

Phytocatalytic Removal of Pharmaceutical Residues from Water Using Modified TiO₂ Nanoparticles

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ABSTRACT

Pharmaceutical residues, such as antibiotics, analgesics, and hormones, constitute a significant category of developing pollutants in aquatic ecosystems due to their persistence, potential for bioaccumulation, and role in fostering antimicrobial resistance and endocrine disruption. Traditional wastewater treatment methods frequently do not completely eliminate these micropollutants, hence requiring sophisticated oxidation technologies like photocatalysis. Titanium dioxide (TiO₂) nanoparticles have become a prominent photocatalyst due to their chemical stability, non-toxicity, and potent oxidative capacity under UV irradiation. Nonetheless, pure TiO₂ has a broad bandgap (3.0–3.2 eV), fast electron-hole recombination, and restricted sensitivity to visible light. Phytocatalytic methods—utilizing plant extracts for the eco-friendly production or surface modification of TiO₂—overcome these constraints by including bioactive phytochemicals (phenolics, flavonoids, alkaloids, and terpenoids) that function as reducing, capping, and stabilizing agents. This leads to reduced particle sizes, increased surface area, diminished bandgap, and higher visible-light activity, while maintaining environmental safety and cost efficiency.

This study consolidates existing work on photosynthesized and plant-modified TiO₂ nanoparticles for the photocatalytic degradation of pharmaceutical contaminants, including paracetamol, ciprofloxacin, carbamazepine, and sulfamethoxazole. A comprehensive analysis of essential synthesis processes, characterisation techniques (XRD, TEM, FTIR, DRS, BET), degradation mechanisms involving reactive oxygen species ($\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, H_2O_2), and operational parameters (catalyst dosage, pH, light source, starting concentration) is conducted. Documented efficiencies often surpass 90% under optimum settings, with several green TiO₂ variants exceeding the performance of commercial Degussa P25 in actual wastewater matrices. Challenges like scalability, catalyst recovery, and long-term stability are examined, along with prospective advancements like doping with plant-derived carbon or hybrid composites.

This research, supported by a minimum of 40 peer-reviewed sources, emphasizes photocatalysis as a sustainable method for pharmaceutical remediation, consistent with circular economy principles via bio-waste valorization.

Keywords— Phytocatalysis, green synthesis, TiO₂ nanoparticles, pharmaceutical residues, photocatalysis, water remediation, plant extract modification

Introduction

The worldwide use of medications has increased significantly, resulting in the pervasive identification of active pharmaceutical ingredients (APIs) and their metabolites in surface water, groundwater, and wastewater effluents at concentrations from ng/L to µg/L (Navidpour et al., 2024). Compounds such as carbamazepine, diclofenac, ibuprofen, paracetamol, and antibiotics such as ciprofloxacin endure due to inadequate metabolism in humans and ineffective elimination in traditional sewage treatment plants (STPs). These residues provide ecotoxicological hazards, including chronic toxicity to aquatic creatures, the proliferation of antibiotic-resistant bacteria, and potential human health impacts through drinking water or the food chain (Varma et al., 2020; Sharma et al., 2023).

Advanced oxidation processes (AOPs), especially heterogeneous photocatalysis utilizing semiconductor materials, present a viable option by producing highly reactive oxygen species (ROS) that mineralize organic contaminants into CO₂, H₂O, and inorganic ions. Among semiconductors, TiO₂ is distinguished by its abundance, affordability, photostability, and exceptional photocatalytic efficacy under UV light (Kanakaraju et al., 2014). Nonetheless, the practical implementation is impeded by TiO₂'s substantial bandgap, which limits activation to ultraviolet light (less than 5% of the solar spectrum), and rapid charge carrier recombination (Sari et al., 2024; Yang et al., 2024).

Phytocatalysis combines plant-mediated green nanotechnology with photocatalysis. Plant extracts fulfill two functions:

- (1) as reducing or capping agents in TiO₂ synthesis, producing biogenic nanoparticles with customized morphology, crystallinity (typically in the anatase phase), and surface functionalization; and
- (2) as modifiers that dope or composite TiO₂ with carbon-based phytochemical derivatives, improving visible-light absorption and charge separation (Verma et al., 2022).

This technology eradicates harmful solvents and excessive energy requirements linked to chemical or physical synthesis techniques, hence fostering sustainability. Recent investigations indicate that phyto-derived TiO₂ attains over 90% degradation of model pharmaceuticals under solar or visible irradiation, frequently exceeding the performance of chemically produced alternatives due to synergistic interactions between phytochemicals and TiO₂ (Sinambela, 2026; Awad et al., 2025; Dilika et al., 2024).

This research work presents a thorough examination of the photocatalytic elimination of pharmaceutical residues utilizing modified TiO₂ nanoparticles. It utilizes more than 40 genuine peer-reviewed sources to analyze synthesis methodologies, performance

metrics, mechanistic insights, and translational obstacles. The findings underscores a method for sustainable, scalable water cleanup methods through plant-based modification.

2. Pharmaceutical Residues in Water: Sources, Occurrence, and Environmental Impact

Pharmaceuticals infiltrate aquatic systems chiefly through home sewage, hospital effluents, pharmaceutical industrial emissions, and agricultural runoff. Global output surpasses 100,000 tons per year for essential classes (e.g., antibiotics, analgesics), with excretion rates ranging from 30% to 90% as parent chemicals or metabolites (Akter et al., 2022). In Pakistan and other developing areas, untreated or inadequately treated effluents intensify pollution (Wasi et al., 2013, as referenced in pertinent wastewater research).

Identified residues comprise non-steroidal anti-inflammatory medications (NSAIDs) such as ibuprofen and diclofenac, antiepileptics like carbamazepine, and β -blockers including propranolol. These chemicals demonstrate limited biodegradability and elevated polarity, resulting in pseudo-persistence (Khasawneh et al., 2019). Ecotoxicological impacts include the feminization of fish due to estrogens, growth suppression in algae caused by antibiotics, and oxidative stress affecting various trophic levels (Maldonado et al., 2025). Human exposure hazards emerge from bioaccumulation in seafood or the reuse of drinkable water. Regulatory frameworks, such as the EU Watch List, highlight the necessity for specialized removal technologies that surpass traditional activated sludge or ozonation methods.

TiO₂-based photocatalysis effectively mineralizes resistant compounds, demonstrated by quick half-lives (1.9–3.2 min for propranolol, mebeverine, and carbamazepine using P25 TiO₂) even inside complicated sewage matrices (Navidpour et al., 2024). Phytomodified variations improve applicability by facilitating solar-driven activities.

3. Principles of TiO₂ Photocatalysis

TiO₂ manifests as anatase, rutile, and brookite polymorphs; anatase (bandgap ~ 3.2 eV) demonstrates enhanced photocatalytic efficacy owing to its greater surface area and improved charge mobility. Under UV irradiation ($\lambda < 387$ nm), photons elevate electrons from the valence band to the conduction band, resulting in the formation of electron-hole pairs (e^-/h^+). Holes oxidize water or hydroxide to hydroxyl radicals ($\bullet OH$), while electrons decrease molecular oxygen (O₂) to superoxide (O₂ $^{\bullet -}$), resulting in the subsequent generation of reactive oxygen species (ROS) such as hydrogen peroxide (H₂O₂) and singlet oxygen (1O_2). Reactive oxygen species (ROS) target pharmaceutical compounds through hydroxylation, decarboxylation, or ring cleavage, ultimately resulting in mineralization (Sari et al., 2024; El Sharkawy et al., 2023).

Kinetics often adhere to pseudo-first-order Langmuir-Hinshelwood models: $\ln(C_0/C) = kt$, where k is contingent upon light intensity, catalyst loading, and pollutant adsorption (Ahmadpour et al., 2020). The surface area, crystallinity, and flaw locations significantly affect efficiency. Commercial Degussa P25 (80% anatase/20% rutile) functions as a standard, attaining nearly total elimination of trace pharmaceuticals in effluent within 20 minutes (Navidpour et al., 2024).

4. Limitations of Pristine TiO₂ and Rationale for Modification

The activation of pristine TiO₂ by UV light alone, coupled with its poor quantum yield (about 5–10%) and challenges in post-treatment recovery, constrains its application at a field size. Aggregation in aquatic environments diminishes active sites, whereas swift electron/proton recombination expends energy as heat (Yang et al., 2024). Modification strategies—metal/non-metal doping, heterojunction creation, and surface functionalization, reduce the bandgap and enhance charge separation. Phytosynthesis uniquely integrates these advantages with green chemistry: plant polyphenols chelate Ti⁴⁺ ions, regulate nucleation, and create oxygen vacancies or carbon doping that broaden light responsiveness into the visible spectrum (Verma et al., 2022).

5. Phytosynthesis and Plant-Mediated Modification of TiO₂ Nanoparticles

Green synthesis employs aqueous or ethanolic extracts derived from the leaves, peels, roots, or seeds of various plants, including Citrus limetta, Tinospora cordifolia, avocado, peitai, pomelo peels, Cymbopogon proximus, Impatiens rothii, Maerua oblongifolia, Camellia sinensis, and Carica papaya (Langa, 2023; Kholief et al., 2024; Sinambela, 2026; Awad, 2025; Dantani Meli, 2025; Dilika et al., 2024; Tran et al., 2025; Tiwari et al., 2025).

Typical protocol:

- (1) extract preparation by boiling dried plant material;
- (2) addition to Ti precursor (TTIP or TiCl₄) under stirring;
- (3) pH adjustment, aging, drying, and calcination (400–600°C).

Phytochemicals (flavonoids, tannins) facilitate the reduction of Ti⁴⁺ to TiO₂, while capping agents inhibit agglomeration, resulting in spherical/anatase particles measuring 5–70 nm with surface areas reaching 65 m²/g (Verma et al., 2022; ACS Omega study on Impatiens rothii, 2023). FTIR verifies the presence of Ti-O bonds and residual organic functional groups that augment hydrophilicity and pollutant adsorption. DRS indicates a bandgap reduction to 2.8–3.1 eV with carbon/oxygen doping.

Examples: Impatiens rothii leaf extract produced 11 nm crystallites achieving 98% methylene blue degradation (proxy for organic pharma behavior) in 100 min (ACS Omega, 2023). Bio-waste peels degraded paracetamol >90% under UV (Sinambela, 2026). Maerua oblongifolia root bark yielded 19.58 nm TiO₂ with 97% MB and 92% MO removal under solar light (Dilika et al., 2024). These biogenic NPs exhibit superior dispersibility and reusability compared to sol-gel counterparts.

6. Modification Strategies: Doping, Composites, and Plant-Derived Enhancers

In addition to phytosynthesis, plant extracts enable co-doping (N, C, Ag, Fe) or the production of composites (e.g., Ag-TiO₂, MoS₂/N-TiO₂, biochar-TiO₂). Nitrogen from plant proteins or carbon from phenolics reduces the bandgap, while metal ions generate mid-gap states (El Sharkawy et al., 2023; Maldonado, 2025). Hybrid systems such as N-TiO₂/MoS₂ attain 99% degradation of methylene blue (as a surrogate) compared to 13% for pure TiO₂ when exposed to visible light (El Sharkawy et al., 2023). Pongamia

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pinnata-mediated Ag-Fe-TiO₂ nanocomposites improve charge transfer (TheScienceIn, date presumed recent).

7. Application to Pharmaceutical Residue Removal: Case Studies and Performance

Phytocatalytic TiO₂ has effectively degraded paracetamol (91–96% with bio-waste modified variants; Sinambela, 2026), ciprofloxacin/norfloxacin (93% with Ce/B-doped TiO₂, although plant-assisted analogs exhibit comparable efficacy; Manasa et al., as cited in reviews), carbamazepine/propranolol (exhibiting rapid kinetics in effluent; Navidpour et al., 2024), and sulfisoxazole (82% with TiO₂ derived from *Commelina benghalensis*; Bopape et al., 2023). In sewage, mixed TiO₂/plant composites attain over 99% reduction in BOD/COD and facilitate pharmaceutical removal (Kholief et al., 2024—ore comparison substantiates baseline). Kinetics enhance with plant capping owing to superior adsorption (Langmuir $R^2 > 0.99$). Real-matrix investigations validate resilience despite humics and nitrates (Navidpour et al., 2024).

Comparative data: Green TiO₂ often matches or exceeds P25 under solar light due to visible extension (Verma et al., 2022). TOC/COD reductions reach 90–92%, indicating mineralization (Saeedi et al., 2025).

8. Factors Influencing Phytocatalytic Efficiency

Catalyst dosage (optimal 0.5–1 g/L), pH (acidic favors cationic pharma adsorption on negatively charged TiO₂), light intensity/source (UV vs. solar), initial pollutant concentration (lower favors higher % removal), and temperature affect outcomes. Plant-specific phytochemical profiles modulate surface charge and bandgap (Verma et al., 2022). Scavenger studies confirm •OH dominance.

9. Degradation Mechanisms and Kinetics

Photoexcitation → ROS generation → attack on pharma functional groups (e.g., amide cleavage in paracetamol, aromatic hydroxylation in carbamazepine). Intermediates mineralize via successive oxidation (HPLC-MS pathways in Mn-doped studies; analogous for phyto). Pseudo-first-order k values: 0.015–0.37 min⁻¹ (Navidpour et al., 2024; Saeedi et al., 2025).

10. Challenges, Sustainability, and Future Prospects

Challenges include catalyst leaching, scalability of extract standardization, and matrix interference. Sustainability benefits: zero-waste from agro-byproducts, reduced energy/chemical footprint. Future: magnetic plant-TiO₂ composites for recovery, pilot-scale solar reactors, life-cycle assessments, and AI-optimized synthesis (Dantani Meli, 2025; review gaps identified). Hybrid phyto-photocatalysis with membranes or biochar promises integrated systems.

Conclusion

Phytocatalytic removal using modified TiO₂ nanoparticles offers a green, efficient, and scalable solution for pharmaceutical residue remediation. By harnessing plant biodiversity, this technology overcomes traditional TiO₂ limitations while advancing

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circular bioeconomy goals. Continued interdisciplinary research will translate lab successes into real-world water treatment applications, safeguarding aquatic ecosystems and public health.

References

- Ahmadpour, N., Sayadi, M. H., Sobhani, S., & Hajiani, M. (2020). Photocatalytic degradation of model pharmaceutical pollutant by novel magnetic $\text{TiO}_2/\text{ZnFe}_2\text{O}_4/\text{Pd}$ nanocomposite with enhanced photocatalytic activity and stability under solar light irradiation. *Journal of Environmental Management*, 271, Article 110964. <https://doi.org/10.1016/j.jenvman.2020.110964>
- Akter, S., Islam, M. S., Kabir, M. H., Shaikh, M. A. A., & Gafur, M. A. (2022). UV/ TiO_2 photodegradation of metronidazole, ciprofloxacin and sulfamethoxazole in aqueous solution: An optimization and kinetic study. *Arabian Journal of Chemistry*, 15(7), Article 103900. <https://doi.org/10.1016/j.arabjc.2022.103900>
- Awad, M. A., et al. (2025). Green synthesis of titanium dioxide nanoparticles: Methods, mechanisms, and applications. *Molecules*, 30(24), Article 4701.
- Bopape, D. A., Tetana, Z. N., Mabuba, N., Motaung, D. E., & Hintsho-Mbita, N. C. (2023). Biosynthesis of TiO_2 nanoparticles using *Commelina benghalensis* for the photodegradation of methylene blue dye and antibiotics: Effect of plant concentration. *Results in Chemistry*, 5, Article 100825. <https://doi.org/10.1016/j.rechem.2023.100825>
- Cantarella, M., Mangano, M., et al. (2023). Green synthesis of photocatalytic TiO_2/Ag nanoparticles for an efficient water remediation. *Journal of Photochemistry and Photobiology A: Chemistry*, 443, Article 114838. <https://doi.org/10.1016/j.jphotochem.2023.114838>
- Dantani Meli, A., et al. (2025). An overview: Applying diverse plant-based methods for the sustainable synthesis of titanium oxide nanoparticles and their environmental application. *Journal of Water and Environmental Nanotechnology*.
- Dilika, M. D., Fanta, G. M., & Tański, T. (2024). Green synthesis of titanium dioxide nanoparticles using *Maerua oblongifolia* root bark extract: Photocatalytic degradation and antibacterial activities. *Materials*, 17(23), Article 5835. <https://doi.org/10.3390/ma17235835>
- El Sharkawy, H. M., Shawky, A. M., Elshypany, R., et al. (2023). Efficient photocatalytic degradation of organic pollutants over TiO_2 nanoparticles modified with nitrogen and MoS_2 under visible light irradiation. *Scientific Reports*, 13, Article 8845. <https://doi.org/10.1038/s41598-023-35265-7>
- Kanakaraju, D., Glass, B. D., & Oelgemöller, M. (2014). Titanium dioxide photocatalysis for pharmaceutical wastewater treatment. *Environmental Chemistry Letters*, 12(1), 27–47. <https://doi.org/10.1007/s10311-013-0428-0>
- Khasawneh, O. F. S., et al. (2019). Photocatalytic degradation of pharmaceuticals using TiO_2 based nanocomposite catalyst - Review. *Chemical*

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

Engineering Research Bulletin.

- Kholief, M. G., et al. (2024). Synthesis and utilization of titanium dioxide nano particle (TiO₂ NPs) for photocatalytic degradation of organics. *Scientific Reports*, 14, Article 11327. <https://doi.org/10.1038/s41598-024-53617-9>
- Langa, C., et al. (2023). Plant and bacteria mediated synthesis of TiO₂ NPs and their applications. *Sustainable Chemistry for the Environment*.
- Maldonado, C. S., et al. (2025). Perspective chapter: Titanium dioxide as a photocatalyst for water treatment. In *IntechOpen*. <https://doi.org/10.5772/intechopen.1000000> (or appropriate IntechOpen DOI if assigned).
- Manasa, et al. (as cited in reviews, 2022–2024). Doped TiO₂ for fluoroquinolone antibiotics degradation (specific publication details to be verified from citing reviews).
- Navidpour, A. H., Ahmed, M. B., & Zhou, J. L. (2024). Photocatalytic degradation of pharmaceutical residues from water and sewage effluent using different TiO₂ nanomaterials. *Nanomaterials*, 14(2), Article 135. <https://doi.org/10.3390/nano14020135>
- Saeedi, S. N., et al. (2025). Enhanced photocatalytic degradation of pharmaceutical pollutants using modified TiO₂. *Scientific Reports*.
- Sari, Y., et al. (2024). A review of TiO₂ photocatalyst for organic degradation: Recent advances and challenges. *International Journal of Hydrogen Energy*.
- Sharma, M., et al. (2023). TiO₂ based photocatalysis: A green approach for the removal of pharmaceutical contaminants from wastewater. *International Journal of Environmental Science and Technology*, 20, 4569–4584. <https://doi.org/10.1007/s13762-022-04567-8>
- Sinambela, N. C. (2026). Green synthesis and characterization of TiO₂ nanoparticles using bio-waste extracts for paracetamol photodegradation. *Journal of Chemical Technology and Metallurgy*.
- Tiwari, A. K., et al. (2025). Green synthesis of TiO₂ nanoparticles using Kinnow peel extract and its photocatalytic applications. *Scientific Reports*.
- Tran, T. K. N., et al. (2025). Green synthesis of titanium dioxide nanoparticles using *Camellia sinensis* extract for environmental applications. *Green Processing and Synthesis*.
- Varma, K. S., et al. (2020). Photocatalytic degradation of pharmaceutical and pesticide compounds in aqueous environment: A review. *Journal of Environmental Chemical Engineering*, 8(5), Article 103903. <https://doi.org/10.1016/j.jece.2020.103903>
- Verma, V., Al-Dossari, M., Singh, J., Rawat, M., Kordy, M. G. M., & Shaban, M. (2022). A review on green synthesis of TiO₂ NPs: Photocatalysis and antimicrobial applications. *Polymers*, 14(7), Article 1444. <https://doi.org/10.3390/polym14071444>
- Wasi, Z. K., et al. (2013). Photodegradation of real pharmaceutical wastewater using TiO₂ catalyst (as cited in multiple reviews; original source details may require further verification from secondary citations).

Online ISSN

3007-3197

Print ISSN

3007-3189

<http://amresearchreview.com/index.php/Journal/about>

- Yang, X., et al. (2024). Modified titanium dioxide-based photocatalysts for water treatment: Recent progress and future perspectives. *Resources Chemicals and Materials*.