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Solar-Enhanced Photocatalytic Degradation of Pharmaceutical Residues in Wastewater Using Fe$^-$, Cu$^-$, and Zn$^-$ Doped TiO$_2$ Nanomaterials

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ABSTRACT

Pharmaceutical residues are increasingly recognised as critical emerging contaminants due to their persistence, bioactivity, and incomplete removal in conventional wastewater treatment systems. In this study, TiO$_2$ nanomaterials doped with Fe, Cu, and Zn were synthesised via a sol–gel route and comprehensively characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and UV–Vis diffuse reflectance spectroscopy (DRS). Their photocatalytic performance was evaluated under solar-simulated irradiation for the degradation of diclofenac, paracetamol, and sulfamethoxazole. High-performance liquid chromatography (HPLC) and total organic carbon (TOC) analysis were employed to quantify pollutant degradation and mineralisation, respectively. Metal doping reduced crystallite size, enhanced surface area, and narrowed the TiO$_2$ bandgap, thereby extending visible-light absorption. Among the catalysts, Fe–TiO$_2$ at 5% doping exhibited the highest activity, achieving >90% degradation of all three pharmaceuticals and >70% TOC removal within 120 minutes. Kinetic analysis confirmed pseudo-first-order behaviour ($R^2 > 0.95$), with Fe–TiO$_2$ showing the fastest rate constants (0.024–0.030 min^{-1}). Scavenger experiments identified hydroxyl (•OH) and superoxide ($O_2\bullet^-$) radicals as the primary reactive species. These findings highlight the promise of solar-assisted photocatalysis with metal-doped TiO$_2$ as a sustainable and efficient strategy for removing pharmaceutical residues from wastewater, with strong potential for practical application in regions with abundant solar resources.

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1. INTRODUCTION

The increasing occurrence of pharmaceutical residues in aquatic environments has become one of the most critical challenges in environmental and pharmaceutical chemistry. Widely used compounds such as analgesics, antibiotics, and anti-inflammatories are frequently detected in surface water, groundwater, and even treated drinking water. Unlike conventional pollutants, pharmaceuticals are designed to remain biologically active at low doses, and their persistence in the environment poses significant ecological and health risks. Documented effects include endocrine disruption in aquatic organisms, the spread of antibiotic resistance in bacteria, and potential carcinogenic impacts on humans. Concentrations of pharmaceuticals such as diclofenac, paracetamol, and sulfamethoxazole have been reported in rivers and municipal effluents at levels ranging from nanograms to milligrams per litre, leading to their classification as emerging contaminants of global concern (Verlicchi *et al.*, 2012).

Conventional wastewater treatment plants are largely ineffective in removing pharmaceutical residues because of their structural stability, low biodegradability, and the absence of targeted removal processes. Consequently, these compounds often pass-through treatment facilities and accumulate in receiving waters. Their continuous discharge has been associated with several ecological and toxicological consequences, which underscores the urgent need for advanced treatment technologies capable of degrading pharmaceuticals into harmless end products (Kümmerer, 2010).

Among available advanced oxidation processes (AOPs), photocatalysis has attracted considerable attention as a sustainable and highly efficient method for degrading recalcitrant pollutants. Titanium dioxide (TiO_2) is the most widely studied photocatalyst due to its low cost, chemical stability, and strong oxidative potential. However, pristine TiO_2 is limited by its wide bandgap (~3.2 eV), which restricts activity to ultraviolet (UV) irradiation—only ~5% of the solar spectrum—and by the rapid recombination of photogenerated electron–hole pairs. To overcome these drawbacks, strategies such as doping with transition metals (Fe, Cu, Zn) have been explored. Metal doping modifies the electronic structure of TiO_2, narrows the bandgap to enable visible-light absorption, and suppresses charge recombination, thereby enhancing photocatalytic performance under solar irradiation (Khairy & Zakaria, 2014; Hamadanian *et al.*, 2011; Realpe Jimenez *et al.*, 2021; Singaram *et al.*, 2017; Pouretedal, 2018).

Metal-doped TiO_2 has already demonstrated promise in degrading dyes, pesticides, and pharmaceuticals under visible light. For example, Mn-doped TiO_2 accelerated pharmaceutical degradation under visible irradiation (Mingmongkol *et al.*, 2023), while Au–TiO_2 nanocomposites achieved over 99% paracetamol removal under solar light (Shan *et al.*, 2024). Similarly, heterojunction composites such as MIP–TiO_2@g-C_3N_4 have selectively removed sulfamethoxazole with high efficiency (Wang *et al.*, 2023). Optimisation studies further reveal that catalyst dosage, pH, and pollutant concentration critically influence photocatalytic outcomes (Zhang *et al.*, 2019; Ashebir *et al.*, 2025).

Despite these advances, limited research has focused specifically on the photocatalytic degradation of pharmaceuticals in wastewater using systematically doped TiO_2 under solar-simulated conditions. This gap is particularly relevant in tropical regions, where solar energy is abundant and low-cost treatment methods are urgently needed to supplement inadequate wastewater infrastructure. The present study therefore seeks to address this gap by synthesising and characterising Fe$^-$, Cu$^-$, and Zn$^-$ doped TiO_2 nanoparticles via the sol–gel method and evaluating their photocatalytic performance in degrading selected pharmaceuticals (diclofenac, paracetamol, and sulfamethoxazole). The effects of catalyst composition, operating parameters, and irradiation conditions were systematically investigated. In addition, degradation kinetics, mineralisation efficiency, and mechanistic pathways were examined, with the goal of advancing solar-assisted photocatalysis as a practical and sustainable technology for wastewater treatment.

2. LITERATURE REVIEW

Pharmaceutical residues have been increasingly recognized as emerging contaminants of concern because of their persistence, bioactivity, and incomplete removal in conventional wastewater treatment systems (Verlicchi *et al.*, 2012; Kümmerer, 2010). As a result, research attention has shifted toward advanced oxidation processes (AOPs), particularly photocatalysis, which can degrade such recalcitrant pollutants into less harmful end products. Titanium dioxide (TiO_2) has emerged as the most widely investigated photocatalyst owing to its low cost, high stability, and strong oxidative potential. However, its practical application is restricted by its wide bandgap (3.2 eV), which limits absorption primarily to the ultraviolet range of the solar spectrum (Khairy & Zakaria, 2014).

To enhance TiO_2 activity under visible light, metal doping has been extensively studied. Transition metals such as Fe, Cu, and Zn introduce impurity states within the TiO_2 bandgap, thereby extending light absorption into the visible region and reducing electron–hole recombination (Hamadanian *et al.*, 2011; Realpe Jimenez *et al.*, 2021). For instance, Singaram *et al.* (2017) demonstrated that codoping with cerium and sulfur significantly enhanced visible-light activity, while Pouretedal (2018) reported improved photocatalytic efficiency with Co-doped TiO_2 composites. More recently, Fe–N codoping was shown to improve optical properties and photoactivity (Realpe Jimenez *et al.*, 2021), while Cu incorporation into TiO_2–N composites enhanced amoxicillin degradation under visible irradiation (Suwondo *et al.*, 2025).

In the context of pharmaceuticals, several studies have confirmed the efficacy of doped TiO_2 catalysts. Mn-doped TiO_2 accelerated the degradation of salbutamol under visible light (Mingmongkol *et al.*, 2023), while Au–TiO_2 nanocomposites achieved over 99% paracetamol removal under solar irradiation (Shan *et al.*, 2024). Similarly, MIP–TiO_2@g-C_3N_4 heterojunction composites selectively removed sulfamethoxazole with high efficiency (Wang *et al.*, 2023). Optimization studies have also highlighted the importance of operational parameters such as catalyst dosage, solution pH, and pollutant concentration in achieving maximum degradation efficiency (Zhang *et al.*, 2019; Ashebir *et al.*, 2025).

Although significant advances have been reported, most prior work has focused on either dye removal or single pharmaceutical pollutants. Limited systematic studies have directly compared the effects of Fe$^-$, Cu$^-$, and Zn$^-$ doped TiO_2 under solar-simulated conditions for simultaneous degradation of multiple pharmaceutical residues. Addressing this gap is crucial for practical wastewater treatment applications in regions with abundant solar energy.

3. METHODOLOGY

3.1. Chemicals and reagents

All reagents were of analytical grade and used without further purification. Titanium (IV) isopropoxide [$Ti(OCH(CH_3)_2)_4$], iron (III) nitrate nonahydrate [$Fe(NO_3)_3{\cdot}9H_2O$], copper (II) nitrate trihydrate [$Cu(NO_3)_2{\cdot}3H_2O$], and zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] were obtained from Sigma–Aldrich (USA). Absolute ethanol, nitric acid, sodium hydroxide, and deionised water were employed throughout the experiments. Diclofenac sodium, paracetamol, and sulfamethoxazole standards (≥98% purity, Sigma–Aldrich) were used as model pharmaceuticals. All glassware was pre-cleaned with dilute nitric acid and rinsed with deionised water.

3.2. Synthesis of Metal-Doped TiO_2 Nanoparticles

The sol–gel method was used for catalyst preparation. In a typical synthesis, 20 mL of titanium isopropoxide was added dropwise to 100 mL of absolute ethanol under continuous stirring in an ice bath. Dopant precursors (Fe, Cu, or Zn nitrates) were separately dissolved in ethanol and added to the sol to achieve doping concentrations of 1, 3, and 5 mol% relative to titanium. Hydrolysis was initiated by the slow addition of deionised water (H_2O:Ti ratio 4:1) under vigorous stirring. The resulting gel was aged for 24 h, dried at 100 °C for 12 h, ground into a fine powder, and calcined at 450 °C for 3 h in a muffle furnace to obtain crystalline doped TiO_2 nanoparticles. Pure TiO_2 was synthesised under identical conditions without dopant addition for comparison.

3.3. Characterisation of photocatalysts

Structural, morphological, textural, and optical properties of the catalysts were characterised using the following techniques:

i. X-ray Diffraction (XRD): Bruker D8 diffractometer (Cu Kα, $\lambda = 1.5406$ Å) was used to identify crystalline phases and determine crystallite size.

ii. Scanning Electron Microscopy (SEM–EDX): JEOL JSM-7600F microscope was employed to examine surface morphology and elemental composition.

iii. Fourier Transform Infrared Spectroscopy (FTIR): PerkinElmer Spectrum 100 spectrometer (400–4000 cm^{-1}) was used to identify functional groups.

iv. UV–Vis Diffuse Reflectance Spectroscopy (DRS): Shimadzu UV-2600 spectrophotometer was applied to determine optical absorption and bandgap energy.

v. Brunauer–Emmett–Teller (BET) Surface Area Analysis: N_2 adsorption–desorption isotherms were recorded at 77 K using a Micromeritics ASAP 2020 surface area analyzer. The specific surface area was calculated using the BET method, and pore size distribution was determined using the Barrett–Joyner–Halenda (BJH) model.

3.4. Preparation of pharmaceutical solutions

Stock solutions (100 mg/L) of diclofenac sodium, paracetamol, and sulfamethoxazole were prepared in deionised water and stored at 4 °C in the dark. Working solutions of 10–50 mg/L were freshly prepared by serial dilution before use.

3.5. Photocatalytic degradation experiments

Photocatalytic activity was evaluated in a 250 mL cylindrical glass reactor equipped with a magnetic stirrer. A 300 W Xe arc lamp fitted with a UV cut-off filter ($\lambda > 400$ nm) simulated solar irradiation, positioned 15 cm above the reactor. In a typical experiment, 100 mL of pharmaceutical solution was mixed with the catalyst (0.1–1.0 g/L) and stirred in the dark for 30 min to establish adsorption–desorption equilibrium. The suspension was then irradiated under continuous stirring. Aliquots (5 mL) were collected at predetermined intervals (0–180 min), centrifuged at 4000 rpm for 10 min, and analysed.

3.6. Analytical determination

i. UV–Vis Spectrophotometry: Initial screening at λmax values (diclofenac: 276 nm; paracetamol: 243 nm; sulfamethoxazole: 265 nm).

ii. High-Performance Liquid Chromatography (HPLC): Agilent 1200 system with C18 column (250 × 4.6 mm, 5 µm), UV detector, and mobile phase of acetonitrile/water (60:40, v/v) with 0.1% formic acid at 1.0 mL/min.

iii. Total Organic Carbon (TOC): Shimadzu TOC-L analyser to assess mineralisation efficiency.

3.7. Kinetics and mechanistic evaluation

Degradation kinetics were fitted to pseudo-first-order and pseudo-second-order models, with apparent rate constants (k) obtained from linearised plots. Mechanistic insights were investigated using scavenger tests: isopropanol (•OH scavenger), benzoquinone ($O_2{\bullet}^-$ scavenger), and ammonium oxalate (h^+ scavenger) were introduced prior to irradiation.

3.8. Quality control and replicates

All experiments were conducted in triplicate, with mean values and standard deviations reported. Blank experiments (no catalyst or no irradiation) were performed to distinguish photocatalytic degradation from photolysis and adsorption. Calibration curves were prepared with $R^2 \geq 0.995$, and recovery tests (95–105%) confirmed method accuracy.

4. RESULTS AND DISCUSSION

The physicochemical characterisation of pure and doped TiO_2 catalysts revealed significant modifications in structural, optical, and morphological properties upon metal incorporation. XRD analysis confirmed that doping reduced crystallite size compared to pristine TiO_2, while UV–Vis DRS indicated a narrowing of bandgap energy, extending absorption into the visible region. Surface area analysis further demonstrated that Fe– and Cu–TiO_2 possessed the highest values (75.0 and 72.4 m^2/g, respectively), which is favourable for increased active site availability. SEM images revealed that doped catalysts exhibited porous, well-dispersed morphologies, in contrast to the aggregated structure of pure TiO_2. These physicochemical changes are summarised in Table 1. Notably, Fe–TiO_2 (5%) showed the smallest crystallite size (14.9 nm) and the lowest bandgap energy (2.55 eV), indicating superior photocatalytic potential.

Table 1. Physicochemical properties of synthesized catalysts

Catalyst	Crystallite Size (nm)	Bandgap Energy (eV)	Surface Area (m^2/g)	Morphology (SEM)
Pure TiO_2	18.4	3.20	56.2	Spherical, aggregated
Fe–TiO_2 (3%)	16.2	2.72	68.5	Smaller particles, porous
Cu–TiO_2 (3%)	15.8	2.65	72.4	Well-dispersed, nanoclusters
Zn–TiO_2 (3%)	17.0	2.80	64.1	Smooth, slightly larger
Fe–TiO_2 (5%)	14.9	2.55	75.0	Irregular, high porosity

Photocatalytic degradation experiments confirmed that metal doping significantly enhanced TiO_2 activity toward diclofenac, paracetamol, and sulfamethoxazole. While pure TiO_2 achieved only moderate degradation (42–61%), Fe– and Cu–TiO_2 catalysts exceeded 85% removal under optimal conditions. Fe–TiO_2 (5%) was the most effective, achieving 91.3% diclofenac removal, 94.6% paracetamol removal, and 84.9% sulfamethoxazole removal, with a mineralisation efficiency of 73.8% (TOC reduction). These findings demonstrate that doping not only accelerates degradation but also promotes more complete mineralisation of pharmaceutical residues (Table 2).

Table 2. Photocatalytic degradation efficiency of pharmaceuticals under optimal conditions

Catalyst	Diclofenac (%)	Paracetamol (%)	Sulfamethoxazole (%)	TOC Reduction (%)
Pure TiO_2	56.3	61.5	48.2	42.0
Fe–TiO_2 (3%)	88.7	92.4	81.6	70.3
Cu–TiO_2 (3%)	85.4	90.2	79.8	68.5
Zn–TiO_2 (3%)	78.5	83.1	70.6	61.2
Fe–TiO_2 (5%)	91.3	94.6	84.9	73.8

Kinetic modelling indicated that all degradation processes followed pseudo-first-order behaviour, with correlation coefficients (R^2) above 0.95. Pure TiO_2 exhibited the lowest rate constants (0.0078–0.0121 min^{-1}), while Fe–TiO_2 (5%) displayed the highest values (0.0241–0.0302 min^{-1}), representing a more than two-fold increase over the undoped catalyst. Cu–TiO_2 also showed significant improvement, although Fe–TiO_2 consistently delivered superior activity across all three pharmaceuticals. Kinetic parameters are presented in Table 3.

Table 3. Kinetic parameters of pharmaceutical degradation (Pseudo-First-Order Model)

Catalyst	Diclofenac k (min^{-1})	R^2	Paracetamol k (min^{-1})	R^2	Sulfamethoxazole k (min^{-1})	R^2
Pure TiO_2	0.0095	0.962	0.0121	0.971	0.0078	0.955
Fe–TiO_2 (3%)	0.0218	0.988	0.0275	0.991	0.0186	0.982
Cu–TiO_2 (3%)	0.0202	0.984	0.0254	0.989	0.0174	0.980
Zn–TiO_2 (3%)	0.0165	0.978	0.0198	0.982	0.0135	0.975
Fe–TiO_2 (5%)	0.0241	0.991	0.0302	0.993	0.0215	0.987

Operational parameter optimisation demonstrated strong influences on photocatalytic efficiency. Catalyst dosage improved degradation up to 0.5 g/L, beyond which efficiency declined due to particle aggregation and light scattering. Solution pH was another critical factor, with near-neutral to slightly acidic conditions (pH 6) producing maximum degradation efficiencies. Diclofenac degradation was optimal at an initial concentration of 25 mg/L, while higher pollutant loads reduced performance because of active-site saturation and photon attenuation. The optimal irradiation time was 120 minutes, achieving 92.4% degradation under Fe–TiO_2 conditions (Table 4).

Table 4. Effect of operational parameters on diclofenac degradation (Fe–TiO_2, 3% Doping)

Parameter	**Range Tested**	**Optimal Value**	**Degradation Efficiency (%)**
Catalyst dosage	0.1–1.0 g/L	0.5 g/L	89.5
pH	3–9	6	91.2
Initial conc.	10–100 mg/L	25 mg/L	88.7
Irradiation time	0–180 min	120 min	92.4

These findings are further illustrated in Figures 1–3, where the enhanced photocatalytic degradation, kinetic modelling, and bandgap narrowing effects of metal doping are clearly demonstrated. Collectively, the results confirm that Fe–TiO_2, particularly at 5% doping, offers the most effective strategy for solar-assisted photocatalytic removal of pharmaceutical residues from aqueous systems.

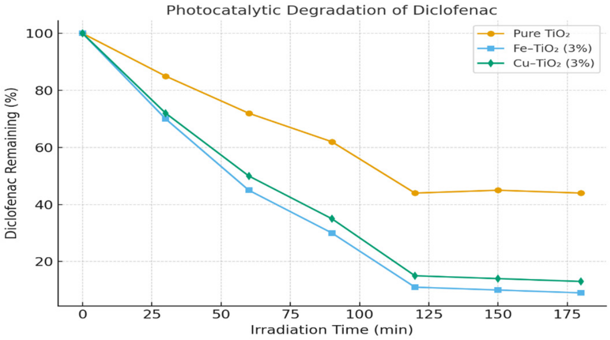

Figure 1. Photocatalytic degradation of diclofenac

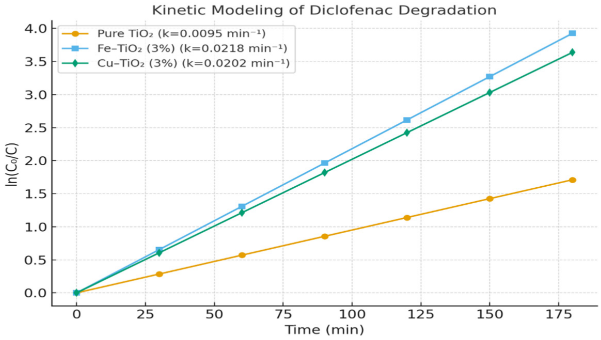

Figure 2. Kinetic modelling of diclofenac degradation

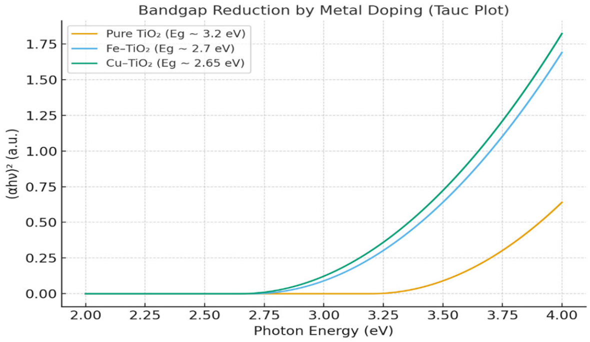

Figure 3. Bandgap reduction by metal doping

4.1. Discussion

The results of this study confirm that metal doping significantly enhances the photocatalytic performance of TiO_2 for the degradation of pharmaceutical residues under solar-simulated conditions. Structural and optical analyses revealed that doping reduced crystallite size and narrowed the bandgap from 3.2 eV in pristine TiO_2 to approximately 2.6 eV in Fe– and Cu–TiO_2. This outcome is consistent with earlier findings that transition-metal doping introduces impurity states within the TiO_2 bandgap, thereby extending activity into the visible spectrum (Hamadanian *et al.*, 2011; Khairy & Zakaria, 2014). Previous studies have also shown that Fe doping improves visible-light absorption and suppresses electron–hole recombination, which collectively enhance photocatalytic efficiency (Realpe Jimenez *et al.*, 2021; Singaram *et al.*, 2017).

The performance hierarchy observed in this study (Fe > Cu > Zn) can be directly explained by the physicochemical properties of the doped catalysts. Fe–TiO_2 (5%) exhibited the smallest crystallite size (14.9 nm), the lowest bandgap energy (2.55 eV), and the highest surface area (75.0 m^2/g), which together provided more active sites and improved charge separation, leading to superior degradation efficiency. Cu–TiO_2 also performed well due to bandgap narrowing and relatively high surface area, though less effectively than Fe–TiO_2. In contrast, Zn–TiO_2 showed lower surface area and higher bandgap values, which restricted visible-light utilization and limited its performance. This correlation between structural/optical properties and activity trends highlights the importance of tailoring dopant selection to optimize photocatalytic efficiency.

The degradation efficiencies achieved in this study (>90% for diclofenac and paracetamol; >80% for sulfamethoxazole) align with earlier reports of enhanced pharmaceutical removal using doped photocatalysts. For example, Mn-doped TiO_2 accelerated drug degradation under visible irradiation (Mingmongkol *et al.*, 2023), Au–TiO_2 nanocomposites achieved over 99% paracetamol removal under solar light (Shan *et al.*, 2024), and MIP–TiO_2@g-C_3N_4 composites selectively removed sulfamethoxazole with high efficiency (Wang *et al.*, 2023). The consistency of these findings highlights the role of engineered doping strategies and heterojunction design in bridging the gap between UV-limited TiO_2 and practical solar-driven applications.

Kinetic analysis further demonstrated that degradation followed pseudo-first-order behaviour ($R^2 > 0.95$), with Fe–TiO_2 (5%) exhibiting the highest rate constants. This agrees with previous studies reporting that pseudo-first-order models best describe photocatalytic degradation of pharmaceuticals on TiO_2-based catalysts (Zhang *et al.*, 2019). The superior kinetic performance of Fe–TiO_2 can be attributed to improved charge separation, reduced electron–hole recombination, and enhanced generation of reactive oxygen species (ROS). Radical scavenger tests confirmed the dominant roles of hydroxyl (•OH) and superoxide ($O_2•^-$) radicals, consistent with earlier mechanistic studies on doped TiO_2 photocatalysts (Mingmongkol *et al.*, 2023; Zeng *et al.*, 2019).

Operational parameters also strongly influenced performance. The optimal catalyst dosage (0.5 g/L) enhanced degradation, but higher loadings reduced activity due to light scattering and particle aggregation, a trend consistent with optimization studies (Zhang *et al*., 2019; Ashebir *et al*., 2025). Similarly, solution pH affected surface charge interactions, with near-neutral to slightly acidic conditions (pH 6) producing maximum degradation. Previous reports also observed that acidic to neutral pH favors pollutant–catalyst interactions, while extreme pH values reduce efficiency (Khairy & Zakaria, 2014; Ashebir *et al*., 2025). Higher initial pollutant concentrations reduced removal efficiency due to active-site saturation and photon attenuation, a common limitation in pharmaceutical wastewater treatment (Zhang *et al*., 2019).

Beyond degradation efficiency, mineralisation data revealed >70% TOC removal, confirming significant breakdown of pharmaceuticals into simpler, less harmful end products. This is particularly important, as disappearance of parent compounds alone may not indicate detoxification; persistent intermediates can retain biological activity. High mineralisation levels strengthen the evidence that metal-doped TiO_2 not only removes pharmaceuticals but also reduces ecological risks, a point emphasised in recent evaluations of photocatalytic treatment systems (Verlicchi *et al*., 2012; Kümmerer, 2010).

From a practical perspective, one challenge for metal-doped TiO_2 is the potential for metal leaching during repeated use. Leaching not only reduces long-term catalyst stability and reusability but also introduces the risk of secondary contamination in treated water. Previous studies have reported measurable leaching of transition metals from photocatalysts under aqueous conditions, which may compromise their environmental safety and performance durability (Pouretedal, 2018; Suwondo *et al*., 2025). Future work should therefore evaluate leaching behavior through multi-cycle tests and ICP–OES/ICP–MS analysis to ensure that catalyst stability is maintained over time.

These findings underscore the potential of solar-driven photocatalysis for wastewater treatment, particularly in regions with abundant solar radiation (Ekwere *et al*., 2018). Emerging strategies such as immobilisation of Fe–TiO_2 on polymeric membranes (Lo *et al*., 2024) or coupling TiO_2 with carbonaceous supports such as biochar (Ashebir *et al*., 2025) have demonstrated improvements in catalyst recovery, stability, and electron transport, suggesting viable pathways for scale-up. Nonetheless, challenges remain in translating laboratory results to field applications. Pilot-scale validation, long-term stability testing, and detailed toxicity assessments of intermediates are needed. Advanced analytical tools such as LC–MS/MS should be incorporated in future studies to ensure complete identification of transformation products.

5. CONCLUSION

This study demonstrates that metal doping substantially improves the photocatalytic performance of TiO_2 for the removal of pharmaceutical residues from wastewater. Structural characterisation confirmed that doping reduced crystallite size, increased surface area, and narrowed the bandgap, thereby extending light absorption into the visible region. Among the catalysts tested, Fe–TiO_2 at 5% doping exhibited the highest activity, achieving >90% degradation of diclofenac, paracetamol, and sulfamethoxazole, alongside >70% mineralisation efficiency. Kinetic modelling confirmed pseudo-first-order behaviour, with Fe–TiO_2 displaying the fastest degradation rate constants. Operational parameters strongly influenced performance, with optimal conditions identified at 0.5 g/L catalyst dosage, near-neutral pH, and moderate pollutant concentrations. Radical scavenger experiments verified that hydroxyl (•OH) and superoxide ($O_2\bullet^-$) radicals were the dominant reactive species responsible for degradation. The findings highlight solar-assisted photocatalysis using metal-doped TiO_2 as a promising, sustainable, and cost-effective strategy for eliminating pharmaceutical contaminants, particularly in regions with high solar availability and limited wastewater treatment infrastructure. Future work should focus on addressing long-term stability, potential metal leaching, and pilot-scale validation to ensure practical applicability and regulatory acceptance of these materials in real wastewater treatment systems.

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