Supplementary Information

Ultrasound-assisted process intensification for the synthesis of nitrogen-doped ZnO photocatalyst and its application to malachite green degradation

Sachin A. Dhakare[1], Dipak U. Giram[2], Ravindra G. Puri[3] & Rajkumar S. Sirsam[1]*

[1]Department of Chemical Engineering, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon 425 001,
Maharashtra, India

[2]Department of Chemical Engineering, Shri Guru Gobind Singhji Institute of Engineering and Technology (SGGSIE&T),
Nanded, 431 606, Maharashtra, India

[3]Department of Paint Technology, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon 425 001, Maharashtra, India

*E-mail:rajkumarsirsam@gmail.com

Received 16 July 2025; accepted 13 February 2026

Table S1 — Literature comparison of nitrogen-doped ZnO photocatalysts for various dye degradation

Name	Method	Pollutant	Sourceoflight	Efficiency (%)	References
Nitrogen-doped ZnO nanoparticles	Solvothermal method	Methyl Orange (MO)	Sunlight	-	Sun *et al.*[1], 2013
Nitrogen-doped ZnO nanoparticles	Sol-gel method	Methylene blue (MB)	Visible light	-	Rajbongshi *et al.* [2], 2014
Nitrogen-doped ZnO microcrystals	Solvothermal method	Rhodamine 6G	Visible light	81.6%	Wu *et al.*[3], 2014
Nitrogen-doped ZnO nanocrystals	Microwave-assisted hydrothermal	RhB	UV Light	-	Byzynski *et al.* [4], 2017
Nitrogen-doped ZnO nanoparticles	Combustion reaction method	Amaranth (AM) & MB	Visible & UV light	88.5% of AM & 89.3% of MB	Sudrajat *et al.* [5], 2017
Nitrogen-doped ZnO nanoparticles	PolymericPrecursormethod	RhB	Ultraviolet &Visible light	78% (UV)/ 48% (Visible)	Oliveira *et al.*[6], 2018
Nitrogen-doped ZnO nanoparticles	Hydrothermal method	MB	UV & Visible light	98.6%	Prabakaran *et al.* [7], 2019
Nitrogen-doped ZnO nanocomposites	Mechanochemical method	MB & RhB	Sunlight	98.11% MB & 86.21% RhB	Kabir *et al.* [8], 2020
Nitrogen-doped ZnO nanoparticles	Sol-gel method	MB	UV& Sunlight	97% and 80%	Tang *et al.*[9], 2020

Table S2 — Comparison of synthesis methods, structural properties, optical characteristics, and photocatalytic performance of nitrogen-doped ZnO materials reported for dye degradation under different light sources

Catalyst	Synthesis Method	Crystallite Size (nm)	Morphology	Band Gap (eV)	Pollutant	Sourceo f light	Efficiency (%)	Rate constant (k)	Ref.
Nitrogen-doped ZnO nanoparticles	Solvothermal method	20-50 nm	Semi-spherical particle	2.75	MO	Sunlight	-	-	1
Nitrogen-doped ZnO nanoparticles	Sol-gel method	7.4 nm	--	3.00	MB	Visible light	-	3.00	2
Nitrogen-doped ZnO microcrystals	Solvothermal method	5-20 µm	Irregular sphere-like particle	3.13	RhB 6G	Visible light	81.6	0.0176	3
Nitrogen-doped ZnO nanocrystals	Microwave-assisted hydrothermal method	2-2.4 µm	Hierarchical flower-like particle	3.12	RhB	UV Light/Visible	-	0.000367 (UV)/0.000511(VL)	4
Nitrogen-doped ZnO nanoparticles	Combustion reaction method	30-60nm	Aggregate structure and spotty ring pattern	1.7	AM & MB	visible and UV light	88.5% AM & 89.3% MB	-	5
Nitrogen-doped ZnO microcrystals	Polymeric precursor method	17-22 nm	Faceted Particle		RhB	Ultraviolet & visible light	78 (UV)/ 48 (Vis)	0.00150(UV)/ 0.000166(Vis)	6
Nitrogen-doped ZnO nanoparticles	Hydrother-mal method	61.6 nm	Cabbage structure	2.9	MB	UV and visible light	98.6/96.2	0.0579 (UV) /0.0585 (Vis)	7
Nitrogen-doped ZnO microcrystals	Mechano chemical method	28 nm	Irregular shape and soft agglomerates	--	MB & RhB	Sunlight	98.1% MB & 86.21% RhB	--	8
Nitrogen-doped ZnO nanoparticles	Sol-gel method	35 nm	Irregular nanorods	2.15	MB	UV& Sunlight	97% and 80%	0.056 (UV)/0.011(Vis)	9

Nitrogen-doped ZnO microcrystals	Ultrasound method	17.67	Smaller aggregates non uniform shape	2.59	MG	Sunlight	96.43	0.0404	Present Study

Table S3 — Comparison of doped ZnO-based photocatalysts (reported in the IJCT journal) for dye degradation under various light sources

Catalyst	Method of synthesis	Targeted pollutant	Light source	Photocatalytic Condition	Efficiency (%)	Rate Constant	Reusability	Ref.
Er-doped ZnO	Mechanochemical Method	TB	Sunlight	Catalyst loading – 150 mg, Dye Concentration-25, 50, 35 ppm, pH-9, Irradiation Time - 3.5,5,6 h	98%	-	3 Cycle	Kaldante *et al.*[10]
Fe-doped ZnO	Co-Precipitation method	EBT	Solar Light	Catalyst loading – 300 mg Dye concentration – 10 ppm pH-4 Irradiation time – 150 min	83.47%	K = 0.0118	-	Giram *et al.*[11]
Fe-doped ZnO/TiO_2	Calcination method	MO	Incandescent Lamp and Sunlight	Catalyst loading- 0.1,0.4,0.6 g Dye concentration- 20 mg/L pH- Irradiation time- 4h	90.68% & 97.14%	-	-	Lin *et al.*[12]
Cu -doped ZnO	Microwave-assisted method	-	--	Catalyst loading - 0.5 g Dye concentration--- pH- -- Reaction time- 8 h	89.9%	-	-	Saranya et al.[13]
N-doped ZnO	Ultrasound Method	MG	Sunlight	Catalyst Loading – 0.15 g /(100 mL) Dye Concentration – 20 ppm pH- 12 Irradiation time – 90 min	96.43%	K= 0.0404	4 Cycle	Present Study

Effect of Initial pH on Photocatalytic Performance

The effect of initial solution pH on dye degradation was studied at acidic (pH 2), neutral (pH 7), and alkaline (pH 12) conditions to understand how pH influences photocatalytic behavior. This study was done to understand how pH affects the photocatalytic behaviour.Moreover, the intent of this study is not to determine the best pH for the treatment of real wastewaters but rather to establish a better understanding of the mechanistic effects of pH on photocatalysis.

Solution pH strongly affects the surface charge of the photocatalyst and the formation of reactive species. At alkaline pH (pH 12), a higher concentration of OH^- ions enhances the generation of highly reactive hydroxyl radicals (•OH), leading to higher degradation efficiency. In addition, the

negatively charged catalyst surface at high pH favors the adsorption of cationic dye molecules, further improving degradation.

At acidic pH (pH 2), the degradation efficiency was much lower due to limited •OH formation, higher electron–hole recombination, and scavenging of reactive species by excess H^+ ions. At neutral pH (pH 7), reasonable degradation efficiency was observed, although the reaction rate was slower than under alkaline conditions.

Practical Considerations

Despite maximum degradation at pH 12, such strongly alkaline conditions are impractical for real wastewater treatment because they need huge volumes of chemicals, raise operational costs, and necessitate post-treatment neutralization. Thus, pH 12 is not recommended for practical applications.

Catalyst Stability and Practical Relevance

During short-term studies at high pH, the photocatalyst remained stable and showed no apparent loss of activity (Fig. 16). However, long-term stability under sustained alkaline conditions has not been studied and should be investigated in future research. Importantly, high degrading performance at near-neutral pH shows that the photocatalyst can be used for actual wastewater treatment without requiring considerable pH adjustments.

References

(1) Sun S, Chang X, Li X & Li Z, Synthesis of N-Doped ZnO Nanoparticles with Improved Photocatalytical Activity, *Ceram Int*, 39 (2013) 5197.

(2) Rajbongshi BM, Ramchiary A & Samdarshi SK, Influence of N-Doping on Photocatalytic Activity of ZnO Nanoparticles under Visible Light Irradiation, *Mater Lett*, 134 (2014) 111.

(3) Wu C, Zhang YC & Huang Q, Solvothermal Synthesis of N-Doped ZnO Microcrystals from Commercial ZnO Powder with Visible Light-Driven Photocatalytic Activity, *Mater Lett*, 119 (2014) 104.

(4) Byzynski G, Melo C, Volanti DP, Ferrer MM, Gouveia AF, Ribeiro C, Andres J & Longo E, The Interplay between Morphology and Photocatalytic Activity in ZnO and N-Doped ZnO Crystals, *Mater Des*, 120 (2017) 363.

(5) Sudrajat H & Babel S, A Novel Visible Light Active N-Doped ZnO for Photocatalytic Degradation of Dyes, *J Water Process Eng*, 16 (2017) 309.

(6) Oliveira JA, Nogueira AE, Goncalves MCP, Paris EC, Ribeiro C, Poirier GY & Giraldi TR, Photoactivity of N-Doped ZnO Nanoparticles in Oxidative and Reductive Reactions, *Appl Surf Sci*, 433 (2018) 879.

(7) Prabakaran E & Pillay K, Synthesis of N-Doped ZnO Nanoparticles with Cabbage Morphology as a Catalyst for the Efficient Photocatalytic Degradation of Methylene Blue under UV and Visible Light, *RSC Adv*, 9 (2019) 7509.

(8) Kabir R, Saifullah MAK, Ahmed AZ, Masum SM & Molla MAI, Synthesis of N-Doped ZnO Nanocomposites for Sunlight Photocatalytic Degradation of Textile Dye Pollutants, *J Compos Sci*, 4 (2020) 49.

(9) Tang C, Chen C, Zhang H, Zhang J & Li Z, Enhancement of Degradation for Nitrogen Doped Zinc Oxide to Degrade Methylene Blue, *Phys B Condens Matter*, 583 (2020) 412029.

(10) Kaldante YD, Shirsat RN & Chaskar MG, A Comparative Photocatalytic Degradation Study of Thymol Blue Dye over Pristine ZnO and Er-Doped ZnO, *Indian J Chem Technol***,** 31 (2024) 175.

(11) Giram D & Das A, Synthesis and Characterization of Fe Doped ZnO Nanoparticles for the Photocatalytic Degradation of Eriochrome Black-T Dye, *Indian J Chem Technol*, 31 (2024) 39.

(12) Lin L & Ali KA, Photocatalytic Degradation of Organic Compounds in Dye Wastewater by Fe^{3+} Doped Nano-ZnO/TiO_2 Composite Photocatalyst, *Indian J Chem Technol*, 31 (2024) 506.

(13) Saranya R, Ali M & JeyalakshmiK, Enhanced Catalytic and Biological Activities of Cu Doped ZnO Nanoparticles Synthesized by Microwave Assisted Method, *Indian J Chem Technol*, 29 (2022) 288.