

Investigation of Tetracycline Removal from Aqueous Environments via Bio-Electro-Fenton Process Using an LDH/CN Cathode

Yang Li, Xiao Liu and Jiahan Tong

North China University of Science and Technology, Tangshan 063210, China

Abstract

The integration of CuFeMn-Layered Double Hydroxide (LDH) with graphitic carbon nitride (g-C₃N₄), designated as CFM/CN, was identified as a potential strategy to enhance the photogeneration of hydrogen peroxide (H₂O₂) and improve the photoelectrocatalytic performance within a Bio-Electro-Fenton (BEF) system. The CFM/CN-BEF system is anticipated to broaden the applicable pH range and augment the overall efficiency of the BEF process, thereby facilitating more effective removal of antibiotics from wastewater. This investigation will systematically evaluate the removal efficiency of tetracycline (TC) as a representative recalcitrant pollutant under a wide range of pH conditions. The findings are expected to provide novel insights into the degradation mechanisms of TC and advance the fundamental understanding of BEF technology for treating refractory organic wastewater.

Keywords

Tetracycline (TC); Layered Double Hydroxide (LDH); Bio-Electro-Fenton (BEF); Microbial Fuel Cell (MFC); Graphitic Carbon Nitride (g-C₃N₄).

1. Preface

Tetracycline antibiotics (TCs), a class of broad-spectrum antibiotics, are either semi-synthetic derivatives or naturally produced by *Streptomyces* species. Owing to their multiple advantages, TCs have been extensively utilized across various sectors, including animal husbandry, aquaculture, and clinical medicine. Consequently, they are frequently detected in substantial concentrations in hospital wastewater. Improper handling or inadequate discharge of these compounds can lead to contamination of aquatic and soil environments, thereby jeopardizing ecological stability and posing significant risks to human health. Therefore, it is imperative to prioritize the development and investigation of effective remediation technologies for tetracycline antibiotic pollution.

Currently, several technological routes exist for the elimination of tetracycline (TC) from wastewater, including adsorption, electrocoagulation, photocatalysis, and the Electro-Fenton (EF) process^{[1]-[2]}. Among these, the EF process, an advanced oxidation process (AOP), has been extensively investigated for the degradation of antibiotics utilizing highly oxidizing hydroxyl radicals ($\cdot\text{OH}$). However, the widespread application of this technology is constrained by its requirement to strictly maintain the pH within a narrow range of 2-3, alongside drawbacks such as electrode corrosion and significant external energy consumption^[3].

Coupling Fenton oxidation with microbial fuel cells (MFCs), known as the Bio-Electro-Fenton (BEF) process, presents a promising alternative. The BEF process is driven by the bioelectricity generated from MFCs, thereby operating without external power input. It enables the in-situ production of H₂O₂ through the oxygen reduction reaction (ORR) and facilitates the regeneration of Fe²⁺ via the reduction of iron at the cathode or on iron-composite electrodes. In contrast to homogeneous Fenton systems, heterogeneous Fenton processes offer a broader

applicable pH range and exhibit lower iron leaching rates. A primary research focus is thus the development of cathode catalysts for heterogeneous BEF systems aimed at further expanding the operable pH range and overcoming challenges associated with catalyst recovery^[4].

Layered double hydroxides (LDHs), two-dimensional ionic lamellar nanomaterials composed of positively charged host layers and interlayer anions, have attracted widespread attention for applications in adsorption, catalysis, photoelectrochemistry, and as ORR electrocatalysts due to their unique layered structure and tunable chemical composition.

Furthermore, the integration of photocatalytic systems can enhance the performance of BEF processes by increasing the yield of H₂O₂. The recent integration of BEF principles into photoelectrochemical systems, specifically through photoelectrochemical coupling, has emerged as a technology characterized by low operational costs and high degradation efficiency. Graphitic carbon nitride (g-C₃N₄, CN), known for its ability to enhance the photogeneration of H₂O₂, can be combined with LDHs to design composite photocatalysts^[5]. This synergy is anticipated to significantly boost overall photoelectrocatalytic performance.

2. Current Research Status

2.1. Applications and Hazards of Tetracycline

2.1.1. Applications of Tetracycline

As broad-spectrum molecular antibacterial agents, tetracycline antibiotics (TCs) exhibit extensive antimicrobial activity. Studies have shown that TCs exert their effects primarily at the molecular structural level by preventing the binding of aminoacyl-tRNA to the ribosomal acceptor site, thereby disrupting subsequent protein synthesis pathways and functional expression.

TCs demonstrate therapeutic efficacy against a wide range of pathogens, including Gram-positive and Gram-negative bacteria, as well as Rickettsia, Chlamydia, Mycoplasma, and Spirochetes. They are also used in the prevention of malaria, which is caused by Plasmodium falciparum. These characteristics make TCs a powerful tool in combating infectious diseases in humans^[6].

Another major application of TCs lies in livestock and poultry farming, where they are directly added to feed as growth-promoting agents^[7]. With strong governmental support for the animal husbandry sector, the industry has experienced significant expansion, leading to a sharp increase in the demand for veterinary antibiotics. According to incomplete statistics, due to the rapid development of animal husbandry, China has become one of the largest producers and consumers of veterinary antibiotics globally. Thus, TCs play a critically important role in both human and veterinary medicine production and usage.

2.1.2. Hazards of Tetracycline

With the continuously increasing use of tetracycline antibiotics (TCs), the issue of antibiotic residues has become increasingly prominent. TCs are widely employed in the treatment of human diseases such as upper respiratory tract infections, as well as in livestock and aquaculture as feed additives to promote growth, improve survival rates, and enhance breeding efficiency. However, this practice has led to the concerning presence of antibiotic residues in food products, posing significant risks.

Despite their benefits, the extensive use of TCs in animal husbandry and aquaculture has resulted in widespread antibiotic residue accumulation^[8]. Even at low concentrations, these residues contribute to the development of antimicrobial resistance (AMR), which not only reduces the efficacy of treatments but also increases medical costs and complicates disease management^[9].

Consequently, both humans and the environment are inevitably exposed to various antibiotic residues, leading to potential harm. Although antibiotics like TCs are essential medicines with relatively low acute toxicity, their chronic exposure raises serious public health concerns. Residual TCs have been detected in common food products including milk, eggs, and meat. Through bioaccumulation and transmission along the food chain, these residues may cause allergic reactions in humans. Some antibiotics even exhibit hormone-like effects and carry significant risks of carcinogenicity, teratogenicity, and mutagenicity. Long-term exposure can lead to adverse health effects such as tooth discoloration and liver damage, while also fostering resistance that compromises internal human microbiota^{[10]-[11]}.

3. Research on the Application of Bio-Electro-Fenton Systems in Antibiotic Wastewater Treatment

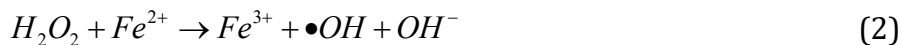
3.1. Introduction to Bio-electro-Fenton Technology

In recent years, the bio-electro-Fenton (BEF) process has garnered widespread attention as an efficient, energy-saving, and green technology for the removal of emerging contaminants such as antibiotics. The BEF system was first proposed by Zhu et al. in 2009^[12]. It typically consists of an anode chamber, a cathode chamber, a proton exchange membrane, and electrode materials. The anode chamber comprises an anode electrode, substrate, and microorganisms, while the cathode chamber contains a cathode electrode, electron acceptors, and organic pollutants. The cathode chamber is continuously aerated to supply dissolved oxygen required for reactions, and the two chambers are separated by a proton exchange membrane.

In the anode chamber, exoelectrogenic bacteria grow and proliferate on the anode, forming a bioanode. These bacteria serve as both biocatalysts and electricity generators. Among various exoelectrogenic bacteria, *Geobacter* and *Shewanella* are common species known for their extracellular electron transfer capabilities. These bacteria form biofilms on the electrode surface and transfer electrons through different mechanisms, including direct electron transfer (via outer membrane redox-active proteins such as c-type cytochromes or conductive pili acting as "nanowires") and mediated electron transfer (using endogenous or exogenous electron shuttles)^[13]. The exoelectrogenic bacteria oxidize substrates (from complex wastewater or simple compounds such as glucose), generating electrons and protons. The protons diffuse through the proton exchange membrane to the cathode chamber, while the electrons are transferred to the anode surface and then conducted to the cathode via an external circuit, where they participate in the oxygen reduction reaction (ORR).

In the cathode chamber, H_2O_2 is generated in situ and reacts with added iron scraps to initiate the Fenton reaction, producing hydroxyl radicals ($\cdot OH$). For instance, in a study treating wastewater containing p-nitrophenol, complete degradation was achieved within 12 hours using this mechanism. The BEF process effectively integrates bioelectrochemical systems with Fenton oxidation. In this system, exoelectrogenic bacteria at the anode oxidize organic matter, simultaneously releasing protons and electrons. The cathode accepts two electrons and protons to produce H_2O_2 in situ, which then reacts with Fe^{2+} to generate $\cdot OH$ for oxidizing organic pollutants. Hydrogen peroxide is produced in situ through the two-electron oxygen reduction reaction (ORR). Under acidic conditions (pH 2–3), H_2O_2 reacts with Fe^{2+} to yield highly oxidizing $\cdot OH$, which non-selectively degrades organic pollutants in wastewater. Simultaneously, electrons facilitate the reduction of Fe^{3+} to Fe^{2+} , as illustrated in Equations (1) to (3):





Depending on the type of reactor, BEF systems can be broadly categorized into several configurations: MFC-coupled electro-Fenton systems, microbial electrolysis cell (MEC)-coupled electro-Fenton systems, microbial reverse-electrodialysis cell (MRC)-coupled electro-Fenton systems, MFC-powered microbial electrolysis cell-electro-Fenton systems, and MFC-driven electro-Fenton systems. Among these, the MFC-coupled electro-Fenton system represents a classic BEF configuration. Compared to conventional electro-Fenton and Fenton processes, its most significant advantage lies in its ability to operate without an external power supply. Electrons are derived from exoelectrogenic bacteria in the anode, resulting in self-sustained current generation, and no external addition of H_2O_2 is required. Thus, the bio-electro-Fenton system demonstrates superior cost-effectiveness and environmental compatibility relative to other systems.

3.2. Selection of Cathode Materials for Bio-electro-Fenton Systems

An effective cathode material can broaden the operable pH range of BEF systems, reduce iron sludge production, lower charge transfer resistance, enhance electrical conductivity, promote the oxygen reduction reaction (ORR), and improve electricity generation performance. Therefore, ideal cathode materials should possess the following characteristics: high ORR catalytic activity, high specific surface area and porosity, high stability and corrosion resistance, good electrical conductivity, as well as low cost and easy availability. Current research indicates that various carbon-based materials—such as carbon felt (CF), graphite plates, carbon nanotubes, and gas diffusion electrodes—can serve as cathodes to improve and enhance ORR for in-situ H_2O_2 generation. These carbon-based catalytic cathodes often require modification, including surface oxygen functionalization^[14], heteroatom doping^[15], carbon-supported single-atom catalysts^[16], and defect or morphology engineering^[17]. Among them, carbon felt is widely used in BEF systems due to its large specific surface area, stable chemical properties, high electrical conductivity, tunable pore size, and resistance to acid and alkali corrosion.

The cathode materials in BEF systems generally consist of two functional components: one is the ORR catalyst that catalyzes the reduction of oxygen to generate H_2O_2 , and the other is the Fenton catalyst that promotes the decomposition of H_2O_2 to produce $\bullet OH$. However, BEF systems often suffer from low H_2O_2 yield and slow degradation kinetics. These limitations are primarily addressed by optimizing the ORR catalyst within the cathode material to improve the efficiency of H_2O_2 production. Studies have shown that layered double hydroxides (LDHs), two-dimensional ionic layered nanomaterials composed of positively charged host layers and interlayer anions, are widely used in adsorption, catalysis, photoelectrochemistry, and as ORR electrocatalysts owing to their unique layered structure and tunable chemical composition. With the introduction of transition metals, LDHs exhibit both oxidative and reductive catalytic activities. They can function as dual-function Fenton catalysts and be used to construct dual catalytic active sites, which accelerate the Fe^{2+}/Fe^{3+} cycle through reduction-regeneration mechanisms^[18]. Transition metals such as Mn, Fe, and Cu, with their multiple valence states and strong electron transfer capabilities, demonstrate excellent catalytic performance and are environmentally benign.

To address the aforementioned challenges in BEF systems, electrode modification is commonly employed to broaden the pH operating range, reduce iron sludge production, and enhance both treatment efficiency and adaptability. Currently, the most prevalent modification strategy involves immobilizing heterogeneous Fenton catalysts on electrodes to create catalytic

cathodes. Therefore, investigating the application of CuFeMn-LDHs as cathode catalysts in BEF systems over a wide pH range is of great significance.

Furthermore, Jiang et al^[19]. found that photocatalytic processes enabled complete degradation of phenol under natural pH conditions. Liu et al. reported that light irradiation extended the operable pH range of photocatalytic reactions to neutral conditions, thereby improving the in-situ generation and utilization efficiency of H₂O₂. Previous studies have proposed that graphitic carbon nitride (g-C₃N₄, CN) can enhance the photogeneration of H₂O₂. Among the five known structural forms of carbon nitride— α -C₃N₄, β -C₃N₄, cubic C₃N₄, pseudo-cubic C₃N₄, and g-C₃N₄,—the g-C₃N₄ configuration is the most stable. As an n-type semiconductor, g-C₃N₄ possesses a moderate bandgap (approximately 2.7 eV), suitable band edge positions, and a broad visible-light absorption range, enabling radical generation through water oxidation and reduction processes. In particular, its tunable bandgap enhances versatility in metal doping and facilitates the construction of heterojunctions with other semiconductors, thereby increasing active sites and improving photocatalytic activity. Research shows that g-C₃N₄, with its π -conjugated layered structure, exhibits good compatibility with various materials, high chemical stability, and flexibility in morphological modification, making it suitable for applications as an effective adsorbent, catalyst, and high-performance photoelectrocatalytic electrode^[20].

Designing composite photocathode catalysts by combining g-C₃N₄ with LDHs has become a research focus due to the excellent catalytic properties of both materials, which synergistically enhance photoelectrocatalytic performance^[21]. This approach improves carrier separation efficiency, facilitates electron transfer, accelerates the reduction rate of metal ions, and exposes more adsorption sites, H₂O₂ generation sites, and Fenton catalytic active sites. In summary, the integration of LDH and g-C₃N₄ to form LDH/CN composites demonstrates the potential to enhance the photocatalytic generation of H₂O₂ and improve the photoelectrocatalytic performance in Bio-electro-Fenton (BEF) systems.

3.3. A Study on the Treatment of Antibiotic Wastewater Using Bio-electro-Fenton Technology

Various technologies for the degradation of antibiotics in wastewater, such as adsorption, advanced oxidation processes (AOPs), and biological treatments, have been extensively studied. Among these, the electro-Fenton (EF) process—a type of AOP—has emerged as one of the most attractive methods for antibiotic removal due to its high degradation efficiency and excellent chemical stability. The EF technology is an electrochemical advanced oxidation process developed by integrating electrocatalysis with the traditional Fenton reaction. In the EF system, oxygen undergoes a two-electron oxygen reduction reaction (ORR) at the cathode under acidic conditions to generate H₂O₂. Subsequent reactions are identical to the traditional Fenton process: H₂O₂ reacts with externally added or in-situ generated Fe²⁺ to produce \cdot OH, which oxidizes organic pollutants into intermediate products and ultimately mineralizes them into CO₂ and H₂O. Importantly, the Fe³⁺ generated during the reaction can be reduced to Fe²⁺ at the cathode, enabling a cyclic process without the need for continuous addition of Fe²⁺ or H₂O₂.

Coupling Fenton oxidation with microbial fuel cells (MFCs) leads to the development of the bio-electro-Fenton (BEF) process, which is driven by MFCs and requires no external power supply. As a result, BEF technology overcomes the drawbacks of traditional Fenton processes, such as high sludge production and risks associated with H₂O₂ transportation. It offers significant advantages including high efficiency, environmental friendliness, energy savings, strong controllability, and good environmental compatibility. Research in this area has been increasing annually, and BEF has been successfully applied to degrade various pollutants. For instance, Midassil et al^[22]. achieved 200% removal of chloroquine and 93% total organic carbon (TOC) elimination using a carbon felt cathode and a boron-doped diamond anode in an EF system. Chen et al^[23]. employed EF as a pretreatment method to enhance the dewaterability of

activated sludge, demonstrating better performance than acid treatment and anodic oxidation, significantly improving sludge dewatering within 40–60 minutes. Yang et al^[24]. reported complete mineralization of 34.5 mg/L imatinib (an anticancer drug) after 8 hours of treatment using a graphene-modified carbon felt cathode.

However, the EF process still has several limitations. Similar to the traditional Fenton reaction, it operates effectively only within a narrow pH range. The current efficiency for H₂O₂ production at the cathode and the catalytic utilization efficiency are relatively low, resulting in limited ·OH generation and reduced degradation efficiency for organic pollutants. Additionally, external addition of Fe²⁺ is still required, and the conversion between Fe²⁺/Fe³⁺ inevitably leads to the formation of iron sludge. To enhance the performance of EF systems, broaden the applicable pH range, reduce iron sludge production, and address challenges in catalyst recovery, the development of efficient cathode catalysts is essential. Recent studies have shown that layered double hydroxides (LDHs), especially with the introduction of transition metals, exhibit both oxidative and reductive catalytic activities. These LDH-based catalysts are considered promising for expanding the pH application range in heterogeneous Fenton-like processes and reducing iron leaching. Transition metals such as Cu, Mn, and Fe, with their multiple valence states and strong electron transfer capabilities, demonstrate excellent catalytic performance and are environmentally benign.

Moreover, Hu et al^[25]. proposed that graphitic carbon nitride (g-C₃N₄) can enhance the photogeneration of H₂O₂. However, the photocatalytic efficiency of g-C₃N₄ is limited by its low specific surface area and high recombination rate of electron-hole (e⁻/h⁺) pairs. Previous studies have shown that designing composite photocatalysts by combining g-C₃N₄, with LDHs can significantly improve photoelectrocatalytic performance. This approach enhances charge carrier separation efficiency, facilitates electron transfer, accelerates the reduction rate of metal ions, and exposes more adsorption sites, H₂O₂ generation active sites, and Fenton catalytic centers. Therefore, LDH/CN composite photocatalysts, composed of g-C₃N₄, and LDHs, can promote the photogeneration of H₂O₂ in BEF systems and enhance photoelectrocatalytic performance, offering a promising strategy to address the limitations of conventional EF systems.

4. Conclusion

Tetracycline antibiotics are widely used in animal husbandry and medical treatment, yet their residual presence poses multiple hazards. Effective removal of these residues is essential to prevent their accumulation in the environment, mitigate damage to ecosystems, improve food safety, reduce human exposure risks through the food chain, and curb the development and spread of bacterial antibiotic resistance. Therefore, the efficient elimination of antibiotic residues remains an urgent issue to be addressed.

This study begins with the electro-Fenton (EF) process, which is first integrated with microbial fuel cell (MFC) technology to form a bio-electro-Fenton (BEF) system. This system is further enhanced by coupling with a composite photocatalyst composed of g-C₃N₄, and LDHs, resulting in the construction of an LDH/CN photo-bio-electro-Fenton system for the degradation of tetracycline antibiotics. This integrated system represents a highly promising approach, enabling cost-effective antibiotic removal over a broad pH range. Moreover, the MFC component provides green and sustainable bio-energy to power the system, aligning with environmental and economic sustainability goals while reducing energy consumption. The proposed system offers novel insights into the degradation performance of tetracycline and the underlying mechanisms of refractory organic wastewater treatment via BEF technology.

References

- [1] A. Balakrishnan, M. Chinthala, R.K. Polagani, D.V.N. Vo, Removal of tetracycline from wastewater using g-C₃N₄, based photocatalysts: a review, *Environ. Res.* 216(2023) 114660.
- [2] Z. Song, Y.L. Ma, C.E. Li, The residual tetracycline in pharmaceutical wastewater was effectively removed by using MnO₂/graphene nanocomposite, *Sci. Total Environ.* 651 (2019) 580–590.
- [3] Brillas, E., 2022. Progress of homogeneous and heterogeneous electro-Fenton treatments of antibiotics in synthetic and real wastewaters. A critical review on the period 2017-2021. *Sci. Total Environ.* 819,153102.
- [4] He, J., Yu, D., Zou, X., Wang, Z., Zheng, Y., Liu, X., et al., 2022. Degradation intermediates of Amitriptyline and fundamental importance of transition metal elements in LDH-based catalysts in Heterogeneous Electro-Fenton system. *Sep. Purif. Technol.* 283, 1202251–12022510.
- [5] Hu, J., Zhang, P., Yang, T., Cai, Y., Qu, J., Yang, X., 2022. Screen superior ultra-thin g-C₃N₄, material for photocatalytic in-situ H₂O₂ production to remove tetracycline. *Appl. Surf. Sci.* 576, 151841.
- [6] Han, C.H., Park, H.D., Kim, S.B., Yargeau, V., Choi, J.W., Lee, S.H., et al., 2020. Oxidation of tetracycline and oxytetracycline for the photo-Fenton process: their transformation products and toxicity assessment. *Water Res.* 172, 115514.
- [7] Wu, Y., Zhao, X., Huang, S., Li, Y., Zhang, X., Zeng, G., et al., 2021. Facile construction of 2D g-C₃N₄, supported nanoflower-like NaBiO₃ with direct Z-scheme heterojunctions and insight into its photocatalytic degradation of tetracycline. *J. Hazard Mater.* 414, 125547.
- [8] Chen, J., Xu, J., Liu, T., Qian, Y., Zhou, X., Xiao, S., et al., 2020. Selective oxidation of tetracyclines by peroxymonosulfate in livestock wastewater: kinetics and non-radical mechanism. *J. Hazard Mater.* 386, 121656.
- [9] Wang, J.-S., Yi, X.-H., Xu, X., Ji, H., Alanazi, A.M., Wang, C.-C., et al., 2022b. Eliminating tetracycline antibiotics matrix via photoactivated sulfate radical-based advanced oxidation process over the immobilized MIL-88A: batch and continuous experiments. *Chem. Eng. J.* 431, 133213.
- [10] Li, S., Yang, Y., Zheng, H., Zheng, Y., He, C.S., Lai, B., et al., 2022c. Introduction of oxygen vacancy to manganese ferrite by Co substitution for enhanced peracetic acid activation and 10₂ dominated tetracycline hydrochloride degradation under microwave irradiation. *Water Res.* 225, 119176.
- [11] Mu G, Liu H, Xu L, et al. Matrix solid-phase dispersion extraction and capillary electrophoresis determination of tetracycline residues in milk[J]. *Food analytical methods*, 2012, 5(1): 148-153.
- [12] Zhu Xiuping, Ni Jinren. Simultaneous processes of electricity generation and p-nitrophenol degradation in a microbial fuel cell[J]. *Electrochemistry communications*, 2009, 11(2): 274–277.
- [13] Fatemeh Soltani, Nahid Navidjouy, Mostafa Rahimnejad. A review on bio-electro-Fenton systems as environmentally friendly methods for degradation of environmental organic pollutants in wastewater[J]. *RSC Advances*, 2022, 12(9): 5184–5213.
- [14] Lu Zhiyi, Chen Guangxu, Siahrostami Sanira, Chen Zhihua, Cui Yi. High-efficiency oxygen reduction to hydrogen peroxide catalysed by oxidized carbon materials[J]. *Nature Catalysis*, 2018, 1: 156–162.
- [15] Qin Meichun, Fan Shiyong, Wang Liang, Gan Gguoqiang, Li Xinyong. Oxygen and nitrogen co-doped ordered mesoporous carbon materials enhanced the electrochemical selectivity of O₂ reduction to H₂O₂[J]. *Journal of Colloid and Interface Science*, 2019, 562(42): 540–549.
- [16] Jung Euiyeon, Shin Heejong, Lee Byoung-Hoon, Efremov Vladimir, Lee Suhyeong, Lee Hyeon Seok, Kim Jiheon, Hooch Antink Wytse, Park Subin, Lee Kug-Seung, Cho Sung-Pyo, Yoo Jong Suk, Sung Yung-Eun, Hyeon Taeghwan. Atomic-level tuning of Co-N-C catalyst for high-performance electrochemical H₂O₂ production[J]. *Nature Materials*, 2020, 19(4): 436–442.
- [17] Liu Yang, Zhang Jianshuo, He Suqiong, Cui Yaqi, Guan Lunhui. Defect engineering of single-walled carbon nanohorns for stable electrochemical synthesis of hydrogen peroxide with high selectivity in neutral electrolytes[J]. *Journal of Energy Chemistry*, 2021c, (3): 118–123.
- [18] Ji, Y., Song, Z., Xu, Y., Zhang, Y., 2022. Cu-Fe LDHs/Bi₂WO₆ composite for superior photo-Fenton Rhodamine B removal through combination of photogenerated electrons and multivalent bimetal redox for accelerating Fe³⁺/Fe²⁺ cycles. *J. Alloys Compd.* 925, 166655.

- [19] Jiang, Z., Wang, L., Lei, J., Liu, Y., Zhang, J., 2019. Photo-Fenton degradation of phenol by CdS/rGO/Fe²⁺ at natural pH with in situ-generated H₂O₂. *Appl. Catal., B* 241, 367–374.
- [20] Liang Fenfen, Zhu Yongfa. Enhancement of mineralization ability for phenol via synergetic effect of photoelectrocatalysis of g-C₃N₄ film[J]. *Applied Catalysis B Environmental*, 2016, 180: 324–329.
- [21] Shakeel, M., Arif, M., Yasin, G., Li, B., Khan, H.D., 2019. Layered by layered Ni-Mn-LDH/g-C₃N₄, nanohybrid for multi-purpose photo/electrocatalysis: morphology controlled strategy for effective charge carriers separation. *Appl. Catal., B* 242, 485–498.
- [22] Midassi S, Bedoui A, Bensalah N. Efcient degradation of chloroquine drug byelectro-Fenton oxidation: Effects of operating conditions and degradationmechanism [J]. *Chemosphere*, 2020, 260:127558.
- [23] Chen Y, Chen H, Li J, Xiao L. Rapid and efficient activated sludge treatment by electro-Fenton oxidation[J].*Water Research*,2019,152:181-190.
- [24] Yang W, Zhou M, Otran N, Li Y, Otruran M A. Electrocatalytic destruction of pharmaceutical imatinib by electro-Fenton process with graphene-based cathode[J].*Electrochimica Acta*,2019,305:285-294.
- [25] Hu, J., Zhang, P., Yang, T., Cai, Y., Qu, J., Yang, X., 2022. Screen superior ultra-thin g-C₃N₄, material for photocatalytic in-situ H₂O₂ production to remove tetracycline. *Appl. Surf. Sci.* 576, 151841.