JOURNAL OF NANOMATERIALS AND DEVICES
Jan-Jun 2025, VOL. 3, ISSUE 1, pp. 24-29
https://doi.org/10.61577/jnd.2025.100005

RESEAPRO JOURNALS

ORIGINAL ARTICLE

OPEN ACCESS

ZIF-67/LDH sandwiched between graphitic nitride sheets for antibiotic removal

Shaikh Sohail and Jyotirmayee Kabi

Department of Chemistry, Institute of Technical Education and Research, SOA University, Odisha, India

ABSTRACT

This research identifies a photocatalyst made up of zeolitic imidazolate framework-67 (ZIF-67) coated with layered double hydroxide (LDH) incorporated in graphitic carbon nitride (GC) nanosheets, formulated precisely for photocatalytic degradation of Tetracycline hydrochloride (TCH), an enduring antibiotic water system contaminant. The composite was synthesised through the hydrothermal method while keeping the ZIF-67/LDH ratio and gCN percentages constant. Material integrity was verified by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and morphological studies. The ternary composite ZLGC prepared showed superior photocatalytic activity towards the degradation of TCH. Trapping experiments carried out using tert-butanol (for •OH), para-benzoquinone (for $•O_2^-$), and EDTA-2Na (for h^+) revealed hydroxyl radicals as the major reactive species. Kinetic experiments revealed increased rates of degradation, which can be attributed to the synergistic action of ZIF-67's adsorption capacity, LDH's structural stability, and gCN's visible light responsiveness. The eco-friendly photocatalyst offers an extremely effective solution to large-scale wastewater treatment, solving the critical problem of antibiotic contamination.

KEY WORDS

Zeolite; Tetracycline; Graphitic carbon nitride; Photodegradation; Layered double hydroxides

ARTICLE HISTORY

Received 09 May 2025;
Revised 29 May 2025;
Accepted 05 June 2025

Introduction

Colour has intrigued humans since ancient times, enhancing the attractiveness, quality, and visual appeal of products. Today, colours have a more significant influence on our lifestyle than ever before, impacting all facets of our daily lives. These colourants are usually obtained from natural sources. Although natural colourants are more environmentally friendly, gentle on the skin, and visually appealing, they have a limited bonding affinity for tissue components [1]. Since the mid-19th century, following the fortuitous invention of the first synthetic organic dye, 'mauveine or aniline purple,' by W.H. Perkin, artificial dyes have progressively replaced those sourced from nature [2]. The annual global production of synthetic dyes exceeds 7.105 million metric tons, with approximately 10% of the total released into the environment as industrial effluents [3]. Dye-laden effluents released into aquatic ecosystems lower dissolved oxygen levels, posing a serious risk to aquatic organisms. They also diminish the transmission of sunlight into water bodies, thus obstructing the photosynthetic activity of aquatic vegetation [4]. Moreover, many synthetic dyes and their metabolic byproducts are toxic, with potential mutagenic and carcinogenic effects on living beings. A multitude of physical, chemical, and biological decontamination strategies (including adsorption, membrane filtration, coagulation-flocculation, advanced oxidation processes, and activated sludge) have been extensively employed to remediate synthetic dyes from textile wastewater [5]. Photocatalysis treatment represents another robust method for the breakdown and mineralisation of synthetic dyes through reactive radicals, utilising various semiconductor photocatalysts, particularly metal oxides like TiO_2 and ZnO, under light irradiation. The photocatalytic degradation process offers several significant advantages, including effectiveness against persistent pollutants, cost efficiency, environmental sustainability, a rapid degradation rate, and high yield [6,7]. It is commonly recognized that the characteristics of the adsorbent/photocatalyst (including porosity, specific surface area, and surface-active sites), operational parameters (such as pH, adsorbent/photocatalyst loading, contaminant concentration, temperature, and reaction time), and the reusability of the adsorbent/photocatalyst are critical factors that influence the performance of both adsorption and photocatalytic degradation in practical applications.

Among the nanomaterials, zeolitic imidazolate framework-67 (ZIF-67), layered double hydroxides (LDHs), and GC are notable for their superior photocatalytic capability. ZIF-67's good pore size and porous structure provide it exceptional porosity, surface area, and catalytic activity. It is made up of cobalt ions and 2-methylimidazole linkers. For the adsorption and breakdown of pollutants, this makes it ideal [8]. ZIF-67 has a high surface area, which allows it to have several active sites [9]. The presence of a hybrid ZIF transition-metal oxide or hybrid ZIF transition-metal/carbon material in ZIF-67 will change its properties from those of the pure material [10]. A variety of approaches, such as the solvothermal method, surfactant-assisted method, sol-gel method, and microwave/ultrasound-assisted methods, have been developed recently to synthesize ZIF-67 and its derivatives with variable shape and porosity [11].These techniques yield ZIF-67 in a nearly pure form and enable real-time control over size and porosity by varying several parameters, including temperature or synthesis time.

A large specific surface area, tunable interlayer spacing, exchangeable anions across layers, simple synthesis, and inexpensive preparation costs are only a few benefits of LDHs' two-dimensional (2D) lamellar structure. LDHs, with their layered anionic clay architecture, possess structural stability, ion-exchange properties, and tunable compositions, making them useful in catalytic systems [12, 13]. LDHs are widely used in a variety of energy and

***Correspondence:** Mr. Shaikh Sohail, Department of Chemistry, Institute of Technical Education and Research, SOA University, Odisha, India.
email: sohailshaikh8093@gmail.com

environmental protection technologies.Electron transport and chemical species exchange between the electrolyte and the electrocatalyst are facilitated by the unique 2D layered structure of LDHs. However, the stacked layered configuration conceals numerous chemical reaction sites, thereby diminishing reaction activity. During chemical reactions, self-stacking may also occur, significantly impairing its electrical conductivity [14].

GC, a metal-free polymeric semiconductor with a bandgap around 2.7 eV, is very effective in photocatalysis with visible light due to its chemical inertness, biocompatibility, non-toxicity, and thermal stability [15]. It is comprised of triazine and heptazine rings. Through the application of these two structures, the carbon and nitrogen atoms are hybridized via sp^2 to form graphitic planes that are stacked to create a lamellar structure. Theoretical calculations indicate GC, composed of heptazine ring structural units, to be more thermodynamically stable compared to GC composed of triazine ring structural units [16]. The stability may be attributed to the lamellar structure and π−π conjugated electronic structure of GC. Its π-conjugated framework, due to sp^2-hybridized carbon and nitrogen atoms, enables effective charge separation as well as visible-light absorption, which identifies GC as a cost-effective and environmentally benign material for environmental purposes [17].

The combined strategic incorporation of ZIF-67, LDH, and GC as a layered composite photocatalyst, ZLGC, leverages their synergistic advantages to address complex environmental challenges. The porous network of ZIF-67 enables the adsorption of organic contaminants, LDH's strong structure guarantees enduring stability under extreme conditions, and GC's photocatalysis enables effective degradation under visible light [18]. Such synergy design is best for the degradation of TCH, a fluoroquinolone antibiotic that is widely present in wastewater because of its resistance, bioaccumulation, and capacity to facilitate antibiotic resistance in aquatic ecosystems [19,20]. TCH recalcitrance poses significant threats to environmental and human health and thus demands advanced remediation strategies [21]. Even though individual nanomaterials like ZIF-67, LDHs, and gCN have been utilized individually for TCH degradation, their combination into a composite of ZIF-67/LDH/GC has not been fully established. Another critical area lacking research is the enhancement of compositional ratios of these materials, understanding the impact of reactive oxygen species (ROS) in degradation mechanisms, and evaluating the scalability and durability of these composites in the context of industrial wastewater management [22].

Recent literature highlights the growing interest in composite photocatalysts for antibiotic removal. For instance, a study by Guo et al [23] demonstrated that GC-based composites with metal oxides enhance antibiotic degradation through improved charge separation and ROS generation, though they noted challenges in maintaining stability under prolonged irradiation. Likewise, Sadiq et al [24] conducted a study on ZIF-67-based composites for antibiotic degradation and, although they verified very high uptake capacity, their composites were, still, not very active under visible light without supplementary semiconductors like gCN. LDH composites have been examined and found by Zhao et al [25] to enhance the degradation of antibiotics when used in NiFe-LDH/GC hybrids. However, the mechanistic information regarding hydroxide radical contributions that might be found was not explored in their research. Hybrid nanomaterials show considerable promise, but they need to be frameworks that furnish an integrated system designed to both adsorb and retain stability prior to and while degrading contaminants using visible light, which may incur a much higher operational cost before full mechanistic contributions are observed.

In the present study, the limitations presented in previous contexts will be accounted for, and a composite photocatalyst that is a ZIF-67-coated LDH/GC (ZLG) is developed through a hydrothermal process for the degradation of TCH. Material characteristics were comprehensively analyzed with X-ray diffraction (XRD) to ensure crystallinity and scanning electron microscopy (SEM) to evaluate binding morphologies. The fabricated, hybrid nanocomposite ZLG demonstrates superior photocatalytic activity for TCH degradation. The primary reactive species in charge of TCH degradation was identified using scavenger tests using EDTA-2Na+ (to scavenge h^+), tert-butanol (to scavenge •OH), and para-benzoquinone (to scavenge $•O_2^-$). Upon combining these various elements, kinetic analyses were found to exhibit a significant improvement in degradation rates (order of magnitude) over their individual constituents, owing to the advantage of the composite. This research forms the foundation for the synthesis of sustainable, high-performance photocatalysts. This technology provides a scalable, environmentally friendly means of degrading antibiotic pollution in wastewater, an advancement in nanotechnology-based environmental remediation.

Materials and Methods

Chemicals required

All the chemicals used were of analytical grade. Methyl imidazole, $Co(NO_3)_2.7H_2O$, EDTA, DMSO, and p-Benzoquinone were obtained from NICE chemicals Ltd. The distilled water utilized throughout the experimentation was obtained from the laboratory.

Characterization techniques

The produced samples underwent analysis via X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) to assess phase purity and identify functional groups. The XRD apparatus was obtained from BRUKER, while the FTIR device utilised was from Agilent 650.

Fabrication of photocatalyst

For the preparation of GC, 2 g of urea were well mixed in 20 ml of distilled water and filtered and dried. The resulting sample was also kept in muffle furnace for a period of 2.5h at 550 °C. Then the resulting yellow powder was retrieved and characterized further. For the synthesis of Z-67, two different beakers with 1g of $Co(NO_3)_2.7H_2O$ and 0.5g of methyl imidazole were taken, individually in 50 mL and 50 mL of methanol, respectively. Both solutions were blended well for a duration of 8h and the produced mixture was left overnight for 24h. The supernatant was spun off, and the remaining solution was centrifuged again and again to precipitate out the impurities. The sample was further dried in an oven for 24h to get ZIF-67. For the preparation

https://doi.org/10.61577/jnd.2025.100005

of ZLD, 0.4g of $NiCl_2$ was mixed in 100 mL of distilled water. Then about 0.48g of the as-prepared ZIF-67 was mixed with the above and transferred to a Teflon-lined autoclave for 12h at 120 °C. To prepare the composite ZLG, the same process was repeated with the addition of 0.2g of GC. The sample was then centrifuged and washed repeatedly to separate the impurities.

Photocatalytic experiments

For conducting photocatalytic experiments, 0.7g of the precursors and the composite were separately introduced into 20 ppm of the prepared 250 mL TCH solutions contained in beakers. These beakers were positioned in sunlight for a total of 80 minutes, and at intervals of 20 minutes, 5mL of the solutions were withdrawn to assess the absorbance values using a UV-Vis spectrophotometer. For the scavenger tests, four beakers were prepared, each containing 1mM of the scavengers EDTA, Sodium benzoate (BzNa), p-Benzoquinone (BQ), and DMSO, which served to quench the holes, hydroxyl radicals, superoxide radicals, and electrons during the photocatalytic experimentation. The following steps were identical to those outlined above.

Results and Discussions

X-ray Diffraction (XRD) is a non-destructive and versatile technique that is crucial for characterizing crystalline materials in fields such as materials science, chemistry, and engineering. XRD yields critical information regarding a material's crystal structure, phase composition, and orientation preference from the analysis of X-ray diffraction patterns [26]. XRD also yields structural details such as an average grain size, crystallinity level, lattice strain, and identification of defects in crystals, using methods such as the Scherrer equation or Williamson-Hall analysis. XRD also provides accurate lattice parameter determination and phase quantification through Rietveld refinement, a principal method in the investigation of nanomaterials, polymers, ceramics, and alloys in different environmental conditions. Figure 1 depicts the X-ray diffraction (XRD) patterns of the samples. For the Z-67 sample, peaks are identified at 2θ = 7.27°, 12.37°, 23.5°, and 35.1°, which correspond to the (003), (006), (009), and (110) planes of the Z-67. ZLD exhibits comparatively amorphous peaks for Z-67 and LDH. The usual GC peak is seen at 13.21° and 27.67°, ascribing to the (100) and (002) planes of GC [27]. For the composite sample ZLG, some peaks are recorded at about 27.68° in relation to GC. Additionally, more peaks are identified at reasonable angles of 7.27°, 12.37°, 23.5°, and 35.1°, indicating an absence of ZLD and the presence of impurities. The lack of other peaks indicates the composite was formed successfully and synthesized at high purity.

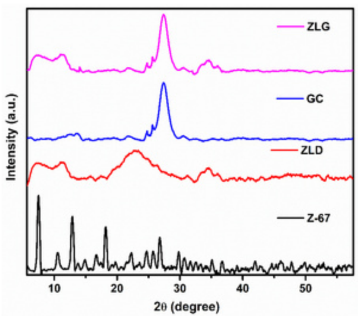

Figure 1. XRD of Z-67, ZLD, GC, and ZLG.

Figure 2 demonstrates that scanning electron microscopy (SEM) demonstrates relatively unique morphological characteristics in GC, ZF-267, ZLD, and their heterojunction (ZLG) for composite applications. The SEM images of the GC morphological characteristics are well supported in the literature as they contain sheet-like structures typical of graphical carbon [15]. In comparison, the SEM images of ZLD show a uniform coating on the ZIF-67 that validated it was successfully deposited on the zeolite of the ZIF-67 framework [28]. The SEM images of ZL showed the composite morphology representing both the sheet-like morphology of GC and ZIF-67 coated on the GC, suggesting that the heterojunction was successfully synthesized, and utilizing the traits of both materials shows that the structure is successful. This heterojunction structure is certainly very important for any potential materials applications as the materials have elements that can be leveraged together [29]. The literature supports the data showing clear anecdotal evidence of the structural traits of GC and ZLD individually and together in the ZLG heterojunction.

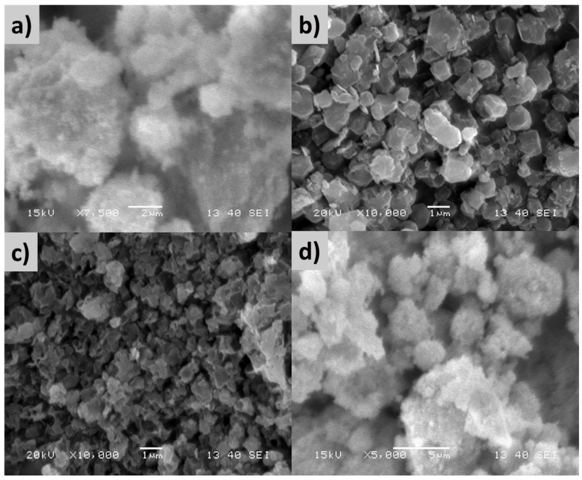

Figure 2. SEM spectra of (a) GC, (b) Z-67, (c) ZLD, and (d) Composite ZLG.

Tetracycline is a wide-spectrum antibiotic for use in humans, animals, and aquaculture to treat infections caused by bacteria. Its significant overuse and persistence in the environment have contributed to its status as an environmental contaminant [13]. Its chemical stability and slow metabolism provide significant excretion of tetracycline residue that ultimately reaches water through wastewater, agricultural runoff, and wastewater from pharmaceutical industries. In aquatic environments, tetracycline concentrations as low as micrograms per litre can disturb microbial communities, inhibit beneficial bacteria, and foster the emergence of antibiotic-resistant strains, which present a global threat to biodiversity and human health by complicating disease treatment [30]. It exhibits high toxicity to aquatic organisms, including algae, freshwater fleas, and fish, causing oxidative stress, apoptosis, altered enzyme activities, and reduced body lengths in amphibians, while also bioaccumulating in the food chain to impact higher trophic levels [31]. Furthermore, when combined with microplastics in polluted waters, it exacerbates cellular damage and metabolic disruptions in marine species, amplifying ecological imbalances. To mitigate these harmful effects, it is crucial to effectively remove tetracycline from water bodies using advanced treatment strategies [32].

https://doi.org/10.61577/jnd.2025.100005

The catalytic efficiency of the precursors GC, Z-67, and ZLD, in conjunction with the composite ZLG, was tracked over a period of 120 minutes for the removal of TCH. It was found that the photocatalytic degradation efficiency of the precursors Z-67 and GC reached 40.615% and 50%, respectively. Notably, the photocatalytic efficacy of the binary composite ZLD attained 62.093%. The synergistic interaction with GC boosts the light-harvesting capability of ZLG to 92.176%. Figure 3a distinctly demonstrates these results and offers a graphical overview of the concentration change of TCH over time (t). The graph of -ln(C/C_0) versus time (t) is illustrated in Figure 3b, where the resulting curves have been linearly fitted to derive the apparent rate constants. This confirms that the photodegradation process follows pseudo-first-order kinetics. The histogram depicted in Figure 3c indicates that the rate constant for the composite is greater than that of the initial components.

Numerous reactive species are present in photocatalytic reactions. These species are investigated in reactions through the application of scavengers. Several scavenger tests are conducted to elucidate the mechanism of the reaction and to ascertain the role of the reactive species involved [33]. In this analysis, scavenger tests were carried out using BzNa (for OH radical), EDTA (for hole), DMSO (for electrons), and BQ (for superoxide radical). It was observed that the degradation percentage fell to 46.2% and 21% with the addition of BQ and BzNa, indicating that hydroxyl radicals are the key reactive species responsible for the photodegradation of TCH, followed by superoxide radicals (Figure 3d). In contrast, the degradation percentages were merely 63.81% and 74.5% in the case of EDTA and DMSO, respectively.

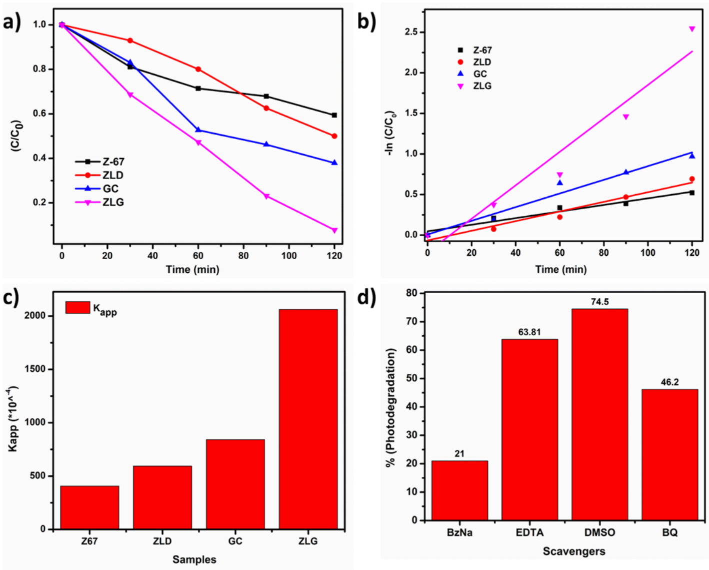

Figure 3. Kinetics plots for photodegradation of TCH (a) C/C_0 plot, (b) -ln(C/C_0) vs t, (c) Apparent rate constants, (d) Scavenger study.

The reusability tests were performed to evaluate the durability of the created ZLG photocatalyst. It was found that after three consecutive cycles, the degradation rate was reduced (Figure 4). This shows that a significant decrease in activity was observed after three repeated cycles. This substantiates the stability of the synthesized photocatalyst.

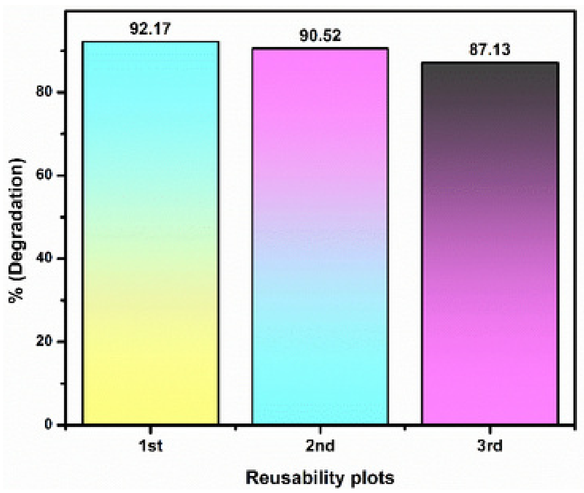

Figure 4. Reusability plot for Zgc.

https://doi.org/10.61577/jnd.2025.100005

Conclusions

This study investigates the synthesis of a zinc-based layered graphene (ZLG) composite photocatalyst via the solvothermal method, highlighting its efficacy in photodegradation applications. The solvothermal synthesis, conducted over 120 minutes, yields a ZLG composite that achieves a remarkable photodegradation efficiency of 92.176% for TCH under sunlight irradiation. Kinetic analysis of the degradation process suggests agreement with a pseudo-first-order kinetic model with linearity observed between the natural log of pollutant concentration and reaction time, indicating a steady reproducible degradation rate. Mechanistic understanding is also provided from scavenger studies, where hydroxyl radicals (.OH) are shown to be the predominant reactive species accountable for the photocatalytic degradation of TCH, underscoring the critical importance of reactive oxygen species in the catalyst's activity. Furthermore, the ZLG composite demonstrates excellent recyclability and quickly degraded TCH with high efficiency over three successive cycles with minimal loss in activity, highlighting the photocatalyst's durability and ability for repeated use for environmental remediation. The ZLG composite's great performance and recyclability demonstrates its promise for broader applications, including water treatment, pollutant degradation, and other photocatalytic reactions. Altogether, the ZLG composite is presented as a promising material for sustainable environmental technologies, meriting additional study for its scale-up and use under varying conditions.

Disclosure Statement

No potential conflict of interest was reported by the author.

References

1. Vega EN, Ciudad-Mulero M, Fernández-Ruiz V, Barros L, Morales P. Natural sources of food colorants as potential substitutes for artificial additives. Foods. 2023;12(22):4102. https://doi.org/10.3390/foods12224102
2. Selvam K, Swaminathan K, Chae KS. Decolourization of azo dyes and a dye industry effluent by a white rot fungus Thelephora sp. Bioresour Technol. 2003;88(2):115-119. https://doi.org/10.1016/S0960-8524(02)00280-8
3. Jasińska A, Paraszkiewicz K, Słaba M, Długoński J. Microbial decolorization of triphenylmethane dyes. InMicrobial degradation of synthetic dyes in wastewaters. Cham: Springer Internat Publ. 2014:169-186. https://doi.org/10.1007/978-3-319-10942-8_8
4. Dutta P, Rabbi M, Sufian M, Mahjebin S. Effects of textile dyeing effluent on the environment and its treatment: A review. Eng Appl Sci Lett. 2022;5:1-17. https://www.doi.org/10.30538/psrp-easl2022.0080
5. Tripathi M, Singh S, Pathak S, Kasaudhan J, Mishra A, Bala S, et al. Recent strategies for the remediation of textile dyes from wastewater: a systematic review. Toxics. 2023 Nov 19;11(11):940. https://doi.org/10.3390/toxics11110940
6. Al Miad A, Saikat SP, Alam MK, Hossain MS, Bahadur NM, Ahmed S. Metal oxide-based photocatalysts for the efficient degradation of organic pollutants for a sustainable environment: a review. Nanoscale Adv. 2024;6(19):4781-4803. https://doi.org/10.1039/D4NA00517A
7. Geldasa FT, Kebede MA, Shura MW, Hone FG. Experimental and computational study of metal oxide nanoparticles for the photocatalytic degradation of organic pollutants: a review. RSC Adv. 2023;13(27):18404-18442. https://doi.org/10.1039/D3RA01505J
8. Sarker T, Tahmid I, Sarker RK, Dey SC, Islam MT, et al. ZIF-67-based materials as adsorbent for liquid phase adsorption-a review. Polyhedron. 2024;260:117069. https://doi.org/10.1016/j.poly.2024.117069
9. Duan C, Yu Y, Hu H. Recent progress on synthesis of ZIF-67-based materials and their application to heterogeneous catalysis. Green Energy & Environment. 2022;7(1):3-15. https://doi.org/10.1016/j.gee.2020.12.023
10. Shan Y, Zhang M, Bai Y, Du M, Guo X, Pang H. Design and synthesis of transition metal oxide/zeolitic imidazolate framework-67 composites. Chem Eng J. 2022;429:132146. https://doi.org/10.1016/j.cej.2021.132146
11. Zhong G, Liu D, Zhang J. The application of ZIF-67 and its derivatives: adsorption, separation, electrochemistry and catalysts. J Mater Chem A. 2018;6(5):1887-1899.
12. Kameliya J, Verma A, Dutta P, Arora C, Vyas S, Varma RS. Layered double hydroxide materials: A review on their preparation, characterization, and applications. Inorganics. 2023;11(3):121. https://doi.org/10.3390/inorganics11030121
13. Xu L, Zhang H, Xiong P, Zhu Q, Liao C, Jiang G. Occurrence, fate, and risk assessment of typical tetracycline antibiotics in the aquatic environment: A review. Sci Total Environ. 2021;753:141975. https://doi.org/10.1016/j.scitotenv.2020.141975
14. Hu X, Zheng W, Wu M, Chen L, Chen S. Composites of metal-organic frameworks (MOFs) and LDHs for energy storage and environmental applications: Fundamentals, progress, and perspectives. Sustain Mater Technol. 2023;37:e00691. https://doi.org/10.1016/j.susmat.2023.e00691
15. Aparajita P, Choudhury S, Sahoo U, Pattnayak S, Padhiari S, Tripathy M, et al. Double charge transfer mechanistic insights into the tailoring of BiOI nanoplates and boron-doped graphitic carbon nitride: a 2D/2D anchored p–n heterojunction nanocatalyst for improved photodegradation. New J Chem. 2023;47(32):15175-15192. https://doi.org/10.1039/D3NJ01122D
16. Yu Y, Huang H. Coupled adsorption and photocatalysis of g-C3N4 based composites: material synthesis, mechanism, and environmental applications. Chem Eng J. 2023;453:139755. https://doi.org/10.1016/j.cej.2022.139755
17. Singh R, Chauhan M, Garg P, Sharma B, Attri P, et al. A critical review on visible light active graphitic carbon nitride (g-CN) based photocatalyst for environment remediation application: A sustainable approach. J Clean Prod. 2023;427:138855. https://doi.org/10.1016/j.jclepro.2023.138855
18. Su P, Zhang J, Xiao K, Zhao S, Djellabi R, Li X, et al. C3N4 modified with single layer ZIF67 nanoparticles for efficient photocatalytic degradation of organic pollutants under visible light. Chin J Catal. 2020;41(12):1894-1905. https://doi.org/10.1016/S1872-2067(20)63620-8
19. Du J, Huang W, Pan Y, Xu S, Li H, Liu Q. Fluoroquinolone antibiotics in the aquatic environment: environmental distribution, the research status and eco-toxicity. Drug Chem Toxicol. 2024;47(6):1325-1340. https://doi.org/10.1080/01480545.2024.2362890
20. Mathur P, Sanyal D, Callahan DL, Conlan XA, Pfeffer FM. Treatment technologies to mitigate the harmful effects of recalcitrant fluoroquinolone antibiotics on the environment and human health. Environ Pollut. 2021;291:118233. https://doi.org/10.1016/j.envpol.2021.118233

https://doi.org/10.61577/jnd.2025.100005

21. Kini V, CS S, Mondal D, Sundarabal N, Nag P, Sadani K. Recent advances in electrochemical sensing and remediation technologies for ciprofloxacin. Environ Sci Pollut Res Int. 2025;32(5):2210-2237. https://doi.org/10.1007/s11356-024-35852-9

22. Alalm MG, Djellabi R, Meroni D, Pirola C, Bianchi CL, Boffito DC. Toward scaling-up photocatalytic process for multiphase environmental applications. Catalysts. 2021;11(5):562. https://doi.org/10.3390/catal11050562

23. Guo X, He S, Meng Z, Wang Y, Peng Y. Ag@ ZIF-8/gC 3 N 4 Z-scheme photocatalyst for the enhanced removal of multiple classes of antibiotics by integrated adsorption and photocatalytic degradation under visible light irradiation. RSC Adv. 2022;12(28):17919-17931. https://doi.org/10.1039/D2RA02194C

24. Sadiq S, Khan I, Humayun M, Wu P, Khan A, Khan S, et al. Synthesis of metal–organic framework-based ZIF-8@ ZIF-67 nanocomposites for antibiotic decomposition and antibacterial activities. ACS omega. 2023;8(51):49244-49258. https://doi.org/10.1021/acsomega.3c07606

25. Zhao GQ, Long X, Hu J, Zou J, Jiao FP. NiFe-layered double hydroxides as a novel hole repository layer for reinforced visible-light photocatalytic activity for degradation of refractory pollutants. Ind Eng. Chem Res. 2021;60(38):13834-13845. https://doi.org/10.1021/acs.iecr.1c02310

26. Ali A, Chiang YW, Santos RM. X-ray diffraction techniques for mineral characterization: A review for engineers of the fundamentals, applications, and research directions. Minerals. 2022;12(2):205. https://doi.org/10.3390/min12020205

27. Aparajita P, Das S, Sahoo U, Choudhury S, Pattnayak S, Mallik S, et al. Combinatorial photoactivity enhancement of ternary nanohybrids: Ag cocatalyst-dispersed monoclinic Bi2O3/g-C3N4 through the synergistic action of induced oxygen defect and porosity for abatement of fluoroquinolones and boosted antimicrobial activity. Appl Eng Mater. 2024;2(7):1748-1765. https://doi.org/10.1021/acsaenm.4c00087

28. Zhang D, Xiang Q, Li X. Electrophoretic fabrication of zeolitic imidazolate framework-67 (ZIF-67) and its derivative coating. Mater Lett. 2019;257:126686. https://doi.org/10.1016/j.matlet.2019.126686

29. Bae SH, Kum H, Kong W, Kim Y, Choi C, Lee B, et al. Integration of bulk materials with two-dimensional materials for physical coupling and applications. Nat Mater. 2019;18(6):550-560. https://doi.org/10.1038/s41563-019-0335-2

30. Paramonov S, Zelikova D, Sklyarova L, Alkhutova I. Environmental risks of micro-contamination of the environment with tetracycline. Pharm Form. 2022;4:76-88. https://doi.org/10.17816/phf106547

31. Tang J, Yang J, Zhao S, Wang X, Xie Z. Toxic effects of tetracycline and its removal by the freshwater microalga Chlorella pyrenoidosa. Agronomy. 2022;12(10):2497. https://doi.org/10.3390/agronomy12102497

32. Duong LT, Nguyen TT, Van Tran T. Combined pollution of tetracyclines and microplastics in the aquatic environment: Insights into the occurrence, interaction mechanisms and effects. Environ. Res. 2024;263:120223. https://doi.org/10.1016/j.envres.2024.120223

32. Schneider JT, Firak DS, Ribeiro RR, Peralta-Zamora P. Use of scavenger agents in heterogeneous photocatalysis: truths, half-truths, and misinterpretations. Phys Chem Chem Phys. 2020;22(27):15723-15733. https://doi.org/10.1039/D0CP02411B

https://doi.org/10.61577/jnd.2025.100005