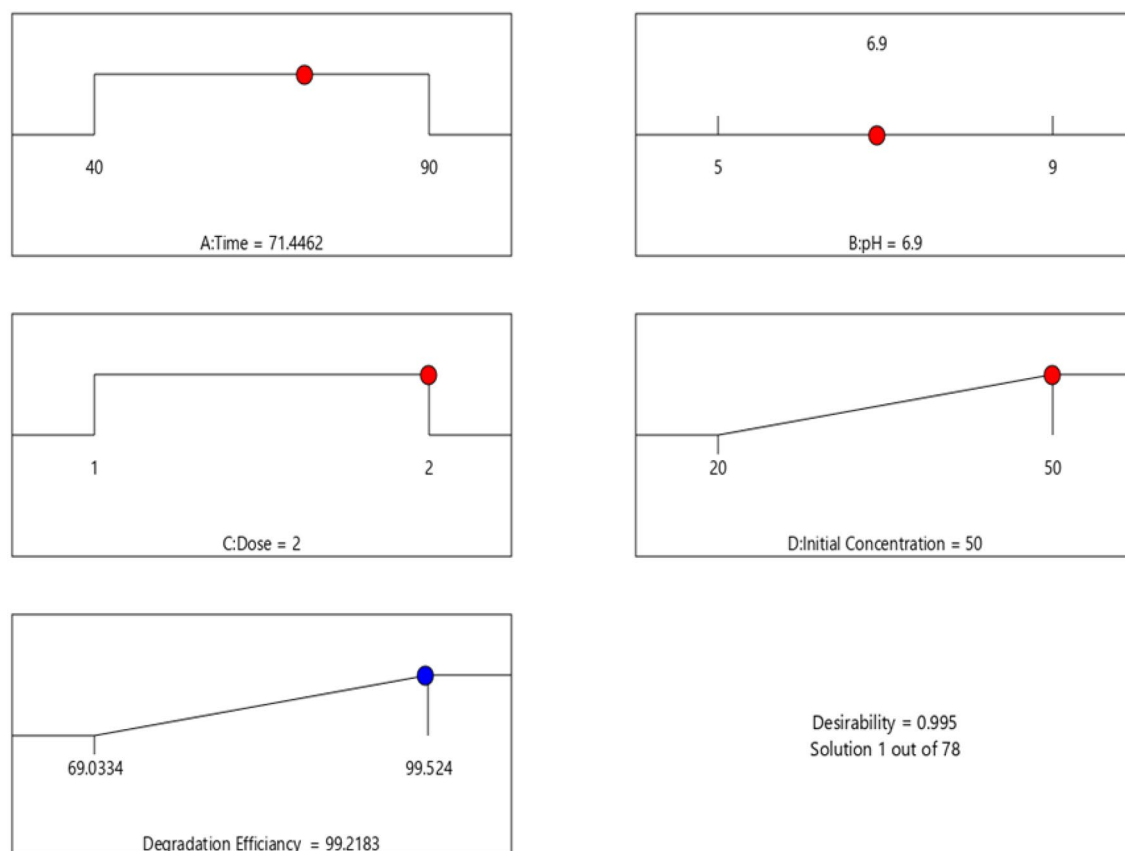


Fig. 11. Process optimization of the degradation process under various parametric conditions against CIX.

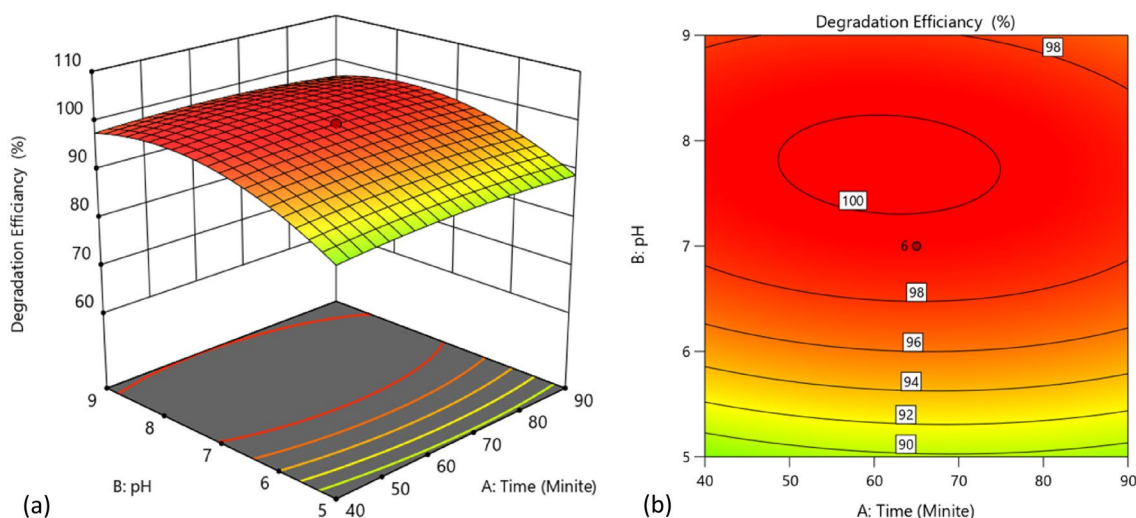


Fig. 12. The 3D response surface (a), and contour map showing the interaction of contact time and pH (b).

varying the catalyst dosage and solution pH, which can greatly increase degradation efficiency. In particular, 99.5% degradation efficiency can be achieved with a catalyst dose of 0.5–2 g/L at about neutral pH. However, light scattering and shielding effects restrict the activation of the photocatalyst, and additional increases in catalyst concentration (> 2 g/L) lower removal effectiveness. These results are consistent with recent discoveries in photocatalytic wastewater/water treatment. For instance, research highlights how crucial it is to enhance light absorption and reactive oxygen species formation by optimizing operational parameters like pH and catalyst dosage⁶⁴. Due to better light harvesting and decreased electron–hole pair recombination, novel visible-light-responsive photocatalysts namely doped TiO_2 and Bi_2WO_6 , have shown improved performance⁶⁵. These

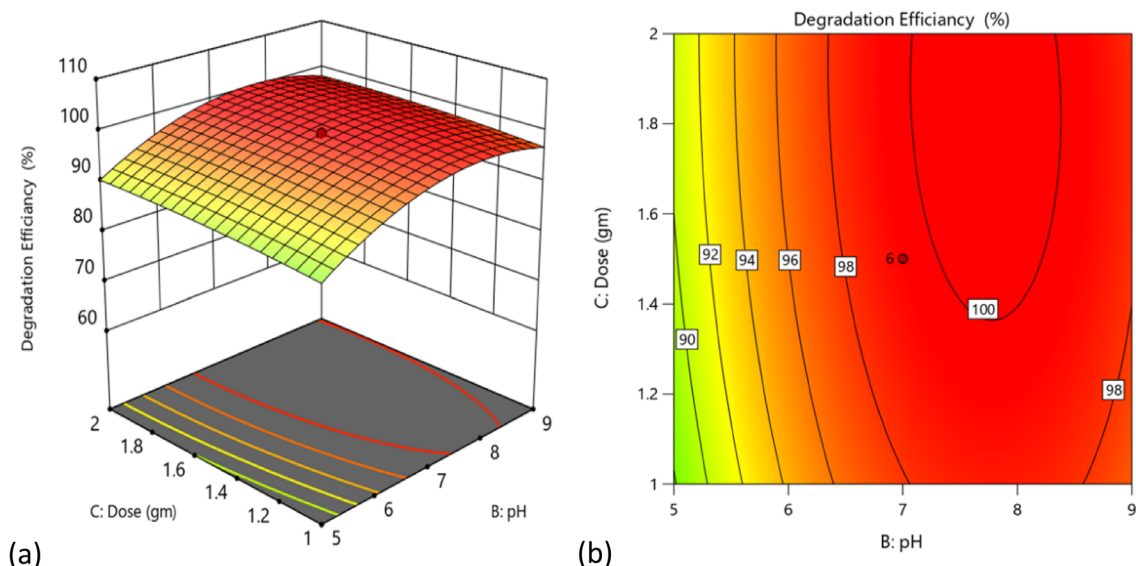


Fig. 13. 3D response surface (a) and contour map showing the interaction of catalyst dose and pH (b).

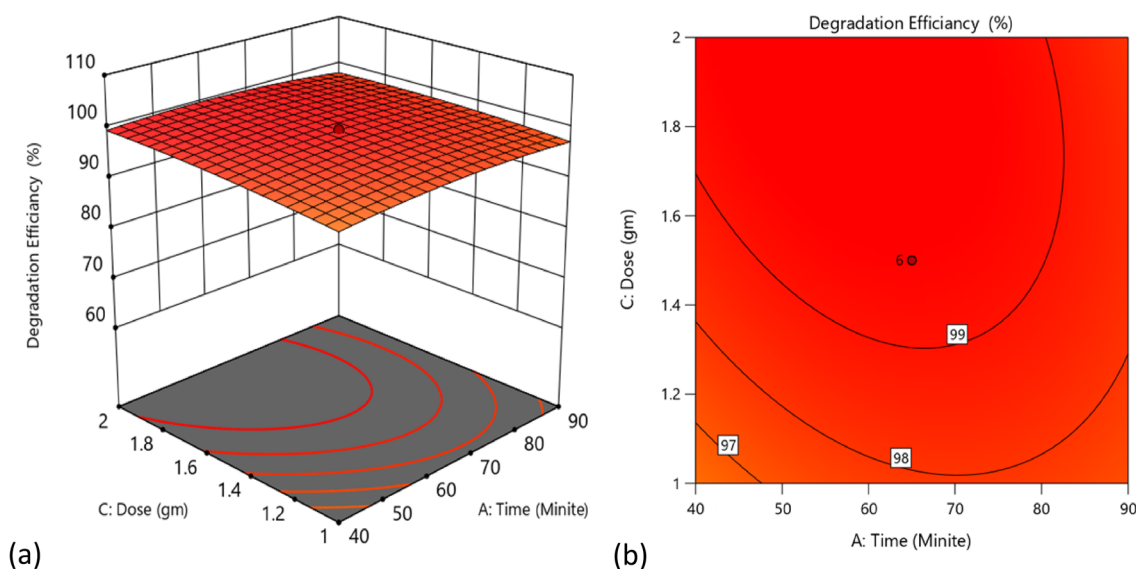


Fig. 14. The 3D response surface (a), and 2D contour map showing the interaction of contact time and catalyst dose (b).

developments strengthen the data showing that balancing surface reactions and avoiding catalyst agglomeration or inefficiencies due to excessive loading requires maintaining proper catalyst concentrations. Moreover, it is commonly known that pH affects photocatalytic efficacy. For example, pH affects the adsorption and degradation processes by influencing the speciation of contaminants and the charge distribution on the catalyst surface⁶⁶.

Effect of time and dose

Under the constant conditions of an initial concentration of 50 mg/L and a solution pH of 7, the interactive effects of contact duration and catalyst dose on the degrading efficiency of CIX were investigated. The results are shown in Fig. 14a and b. The results showed a distinct pattern: increasing the catalyst dose from 0.5 to 2 g/L and extending the contact time from 40 to 90 min improved the degradation efficiency from 69 to 99.5%. However, degradation begins to decrease when the dose is increased above 2 g/L, which may be due to the photocatalyst's density shielding the light. More active sites on the catalyst surface allow for better adsorption and subsequent degradation of CIX molecules. This explains the observed increase in degradation efficiency with a higher catalytic dose. This is in line with research by Chen et al., who found that greater catalyst doses led to higher removal efficiencies of different pollutants because they resulted in more surface area and reaction-ready active sites⁶⁷. Furthermore, the catalyst has a high chance of interacting with the CIX molecules due to

the extended contact period, which improves degradation. This result is consistent with the findings of Kumar et al., who found that extended contact durations increase the overall degradation by improving the interaction between the adsorbent and the target pollutant⁵⁹. Increasing the catalyst dose and contact duration both have a synergistic impact, indicating that these parameters must be optimized to maximize the degrading efficiency of CIX in wastewater treatment systems. Notably, the degrading efficiency significantly improved within the designated ranges, emphasizing how crucial it is to carefully balance these factors to get the best outcomes. The quadratic regression models employed in RSM, which predict that longer contact times and higher catalyst doses have a favorable impact on degrading efficiency, are consistent with the interaction effects seen in this investigation. Additionally, the outcomes support the conclusions of related research, like that conducted by Gupta and Suhas, who highlighted the crucial role that catalyst dosage and contact time play in the adsorption and degradation processes of different organic pollutants⁶⁸.

Effect of time and initial concentration

With constant parameters of a catalyst dose of 2 g/L and a solution pH of 7, this study investigated the combined effects of contact time and starting concentration on the degrading efficiency of CIX. The outcome is shown in Fig. 15a and b. The findings showed that as contact duration increased and starting concentration decreased, degradation efficiency dramatically improved. In particular, when the starting concentration dropped from 50 to 20 mg/L and the contact time increased from 40 to 90 min, the degradation efficiency rose from 84 to 99.9%. According to research by Chen et al., the catalyst's active sites become saturated at greater concentrations, which explains the negative relationship between starting concentration and degradation efficiency⁶⁹. The interaction between initial concentration and contact duration emphasizes how crucial it is to optimize both variables to maximize degradation efficiency. According to Nie et al., more efficient degradation results from lower starting concentrations because the catalyst's active sites are not overloaded. Longer contact times also guarantee that the adsorbent has enough time to engage with the pollutant, which boosts the effectiveness of degradation⁷⁰. These results are in line with the predictions of the RSM quadratic regression models, which imply that degradation efficiency is positively impacted by longer contact durations and lower initial concentrations. Additionally, the findings are consistent with other research, including that of Yahya et al., who highlighted the importance of starting concentration and contact duration in the adsorption and degradation of organic pollutants⁷¹. In conclusion, our work shows that enhancing the degrading efficiency of CIX requires careful consideration of contact time and initial concentration.

Effect of initial concentration and pH

With constant parameters of a catalyst dose of 1.5 g/L and a contact time of ~72 min, this investigation examined the interaction effects of solution pH and starting concentration on the degrading efficiency of CIX. The results are shown in Fig. 16a and b, the findings showed that lower starting concentrations and a drop in pH greatly increased breakdown efficiency. In particular, when the pH dropped from 11 to 3, the degradation efficiency rose, reaching a remarkable 99.98% efficiency at pH ~6.9. The catalyst surface's increased protonation, which improves its contact with the CIX molecules, is responsible for this improved performance at pH values close to neutral. Zhang et al. reported similar results, observing that the enhanced adsorption capacity of the catalyst

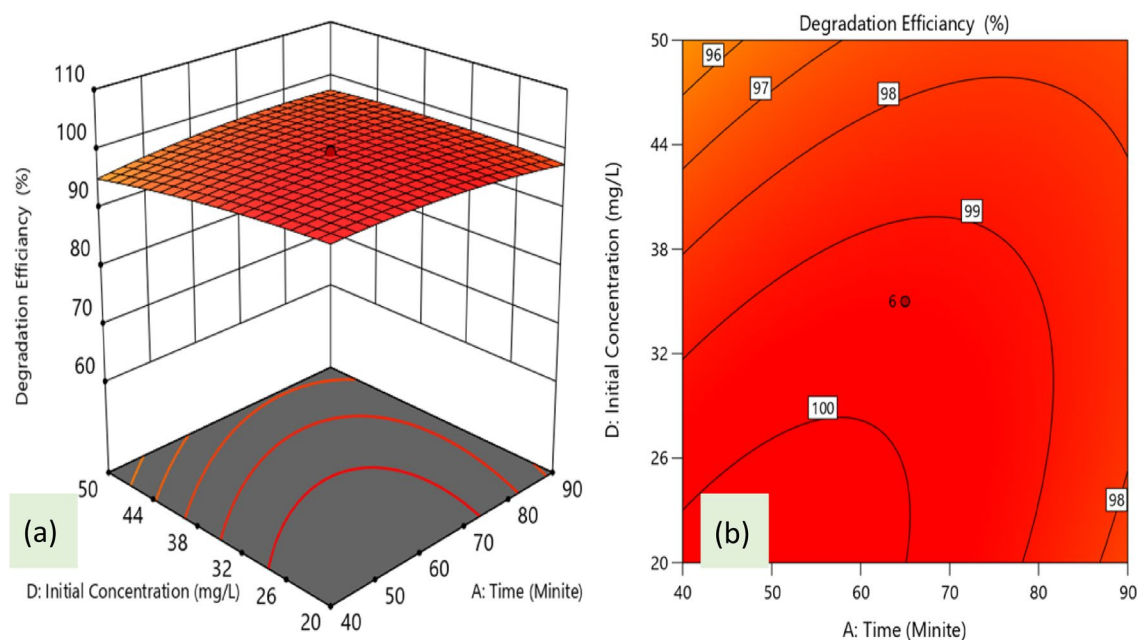


Fig. 15. The 3D response surface (a), and 2D contour map showing the interaction of contact time and initial concentration (b).

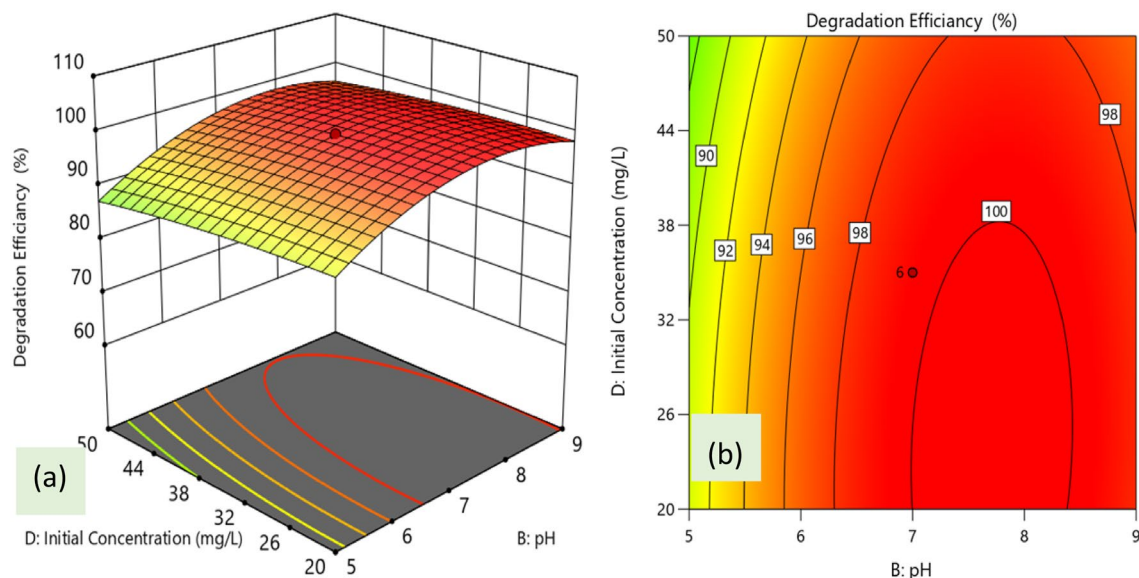


Fig. 16. The 3D response surface (a), and 2D contour map showing the interaction of initial concentration and pH (b).

promoted the breakdown of organic contaminants in acidic conditions⁴⁶. The study also demonstrated that better degradation efficiencies were attained at lower starting concentrations. For instance, compared to greater concentrations, a starting concentration of 20 mg/L produced a noticeably higher degradation efficiency. This is in line with the findings of Liu et al., who discovered that improved degrading performance results from more effective use of the catalyst's active sites at lower pollutant concentrations⁷². According to the interaction effects between pH and starting concentration, maximizing degradation efficiency requires careful consideration of these parameters. According to Chen et al.⁶⁹, the greater catalytic activity and increased availability of reactive species under neutral conditions can account for the increased efficiency at neutral pH levels. Furthermore, the increased degradation efficiency shown at lower neutral concentrations suggests that lowering the pollutant load makes better use of the catalyst's capacity. The quadratic regression models employed in RSM, which predict that neutral pH and lower beginning concentrations favorably increase degradation efficiency, support these findings. The findings are consistent with earlier research, including that conducted by Sharma et al.⁷³, who highlighted the significance of pH and starting concentration in maximizing the degradation process for a range of organic pollutants. In conclusion, this study shows how important pH and initial concentration are to maximizing CIX degradation efficiency. The need for careful regulation of these parameters in wastewater treatment procedures is highlighted by the notable improvements shown with neutral pH and lower initial concentrations.

Effect of initial concentration and dose

Both the initial concentration of the target pollutant and the catalyst dosage have a substantial impact on the adsorbent's degrading efficiency; the outcome is shown in Fig. 17a and b. As mentioned above, this investigation showed that the degradation efficiency improves up to the limiting dose as the catalyst dose increases. This effect is explained by the increased availability of active sites on the adsorbent surface, which increases the catalyst dose while improving the capacity for pollutant uptake. Similar findings have been documented in the literature. For example, Tran et al. discovered that raising the activated carbon dose from 0.1 to 1.0 g/L significantly increased the removal efficiency. This is because of the larger surface area and quantity of adsorption-ready active sites⁷⁴. Likewise, the degradation efficiency falls when the pollutant's starting concentration rises from 20 to 50 mg/L. The adsorbent's active sites being saturated at greater pollutant concentrations explains this pattern. Higher degradation efficiency results from the availability of enough active sites to hold the pollutant molecules at lower initial concentrations. Degradation efficiency decreases as the concentration rises because the ratio of pollutant molecules to accessible active sites becomes unbalanced. The literature has extensively shown the inverse link between initial concentration and removal efficiency. For example, Ghaedi et al. discovered that the removal effectiveness of heavy metals such as lead and cadmium decreased with rising starting concentrations, as a result of the adsorbent's adsorption sites becoming saturated⁷⁵. Furthermore, greater initial concentrations may cause pollutant molecules to compete more aggressively for the few available active sites, which would further lower the overall degradation efficiency. Adsorption kinetics can also be influenced by the initial concentration since mass transfer constraints may cause slower adsorption rates at higher concentrations. The results of Tsai and Tseng, who found that the adsorption rate of dyes onto chitosan dropped as initial dye concentrations increased, offer support for this. They attributed this to a decrease in mass transfer rate and an increase in competition for adsorption sites⁷⁶. In conclusion, our results are consistent with previous research showing that larger initial concentrations of the pollutant have a detrimental effect on the adsorption process of photocatalysts. This is because of site saturation and competitive adsorption, even while increasing the photocatalyst dose improves

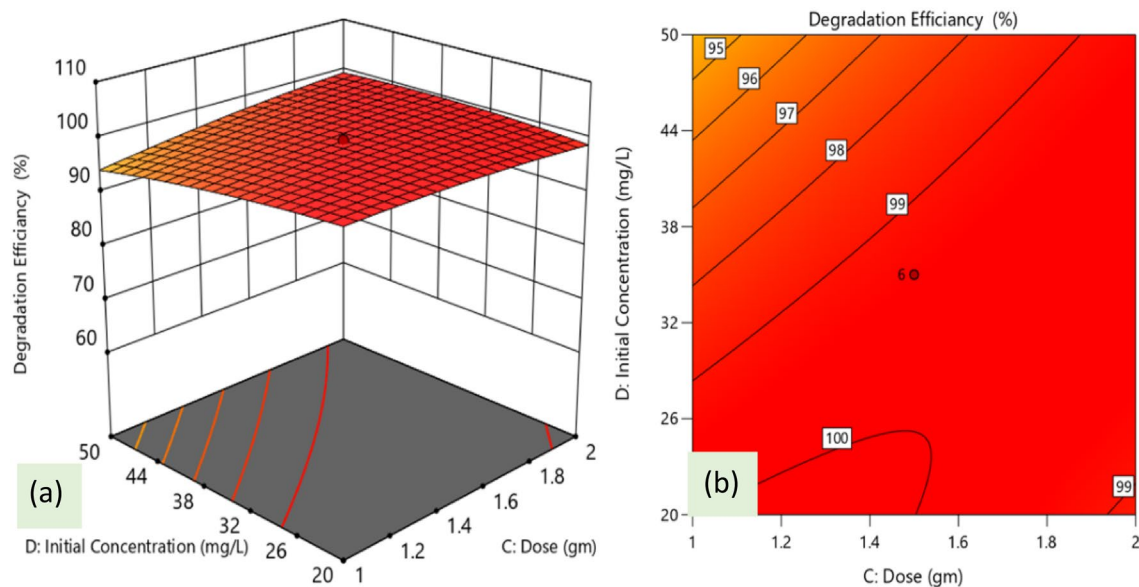


Fig. 17. The 3D response surface (a) and 2D contour map shows the interaction of initial concentration and catalyst dose (b).

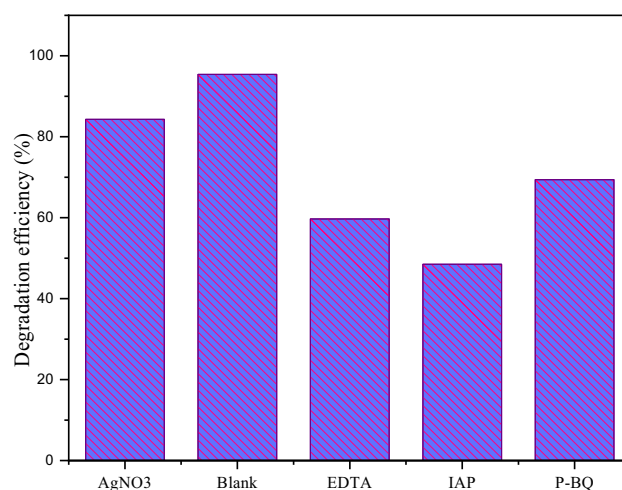


Fig. 18. The influence of different scavengers on the degradation of CIX by N-doped TiO₂/BC nanocomposite.

removal efficiency. Achieving optimal degradation efficiency in real-world applications requires optimizing both the adsorbent dose and the initial pollutant concentration.

Scavenger tests

To investigate the degradation mechanisms of CIX residues, a series of laboratory experiments were conducted using specific chemical scavengers targeting reactive species in synthetic CIX solutions, and the result is presented in Fig. 18. Hydroxyl radicals ($\cdot\text{OH}$) were targeted using isopropanol (IPA), a common $\cdot\text{OH}$ scavenger. Silver nitrate (AgNO_3) was used to quench electrons (e^-), and ethylenediaminetetraacetic acid (EDTA) was applied to scavenge photogenerated holes (h^+). The results indicated that $\cdot\text{OH}$ was a significant contributor to CIX degradation, achieving a degradation efficiency of 61.7%. The second, the most influential species, was found to be h^+ , with a degradation efficiency of 40.3%, suggesting that charge carriers play a critical role in the breakdown of CIX molecules, which agrees with⁷⁷. These findings reveal that while h^+ contributes to degradation, the involvement of $\cdot\text{OH}$ radicals is more substantial in the overall photocatalytic process. Further supporting this, under light irradiation, e^- and h^+ are generated in the conduction and valence bands of the N-doped TiO₂/BC nanocomposite. Electrons reduce oxygen molecules to form $\text{O}_2^{\cdot-}$, which subsequently reacts with H^+ to form $\cdot\text{OH}$. Simultaneously, holes oxidize hydroxide ions or water to generate additional $\cdot\text{OH}$. Notable degradation by-products of CIX included cyclopropylamine, pyridine derivatives, and carboxylic acids. The

porous structure of biochar adsorption facilitates close contact between CIX molecules and reactive sites, thus improving degradation efficiency into less harmful products (CO_2 and H_2O).

Kinetics study

Understanding the degradation processes of CIX utilizing an N-doped TiO_2/BC nanocomposite requires kinetics research of photocatalysts. Because it effectively takes reactant adsorption onto the catalyst surface and ensuing reaction dynamics into account. The Langmuir–Hinshelwood (L–H) model is a popular paradigm for researching these kinetics. When evaluating the N-doped TiO_2/BC nanocomposite's performance, critical parameters such as the correlation coefficient R^2 and the apparent rate constant k_{app} offer crucial insights into the reaction kinetics. A strong match to the pseudo-first-order reaction model is shown by the measured k_{app} of 0.0233, indicating a relatively controlled reaction, typical for pseudo-first-order kinetics which is Your k_{app} value of 0.0233 s^{-1} is very close to $2.45 \times 10^{-2} \text{ s}^{-1}$ reported in the literature. This similarity suggests that your reaction's kinetics are consistent with those observed in similar pseudo-first-order reactions at 25°C ⁷⁸. R^2 value of 0.983, which shows a close alignment with the L–H model's views as enumerated in Eq. 4. The pseudo-first-order model was selected due to the strong linear correlation observed in our data. However, we acknowledge that the L–H model is commonly used for surface-mediated reactions. To ensure robustness, we tested the L–H model, but our data did not show significant deviation from pseudo-first-order kinetics, suggesting that surface adsorption was not the rate-limiting step. This aligns with previous studies' reports with similar trends for comparable systems⁷⁹. The high R^2 value supports this kinetic model's validity in depicting the degradation process, which is consistent with results from related investigations that showed TiO_2 -based composites had R^2 values above 0.981 when organic pollutants were photo-catalytically degraded. The N-doped TiO_2/BC nanocomposite exhibits moderate to high activity under experimental conditions, according to the K_{app} value, which represents the photocatalyst's efficiency. According to research, doping TiO_2 usually improves light absorption and charge separation, which increases photocatalytic activity⁸⁰. In particular, N-doping lowers the bandgap, making it possible to activate using visible light. By expanding the surface area that is available and improving the adsorption capacity, BC further improves photocatalytic performance. These synergistic effects are consistent with observations in the literature showing that composites may efficiently break down different medications and contaminants however, as recent reviews of photocatalytic mechanisms have discussed, it is crucial to recognize the limitations of the L–H model, such as its presumptions about constant active site availability and the need to take into account variables like mass transfer and light intensity, especially in more complex systems⁸¹.

$$\ln(C_0/C_t) = K_{\text{app}}t \quad (4)$$

In the given context, C_0 and C_t represent the initial and final concentrations of the reactant at a specific reaction time t . The apparent first-order rate constant k_{app} is determined as the slope of the linear plot of $\ln(C_0/C_t)$ versus reaction time. For the degradation of CIX, as illustrated in Fig. 19, a rate constant of 0.0233 min^{-1} was obtained.

Application for real wastewater

In this study, the application of the N-doped TiO_2/BC nanocomposite catalyst for real wastewater treatment was evaluated under both UV and natural sunlight irradiation. Comparison of N-doped TiO_2/BC nanocomposite with other photocatalysts as indicated in Table 4. They show the variations in pharmaceutical wastewater quality regarding color, comparing samples before and after treatment. The RSM model was used to determine the experimental conditions for the wastewater treatment, which comprised a catalyst dosage of 2 g/L, a pH of 6.9, an initial CIX of 50 mg/L, and a contact time of 72 min. The findings demonstrated that the nanocomposite's photocatalytic efficacy was almost the same in both UV and ambient sunlight, with removal efficiencies of 86.87 and 87.29%, respectively. This evidence that the N-doped TiO_2/BC nanocomposite catalyst works very well in natural sunshine, achieving one of the main goals of this study, which was to change the catalyst's band gap to

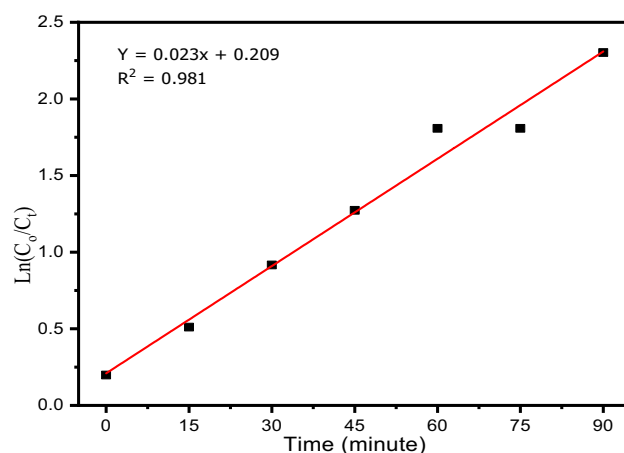


Fig. 19. Pseudo-first-order kinetic model for CIX degradation using N-doped TiO_2/BC nanocomposite.

Catalyst used	Types of pollutants	Light source	Initial conc. (mg/L)	pH	Catalyst dosage (g/L)	Time (min)	Degradation efficiency (%)	References
TiO ₂	CIX	UV	5.02	5.04	0.45	75.8	88.3	89
CdS/g-C ₃ N ₄ /rGO/CMC	CIX	UV	8	6.1	0.6	35	81.93	22
CuO/UV-C	CIX	UV	11.2	8.17	0.08		93.18	90
MMT/CuFe ₂ O ₄	CIX	UV	32.5	3	0.78	47.5	83.7	91
Bi ₂ WO ₆ /GNPs	CIX	Visible	20	3	0.1	140	60	65
BiFeO ₃	CIX	UV	1	6	2.5	46	100	64
N-doped TiO ₂ /BC	CIX	UV	50	6.9	2	71	98.89	This study
N-doped TiO ₂ /BC	CIX	Visible	50	6.9	2	71	97.6	This study

Table 4. Comparison of N-doped TiO₂/BC nanocomposite with other photocatalysts.

allow for effective photocatalytic activity in natural sunlight. These findings are consistent with earlier research showing the efficiency of N-doped TiO₂-based catalysts for sunlight-driven photocatalysis⁸². Because of the narrowing of the band gap and the formation of new energy states that made it easier to absorb visible light, Zhang et al. found that N-doped TiO₂ demonstrated better photocatalytic activity under visible light than bare TiO₂⁸³. Similarly, Liu et al. found that N-doped TiO₂ composites improved photocatalytic efficiency in natural sunlight when combined with carbon materials like graphene or charcoal, achieving removal efficiencies of more than 80% for pollutants, including dyes and heavy metals⁸⁴. The near-identical photocatalytic performance under UV and natural sunlight observed in this study highlights the success of doping TiO₂ with nitrogen and incorporating BC as a composite material⁸⁵. The BC likely helps to extend the absorption spectrum of the catalyst, enhancing its ability to utilize visible light. Moreover, the N-doping effectively reduces the band gap of TiO₂, facilitating electron excitation under visible light, which is critical for practical applications that rely on natural sunlight. On the other hand, because of their large band gap (usually > 3.0 eV), many photocatalysts, including unaltered TiO₂, are mainly active under UV light⁸⁶. Given that UV radiation makes up a very small portion of sunlight, this restriction has proven to be a major obstacle for large-scale, sustainable photocatalytic operations. The development of photocatalysts for practical environmental applications has advanced significantly with the N-doped TiO₂/BC nanocomposite's ability to perform nearly equally under UV and sunlight irradiation. This is in line with the objectives of several recent studies, including Chen et al.'s, which stressed the significance of creating photocatalysts with increased visible light activity to overcome the financial and energy limitations of employing UV light in extensive water treatment systems⁶⁹. In conclusion, the study's findings demonstrate that the N-doped TiO₂/BC nanocomposite is a promising material for sustainable, solar-driven photocatalysis in addition to being an efficient photocatalyst for wastewater treatment. This work closes a significant gap in the development of economical and ecologically friendly water treatment systems by adding to the ongoing effort to alter the electrical characteristics of photocatalytic materials to better capture natural sunlight.

Comparison with recent literature

The proposed N-doped TiO₂/biochar composite was synthesized using a sol-gel method, known for its simplicity and ability to achieve high uniformity. In contrast, graphene-TiO₂ composites are often synthesized via hydrothermal or impregnation methods, which can present challenges in achieving uniform dispersion of dopants. Our sol-gel approach ensures better dispersion, potentially enhancing photocatalytic activity⁸². In terms of degradation efficiency, our composite achieved a COD reduction from 2498 to 197.3 mg/L and a TOC reduction from 1050 to 155 mg/L. These results are comparable to or exceed those reported for graphene-based TiO₂ catalysts. For instance, an activated carbon/graphene oxide/TiO₂ composite achieved a degradation efficiency of 78% after 80 min, while our composite demonstrated a higher reduction under similar conditions⁸⁷. Regarding reusability, our catalyst retained over 85% efficiency after five cycles, indicating good stability. This performance surpasses some graphene-TiO₂ systems, which have shown significant deactivation due to surface fouling. Additionally, doped TiO₂ photocatalysts, such as nitrogen and boron co-doped TiO₂ nanoparticles, have demonstrated high reusability and durability. These comparisons highlight the effectiveness of our composite in wastewater treatment applications⁸⁸. In summary, the N-doped TiO₂/biochar composite synthesized via the sol-gel method exhibits superior degradation efficiency and reusability compared to some graphene-based and doped TiO₂ systems. These findings suggest that our composite is a promising candidate for wastewater treatment applications, and more comparisons are presented in Table 4.

To sum up the finding, the proposed N-doped TiO₂/BC nanocomposite holds promising applications in pharmaceutical industry wastewater treatment, particularly for mitigating the inhibitory effects of common interfering anions such as sodium dodecyl sulfate (SDS), Cl⁻, SO₄²⁻, and NO₃⁻. The nanocomposite's enhanced photocatalytic performance stems from the synergistic effects of N-doping, which improves visible-light absorption, and BC's high adsorption capacity, which reduces competitive anion interference. This method is particularly suitable for industrial-scale applications, including pretreatment systems to minimize anion load before biological treatment, integration into hybrid AOPs for improved degradation efficiency, and decentralized wastewater treatment in pharmaceutical manufacturing units due to its reusability and stability⁹². Our findings underscore the importance of developing anion-resistant photocatalytic systems and suggest the potential for further optimization through pre-adsorption stages or tailored catalyst design. Future studies will focus on pilot-scale validation and economic feasibility to facilitate real-world implementation.

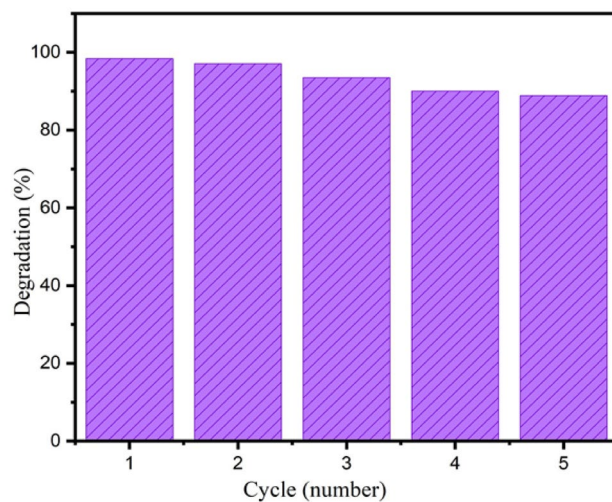


Fig. 20. Reusability of N-doped TiO₂/BC nanocomposite for degradation of CIX.

Reusability test

Using the ideal process parameters derived from the RSM model, the reusability of the N-doped TiO₂/BC nanocomposite catalyst was assessed for five cycles. A pH of 6.9, a contact time of 72 min, an initial CIX concentration of 50 mg/L, and a catalyst dosage of 2 g/L were the factors that produced the following outcomes. The catalyst's high degrading efficacy of 98.4% in the first cycle gradually decreased to 88.9% in the fifth cycle, indicating a little decrease in activity with repeated use (Fig. 20). Among the reasons for this decrease in performance are active site leaching, catalyst deactivation, or the accumulation of contaminants on the catalyst surface. These findings are consistent with earlier research on closely related nanocomposite catalysts. According to Zhang et al., the N-doped TiO₂/GO composite maintained a high catalytic efficiency (about 97% after the first cycle), but after five cycles, the efficiency dropped to about 85%⁴⁶. In a similar vein, Li et al. found that their N-doped TiO₂-based composite's catalytic activity decreased across several cycles, with a performance decline of 10–15% by the fifth cycle, which they attributed to the loss of active sites and surface area⁹³. The N-doped TiO₂/BC nanocomposite is a promising candidate for repeated use in environmental applications, as indicated by the relatively small decline in performance observed in the current study. Further optimization of the synthesis and operating conditions may improve stability and reusability. These results emphasize the importance of using reliable catalysts and optimizing process parameters for real-world, long-term uses in wastewater/water treatment and other catalytic processes.

Conclusions

Using an N-doped TiO₂/BC nanocomposite, this study effectively examined the photolytic elimination of CIX under both UV and visible light irradiation. For synthetic solutions, the results showed impressive degradation efficiencies of 98.87% under UV light and 96.89% under natural sunshine. The RSM's second-degree polynomial model, which was created with CCD, successfully examined the experimental data. To optimize the process, key parameters affecting degradation efficiency, such as CIX concentration, contact time, nanocomposite dose, and pH were thoroughly investigated. A contact time of 72 min, a pH of 6.9, a nanocomposite dosage of 2 g/L, and an initial CIX content of 50 mg/L were found to be the ideal parameters for maximal degradation. The model anticipated a 99.2% deterioration efficiency and a 0.995 attractiveness value under these circumstances. This prediction was validated by later validation trials, which demonstrated the accuracy and dependability of the model with an actual degradation efficiency of 98.87%. Furthermore, genuine pharmaceutical wastewater was successfully treated with the modified settings, yielding degradation efficiencies of 84.29% and 86.87% under sunshine and UV irradiation, respectively. These results support the N-doped TiO₂/BC nanocomposite's promise as a material that effectively degrades CIX in the visible and ultraviolet light spectrums. The success of this system is further supported by the R² value of 0.983 and the strong fit of the observed rate constant ($k_{app} = 0.0233$) to the pseudo-first-order reaction model. All things considered, this study demonstrates the effectiveness of the N-doped TiO₂/BC nanocomposite for environmental remediation applications, offering a viable way to break down pharmaceutical pollutants.

Data availability

All data are fully available without restriction from the corresponding author.

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References

- Ansari, M. J. et al. Emerging optical and electrochemical biosensing approaches for detection of ciprofloxacin residues in food and environment samples: A comprehensive overview. *J. Mol. Liq.* **354**, 118895 (2022).
- Wang, R. et al. Mechanistic exploration of COVID-19 antiviral drug ritonavir on anaerobic digestion through experimental validation coupled with metagenomics analysis. *J. Hazard Mater.* **479**, 135603. <https://doi.org/10.1016/j.jhazmat.2024.135603> (2024).
- Massima Mouele, E. S. et al. Removal of pharmaceutical residues from water and wastewater using dielectric barrier discharge methods—A review. *Int. J. Environ. Res. Public Health* **18**, 1683 (2021).
- Khasawneh, O. F. S. & Palaniandy, P. Occurrence and removal of pharmaceuticals in wastewater treatment plants. *Process. Saf. Environ. Prot.* **150**, 532–556 (2021).
- Kumar, R. et al. Advancing pharmaceutical wastewater treatment: A comprehensive review on application of catalytic membrane reactor-based hybrid approaches. *J. Water Process. Eng.* **58**, 104838 (2024).
- Moosivand, A., Ghatari, A. R. & Rasekh, H. R. Supply chain challenges in pharmaceutical manufacturing companies: Using qualitative system dynamics methodology. *Iran. J. Pharm. Res. IJPR* **18**, 1103 (2019).
- Zhang, C., Barron, L. & Sturzenbaum, S. The transportation, transformation and (bio) accumulation of pharmaceuticals in the terrestrial ecosystem. *Sci. Total Environ.* **781**, 146684 (2021).
- Zenker, A. et al. Bioaccumulation and biomagnification potential of pharmaceuticals with a focus to the aquatic environment. *J. Environ. Manage* **133**, 378–387 (2014).
- Majumder, M. A. A. et al. Antimicrobial stewardship: Fighting antimicrobial resistance and protecting global public health. *Infect. Drug Resist.* **13**, 4713–4738 (2020).
- Samal, K., Mahapatra, S. & Ali, M. H. Pharmaceutical wastewater as emerging contaminants (EC): Treatment technologies, impact on environment and human health. *Energy Nexus* **6**, 100076 (2022).
- Moghaddam, A. et al. Biodegradation of pharmaceutical compounds in industrial wastewater using biological treatment: A comprehensive overview. *Int. J. Environ. Sci. Technol.* **20**, 5659–5696 (2023).
- Zainab, S. M., Junaid, M., Xu, N. & Malik, R. N. Antibiotics and antibiotic resistant genes (ARGs) in groundwater: A global review on dissemination, sources, interactions, environmental and human health risks. *Water Res.* **187**, 116455 (2020).
- Sangamner, R. et al. A critical review of conventional and emerging wastewater treatment technologies. *Sustain. Water Resour. Manag.* **9**, 58 (2023).
- Yao, Y., Wei, Y., An, L. & Zhou, J. Effect of inoculum on anaerobic Co-digestion of vegetable processing wastes and cattle manure at high solids concentration. *Waste Biomass Valorization* **9**, 2091–2098 (2018).
- Satyam, S. & Patra, S. Innovations and challenges in adsorption-based wastewater remediation: A comprehensive review. *Heliyon* **10**, e29573 (2024).
- Priya, A. K. et al. Occurrences and removal of pharmaceutical and personal care products from aquatic systems using advanced treatment—A review. *Environ. Res.* **204**, 112298 (2022).
- Quddus, F. et al. Environmentally benign nanoparticles for the photocatalytic degradation of pharmaceutical drugs. *Catalysts* **13**, 511 (2023).
- Koe, W. S. et al. An overview of photocatalytic degradation: Photocatalysts, mechanisms, and development of photocatalytic membrane. *Environ. Sci. Pollut. Res.* **27**, 2522–2565 (2020).
- Aracha, C. B., Altin, I., Bacaksiz, E. & Stathopoulos, V. N. Titanium dioxide (TiO₂)-based photocatalyst materials activity enhancement for contaminants of emerging concern (CECs) degradation: In the light of modification strategies. *Chem. Eng. J. Adv.* **10**, 100262 (2022).
- Saravanan, A. et al. Degradation of toxic agrochemicals and pharmaceutical pollutants: Effective and alternative approaches toward photocatalysis. *Environ. Pollut.* **298**, 118844 (2022).
- Subramaniam, M. N., Wu, Z., Goh, P. S. & Zhou, S. The state-of-the-art development of biochar based photocatalyst for removal of various organic pollutants in wastewater. *J. Clean Prod.* **429**, 139487 (2023).
- Qarajehdaghi, M., Mehrizad, A., Gharbani, P. & Shahverdizadeh, G. H. Quaternary composite of CdS/g-C₃N₄/rGO/CMC as a susceptible visible-light photocatalyst for effective abatement of ciprofloxacin: Optimization and modeling of the process by RSM and ANN. *Process Saf. Environ. Prot.* **169**, 352–362 (2023).
- Saeed, M., Muneer, M., Haq, A. & ul, Akram N., Photocatalysis: An effective tool for photodegradation of dyes—A review. *Environ. Sci. Pollut. Res.* **29**, 293–311 (2022).
- Wong, E. C. et al. Methods for identifying health research gaps, needs, and priorities: A scoping review. *J. Gen. Intern. Med.* **37**, 198–205 (2021).
- Nassis, E. & Gruffy, L. Factorial design: design, measures, classic example. In *Translational Sports Medicine* 269–274 (Elsevier, 2023).
- Zhang, Y. et al. Bagasse-based porous flower-like MoS₂/carbon composites for efficient microwave absorption. *Carbon Lett.* **35**, 145–160 (2024).
- Yao, Y., Chen, S. & Kafle, G. K. Importance of “weak-base” poplar wastes to process performance and methane yield in solid-state anaerobic digestion. *J. Environ. Manage.* **193**, 423–429. <https://doi.org/10.1016/j.jenvman.2017.02.025> (2017).
- Ahmad, I. et al. Semiconductor photocatalysts: A critical review highlighting the various strategies to boost the photocatalytic performances for diverse applications. *Adv. Colloid Interface Sci.* **311**, 102830 (2023).
- Náfrádi, M., Veréb, G., Firak, D. S. & Alapi, T. Photocatalysis: Introduction, mechanism, and effective parameters. In *Green Photocatalytic Semiconductors: Recent Advances and Applications* 3–31 (2022).
- Coha, M. et al. Advanced oxidation processes in the removal of organic substances from produced water: Potential, configurations, and research needs. *Chem Eng J* **414**, 128668 (2021).
- Khan, M. M. Principles and mechanisms of photocatalysis. In *Photocatalytic Systems by Design* 1–22 (Elsevier, 2021).
- Ihsanullah, I. et al. Removal of pharmaceuticals from water using sewage sludge-derived biochar: A review. *Chemosphere* **289**, 133196 (2022).
- Pirsaheb, M. et al. Optimization of photocatalytic degradation of methyl orange using immobilized scoria-Ni/TiO₂ nanoparticles. *J. Nanostruct. Chem.* **10**, 143–159 (2020).
- Qiu, L. et al. A review on biochar-mediated anaerobic digestion with enhanced methane recovery. *Renew. Sustain. Energy Rev.* **115**, 109373. <https://doi.org/10.1016/j.rser.2019.109373> (2019).
- Fito, J., Kefeni, K. K. & Nkambule, T. T. I. The potential of biochar-photocatalytic nanocomposites for removal of organic micropollutants from wastewater. *Sci. Total Environ.* **829**, 154648. <https://doi.org/10.1016/j.scitotenv.2022.154648> (2022).
- Ashebir, H., Nure, J. F., Worku, A. & Msagati, T. A. M. Prosopis Juliflora biochar for adsorption of sulfamethoxazole and ciprofloxacin from pharmaceutical wastewater. *Desalin. Water Treat.* **320**, 100691 (2024).
- Zhao, P. et al. Assessment of bamboo charcoal/nano-TiO₂ (BC/TiO₂) composite material and its application in photocatalytic coating. *J. Inorg. Organomet. Polym. Mater.* **29**, 799–805 (2019).
- Asahi, R., Morikawa, T., Irie, H. & Ohwaki, T. Nitrogen-doped titanium dioxide as visible-light-sensitive photocatalyst: Designs, developments, and prospects. *Chem. Rev.* **114**, 9824–9852 (2014).
- Yamagishi, T., Kurimoto, Y. & Yamauchi, S. A method for visualizing cesium ions adsorbed on wood charcoal using SEM–EDX. *Wood Sci. Technol.* **51**, 413–429 (2017).

40. Zhang, H. et al. H₂ production from coal by enriching sugar fermentation and alkane oxidation with hyperthermophilic resistance microbes in municipal wastewater. *Chem. Eng. J.* **489**, 151487. <https://doi.org/10.1016/j.cej.2024.151487> (2024).
41. Zhu, K. et al. Catalytic oxidation of clofibric acid by peroxydisulfate activated with wood-based biochar: Effect of biochar pyrolysis temperature, performance and mechanism. *Chem. Eng. J.* **374**, 1253–1263 (2019).
42. Fatholahi, P. et al. Removal of erythromycin antibiotic from the aqueous media using magnetic graphene oxide nanoparticles. *Desalin. Water Treat.* **303**, 142–150. <https://doi.org/10.5004/dwt.2023.29750> (2023).
43. Mhemid, R. K. S., Salman, M. S. & Mohammed, N. A. Comparing the efficiency of N-doped TiO₂ and commercial TiO₂ as photo catalysts for amoxicillin and ciprofloxacin photo-degradation under solar irradiation. *J. Environ. Sci. Health Part A* **57**, 813–829 (2022).
44. Safari, M. et al. Solar photocatalytic degradation of amoxicillin using Ni/TiO₂ nanocatalyst stabilized on ceramic plates. *Desalin. Water Treat.* **270**, 163–171. <https://doi.org/10.5004/dwt.2022.28787> (2022).
45. Ashebir, H., Tibebe, S., Bedada, D. et al. Advanced methylene blue adsorption with a tailored biochar/graphene oxide/magnetite nanocomposite: Characterization, optimization, and reusability. *Biomass Convers. Biorefinery* 1–22 (2024).
46. Zhang, X., Wang, J., Dong, X.-X. & Lv, Y.-K. Functionalized metal-organic frameworks for photocatalytic degradation of organic pollutants in environment. *Chemosphere* **242**, 125144 (2020).
47. Wu, J., Ren, J., Pan, W. et al. Preparation and Characterization of Titanium-Based Photocatalysts. In *Photo-catalytic Control Technologies of Flue Gas Pollutants* 13–44 (2019).
48. Yang, J., Kang, F., Wang, X. & Zhang, Q. Design strategies for improving the crystallinity of covalent organic frameworks and conjugated polymers: A review. *Mater. Horizons* **9**, 121–146 (2022).
49. Trukhan, N. N. et al. FTIR spectroscopic study of titanium-containing mesoporous silicate materials. *Langmuir* **21**, 10545–10554 (2005).
50. Abdelfattah, I. & El-Shamy, A. M. A comparative study for optimizing photocatalytic activity of TiO₂-based composites with ZrO₂, ZnO, Ta₂O₅, SnO, Fe₂O₃, and CuO additives. *Sci. Rep.* **14**, 27175 (2024).
51. Morales, H. M. et al. Synthesis and characterization of titanium nitride-carbon composites and their use in lithium-ion batteries. *Nanomaterials* **14**, 624 (2024).
52. Zhang, W. et al. Role of vacancy defects and nitrogen dopants for the reduction of oxygen on graphene. *ACS Catal.* **14**, 11065–11075 (2024).
53. Coates, J. Interpretation of infrared spectra, a practical approach. *Encycl. Anal. Chem.* **12**, 10815–10837 (2000).
54. Guan, S. et al. Oxygen vacancies induced band gap narrowing for efficient visible-light response in carbon-doped TiO₂. *Sci. Rep.* **13**, 14105 (2023).
55. Khan, I. et al. Synergizing black gold and light: A comprehensive analysis of biochar-photocatalysis integration for green remediation. *Carbon Capture Sci. Technol.* **13**, 100315 (2024).
56. Alahmad, W. et al. Modeling sustainable photocatalytic degradation of acidic dyes using Jordanian nano-Kaolin-TiO₂ and solar energy: Synergetic mechanistic insights. *Heliyon* **10**, 36978 (2024).
57. Suhan, M. B. K. et al. Sustainable pollutant removal and wastewater remediation using TiO₂-based nanocomposites: A critical review. *Nano-Struct. Nano-Objects* **36**, 101050 (2023).
58. Alam, A. et al. Photocatalytic degradation of the antibiotic ciprofloxacin in the aqueous solution using Mn/Co oxide photocatalyst. *J. Mater. Sci. Mater. Electron.* **33**, 4255–4267 (2022).
59. Kumar, A. et al. Bio-inspired and biomaterials-based hybrid photocatalysts for environmental detoxification: A review. *Chem. Eng. J.* **382**, 122937 (2020).
60. Alalm, M. G. & Boffito, D. C. Mechanisms and pathways of PFAS degradation by advanced oxidation and reduction processes: A critical review. *Chem. Eng. J.* **450**, 138352 (2022).
61. Verma, M. & Haritash, A. K. Photocatalytic degradation of Amoxicillin in pharmaceutical wastewater: A potential tool to manage residual antibiotics. *Environ. Technol. Innov.* **20**, 101072 (2020).
62. Silva, V. & Cardoso, J. S. *Response Surface Methods-Theory, Applications and Optimization Techniques: Theory, Applications and Optimization Techniques* (BoD-Books on Demand, 2024).
63. Zhang, H. et al. Sharpening nanofiltration: Strategies for enhanced membrane selectivity. *ACS Appl. Mater. Interfaces* **12**, 39948–39966 (2020).
64. Mostafaloo, R., Asadi-Ghalhari, M., Izanloo, H. & Zayadi, A. Photocatalytic degradation of ciprofloxacin antibiotic from aqueous solution by BiFeO₃ nanocomposites using response surface methodology. *Glob. J. Environ. Sci. Manag.* **6**, 191–202 (2020).
65. Li, C. et al. Doping effect of phosphate in Bi₂WO₆ and universal improved photocatalytic activity for removing various pollutants in water. *Appl. Catal. B Environ.* **188**, 39–47 (2016).
66. Xiong, L. & Tang, J. Strategies and challenges on selectivity of photocatalytic oxidation of organic substances. *Adv. Energy Mater.* **11**, 2003216 (2021).
67. Gong, F. et al. An effective heterogeneous iron-based catalyst to activate peroxydisulfate for organic contaminants removal. *Chem. Eng. J.* **267**, 102–110 (2015).
68. Mishra, K. et al. Hybrid semiconductor photocatalyst nanomaterials for energy and environmental applications: fundamentals, designing, and prospects. *Adv. Sustain. Syst.* **7**, 2300095 (2023).
69. Chen, D. et al. Photocatalytic degradation of organic pollutants using TiO₂-based photocatalysts: A review. *J. Clean. Prod.* **268**, 121725 (2020).
70. Nie, X. et al. Highly efficient adsorption and catalytic degradation of ciprofloxacin by a novel heterogeneous Fenton catalyst of hexapod-like pyrite nanosheets mineral clusters. *Appl. Catal. B Environ.* **300**, 120734 (2022).
71. Yahya, N. et al. A review of integrated photocatalyst adsorbents for wastewater treatment. *J. Environ. Chem. Eng.* **6**, 7411–7425 (2018).
72. Liu, X. et al. Efficient photocatalytic H₂ production via rational design of synergistic spatially-separated dual cocatalysts modified Mn_{0.5}Cd_{0.5}S photocatalyst under visible light irradiation. *Chem. Eng. J.* **337**, 480–487 (2018).
73. Sharma, R. K. et al. Silver nanomaterials: Synthesis and (electro/photo) catalytic applications. *Chem. Soc. Rev.* **50**, 11293–11380 (2021).
74. Tran, M. L., Nguyen, C. H., Fu, C.-C. & Juang, R.-S. Hybridizing Ag-doped ZnO nanoparticles with graphite as potential photocatalysts for enhanced removal of metronidazole antibiotic from water. *J. Environ. Manage.* **252**, 109611 (2019).
75. Sadeghfar, F. & Ghaedi, M. Photocatalytic treatment of pollutants in aqueous media. In: *Interface Science and Technology* 725–759 (Elsevier, 2021).
76. Tsai, C.-G. & Tseng, W. J. Preparation of TiN-TiO₂ composite nanoparticles for organic dye adsorption and photocatalysis. *Ceram. Int.* **46**, 14529–14535 (2020).
77. Phoon, B. L. et al. Conventional and emerging technologies for removal of antibiotics from wastewater. *J. Hazard Mater.* **400**, 122961. <https://doi.org/10.1016/j.jhazmat.2020.122961> (2020).
78. Trapp, O. Unified equation for access to rate constants of first-order reactions in dynamic and on-column reaction chromatography. *Anal. Chem.* **78**, 189–198 (2006).
79. Kravanja, Z. *26th European Symposium on Computer Aided Process Engineering: Part A and B* (Elsevier, 2016).
80. Galedari, M., Ghazi, M. M. & Mirmasoomi, S. R. Photocatalytic process for the tetracycline removal under visible light: Presenting a degradation model and optimization using response surface methodology (RSM). *Chem. Eng. Res. Des.* **145**, 323–333 (2019).

81. Tran, H. D., Nguyen, D. Q., Do, P. T. & Tran, U. N. P. Kinetics of photocatalytic degradation of organic compounds: A mini-review and new approach. *RSC Adv.* **13**, 16915–16925 (2023).
82. Khlyustova, A. et al. Doped TiO₂: The effect of doping elements on photocatalytic activity. *Mater. Adv.* **1**, 1193–1201 (2020).
83. Zhang, J., Tian, B., Wang, L., et al. Photocatalysis. In *Lecture Notes in Chemistry* 1–17 (Springer, 2018).
84. Liu, J. et al. A review on bidirectional analogies between the photocatalysis and antibacterial properties of ZnO. *J. Alloys Compd.* **783**, 898–918 (2019).
85. Byun, J. & Zhang, K. A. I. Designing conjugated porous polymers for visible light-driven photocatalytic chemical transformations. *Mater. Horizons* **7**, 15–31 (2020).
86. Chakraborty, A. K., Ganguli, S. & Sabur, M. A. Nitrogen doped titanium dioxide (N-TiO₂): Electronic band structure, visible light harvesting and photocatalytic applications. *J. Water Process. Eng.* **55**, 104183 (2023).
87. Prado Mendonça, T. A. et al. Efficient photocatalyst based on activated carbon/graphene oxide/TiO₂ synthesized under acidic conditions for environmental remediation. *J. Photochem. Photobiol. A Chem.* **462**, 116244. <https://doi.org/10.1016/j.jphotochem.2024.116244> (2025).
88. Das, A., Adak, M. K., Mahata, N. & Biswas, B. Wastewater treatment with the advent of TiO₂ endowed photocatalysts and their reaction kinetics with scavenger effect. *J. Mol. Liq.* **338**, 116479. <https://doi.org/10.1016/j.molliq.2021.116479> (2021).
89. Parmar, N. & Srivastava, J. K. Process optimization and kinetics study for photocatalytic ciprofloxacin degradation using TiO₂ nanoparticle: A comparative study of artificial neural network and surface response methodology. *J. Indian Chem. Soc.* **99**, 100584 (2022).
90. Khoshnamvand, N., Kord Mostafapour, F., Mohammadi, A. & Faraji, M. Response surface methodology (RSM) modeling to improve removal of ciprofloxacin from aqueous solutions in photocatalytic process using copper oxide nanoparticles (CuO/UV). *AMB Express* **8**, 1–9 (2018).
91. Al-Musawi, T. J. et al. Photocatalytic degradation of ciprofloxacin by MMT/CuFe₂O₄ nanocomposite: Characteristics, response surface methodology, and toxicity analyses. *Environ. Sci. Pollut. Res.* **30**, 70076–70093 (2023).
92. Suwannaruang, T. et al. Visible-light-driven photodegradation of Pt-derivative anticancer drug carboplatin over La-Fe-modified SrTiO₃ with simultaneous doping and enhanced Pt-photodeposited catalyst. *J. Water Process. Eng.* **71**, 107387. <https://doi.org/10.1016/j.jwpe.2025.107387> (2025).
93. Li, Y., Gao, C., Long, R. & Xiong, Y. Photocatalyst design based on two-dimensional materials. *Mater. Today Chem.* **11**, 197–216 (2019).

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Author contributions

All authors have contributed to this paper, including the concept development by HA and JN, draft preparation and revision by HA, SB, PD, AW, JN, and TM, and approved submission by HA, SB, AW, PD, JN, and TM.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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