

Article

Photodegradation of Sulfamethoxazole and Enrofloxacin under UV and Simulated Solar Light Irradiation

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Abstract: Antibiotics, as typical emerging contaminants, are frequently detected in the aquatic environment due to their widespread and massive use, posing potential risks to aquatic ecology and human health. To characterize the photodegradation behavior of typical antibiotics in water environment, sulfamethoxazole (SMX) and enrofloxacin (ENR) were selected in this study, and the photodegradation behaviors of these two antibiotics under UV and simulated solar light irradiation were investigated. The degradation rates of SMX under the two light sources were 0.235 min^{-1} and 0.024 min^{-1} , respectively, and ENR were 0.124 min^{-1} and 0.043 min^{-1} , respectively. Furthermore, the effects of typical influencing factors including different light intensities, initial concentrations, inorganic anions, and natural organic matter on the photodegradation behaviors of these two antibiotics were studied. The effect of several active substances was explored by adding several quenching agents, and the photodegradation pathway was proposed. The study of the photodegradation characteristics and mechanisms of these two antibiotics may help to provide a reference for the subsequent development of innovative and efficient photocatalytic materials and techniques to remove antibiotics from water.

Keywords: photodegradation; sulfamethoxazole; enrofloxacin; simulated solar light



Citation: Lin, X.; Zhou, W.; Li, S.; Fang, H.; Fu, S.; Xu, J.; Huang, J.

Photodegradation of Sulfamethoxazole and Enrofloxacin under UV and Simulated Solar Light Irradiation. *Water* **2023**, *15*, 517. <https://doi.org/10.3390/w15030517>

Academic Editor: Constantinos V. Chrysikopoulos

Received: 22 December 2022

Revised: 12 January 2023

Accepted: 24 January 2023

Published: 28 January 2023



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1. Introduction

As more and more studies [1–3] have suggested, organic micropollutants have become an important constraint on the quality and safety of the water environment. Antibiotics are a large typical class of organic micropollutants which have been detected with high frequency in various kinds of aquatic environment including drinking water [4,5], wastewater [6], surface water [7–9], and underground water [10] in various countries and regions including the United States, Europe, China, and Australia. A total of 70 antibiotics were detected and 13 antibiotics were frequently detected in surface water of the seven major rivers in China, with a maximum concentration of $360 \mu\text{g}\cdot\text{L}^{-1}$ [11].

The existence of antibiotics has become one of the major problems in the water environment, and will affect the survival of microorganisms and cause problems of antibiotic-resistant genes (ARGs) and antibiotic-resistant bacteria, thereby changing the microbial community in the water environment and potentially threatening the stability of the water ecosystem and human health. Many approaches including traditional techniques and newly developed methods such as adsorption, coagulation/flocculation/sedimentation, ozonation, photocatalytic degradation, electrochemical oxidation, and combined processes have been developed and applied to remove antibiotics from water [12–14]. Among them, photodegradation is an important pathway for the transformation of antibiotics in the natural aquatic environment, with many antibiotics including sulfonamides (SAs), quinolones

(QNs), macrolides (MLs), and others exhibiting significant photolysis under strong solar irradiation [15,16]. Photolysis proved to be efficient in the removal of antibiotics in water [17–19]. At present, the research on the photodegradation and photocatalytic degradation of antibiotics is still insufficient. It is necessary to carry out in-depth research on the photodegradation behavior of various typical antibiotics, and to develop corresponding technologies to remove the antibiotics in the aquatic environment and the risks they may pose to the aquatic ecology and human health.

Some recent studies have provided information about the photodegradation activity of different antibiotics. Many antibiotics, such as sulfamethoxazole (SMX), were observed to be photodegraded quickly in ultrapure water under simulated solar irradiation [20]. Several studies evaluated the matrix effect of some environmental factors including pH, concentrations, fulvic acids, and suspended matter on the photodegradation of antibiotics [20–22]. Although these studies reported the information about the degradation of certain antibiotics, they did not comprehensively explore the photodegradation characteristics of typical antibiotics under various light sources, the influence of different factors, and photodegradation mechanisms, which limits the application and engineering practices of relative photocatalytic technologies.

Therefore, this study aimed to investigate the photodegradation behavior of typical antibiotics including the influence on their photodegradation of various factors and the reaction mechanism. Sulfonamides and fluoroquinolones are the two kinds of antibiotics most frequently used and detected in surface water and wastewater in many countries [23,24]. Two typical antibiotics, sulfamethoxazole (SMX) and enrofloxacin (ENR), were selected as the research objects. First, the photodegradation reactions of SMX and ENR under different light sources including UV, simulated solar light, and simulated visible light conditions were studied. Subsequently, the effects and mechanisms of different factors including light intensities, initial concentrations of antibiotics, common inorganic anions, and natural organic matter in water on the photodegradation behavior of the two antibiotics were investigated. In order to further reveal the photolysis reaction mechanism of these two antibiotics, the photodegradation mechanism and byproducts were analyzed. The study could provide valuable information and reference for the development and application of efficient photocatalytic degradation technologies and materials, so as to alleviate the potential risks posed by emerging contaminants or micropollutants.

2. Materials and Methods

2.1. Materials and Reagents

Sulfamethoxazole (analytic standard) and enrofloxacin (analytic standard) were purchased from Sigma-Aldrich. Acetonitrile, methanol, and ethyl acetate were at least HPLC-grade and obtained from Sigma-Aldrich. Humic acid, sodium chloride, sodium sulfate, sodium nitrate, isopropyl alcohol, tert-Butanol (tBA), EDTA Disodium Salt (EDTA-2Na), and sodium azide were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water (resistivity $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$ at $25 \text{ }^\circ\text{C}$) was derived by a Merck Millipore water purification system and was used in related experiments. More details about the materials and reagents used in this study are introduced in Table S1.

2.2. Photodegradation of SMX and ENR

The photodegradation experiments of SMX and ENR were carried out under UV and simulated solar light supplied by a photochemical reactor (Phchem III, NBeT, Beijing NBET Technology Co., Ltd., Beijing, China) equipped with a 500 W UV lamp and 500 W Xenon lamp, respectively, as shown in Figure S1. A 50 mL measure of SMX or ENR aqueous solution was added into a 75 mL quartz tube and used to conduct photodegradation experiments. To explore the effect of different initial concentration of SMX or ENR on their photodegradation, different amounts of SMX or ENR were added to prepare solutions with $1\text{--}10 \text{ mg}\cdot\text{L}^{-1}$ SMX or ENR.

Micro-pollutants such as antibiotics have different photodegradation characteristics under different light sources due to the different emission spectral ranges and absorption spectra of chemicals. Considering that ultraviolet light and solar light are the two most common light sources in wastewater treatment processes and nature, ultraviolet light (with a 300 nm filter) and a xenon lamp (with a 400 nm filter) were adopted to study the photodegradation behavior of two typical antibiotics (SMX and ENR) under UV and simulated solar light irradiation.

2.3. Detection of SMX and ENR with HPLC

SMX and ENR were analyzed by high-performance liquid chromatography (HPLC) (Agilent HPLC 1200, Agilent Technologies, Santa Clara, USA) equipped with a variable wavelength detector (VWD) and a Shim-pack VP-ODS column (250 mm × 4.6 mm). The mobile phase for the detection of SMX consisted of acetonitrile (A) and 0.1% formic acid (B) with a ratio of 40:60 (*v/v*) at a flow of 1.0 mL·min⁻¹. The mobile phase for the detection of ENR consisted of acetonitrile (A) and 0.1% formic acid (B) with a ratio of 20:80 (*v/v*) at a flow of 1.0 mL·min⁻¹. The detection wavelength for SMX and ENR were set at 270 nm and 280 nm, respectively.

2.4. Photolysis Reaction Kinetic Curve

Substantial studies revealed that the photolysis reaction obeyed the kinetics of first-order reaction [18,25], and the concentration with time could be fitted with the following equations.

$$C/C_0 = e^{-kt} \quad (1)$$

$$-\ln(C/C_0) = kt \quad (2)$$

where C_0 represents the initial concentration of the pollutant (mg·L⁻¹), C represents the real-time concentration of the chemical (mg·L⁻¹), k represents the reaction rate constant, and t represents the reaction time (min).

3. Results and Discussions

3.1. Photodegradation and Kinetic Curves under Different Light Irradiation

UV light has a short wavelength and high photon energy, and many organic pollutants can be photodegraded significantly under UV light. UV-based advanced oxidation technology systems have also been widely studied and applied. According to the UV/Vis spectra of SMX and ENR (Figure S2), the absorption spectrum of the two antibiotics is mainly in the UV light region. Thus, photodegradation under UV light is theoretically easier and obvious. Under UV light, the time-dependent and kinetic fitting curves of the reaction concentrations of SMX and ENR are shown in Figure 1a,b, respectively. Both SMX and ENR were rapidly and obviously photodegraded, with the degradation efficiency reaching 96.6% and 81.8% within 15 min under UV light, respectively. The photodegradation reactions obeyed the pseudo-first-order kinetic law, with the fitted photodegradation reaction rate constants of SMX and ENR being 0.235 min⁻¹ and 0.124 min⁻¹, respectively. A relevant study [26] showed that different wavelengths of ultraviolet light had different photodegradation rates for organic micro-pollutants such as antibiotics, and the degradation rates of SMX and trimethoprim were vacuum UV > UV-C > UV-A, and the shorter the wavelength was, the stronger the ability of ultraviolet light to degrade organic micro-pollutants. Considering that the UV light generated by the high-pressure mercury lamp used in this study covers a wide range of UV wavelengths, the degradation effects under UV reported in related studies were basically similar to those in this study.

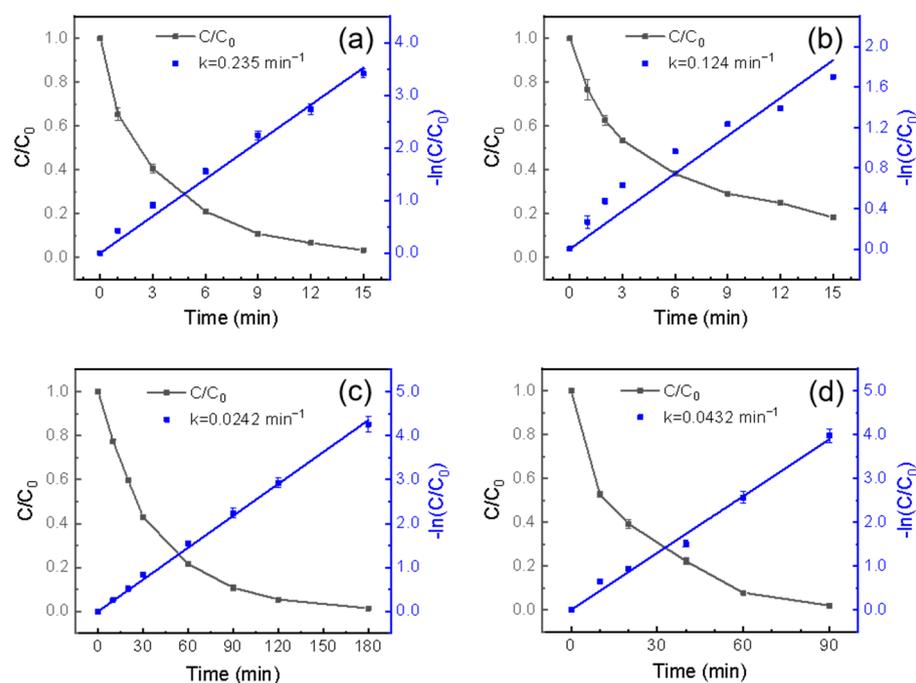


Figure 1. The photodegradation of (a) SMX and (b) ENR under UV irradiation, and (c) SMX and (d) ENR under simulated solar light.

Under simulated solar light irradiation, the concentration variations in SMX and ENR during the photodegradation reaction and the reaction kinetics fitting curves are shown in Figure 1c,d, respectively. The photodegradation rates of SMX and ENR under simulated solar light conditions were significantly slower than that under UV conditions, although the degradation was still obvious, and the degradation could be basically completed in correspondingly longer time. Kinetic fitting also showed that the degradation reactions of both were very consistent with pseudo-first-order kinetics, and the reaction rate constants were 0.0247 min^{-1} and 0.0430 min^{-1} , respectively.

The photodegradation behavior of antibiotics such as SMX and ENR in water had also been reported by several other studies. Oliveira et al. [20] used a 1500 W xenon lamp and a UV filter to simulate the solar light irradiation, and studied the photodegradation of SMX with an initial concentration of $100 \mu\text{g}\cdot\text{L}^{-1}$ in ultrapure water, and found that the reaction was highly consistent with pseudo-first-order kinetics. The reaction rate constant was measured to be $0.24\text{--}1.4 \text{ h}^{-1}$. The study by Niu et al. [22] also showed that the photodegradation reaction of SMX under a xenon lamp conformed to pseudo-first-order kinetics, and the reaction rate constant was 0.014 min^{-1} when the initial concentration was $5 \text{ mg}\cdot\text{L}^{-1}$. In the study of the photodegradation of ENR by Sturini et al. [27], the photodegradation reaction rate constant in tap water was measured to be $0.013\text{--}0.24 \text{ min}^{-1}$ under simulated solar light irradiation. The photodegradation reaction rates of the two antibiotics in this study under simulated solar light were basically similar to those reported in the literature, which indicated that the antibiotics had the potential to be photodegraded in nature, but the photodegradation of the antibiotics in the actual water was also affected by other composition and factors in the water environment.

3.2. Effect of Several Factors on the Photodegradation

In addition to the photodegradation characteristics of antibiotics under different light sources, several other important influencing factors were also taken into account in this study, including different light intensities, initial concentrations of antibiotics, common inorganic anions, and natural organic matter in water. In the experiment, a xenon lamp was used to simulate solar light as the light source, the current of the light source device was set to 8 A, and the reaction temperature was set to $25 \text{ }^\circ\text{C}$.

3.2.1. Photodegradation under Different Light Intensities

Light intensity directly affects the photodegradation rate of pollutants. In the experiment, the light intensity of the xenon lamp was changed by adjusting the current of the xenon lamp device, the xenon lamp was used to simulate the solar light condition, and four groups of different currents were set. As shown in Figure 2, the photodegradation rate of both SMX and ENR increased with the increase in current. The rate constant of the photodegradation reaction of SMX and ENR increased with increasing current. When the current intensified, the irradiation intensity of the xenon light source enhanced, and the number of photons per unit area and the absorption of photons by the pollutants in the reaction system also rose, resulting in an increase in the photolysis rate of the pollutants.

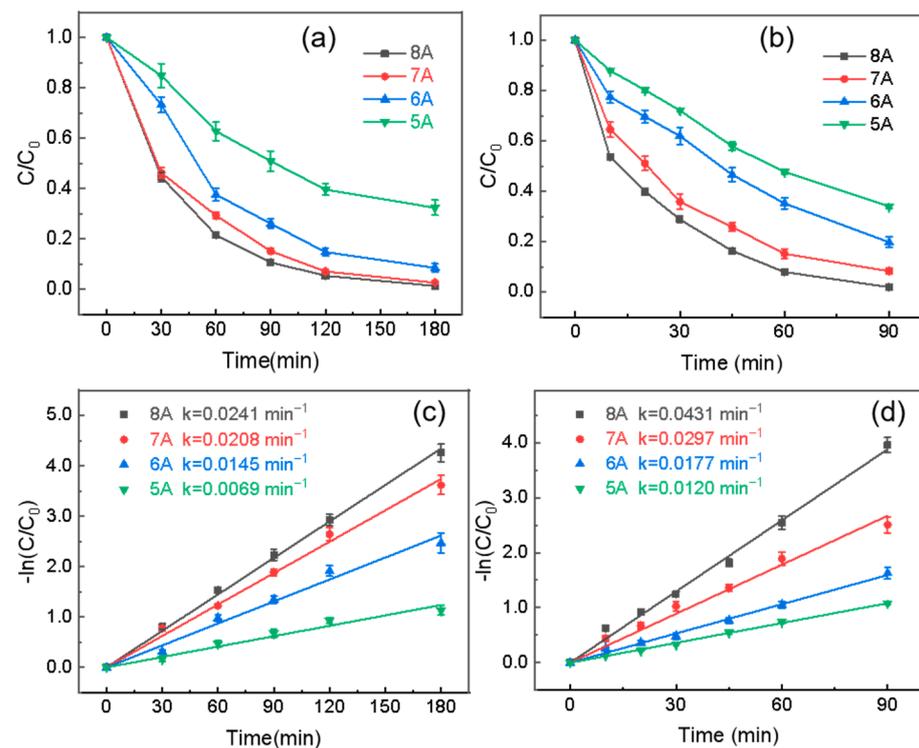


Figure 2. Effect of different currents on the photodegradation of (a) SMX and (c) ENR, and kinetic curves of (b) SMX and (d) ENR.

3.2.2. Effect of Initial Antibiotic Concentration

The initial concentration of the antibiotic affects the rate of its photodegradation reaction. In the study, the photolysis reaction rates during the photodegradation with different initial concentrations of antibiotics were investigated. The concentration variations in the two antibiotics and the corresponding kinetic fitting results are shown in Figure 3. The photodegradation rate constants of SMX and ENR generally decreased with an increase in their initial concentrations. When the initial concentration was $1 \text{ mg}\cdot\text{L}^{-1}$, the degradation constants of SMX and ENR were 0.0294 min^{-1} and 0.0768 min^{-1} , respectively, and the degradation rates of these two pollutants decreased when the concentration gradually increased. This was mainly because, when the initial concentration was low, the pollutants could fully absorb photons and react with the active groups in the reaction system. The group had a competitive effect, which reduced the unit degradation rate.

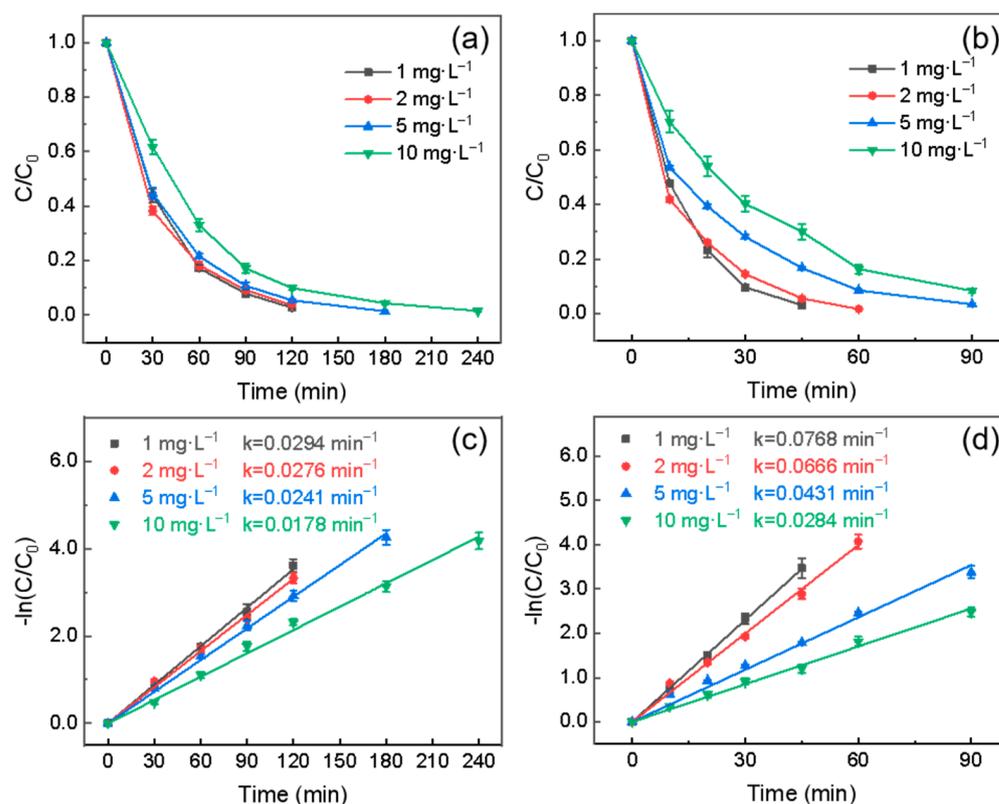


Figure 3. Effect of initial concentration of (a) SMX and (b) ENR on their photodegradation, and kinetic curves of (c) SMX and (d) ENR.

3.2.3. Effects of Common Inorganic Anions

The presence of common inorganic ions in water also affects the photodegradation reaction process and rate of pollutants. In the study, three common anions, Cl^- , SO_4^{2-} , and NO_3^- in natural water were selected as the objects to investigate the effects of different anions on the photodegradation of SMX and ENR under simulated solar light condition, with the results shown in Figure 4.

The three inorganic anions had inhibitory effects on the photodegradation of typical antibiotics. The degradation constant inhibition rates of Cl^- for SMX and ENR were 15.5% and 36.4%, respectively. The inhibitory effect of Cl^- on the photodegradation of antibiotics is mainly due to its competitive absorption of photons and the quenching effect of hydroxyl radicals. After reacting with $\cdot\text{OH}$, Cl^- with weak oxidation performance is generated, thereby reducing the photodegradation rate. The study of Oliveira et al. [20] also showed that the photodegradation rate of SMX in NaCl (21%) and synthetic brine was significantly lower than that in ultrapure water. Under the same pH of 7.3, the reaction constant dropped from 0.24 h^{-1} to 0.14 h^{-1} and 0.13 h^{-1} . Yang et al. [28] proved that Cl^- had an inhibitory effect on the photodegradation of SMX. Compared with the half-life in the blank experimental group, which was 112 min, the half-life under the condition of 0.342 M Cl^- was extended to 135 min, and the half-life under the condition of 0.582 M Cl^- was extended to 135 min. When it was increased to 212 min, SO_4^{2-} had a more obvious inhibitory effect, and the half-lives at the two concentrations were 313 min and 409 min, respectively.

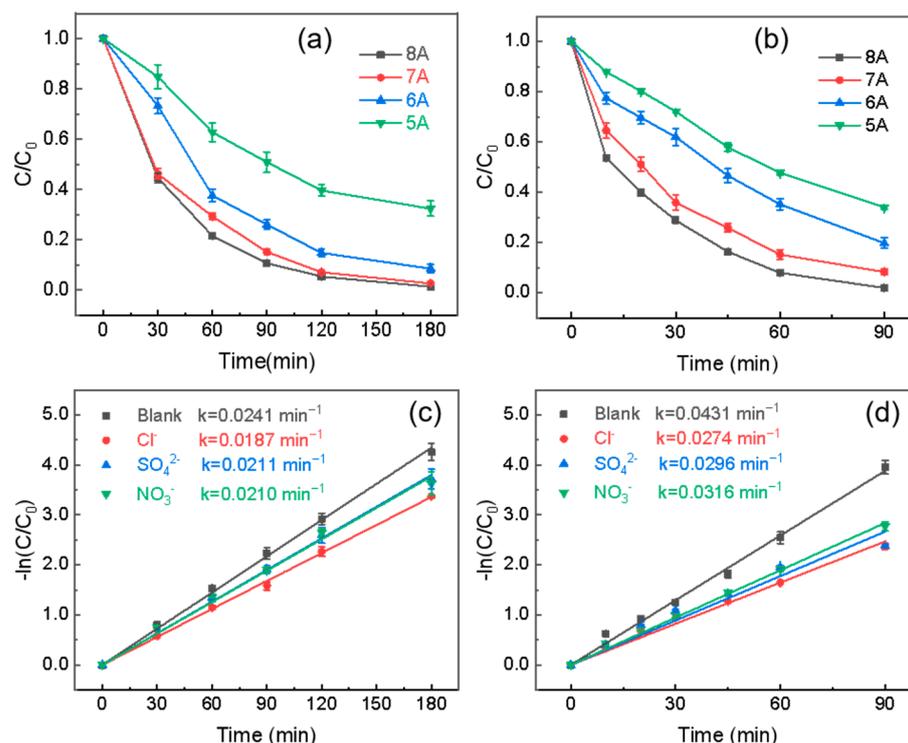


Figure 4. Effect of inorganic anions on the photodegradation of (a) SMX and (b) ENR, and kinetic curves of (c) SMX and (d) ENR.

3.2.4. Effects of Natural Organic Matter in Water

The presence of natural organic matter in water can affect the photodegradation reaction of pollutants. In natural water bodies, humic acid and fulvic acid account for up to 80% of the total dissolved organic matter [29]. Humic acid was used to simulate natural organic matter, to study its effect on the photodegradation reaction of two typical antibiotics. In the experiment, $1 \text{ mg}\cdot\text{L}^{-1}$, $2 \text{ mg}\cdot\text{L}^{-1}$, $5 \text{ mg}\cdot\text{L}^{-1}$, and $10 \text{ mg}\cdot\text{L}^{-1}$ of humic acid were added, respectively, and other conditions remained the same.

As shown in Figure 5, after adding different concentrations of humic acid, the photodegradation reactions of SMX and ENR were significantly inhibited, with the highest inhibition rates reaching 45.6% and 77.8%, respectively. Oliveira et al. [20] studied the effects of three components of humic substances in water on the photodegradation of SMX. After 1 h of illumination, under the condition of pH 5.0, the degradation rate of SMX was about 80% compared with ultrapure water, containing $20 \text{ mg}\cdot\text{L}^{-1}$. The degradation rates of SMX in the humic acid HA and fulvic acid FA systems dropped to about 47% and 50%, respectively. The analysis of the effects of the three components showed that the humic acid HA had the most light absorption in the reaction system, thus showing the strongest inhibitory effect on SMX photodegradation. The study reported by Li et al. [30] also confirmed that humic acid reduces the photolysis rate of ENR.

Natural organic matter has photosensitivity. Under the irradiation of a light source, organic matter transforms into a transient excited state, which can react with oxygen in the solution to form active substances, or directly react with organic matter, resulting in an increase in the rate of photodegradation. In general, however, DOMs can reduce the photodegradation rate of pollutants through three distinct effects: internal filtration, removal or quenching of reactive species, and inhibition of pollutant transformation through the reduction of 3CDOM^* [20,31]. Zhao et al. [32] studied the effects of Pahokee peat humic acid and Sigma-Aldrich humic acid on the photodegradation of SMX, and believed that, in addition to the competition for photons, quenching and masking effects may be the main reason accounting for the inhibition of SMX photodegradation. Humic acid has a large specific

surface area and more surface reaction sites, and has good adsorption performance, which will adsorb some pollutants and lead to a decrease in the photodegradation rate of pollutants.

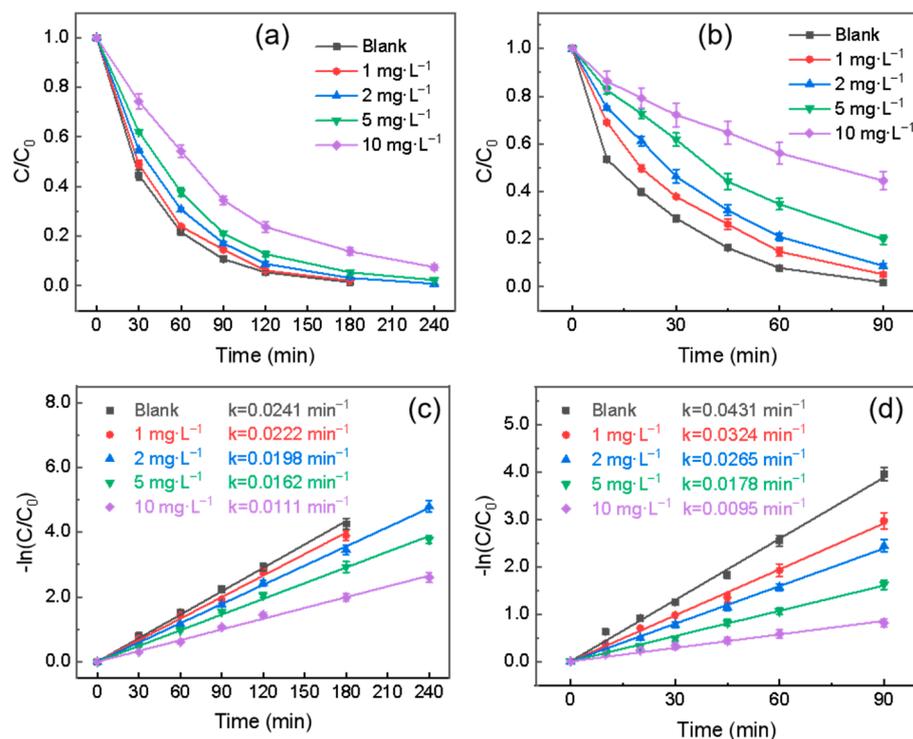


Figure 5. The impact of different amounts of humic acid on the photodegradation of (a) SMX and (c) ENR, and kinetic curves of (b) SMX and (d) ENR.

3.3. Quenching Experiments

The photolysis reactions of pollutants including antibiotics generally include direct photolysis and indirect photolysis. In order to understand the photodegradation mechanism of the two antibiotics, quenchers were added to remove or quench the oxidative groups generated during the reaction, and the effect on the reaction rate was analyzed to examine the reactive oxidative species generated during the reaction and propose the photodegradation reaction mechanism of these two antibiotics. In the experiment, tert-butanol (5 mM) and isopropanol (5 mM) were added as quenchers for $\cdot\text{OH}$, p-benzoquinone (0.1 mM) was added as a quencher for $\cdot\text{O}_2^-$, and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, 5 mM) was used as a quencher for oxidation holes [33].

As shown in Figure 6, after adding quenchers, the reaction rates in the photodegradation reaction stage were all lower than those of the blank control group without the addition of quenchers. Among them, the reaction rate of the experimental group added with EDTA-2Na had the smallest decrease. Although it acted as a quencher of oxidation holes, it did not indicate that there were oxidation holes in the reaction system and had an effect, and the reaction rate of this group was inhibited (about 11.6% and 7.9%, respectively) due to the interference effect of EDTA-2Na itself. In contrast, tert-butanol, isopropanol, and p-benzoquinone inhibited the reaction more significantly. Both tert-butanol and isopropanol were used as quenchers for $\cdot\text{OH}$. In the experimental group with these two quenchers added, the SMX reaction rate constant decreased by 27.0% and 18.3%, respectively, and the ENR decreased by 22.7% and 21.3%, respectively, which indicated that $\cdot\text{OH}$ was produced in the reaction. After the addition of p-benzoquinone, the photodegradation constants of SMX and ENR were reduced to 0.0191 min⁻¹ and 0.0376 min⁻¹, respectively, and the photodegradation inhibition rates were 20.7% and 13.0%, respectively, which confirmed the existence of $\cdot\text{O}_2^-$ in the reaction.

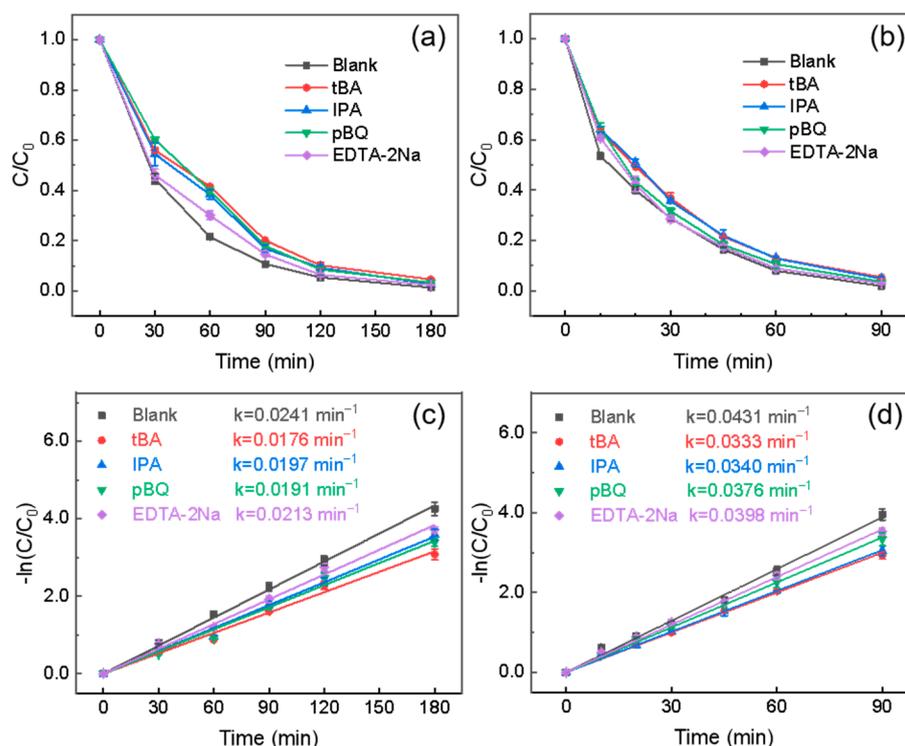


Figure 6. The concentration curves of (a) SMX and (b) ENR in their photodegradation after adding several quenchers, and kinetic curves of (c) SMX and (d) ENR photodegradation.

Each quencher had a limited inhibitory effect on the photodegradation reaction, indicating the coexistence of oxidative groups such as $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ in the reaction. However, the cumulative inhibition rate was also significantly less than 100%, which indicates that there was not only indirect photodegradation but also direct photodegradation in the photodegradation reaction.

3.4. Analysis of Photodegradation Products

There were both direct photodegradation reactions and indirect photodegradation reactions in the degradation process of the two typical antibiotics. The direct photodegradation reaction was that after the antibiotic molecule absorbed light energy and became an excited state (SMX* or ENR*), it directly degraded to form the corresponding product. In the indirect photodegradation process, after the antibiotic molecule absorbed light energy, the excited state interacted with water molecules or oxygen in the water to generate $\cdot\text{OH}$, $\cdot\text{O}_2^-$, and $^1\text{O}_2$ active groups, and then, under the action of these active groups, it was converted into degradation byproducts. Taking SMX as an example, the photodegradation pathway was proposed, as shown in Figure 7. The photodegradation of ENR also included a direct photodegradation process and an indirect photodegradation process, and the photolysis reaction mechanism was basically similar.

Through the natural photodegradation process in water, SMX and ENR were nearly completely degraded and removed in good time. The degradation rate of SMX under simulated solar light was relatively fast, and the degradation ratio was close to 100% in about 2 h. However, HPLC analysis showed that, during the degradation of the two typical antibiotics, after the samples prepared with ultrapure water were degraded, in addition to the chromatographic peaks corresponding to the parent substances of SMX or ENR, there were several other chromatographic peaks in the liquid chromatography analysis whose size and shape also changed with the reaction process, and existed until the end of the reaction. It is suggested that, in the reaction process, the antibiotic parent substance was continuously degraded and transformed into other organic substances and

degradation products, and the types and concentrations of the degradation products were also constantly changing.

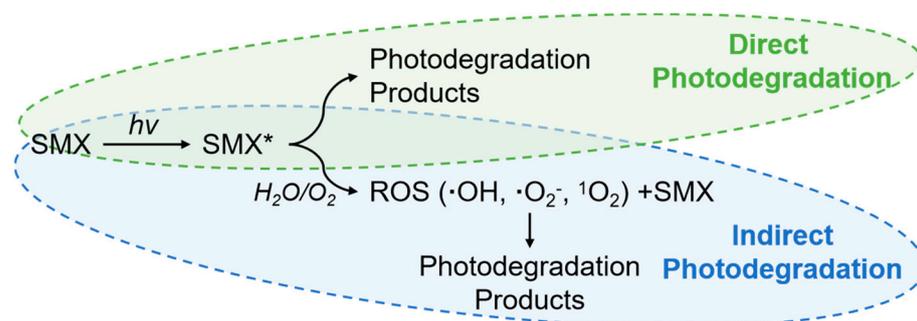


Figure 7. The proposed pathway for photodegradation of SMX.

4. Conclusions

Taking SMX and ENR as two typical representatives of antibiotics as the research objects, their photodegradation under UV and simulated solar light were studied. The degradation rates of SMX under the two light sources were 0.235 min^{-1} and 0.024 min^{-1} , respectively, and for ENR were 0.124 min^{-1} and 0.043 min^{-1} , respectively. The increase in light intensity helped to increase the photodegradation reaction rates of SMX and ENR, while the photodegradation rates showed a decreasing trend with the increase in the initial concentration. The three inorganic anions Cl^- , SO_4^{2-} , and NO_3^- , and natural organic matter (humic acid), all had inhibitory effects on the photodegradation of typical antibiotics. Each quencher had a limited inhibitory effect on the photodegradation reaction. The cumulative inhibition rate was also significantly less than 100%, indicating that not only indirect photodegradation but also direct photodegradation existed in the photodegradation reaction. This study showed that enhancing the photodegradation of pollutants such as antibiotics could effectively speed up their degradation in water, thereby reducing the ecological and health risks they cause. The research could provide a reference for the development of corresponding efficient photocatalytic degradation materials and technologies.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15030517/s1>, Table S1: Details of the materials and reagents; Figure S1: Schematic diagram of the main part of the photochemical reactor (NBeT, PhchemIII); Figure S2: The UV/Vis spectra of SMX and ENR.

Author Contributions: Conceptualization, X.L.; methodology, X.L. and J.X.; software, X.L.; validation, X.L. and J.X.; formal analysis, X.L.; resources, W.Z., S.L. and J.X.; data curation, X.L.; writing—original draft preparation, X.L.; writing—review and editing, X.L., W.Z. and J.X.; visualization, X.L.; supervision, J.X.; project administration, H.F., S.F. and J.H.; funding acquisition, S.L., H.F., S.F. and J.X. All authors have read and agreed to the published version of the manuscript. **Funding:** This research was supported by the scholarship from the China Scholarship Council (CSC) (Grant No.201906260067) and scientific program of PowerChina Huadong Engineering Corporation Limited (KY2018-SHJ-02).

Data Availability Statement: Data will be made available on request.

Conflicts of Interest: The authors declare no conflict of interest.

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