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Mechanistic Insights into Photodegradation of the Quinolone Antibiotic Cinoxacin in the Aqueous

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ABSTRACT: *The environmental persistence and transformation pathways of quinolone antibiotics are critical issues for ecological risk assessment. This study investigated the photodegradation of cinoxacin, a frequently detected yet less-studied quinolone, by combining kinetic experiments, product identification, and quantum chemical calculations to unravel its aquatic photochemical behavior. Results indicate that photodegradation kinetics are profoundly influenced by solution pH, which regulates the chemical speciation of cinoxacin. The protonated form prevalent under acidic conditions degrades faster, with the vinyl group departure identified as the dominant pathway (energy barrier: 5.6 kcal/mol).* NO_2^- *significantly promotes degradation through photosensitization, whereas common metal cations (e.g.,* Cu^{2+}*) and humic acid inhibit the process via coordination complexation and radical scavenging, respectively. Three potential reaction pathways, decarboxylation,vinyl group departure, and oxygen-heterocycle ring-opening, were computationally simulated. The theoretical energy profiles are consistent with the experimentally identified intermediates, confirming the proposed mechanisms. This research elucidates the pH-dependent pathway switching and the role of co-existing water constituents in cinoxacin photolysis, providing a fundamental mechanistic understanding essential for predicting the environmental fate and designing remediation strategies for this class of emerging contaminants.*

KEY WARDS: *Cinoxacin; Photodegradation, Transition state theory, Reaction pathway*

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I. INTRODUCTION

Quinolones (QNs), a class of broad-spectrum antibacterial drugs, are widely used in human medicine and animal husbandry. Their widespread use and continuous release have led to increasingly severe environmental pollution and bacterial resistance. QNs have been detected in various environmental media[1-3], including surface water, groundwater, soil, landfill surroundings, and forested areas, with concentrations ranging from ng/L to μg/L. Thesefindings highlight their environmental persistence in the environment and potential ecological risks. Among numerous degradation pathways, photodegradation is one of the key natural processes for transforming QNs in aquatic environments. Its efficiency and mechanisms are regulated by multiple factors, including the antibiotic's chemical speciation, environmental pH[4], coexisting ions, and reactive oxygen species (ROS)[5]. Although the photochemical properties of some common QNs (e.g., ciprofloxacin and norfloxacin) have been preliminarily investigated, research on their degradation pathways and environmental effects has remained focused on a few model compounds. This limited scope underscores the necessity of investigating other prevalent yet understudied QNs.

Cinoxacin, a quinolone antibiotic belonging to the cinnoline carboxylic acid class, exerts its antibacterial effect by inhibiting bacterial DNA synthesis and is clinically used to treat urinary tract infections. In recent years, the average total concentration of quinolone antibiotics detected in surface water bodies of the Yellow River basin has been reported as 223.51 ng/L, among which cinoxacin accounts for a relatively high proportion[6]. This compound has been frequently detected in influent and effluent samples from typical wastewater treatment plants, with concentrations ranging from 14.3 ng/L to 117 ng/L[7], indicating incomplete removal during conventional wastewater treatment processes and a potential for continuous discharge into aquatic environments, thereby posing long-term ecological risks. However, compared with other common QNs, studies on the degradation behavior and reaction mechanism of cinoxacin under natural light conditions are still relatively scarce. In particular, the transformation pathways, and microscopic reaction mechanisms of cinoxacin under the influence of complex environmental factors have not been systematically elucidated. This hinders accurate predictions of its environmental persistence, degradation product toxicity, and ecological effects, and constrains the development of targeted environmental remediation strategies.

Therefore, this study systematically investigates the photodegradation kinetics and mechanisms of cinoxacin in aquatic environments through a multi-faceted strategy combining experimental analysis and theoretical calculations. The effects of key environmental factors such as initial concentration, pH, metal ions and anions (e.g., NO_2^-) on the photodegradation behavior of cinoxacin are investigated in water. Utilizing high-performance liquid chromatography-mass spectrometry (HPLC-MS), photolysis intermediates are identified and potential degradation pathways are proposed. Combined with quantum chemical calculations, the energy barriers of different potential reaction pathways were simulated and compared to elucidate the rationality of dominant degradation channels at the electronic structure level. This study not only has the potential to address the research gap concerning the photochemical environmental behavior of cinoxacin, but also provides new methods and perspectives for a deeper understanding of the photochemical transformation patterns of QNs. Consequently, it offers a crucial scientific basis for developing efficient and precise environmental pollution control technologies and ecological risk assessment systems.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

2.1 Identifying and removing the trend in the mean daily soil water level.

2.1.1 Influence of environmental factors.

In order to systematically investigate the photodegradation behavior of cinoxacin in aqueous solution and the influence of key environmental factors, the effects of initial concentration, pH (adjusted using 0.1 mol/L NaOH and HCl solutions), cations (Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}), anions (Cl^-, CO_3^{2-}, SO_4^{2-}, NO_2^-) and humic acid (HA) were evaluated. To investigate the influence of the initial concentration on the photodegradation reaction, solutions with concentrations of 10, 20, and 40 mg/L were prepared. Five different pH values within the range of 3 to 11 were tested. The cations and anions wereused in the form of chloride and sodium salts, respectively, and the concentrations of cinoxacin, cations, and anions were all set at 20 mg/L.The concentration of cinoxacin in the reaction system was determined by UV-Vis spectroscopy and quantified based on the standard curve. The photolysis experiments were conducted under a xenon light source (PLS-SXE300/300UV). Samples were taken and analyzed at 0, 15, 30, 45, and 60 min of illumination. Except for the pH-dependent experiments, all other experiments were conducted at pH 6. Analytical-grade chemical reagents and ultra-pure water were used in all experiments.

2.1.2 Identification and Analysis of Photodegradation Intermediates.

A cinoxacin (CIN) solution (20 mg/L) was irradiated with a xenon lamp for 0, 20 and 60 min. The degradation products were then analyzed by HPLC-MS. HPLC analysis was performed using an Agilent 1290 Infinity system equipped with an autosampler, a binary pump, and a diode array detector (DAD), with the detection wavelength set at 268 nm. Chromatographic separation was conducted on a reversed-phase C18 column (250 mm × 4.6 mm, 5 μm) with a methanol-water gradient elution program (20% to 95% methanol) at a flow rate of 0.8 mL/min and an injection volume of 10 μL. High-resolution mass spectrometry (HRMS) analysis was performed in positive ion full-scan mode.Based on the HPLC-MS product analysis, the photodegradation pathway of cinoxacin was systematically elucidated.

2.2 *Computational Methodology*.

All calculations were carried out using the Gaussian 09 software package[8].The ground-state (S_0) geometries were optimized using density functional theory (DFT) at the B3LYP-D3/def2SVP level, incorporating Grimme's D3 dispersion correction. Excited-state properties were assessed with time-dependent DFT (TD-DFT), employing the same functional and basis set. To simulate aqueous conditions, the IEF-polarizable continuum model (IEF-PCM) was utilized[9]. Vibrational frequency analyses performed at the same theoretical level confirmed stationary points. Minimum-energy structures exhibited no imaginary frequencies, whereas transition states (TS) were characterized by a single imaginary frequency. For selected TS structures, intrinsic reaction coordinate (IRC) calculations were performed to validate reaction pathways. Final single-point energy evaluations for reactants, transition states (TS), and products were conducted using the B3LYP-D3/def2TZVP method, providing comprehensive thermodynamic data for the reactions.

III. RESULTS AND DISCUSSIONS

3.1 *Photodegradation Kinetics of Cinoxacin.*

The photodegradation behavior of cinoxacin was systematically evaluated under various controlled conditions. Based on different reaction pathways, the photodegradation of antibiotics in water can be categorized into direct photolysis, sensitized photolysis, and indirect photolysis[10]. The initial concentration is a key factor influencing the degradation kinetics and the dominant mechanism: increasing the concentration usually reduces the number of photons available for a single molecule and the total amount of reactive oxygen species (ROS) in the system. A decrease in the observed reaction rate constant with increasing concentration typically indicates the significant contribution of sensitized photolysis, whereas the opposite trend suggests the dominance of direct photolysis[11]. Therefore, clarifying the effect of initial concentration on the photodegradation kinetics of cinoxacin is essential for identifying the dominant reaction mechanism.

To establish a basis for quantification, the spectral properties of cinoxacin were first characterized. In this study, UV-vis and fluorescence/phosphorescence spectra were used to characterize the spectral characteristics of cinoxacin (Fig. 1), based on which a standard curve was plotted for subsequent concentration quantification. As shown in Fig. 1a-b, after 60 minof irradiation, the degradation rates were 11.3%, 18.1%, and 21.4% for initial concentrations of 10, 20, and 40 mg/L, respectively. The degradation rate increased with the initial concentration, which contrasts with the behavior of most quinolones reported in the literature. It is speculated that the cinoxacin molecule may contain groups (carboxyl group or double bond) that are more easily photoexcited, or that it may be more prone to intramolecular energy transfer after excitation, leading to more significant chain reactions at higher concentrations and thus accelerating the overall degradation process[12]. This observed positive correlation suggests a complex photodegradation mechanism potentially involving concentration-dependent processes.

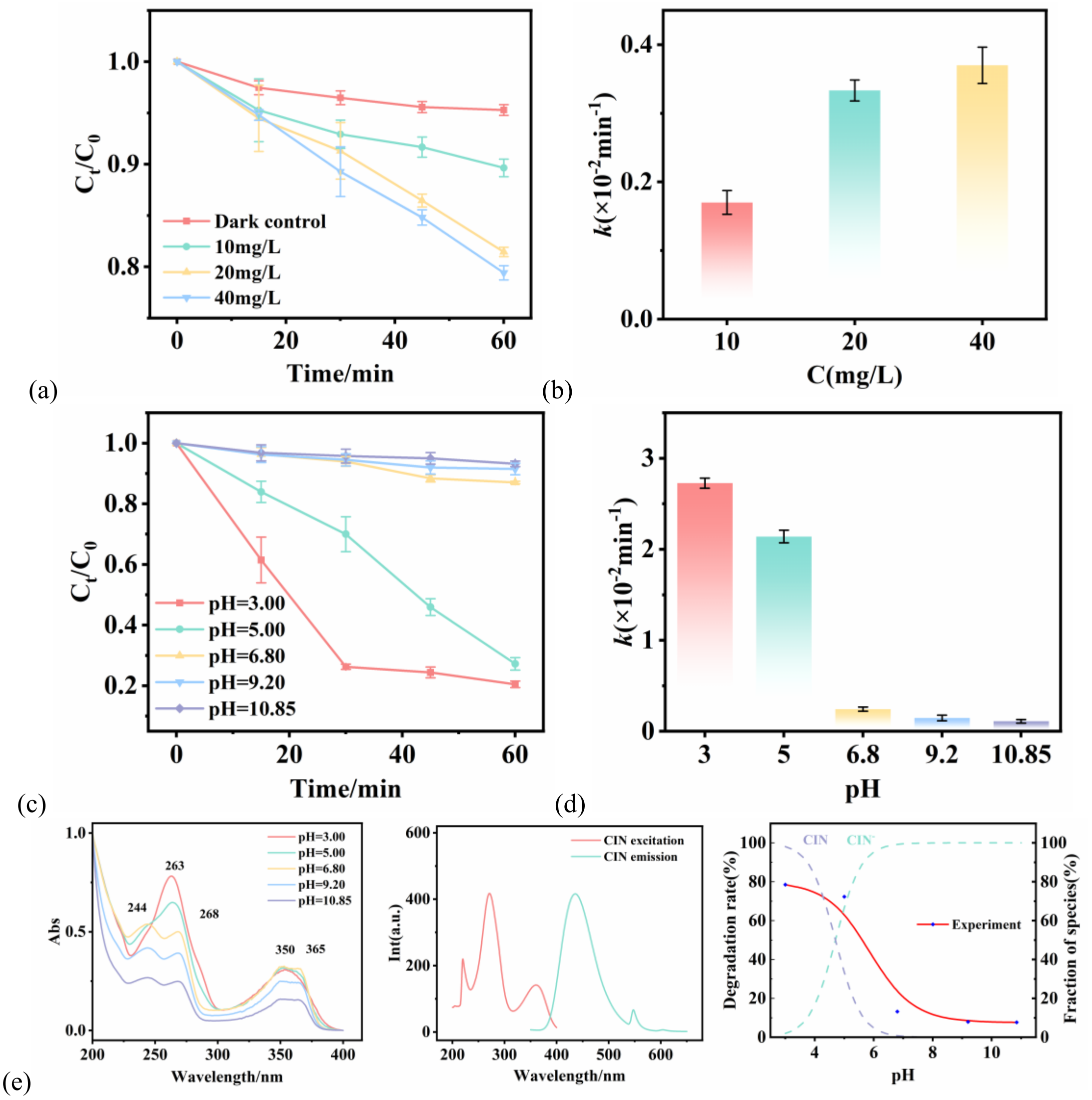


Figure 1: Photodegradation reactions of cinoxacin under different initial concentrations (a-b), photodegradation reactions under different solution pH values (c-d), the optical analysis of cinoxacin and the ion distribution curves and degradation rates under different pH values (e).Error bars indicate the standard deviation of three replicate experiments.

3.2 *pH Influence on Photodegradation Efficiency.*

Cinoxacin can exist in two forms depending on the solution pH: molecular form and anion form. To investigate the effect of pH on the photodegradation process, five CIN solutions with pH values ranging from 3 to 11 were prepared by adjusting the pH with sodium hydroxide and hydrochloric acid, and then exposed to a xenon light source for 0, 15, 30, 45, and 60 min. The residual concentrations were determined using a standard curve. As shown in Fig. 1c-d, the photodegradation rate of CIN gradually decreased with increasing solution pH during the 60 min irradiation.

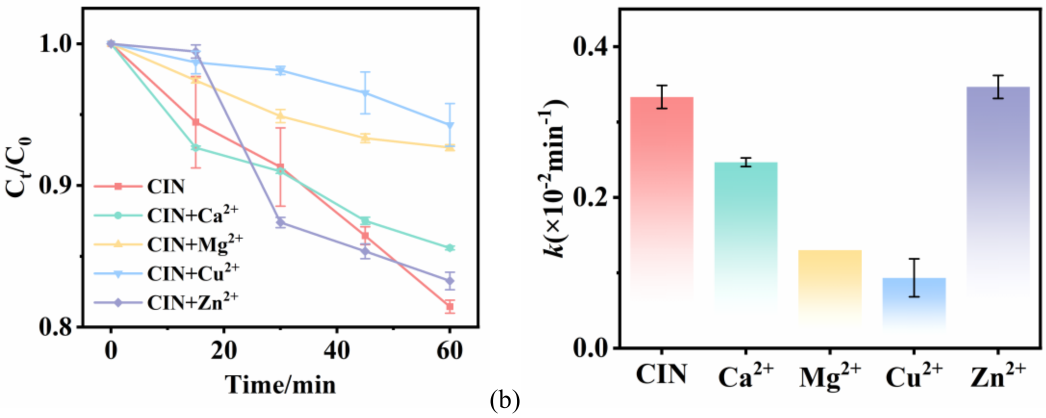
The species distribution was analyzed to interpret the pH-dependent behavior. The species distribution curve of CIN was plotted according to the pKa (4.7)[13] and the degradation rate versus pH curve was predicted by fitting the photolysis data (Fig. 1e). When the pH was below 4.7, CIN existed primarily in molecular form in the aqueous solution and exhibited maximum absorption at 263 nm under acidic conditions. The molecular form of CIN has stronger light absorption and is more likely to absorb photons to reach an excited state, resulting in a faster observed photodegradation rate under acidic conditions. As the pH increased, the anionic form became dominant, with the absorption peaks shifted to 244 nm, 268 nm and 350 nm under neutral and alkaline conditions. This spectral change may be related to its existing form in different pH solutions and the associated energy changes in the ground state and excited state, which consequently lead to differences in reaction rates. Thus, differences in quantum yield caused by pH-regulated changes in the chemical form of CIN are the main reason for the significant variation in the photodegradation behavior under different pH conditions. Since the pH in natural water environments typically ranges from 6 to 8, subsequent experiments were conducted at pH 6 to simulate near-natural conditions, balancing degradation efficiency with environmental relevance while ensuring effective pollutant degradation and minimizing secondary pollution risks.

3.3 *Effects of Common Aquatic Constituent.*

Photodegradation serves as an important pathway for antibiotics degradation in water. Components such as metal ions, inorganic ions, and natural organic matter commonly present in natural water bodies can affect the photodegradation kinetics of antibiotics through various mechanisms such as photosensitization, reactive oxygen species generation, and coordination complexation. In this study, natural water chemical conditions were simulated to evaluate the effects of representative dissolved substances on the photodegradation of cinoxacin, and the underlying mechanisms were elucidated based on the kinetic data.

3.3.1Role of Metal Cations.

The influence of metal cations on the photodegradation of CIN was investigated, and the results are shown in Fig. 2. Ca^{2+}, Mg^{2+} and Cu^{2+} all exhibited inhibitory effects on the photodegradation of CIN. After 60 min, the degradation rates decreased by 3.6%, 10.6%, and14.1%, respectively. Little effect of Zn^{2+} on the CIN photodegradation was observed in the experiments.The common 3-carboxyl and 4-carbonyl groups in quinolone antibiotics can serve as coordination sites, forming 1:1 or 1:2 complexes with divalent metal ions[14]. This complexationprocess is regulated by solution pH, which affects the composition and stability of the complexes[15]. Under aqueous conditions, the ionic form of CIN is conducive to the electrostatic attraction and coordination with metal ions. Among the four metal ions, Cu^{2+} exhibited the strongest inhibitory effect, highlighting the importance of metal complexation in modulating photodegradation kinetics. This can be attributed to two aspects: first, its vacant d orbitals endow it with a stronger excited state quenching ability; and second, it forms a relatively stable coordination complex with CIN. These factors jointly resulted in a significant reduction in the photodegradation rate.

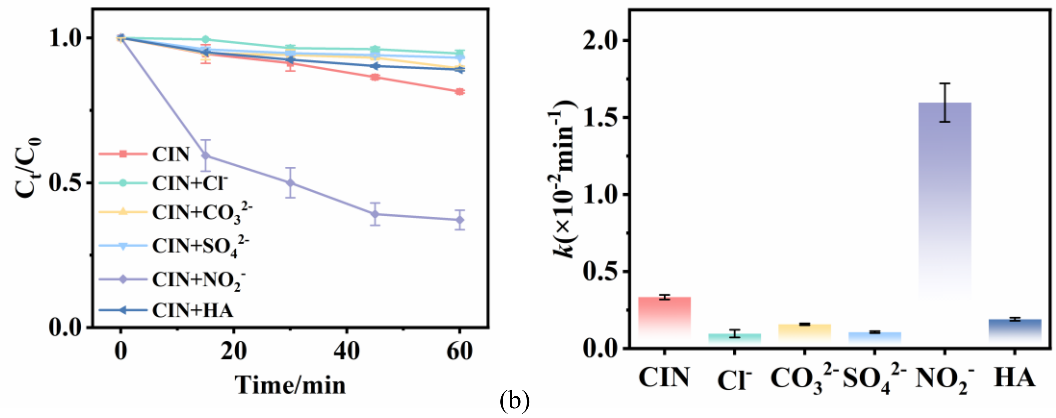


(a) (b)

Figure 2: Photodegradation reactions of cinoxacin in the presence of different cations. Error bars indicate the standard deviation of three replicate experiments.

3.3.2Effects of Anions and Humic Acid.

The effects of different anions and humic acid (HA) on the photodegradation of CIN are shown in Fig.



(a) (b)

Figure 3: Photodegradation reactions of cinoxacin in the presence of different anions and HA. Error bars indicate the standard deviation of three replicate experiments.

NO_2^- significantly promoted the photodegradation of CIN in water, as it can generate various reactive free radicals (e.g., ·OH, NO·) upon irradiation[16]. Under lightirradiation, the free radicals generated by NO_2^- possess relatively high oxidation potentials. NO_2^- acts as both a source and a scavenger of ·OH, playing a dual role in photolysis. However, in this experiment, its photosensitizing effect on CIN outweighed its quenching effect.

$$NO_2^- + hv \rightarrow [NO_2^-]^*$$
$$[NO_2^-]^* \rightarrow NO\cdot + O\cdot^-$$
$$O\cdot^- + H_2O \rightarrow \cdot OH + OH^-$$
$$NO\cdot + \cdot OH \rightarrow HNO_2$$
$$\cdot OH + NO_2^- \rightarrow NO_2\cdot + OH^-$$

Cl^-, SO_4^{2-}, CO_3^{2-} and HA all exhibited inhibitory effects on the photodegradation of CIN. The reaction between ·OH with Cl^- produces new chlorine radical speciesat a relatively high rate, thereby affecting the photodegradation process.

$$Cl^- + \cdot OH \rightarrow ClHO\cdot^-$$
$$ClHO\cdot^- + H_+ \rightarrow Cl\cdot + H_2O$$
$$Cl^- + Cl\cdot \rightarrow \cdot Cl_2^-$$

HA, CO_3^{2-} and Cl^- act as effective scavengers of reactive oxygen species, competitively consuming the oxidative free radicals involved in the degradation reaction, thereby interrupting the free radical chain reaction and reducing the degradation rate[17]. HA was found to reduce the light absorption of cinoxacin via the light-shielding effect[18]. These results demonstrate that common water constituents can significantly alter CIN photodegradation through competing radical pathways and light attenuation.

***Table I*. Photodegradation data of cinoxacin under different environmental conditions.**

Impact factors	Ingredients	Degradation rate	k(×10-2min-1)
Initial concentration	10 mg/L	11.3%	0.17±0.02
	20 mg/L	18.1%	0.33±0.02
	40 mg/L	21.4%	0.37±0.03
pH value	3.00	78.5%	2.73±0.06
	5.00	72.2%	2.14±0.07
	6.80	13.2%	0.24±0.02
	9.20	8.0%	0.15±0.03
	10.85	7.7%	0.11±0.02
Cations	CIN	18.1%	0.33±0.02
	CIN + Ca^{2+}	14.5%	0.25±0.01
	CIN + Mg^{2+}	7.5%	0.13
	CIN + Cu^{2+}	4.0%	0.09±0.03
	CIN + Zn^{2+}	18.2%	0.35±0.02
Anions and HA	CIN + Cl^-	4.2%	0.10±0.03
	CIN + CO_3^{2-}	10.8%	0.17±0.01
	CIN + SO_4^{2-}	6.9%	0.11±0.01
	CIN + NO_2^-	63.3%	1.60±0.12
	CIN + HA	11.3%	0.19±0.01

3.4 *LC-MS analysis of Photodegradation Pathways.*

Based on HPLC-MS analysis and existing studies on the photodegradation pathways of quinolone antibiotics, three mainintermediates generated during the photodegradation of cinoxacin were identified. On the basis of these findings, three potential photodegradation pathways of CIN in water under simulated sunlight were proposed, as illustrated in Fig. 4.

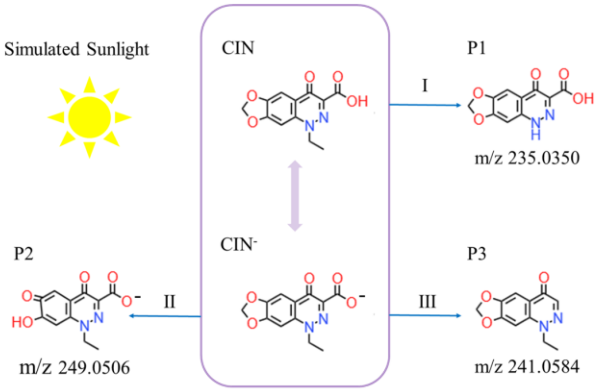


Figure 4: The degradation pathway of cinoxacin.

Pathway I involved the departure of the ethyl group from the structure of CIN, forming an intermediate with m/z 235 (P1)[12]. Pathway II showed a ring-opening reaction of the oxygen heterocyclic ring in CIN, generating a characteristic ion with m/z 249 (P2), which corresponds to a compound with a molecular weight of 248. This indicates that additional oxygen was incorporated during the photoreaction, which was consistent with the subsequent theoretical calculation analysis. Pathway III was the decarboxylation of CIN, yielding an intermediate with m/z 241 (P3). This pathway represents a typical photodegradation reaction for quinolone drugs, similar to the photodegradation mechanisms reported for norfloxacin (NOR) and ofloxacin (OFL)[19, 20]. The identification of these intermediates provides a foundation for proposing specific degradation pathways.

Table II: Summary of intermediate degradation products of cinoxacin in water.

Compound	Mode	m/z	Error (ppm)	RT/min	Intensity
CIN	ESI+	263.0663	-0.1	25.76	264054
P1	ESI+	235.0350	2.4	25.77	447
P2	ESI+	249.0506	0.9	24.87	4919
P3	ESI+	241.0584	-0.2	25.77	1010

3.5 *Theoretical Insights into Reaction Mechanisms.*

3.5.1Molecular electrostatic potential analysis.

Molecular electronic potential (MEP) analysis visually displays the distribution of surface charges on molecules, effectively revealing the reactive sites for electrophilic/nucleophilic reactions and intermolecular interactions[21]. The MEP analysis of cinoxacin is shown in Fig. 5a. The golden dots represent the extreme points of positive charge, while the blue dots represent the extreme points of negative charge. The blue area (negative potential) is mainly concentrated around the oxygen atoms of the carboxyl group, indicating that the adjacent carbon atoms carry partial positive charges and are susceptible to nucleophilic attack. Conversely, carbon atoms in red areas are vulnerable to electrophilic attack. Notably, distinct negative potential points are observed near the oxygen atoms of the oxygen heterocycle. This suggests that the connected carbon atoms may be sensitive to nucleophiles (e.g., OH^-), which provides a theoretical basis for proposing the ring-opening reaction pathway of the oxygen heterocycle.

3.5.2Reaction pathway.

To elucidate the photodegradation mechanism of cinoxacin at the microscopic level, three possible photochemical reaction pathways were proposed and calculated (Fig. 5b). Path-1 involves proton transfer between the carboxyl group and a nearby water molecule, forming $-COO^-$, followed by decarboxylation. The C-C bond length increases from 1.51 Å in the reactant to 2.18 Å in the transition state, and ultimately reaches 3.15 Å in the product. The reaction energy barrier is 23.2 kcal/mol, and the product energy is 18.4 kcal/mol higher than that of the reactant, indicating that this is an endothermic reaction. Protonation of the N atom within the molecule facilitates the photoionization of its ethane moiety, yielding vinyl groups. Subsequently, the departure ofa vinyl group leads to Path-2. The initial bond length of the N-C bond in the reactant (1.56 Å) gradually extends to 2.10 Å in transition state and ultimately to 4.74 Å in the product. The reaction energy barrier is 5.6

kcal/mol, and the product energy is 12.4 kcal/mol lower, making this an exothermic reaction. The calculation results show that Path-2 is more favorable under acidic conditions, while Path-1 is more likely to occur under alkaline conditions. This is because cinoxacin exists in ionic form (pH > pKa) that favors Path-1, and in its molecular form (pH < pKa) that favors Path-2. The activation energies required for the two reactions satisfy $E_{aPath-2}<E_{aPath-1}$, indicating that the degradation rate of cinoxacin is faster in acidic environments. The calculation results are highly consistent with the experimental phenomenon observed in Section 3.2.

Based on product analysis and MEP results, ring-opening reactions of the oxygen heterocycle were also explored.Path-3 involves OH^- attack on a C atom of the oxygen heterocycle, leading to ring opening and formation of a product containing a carbonyl and a phenolic structure. The C-O bond (1.43 Å) in the reactant extends to 1.84 Å, and then an intermediate with an interatomic spacing of 2.66 Å is formed. Subsequently, another C-O bond (1.48 Å) in the intermediate extends to 1.85 Å, ultimately forming a product with an interatomic spacing of 2.76 Å. The first step has an energy barrier of 10.9 kcal/mol, and the second step has a barrier of 3.0 kcal/mol; the overall pathway is exothermic.

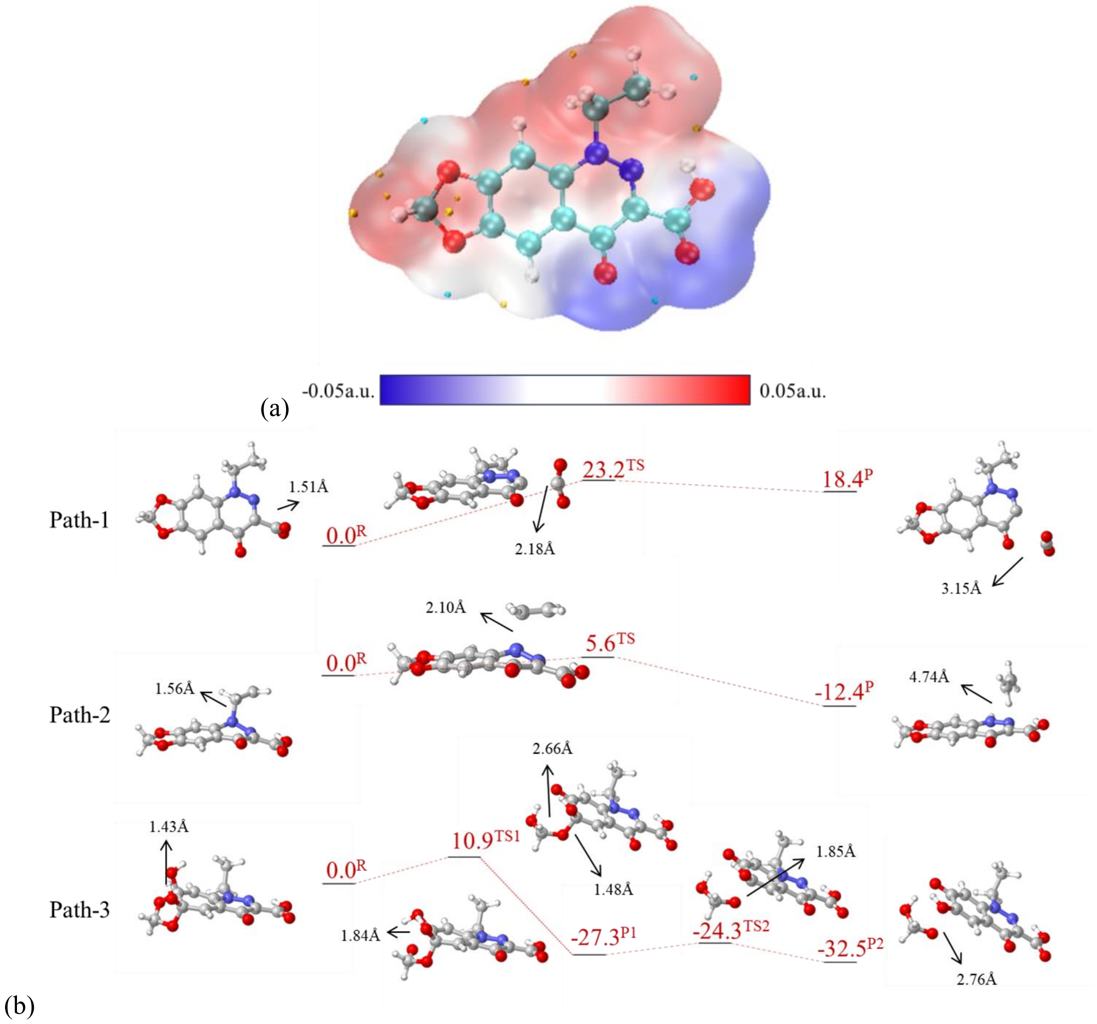


Figure 5: Electrostatic potential analysis of cinoxacin (a), Light reaction pathway of cinoxacin (b).

Theoretical calculations revealed the microscopic reaction pathways and energy barriers for cinoxacin photodegradation. The calculations indicated that alkaline conditions favor the high-barrier decarboxylation pathway (Path-1), while acidic conditions favor the low-barrier vinyl departure pathway (Path-2). This directly explains the experimental kinetic observation of faster degradation under acidic conditions. Under simulated environmental conditions (near-neutral to slightly acidic), vinyl departure (Path-2, barrier 5.6 kcal/mol) and oxygen heterocycle ring-opening (Path-3) are the most energetically favorable competitive primary reactions, which is consistent with the main product types identified by LC-MS. The synergy between experimental data and theoretical modeling provides a robust mechanistic understanding of cinoxacin photodegradation.

IV. CONCLUSIONS AND RECOMMENDATIONS

This study comprehensively revealed the photodegradation behavior of cinoxacin in aquatic environments through an integrated experimental and theoretical approach. The key findings demonstrated that solution pH served as the predominant factor governing the degradation pathway by dictating the molecular speciation of cinoxacin. Under acidic conditions (pH < pKa), the protonated molecular form facilitated the kinetically favored vinyl group departure pathway, which was characterized by a low activation energy of 5.6 kcal/mol. Conversely, under alkaline conditions, the anionic form shifted the preference toward a decarboxylation pathway. Among common aqueous constituents, nitrite (NO_2^-) acted as a potent photosensitizer, enhancing degradation via the generation of photochemically produced reactive oxygen species (e.g., ·OH). In contrast, metal cations (notably Cu^{2+}) and humic acid exhibited inhibitory effects, primarily through excited-state quenching, complexation, and light shielding. Quantum chemical calculations, validated by HPLC-MS product identification, successfully elucidatedthe energetic landscape of competing pathways, including ring-opening reactions of the oxygen heterocycle. This work clarifies the specific environmental transformation mechanisms of cinoxacin and provides a mechanistic framework for predicting the photochemical fate of quinolone antibiotics.

REFERENCES

[1]. Wu, X., Yuan, Z. Wang, S., (2023). "Prioritization, sources, and ecological risk of typical antibiotics in the Huai River, a Chinese major river: a warning about aquaculture", Environmental Science and Pollution Research, 30 (23), 64254-64264.

[2]. Chen, L., Lang, H., Liu, F., (2018). "Presence of Antibiotics in Shallow Groundwater in the Northern and Southwestern Regions of China", Ground water, 56 (3), 451-457.

[3]. Wang, Y., Lei, Y., Liu, X., (2022). "Sulfonamide and tetracycline in landfill leachates from seven municipal solid waste (MSW) landfills: Seasonal variation and risk assessment", The Science of the total environment, 825, 153936.

[4]. Rodríguez-López, L., Cela-Dablanca, R., Núñez-Delgado, A., (2021). "Photodegradation of Ciprofloxacin, Clarithromycin and Trimethoprim: Influence of pH and Humic Acids", Molecules (Basel, Switzerland), 26 (11).

[5]. Cai, T., Zhang, X., Zhang, S., (2023). "Photochemical behaviors of dissolved organic matter in aquatic environment: Generation, characterization, influencing factors and practical application", Environmental research, 231 (Pt 2), 116174.

[6]. An, X. D., Wu, J. Q., Pang, Y.. Tao, Y. R., (2025). "[Distribution and Risk Assessment of Antibiotics in Surface Waters of the Yellow River Basin]", Huan jing ke xue= Huanjing kexue, 46 (10), 6244-6253.

[7]. Wang, F., Lin, J., He, S., (2025). "Distribution characteristics, removal efficiency and risk assessment of antibiotics in typical sewage treatment stations in Hainan Province", Environmental Chemistry, 44 (9), 3253-3266.

[8]. Frisch, M. J., Trucks, G. W., Schlegel, H. B.. Scuseria, G. E., (2009). "Gaussian 09 Rev. A.02".

[9]. Tomasi, J., Mennucci, B.. Cance`s, E., (1999). "The IEF version of the PCM solvation method: an overview of a new method addressed to study molecular solutes at the QM ab initio level", Journal of Molecular Structure (Theochem) 464, 211-226.

[10]. Zhang, Z., Xie, X., Yu, Z.. Cheng, H., (2019). "Influence of chemical speciation on photochemical transformation of three fluoroquinolones (FQs) in water: Kinetics, mechanism, and toxicity of photolysis products", Water Research, 148, 19-29.

[11]. Zhang, H., Song, X., Liu, J.. Hao, C., (2019). "Photophysical and photochemical insights of the photodegradation of norfloxacin: The rate-limiting step and the influence of Ca(2+) ion", Chemosphere, 219, 236-242.

[12]. Tyutereva, Y. E., Snytnikova, O. A., Fedunov, R. G., (2023). "Direct UV photodegradation of nalidixic acid in aqueous solutions: A mechanistic study", Chemosphere, 334, 138952.

[13]. Scavone, J. M., Gleckman, R. A.. Fraser, D. G., (1982). "Cinoxacin: mechanism of action, spectrum of activity, pharmacokinetics, adverse reactions, and therapeutic indications", Pharmacotherapy, 2 (5), 266-72.

[14]. Huang, X., Xiong, Y., Peng, K., (2016). "The progress of antibiotics removal performance under the complexion effect of metal ions", Environmental Chemistry, 35 (1), 133-140.

[15]. Xiangfeng, H., Yongjiao, X., Kaiming, P., (2016). "The progress of antibiotics removal performance under the complexion effect of metal ions", Environmental Chemistry, 35 (1), 133-140.

[16]. Yang, G., Xu, C., Yang, L., (2023). "Degradation of Orange IV by UV photolysis in nitrite-containing wastewater: Influencing factors, mechanism, and response surface methodology", Process Safety and Environmental Protection, 169, 592-603.

[17]. Lian, L., Yao, B., Hou, S., (2017). "Kinetic Study of Hydroxyl and Sulfate Radical-Mediated Oxidation of Pharmaceuticals in Wastewater Effluents", Environmental science & technology, 51 (5), 2954-2962.

[18]. Han, Y., Li, L., Jin, L., (2023). "Direct and indirect photodegradation of bisphenol A in the presence of natural water components", Environmental geochemistry and health, 46 (1), 18.

[19]. Chen, X., Yao, J., Xia, B., (2020). "Influence of pH and DO on the ofloxacin degradation in water by UVA-LED/TiO(2) nanotube arrays photocatalytic fuel cell: mechanism, ROSs contribution and power generation", Journal of hazardous materials, 383, 121220.

[20]. Lian, L., Jiang, B., Xing, Y.. Zhang, N., (2021). "Identification of photodegradation product of organophosphorus pesticides and elucidation of transformation mechanism under simulated sunlight irradiation", Ecotoxicology and environmental safety, 224, 112655.

[21]. Lian, L., Jiang, B., Xing, Y.. Zhang, N., (2021). "Identification of photodegradation product of organophosphorus pesticides and elucidation of transformation mechanism under simulated sunlight irradiation", Ecotoxicology and environmental safety, 224.