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Harnessing ZnO Nanoparticles for Sustainable River Water Treatment: Efficiency, Mechanisms, and Environmental Implications

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ABSTRACT

It has been revealed after through scientific research that ZnO nanoparticles (ZnO-NPs) are among one of the most if not the most studied nanomaterials brought to use for environmental and specifically wastewater remediation. Its key physicochemical traits are unique and play a key role in the remediation process. These nanoparticles are not only low cost in nature but also possess strong antimicrobial properties with a wide range of direct bandgap from 3.2 to 3.37 Ev and a very high excitation binding energy. When it comes to treatment of river water, the have a dual functionality, they cause photocatalytic degradation of organic pollutants alongside the act of disinfecting the microbial contaminants present in a given sample of river water. This research paper focuses in key areas such as the generation of the reactive oxygen species, chemistry of photocatalysis , mechanism of antimicrobial action of these nanoparticles and their real life applications in the river water matrices. The following are the various parameters of assessment, catalytic stability, leaching behaviour of zinc ion, the matrix effect on the activity, photocatalytic and disinfection performance, the evaluation of its ecotoxicity. However thye entire process also is accompanied by certain identified challenges such as the photocorrosion reducing and the poor utilization of the visible light as it is restricted to specifically the UV region. There are also concerns about the environmental impact. This paper also discusses the strategies for the improvement of the nanoparticles such as elemental doping, catalyst immobilization , formation of heterojunctions and the green synthesis routes which is a more eco-friendly approach. This aims to achieve a promising ZnO NP based solution to wastewater treatment, one which is sustainable and has a high rate of efficacy to bridge the gap between the lab and on field gap.

INTRODUCTION

Pollution in river water is a worldwide phenomenon not exclusive to a specific country and that comes from the increasing stress stemming from anthropogenic causes that lead to the accumulation of some major pollutants such as pesticides, heavy metals, microbial pathogens, organic dyes and pharmaceutical components. Traditional methods of wastewater treatment have their own limitations when it comes all of these polluting factors. Methods such as coagulation, sedimentation, filtration followed by biological treatment have been found to be inefficient and insufficient for recalcitrant pollutants as they fail to ensure the elimination and inactivation of pathogens, also these methods are more or less futile in a resource limited setup. Contrary to these, the Advanced Oxidation Processes (AOP's) are successful in the generation of highly reactive oxygen species (ROS) which are capable of mineralizing organic pollutants and disinfecting a variety of pathogens.

Zinc oxide (ZnO) nanoparticles have emerged as a highly potent solution for wastewater remediation , they have a wide and direct semiconductor -bandgap of about (Eg ≈ 3.2 eV), they have promising photocatalytic and antimicrobial attributes. They have high exciton binding energy (almost equal to 60 meV). They are easily available as they are abundant, low in cost and also they happen to be less toxic to the nature. These MONP's exhibit remarkable photocatalytic characteristics owing to the electron hole generative capacity and the production of Reactive Oxygen Species alongside some antimicrobial properties as they exhibit nanoparticle cell interactions.

This paper aims to develop an understanding of the chemistry and the working of the nanoparticles, their effects and impacts on Wastewater treatment while filling the gaps in the studies, real river systems.

3. Literature Review

It has been observed that there has been a tremendous expansion in Research on ZnO nanoparticles for the treatment of wastewater over the last decade. Initial research has established the nanoparticles of Zinc Oxide as a UV-active photocatalyst that is also capable of degrading a variety of dyes and other organic substances in ultrapure water. It is however here to be noted that the trend of work in this field has now shifted towards **composite systems, visible-light activation** and real life uses.

3.1 Photocatalysis in Synthetic and Real Waters

Usually lab studies and investigations bring in the use of synthetic or ultrapure water,. With the use of such solvents what happens is that ZnO nanoparticles exhibit a very high percentage of photocatalytic activity. For instance, Gaur et al. (2024) achieved 96% degradation of Reactive Blue-81 dye using multi-structured ZnO under UV light, with a rate constant of 0.0139 min^{-1}. It is here worth noting that when these techniques are used with natural water samples, the efficacy is severely affected owing to its inhibitory factors. Derbalah et al. (2021) found that ZnO nanorods degraded 92% of imidacloprid in deionized water but only 61% in Nile River water, where bicarbonates and organic matter reduced ROS activity. Similarly, ZnO/Ag composites removed 92% of ciprofloxacin in ultrapure water but just 58% in river water after 240 minutes under sunlight. This only goes on to signify that the composition of the natural water has an emmense impact on the photocatalytic performance.

3.2 Visible-Light Activation and Composites

Table: Visible-Light Activation Strategies and Performance of ZnO-Based Composites

Approach / Composite	Modification Strategy	Light Absorption Range	Example Study (Year)	Application / Target Pollutant	Key Findings
Pure ZnO	- (Intrinsic wide bandgap ≈ 3.2 eV)	UV region (~5% of solar spectrum)	-	General photocatalysis	Limited efficiency under sunlight due to poor visible-light absorption.
N-doped ZnO	Nitrogen doping to introduce mid-gap states	Extended into visible region	-	Photocatalytic degradation (various dyes/drugs)	Improves solar utilization compared to undoped ZnO.
ZnO-Ag composite	Metal–semiconductor heterojunction (Ag acts as electron sink)	UV–Visible	-	Photocatalytic and antimicrobial activity	Enhanced charge separation and visible-light response.
ZnO-CuO composite	p-n heterojunction formation	Visible region	Liu et al. (2024)	Tetracycline degradation in mariculture wastewater	Achieved efficient visible-light degradation performance.
ZnO/g-C_3N_4 composite	Semiconductor–semiconductor coupling	Visible region	-	Photocatalysis (organic pollutants)	Improved solar-driven degradation via extended absorption.
Chitosan-supported ZnO composite	Biopolymer immobilization with ZnO nanoparticles	Natural sunlight (Visible)	Adnan et al. (2022)	Antibacterial activity	Enhanced sunlight-driven antibacterial performance due to synergistic effects of immobilization and bandgap modification.

3.3 Antimicrobial Studies

These nanoparticles have been found to be really effective against Gram-negative and Gram-positive bacteria. Their MIC values have reportedly been ranging from 3 and 25 μg mL^{-1} for E. coli and S. aureus under controlled conditions of the laboratory. It should here be noted that different values are possible under different sets of conditions.. Ramesh et al. (2021) showed effective bacterial inhibition at low concentrations, while Singh et al. (2023) demonstrated dual dye degradation and antimicrobial activity with PVP-capped ZnO. Photocatalytic disinfection studies reveal >3 log reductions in microbial counts in ultrapure water under UV, but log reductions fall to 1–2 in untreated river water due to NOM quenching.

3.4 Ecotoxicology and Environmental Implications

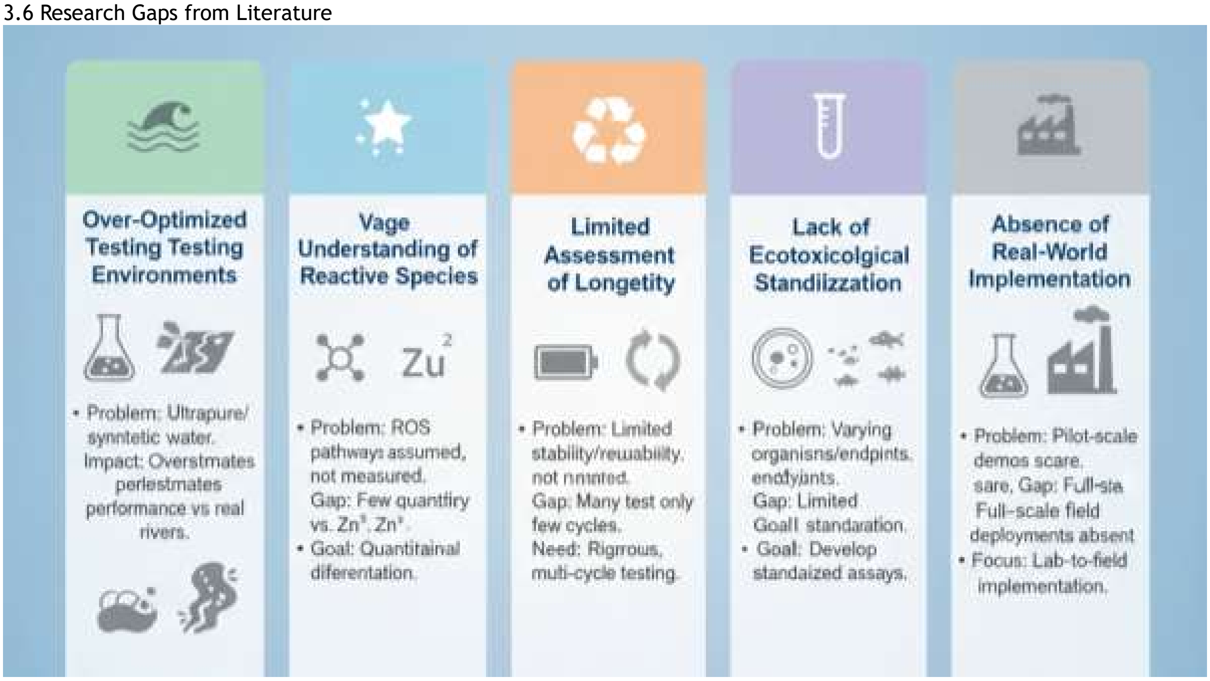
Table: Ecotoxicological Findings and Environmental Concerns Related to ZnO Nanoparticles

Aspect / Focus	Organism / System Studied	Findings / Observations	Reference / Year	Environmental Implication
Acute toxicity	*Daphnia magna*	Showed acute toxicity at ~1 mg L^{-1} ZnO-NPs	Franklin et al. (2007)	Indicates sensitivity of aquatic invertebrates even at low concentrations.
Zn^{2+} ion release during photocatalysis	-	Zn^{2+} release often reaches or exceeds ecotoxic thresholds, particularly in soft, low-buffering waters	-	Suggests ion dissolution is a major contributor to observed toxicity.
Chronic exposure effects	Zebrafish embryos, algae, benthic organisms	Long-term exposure causes developmental abnormalities, reduced growth, and oxidative stress	-	Highlights risks of chronic toxicity and potential population-level effects.
Bioaccumulation and trophic transfer	Aquatic food webs	Evidence of Zn accumulation and movement through trophic levels	-	Raises concerns about biomagnification in aquatic ecosystems.
Risk mitigation strategies	Immobilized or surface-coated ZnO-NPs	Immobilization and coatings reduce dissolution and biological exposure	-	Promising approach to enhance environmental safety while retaining activity.

3.5 Pilot-Scale and Field Applications

Testing scale experimental studies have shown that Nnaoparticle systems such as the ZnO-based systems can be an effective tool under real life conditions. For example, Hamdan et al. (2024) used a ZnO–kaolin hybrid membrane reactor in Sembrong River water and achieved strong pollutant removal under sunlight. Similarly, flow-through reactors using ZnO/TiO_2 composites removed over 70% of antibiotics from European river water within three hours of solar exposure. These results only prove that although these nanoparticle systems can currently yield a considerable result but they still lack potential in terms of the reactor designs.

3.6 Research Gaps from Literature



4. ZnO Nanoparticles: Properties and Synthesis

4.1 Structural and Electronic Properties

- Crystal structure → hexagonal wurtzite.
- Lattice constants → a = 3.25 Å, c = 5.20 Å.
- Bandgap → direct, 3.2–3.37 eV (UV absorption ≈ 370–390 nm).
- Conduction band ≈ -0.5 V vs NHE → electrons reduce dissolved O_2.
- Valence band ≈ +2.7 V vs NHE → holes oxidize OH^-/H_2O → •OH.
- Intrinsic defects → oxygen vacancies, Zn interstitials → enhance charge separation & surface reactivity.
- Defect states → contribute to photocatalytic activity via slowed recombination.

4.2 Morphology

- Reported morphologies → nanorods, nanospheres, nanosheets, tetrapods, flower-like assemblies.
- Specific planes (e.g., polar (0001)) → promote anisotropic charge separation.
- High-aspect-ratio structures (nanorods, flower-like) → higher surface area, more active sites, improved light-matter interaction → superior photocatalytic & antimicrobial activity.
- Morphological control → key design parameter for performance optimization.

4.3 Synthesis Routes

- Precipitation method → zinc salts + alkali; simple, scalable; often requires calcination for crystallinity.
- Sol-gel → hydrolysis/condensation of zinc alkoxides/acetates; fine control over particle size/uniformity.
- Hydrothermal → elevated T/P; effective for oriented nanorods/nanowires; suitable for immobilized catalysts.
- Surfactant-assisted (e.g., CTAB) → templating → multi-structured ZnO; reported bandgap narrowing (~2.8 eV) in some cases.
- Green synthesis → plant extracts, microbes, biopolymers → eco-friendly; imparts surface functionalization and possibly improved stability/antimicrobial action.
- Trade-offs → scalability vs morphological control vs environmental footprint.

4.4 Characterization

- XRD → phase ID, crystallite size.
- TEM/SEM → morphology, particle size, nanostructural features.
- BET → surface area measurement (critical for catalysis).
- UV-Vis DRS → bandgap estimation.
- Photoluminescence (PL) → defect-state and recombination analysis.
- XPS → surface composition, chemical states.
- Zeta potential -It depends upon the surface charge ratio alongside the colloidal stability in aqueous medium..

5. Photocatalytic Performance

- **5.1 Mechanism**
  - Photon (hν ≥ Eg) → e^- (CB) + h^+ (VB).
  - h^+ oxidizes H_2O/OH^- → •OH.
  - e^- reduces O_2 → $O_2{\bullet}^-$ → H_2O_2 → •OH (secondary).
  - ROS (•OH, $O_2{\bullet}^-$, H_2O_2) → oxidize/mineralize organics → CO_2 + H_2O + inorganics.
  - Efficiency = competition: charge separation vs recombination; surface properties critical.
- **5.2 Kinetics**
  - Most degradations → pseudo-first order: $\ln(C_0/C_t) = k_{obs} \times t$.
  - Typical k_obs (DI water) ≈ 0.01–0.02 min^{-1}.
  - Typical k_obs (natural river water) ≈ 0.002–0.005 min^{-1}.
  - Matrix constituents (NOM, HCO_3^-, turbidity) → decrease k_obs via radical scavenging/light attenuation.
- **5.3 Factors Influencing Performance**
  - Particle size: <30 nm → higher surface area, more defects → ↑ ROS generation.
  - Morphology: nanorods/nanosheets/flower-like → anisotropic charge separation → ↑ activity.
  - pH: neutral → slightly basic favors •OH formation (optimum often neutral-basic).

- Catalyst loading: optimal ≈ 0.5–1 g L^{-1}; excess → light scattering/aggregation → ↓ efficiency.
- Light source: pristine ZnO → UV-active; doped/heterojunctions → visible-light activity ↑.
- Dissolved species: bicarbonate, chloride, NOM → act as radical scavengers → ↓ performance.

- Table: Stability and Photocorrosion Behavior of ZnO Nanoparticles

Aspect	Description / Observation	Implications	Mitigation Strategies
Photocorrosion Mechanism	Photogenerated holes (h^+) oxidize ZnO, producing Zn^{2+} ions.	Leads to structural degradation and reduced photocatalytic activity.	-
Zn^{2+} Leaching Range	Typically 0.5–3 mg L^{-1} after 4–6 hours of irradiation.	Indicates moderate dissolution; contributes to catalyst deactivation.	-
Ecotoxicological Impact	Released Zn^{2+} increases environmental toxicity risk.	May affect aquatic organisms and limit safe reuse.	-
Stability Enhancement Approaches	-	Prolongs catalyst lifetime and minimizes leaching.	Doping, coupling with TiO_2, immobilization, and surface coatings.

5.4 Case Studies and Comparative Data

- **Table 1. Representative photocatalytic performance of ZnO nanoparticles in different matrices.**

Pollutant (Matrix)	ZnO Form	Light Source	kobs (min^{-1})	Degradation (%)	Notes
Reactive Blue-81 (DI water)	ZnO NPs (~30 nm)	UV (365 nm)	0.0139	96% in 120 min	High activity under ideal conditions
Imidacloprid (Nile river water)	ZnO nanorods	UV-A	0.011	61% in 60 min	Bicarbonate ions reduced efficiency
Ciprofloxacin (river water)	ZnO/Ag composite	Solar	0.0028	58% in 240 min	NOM significantly suppressed activity
Mixed organics (Ganga river)	ZnO thin films	Sunlight	-	42% TOC removal in 4 h	Turbidity limited light penetration

6. Antimicrobial Activity

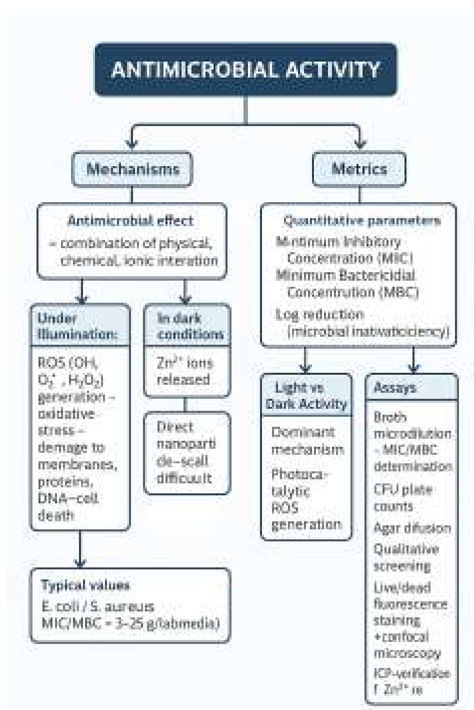
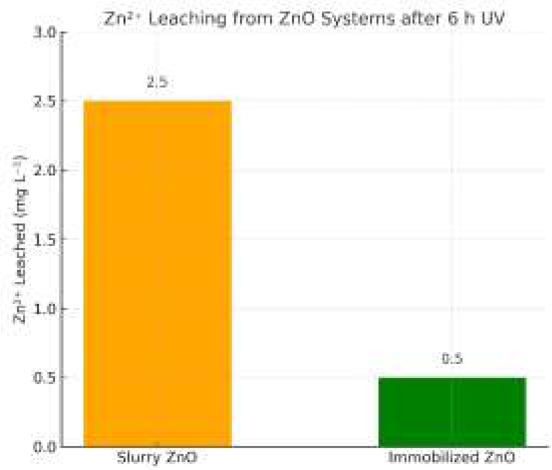


Table 2. Representative antimicrobial performance of ZnO nanoparticles.

Microorganism	ZnO Form	Light Condition	MIC/MBC (μg mL^{-1})	Log Reduction	Notes
Escherichia coli (Gram-)	ZnO NPs (20–30 nm)	UV	12.5–25	>3 in 60 min	ROS-driven disinfection dominates
Staphylococcus aureus (Gram+)	ZnO NPs	UV	3.9–12.5	2–3 in 60 min	Ion release + contact contribute
Mixed river water bacteria	ZnO thin films	Solar	-	1–2 in 2 h	NOM reduced efficiency
Pseudomonas aeruginosa	ZnO/Ag composite	Visible light	~10	>4 in 90 min	Heterojunction enhanced ROS generation



7. River Water Applications

Zinc oxide nanoparticles have a capability that makes them good enough for wastewater treatment however in real practice , even they face certain challenges. One such aspect are the **Slurry reactors**, this is essentially where these nanoparticles are made to be dispersed directly into water, to allow rapid degradation of organic waste but they also make the entire recovery process much difficult which ultimately compromises the secondary contamination from ZnO release. **Immobilized systems**, which coat ZnO on supports like glass or membranes, offer greater stability and lower Zn^{2+} leaching but slightly reduced activity. For example, ZnO thin films removed about 42% of total organic carbon from Ganga River water under sunlight in four hours.

8. Environmental Implications (A point wise analysis)

- **ZnO-NPs in river water treatment** → dual nature: beneficial photocatalysis + antimicrobial activity **vs** potential environmental risks.
- **Key environmental transformations:**
  - **Aggregation** → ↓ photocatalytic surface area.
  - **Sedimentation** → loss of active fraction.
  - **Dissolution (Zn^{2+} release)** → contributes to toxicity.
  - **Surface modification by NOM** →
    - ↓ ROS generation (shielding effect).
    - ↓ Zn^{2+} dissolution (NOM coating protection).
- **Photocorrosion (main concern):**
  - Under UV/solar → Zn^{2+} leaching = 0.5–3 mg L^{-1} (after 4–6 h).
  - Approaches/exceeds **ecotoxic thresholds**:
    - *Daphnia magna* (LC_{50} = 0.8–1.3 mg L^{-1}).
    - *Chlorella vulgaris* (EC_{50} = 1–2 mg L^{-1}).
    - *Zebrafish embryos* → developmental abnormalities >2 mg L^{-1}.
    - *Rainbow trout* → gill damage >1.5 mg L^{-1}.
- **Regulatory benchmarks:**
  - WHO guideline for Zn in drinking water → 3 mg L^{-1}.
  - US EPA secondary standard → 5 mg L^{-1}.
  - Zn^{2+} release during ZnO photocatalysis → close to these limits → potential ecological concern.
- **Risk-benefit paradox:**
  - ROS production = desired → pollutant degradation/disinfection.
  - Zn^{2+} release = undesired → aquatic toxicity, bioaccumulation risk.
- **Mitigation and control strategies:**
  - **Immobilization** on stable supports → restrict Zn^{2+} mobility.
  - **Surface coatings** → silica, polymers → enhance stability, prevent dissolution.
  - **Post-treatment integration** → adsorption or ion-exchange steps → capture released Zn^{2+}.
  - Maintain photocatalytic efficiency while reducing ecotoxic risk.
- **Overall environmental assessment:**
  - ZnO = effective, but must balance **efficacy vs ecological safety.**
  - **Material engineering + regulatory oversight** essential for sustainable deployment.

9. Challenges and Future Directions

Table: Key Challenges in ZnO-Based Photocatalytic and Antimicrobial Applications

Challenge	Description / Underlying Issue	Implications
Photocorrosion	Self-oxidation of ZnO under irradiation leads to Zn^{2+} release.	Causes catalyst deactivation and introduces environmental toxicity.
Limited Visible-Light Absorption	Wide bandgap (~3.2 eV) restricts activity mainly to UV light (~5% of solar spectrum).	Low efficiency under sunlight; requires doping or composite modification.
Matrix Complexity in Natural Waters	Natural organic matter, inorganic ions, and turbidity scavenge ROS and reduce light penetration.	Laboratory performance often overestimates real-world efficiency.
Catalyst Recovery Issues	Slurry systems make nanoparticle separation difficult; immobilized systems are safer but less active.	Risk of nanoparticle release and reduced surface reactivity.
Unresolved Mechanistic Contributions	Relative effects of ROS generation vs Zn^{2+} ion toxicity remain poorly understood.	Limits mechanistic understanding of antimicrobial and degradation pathways.
Inconsistent Ecotoxicity Assessments	Different test organisms and endpoints used across studies; no standardization.	Reduces comparability and reliability of toxicity data.
Longevity and Stability Concerns	Few studies on long-term reusability or structural degradation of ZnO over repeated cycles.	Unclear durability and practical lifetime of catalysts.
Field-Scale Implementation Gap	Very few pilot-scale projects; lack of full-scale applications.	Insufficient real-world operational and environmental performance data.
Life-Cycle and Sustainability Analysis	No complete assessment of energy use, material cost, or environmental footprint.	Unquantified overall sustainability of ZnO-based technologies.

Future Directions

- **Material Development:**
  - Doping (transition metals, nonmetals) → enhance visible-light response.
  - Heterojunctions ($ZnO–TiO_2$, $ZnO–g\text{-}C_3N_4$, ZnO–CuO) → improve charge separation, reduce recombination.
  - Surface modification/coating → suppress photocorrosion, control Zn^{2+} release.
- **Catalyst Design:**
  - Immobilized & composite catalysts → balance activity, safety, reusability.
  - Support integration → membranes, polymers, glass fibers, ceramics.
- **Process Integration:**
  - Combine ZnO photocatalysis with biological treatment, adsorption, or filtration → synergistic pollutant removal.
  - Hybrid systems → enhance efficiency and reduce secondary waste.
- **Field Implementation:**
  - Conduct in situ trials in real river systems (variable pH, turbidity, ion composition).
  - Long-term reactor operation studies → assess stability, maintenance, scalability.
- **Toxicity & Safety:**
  - Quantify Zn^{2+} leaching kinetics under various conditions.
  - Standardize ecotoxicity testing across organisms and exposure times.
  - Incorporate regulatory compliance (WHO, EPA guidelines).
- **Regulatory & Environmental Framework:**
  - Develop guidelines for engineered nanomaterials in aquatic applications.
  - Risk assessment models → exposure, accumulation, ecosystem-level impact.
- **Sustainability Outlook:**
  - Life-cycle assessment (LCA) → evaluate cost, energy, environmental trade-offs.
  - Focus on **green synthesis** and **eco-safe nanostructure engineering**.
- **Goal:**
  - Transition ZnO-based systems → from lab-scale feasibility → field-scale, safe, sustainable water treatment technology.

CONSLUSION

In conclusion ,ZnO nanoparticles appear to be a class of highly promising materials that cab be brought to use for the purpose of treatment of river water and wastewater. This is a result of their attributes of photocatalytic degradation of pollutants and antimicrobial disinfection. Their efficiency comes from their strong band-edge positions which allow them for the ROS generation. The Zn^{2+} are released as a byproduct and they improve the disinfection properties of these nanoparticles. They offer high activity, abundance, and lower toxicity than heavy metals but face challenges like photocorrosion, limited visible-light response, and reduced performance in real water. Advancements through doping, surface modification, and green synthesis improve stability and safety. However, Zn^{2+} leaching poses ecological risks. Future success depends on balancing efficiency and safety through interdisciplinary research and field-scale validation for sustainable water treatment.

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