Molecular iodine enhancing sulfadiazine photodegradation in water under UVA irradiation

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Abstract. Photodegradation of sulfadiazine (SD), a typical sulfonamide antibiotic (SA) frequently detected in the aquatic environment, under UVA irradiation enhanced by molecular iodine was investigated. Herein, molecular iodine I₂ and coexisting I⁻ were provided by hydrogen peroxide and potassium iodide in acidic solution. During the treatment, highly reactive iodine radicals (I⁻, I₂·, I−2·) produced by UVA photolytic activation of both I₂ and I⁻, were verified as the dominated oxidant species against the decomposition of SD in aqueous solution. Besides, SD removal was found to be affected by the initial pH value, KI and H₂O₂ added concentrations.

1. Introduction
Sulfonamides (SAs), a kind of synthetic antibiotic drugs including a sulfonamide group, have been widely applied in veterinary and clinical medicine for a long time, ascribing to both their convenience in utilization and broad spectrums in antibacterial property [1]. Currently, the increasing residuals of SAs in the environment, primarily releasing from animal and human excrements, has been arousing global concerns gradually [2,3]. Even the residual level of SAs in the environment is considerably low, the fact that the direct toxicity to microorganisms and the subsequent generation of antimicrobial genes and/or microorganisms, due to their persistence, threatens the ecosystem's stabilization and human health cannot be ignored [4]. Moreover, it has been proved that SAs show the highest drug resistance compared to tetracyclines and other antibiotics [5].

However, wastewater treatment plants (WWTPs), primarily using activated sludge (AS), show relatively low removal efficiency of SAs, with the occasional case that the concentration in effluent is higher than that in influent [1]. As a response, advanced oxidation processes (AOPs), such as sonolysis [6], Fenton reactions [7], ozonation [8] and photocatalysis (heterogeneous/homogeneous) under ultraviolet (UV) [9], visible light [10] or gamma radiation [11], primarily based on the strong oxidizing hydroxyl radicals (HO· (E°(HO·/H₂O)=2.8 V)), have been proved to be a newly approved method to remove refractory compounds from aqueous solution [6,12]. With the development of the research, some other active substances, like sulfate and carbonate radicals (SO₄²⁻· (E°(SO₄²⁻·/SO₄²⁻)=2.6 V), CO₃⁻/HCO₃⁻ (E°=1.78 V)), motivated by light irradiation, have been proved to be selective transient species against sulfamethazine [9], diethyl phthalate [13] and bisphenol A [14]. Besides, iodineradicals I⁻ (E°=1.33 V) as well as I₂· (E°=1.03 V), excited by UV or visible light irradiation, were also reported to act a potentially direct role to the removal of persistent compounds [15-17]. However, any research on the treatment of antibiotic drugs mainly based on iodine radicals, excited by light irradiation, has not been reported yet.
According to Hu et al. [17], hydrogen peroxide (H$_2$O$_2$) and I$^-$ (provided by potassium iodide (KI) in our work) can be used as the source of molecular iodine in acidic solution (equations (1) and (2)). Subsequently, the coexisting I$_2^-$ (equation (3)) largely increases the solubility of I$_2$ in aqueous solution. In our work, UVA light ($\lambda=365$ nm) was utilized to motivate molecular iodine to produce highly active iodine radicals (equations (4) and (5)). And the photodegradation of sulfadiazine (SD), a typical kind of SAs, in aqueous solution enhanced by iodine radicals was investigated. Besides, the main active substances acting on SD photodegradation were validated, and affecting parameters including initial pH value, H$_2$O$_2$ and KI added concentrations were evaluated.

\[
\begin{align*}
H_2O_2 + I^- + H^+ & \rightarrow HIO + H_2O \\
I^- + HIO + H^+ & \rightarrow I_2 + H_2O \\
I_2 + I^- & \rightarrow I^- \\
I_2 + h\nu & \rightarrow 2I^- \\
I^- + h\nu & \rightarrow I^- + I\
\end{align*}
\]

2. Materials and methods

2.1. Reagents

All chemicals used in this study have been illustrated in our previous research [18]. Herein, the main properties of the target compound, sulfadiazine (C$_{10}$H$_{14}$N$_3$O$_2$S, ≥99%), was demonstrated in table 1.

| Compound  | Structure           | Structural formula | $m_w^a$ (g/mol) | $\lambda_{max}^b$ (nm) |
|-----------|---------------------|--------------------|----------------|------------------------|
| sulfadiazine | ![structure](image) | C$_{10}$H$_{14}$N$_3$O$_2$S | 250.28 | 269 |

$^a m_w$ denotes sulfadiazine’s molar mass.

$^b \lambda_{max}$ denotes sulfadiazine’s maximum absorption sulfadiazine.

2.2. Sulfadiazine photodegradation experiments

Photodegradation experiments were conducted in a glass beaker (250 mL) radiated with a UVA lamp ($\lambda=365$ nm, 18 W, Beijing ZhongYiBoTeng Tech Co. Ltd., China). The distance between the liquid level and the lamp was fixed at 10 cm. Unless otherwise noted, all reactions were performed under atmospheric conditions, the initial concentrations of SD was 10 mg/L$^{-1}$, H$_2$O$_2$ and KI added concentrations were 120.0, 2.4 mmol.L$^{-1}$, respectively. Besides, 0.5 mol.L$^{-1}$ HCl or NaOH solution was used to adjust the initial pH to 3.2 if not specified. At set irradiation time intervals, 1 mL samples were withdrawn quickly after stirring and filtered with 0.22 μm micro-filter before quantification as described below. Removal (%) of SD, obtaining from the arithmetic mean of three replications, was calculated based on equation (6).

\[
\text{Removal (\%)} = \frac{[SD]_0 - [SD]_t}{[SD]_0} \times 100\%
\]

Where [SD]$_0$ denotes the initial concentration of SD, and [SD]$_t$ denotes its concentration at time t (min).

2.3. Analytical methods
High Performance Liquid Chromatography (HPLC), described in our previous report [19], was used to the quantification of SD. Herein, conditions are different in that acetonitrile and water (25%:75% in volume) were the components of the mobile phase with 0.30 mL/min flow rate, the detection wavelength was 269 nm. Method to illustrate the behavior of iodine (I$_2$ and I$^-$) was also described in our previous report [19].

3. Results and discussion

3.1. Comparable degradation systems of SD

The degradation of SD under a series of comparable systems is shown in figure 1, and it should be noted that except for the photodegradation experiments, all other experiments were carried out in the dark.

![Figure 1. The degradation of SD under a series of comparable systems.](image)

Figure 1 shows that H$_2$O$_2$ alone hardly worked on SD while 16.3% removal of SD was obtained under UVA irradiation alone. Similarly, SD removal in UVA/H$_2$O$_2$ system was only 15.0% after 120 min of treatment, which is due to the fact that the covalent bond HO-OH in H$_2$O$_2$ could not be broken to form HO- [E$^0$(HO-/H$_2$O) = 2.80 V] unless under the light irradiation with the emission wavelength less than 260 nm [19]. Besides, because of the photon absorption of I$^-$, it may compete with the photodegradation of SD in the UVA/KI system, resulting in the lower SD removal [20]. Interestingly, H$_2$O$_2$/KI system effectively improved the degradation of SD with 81.4% removal in 120 min. As mentioned above, I$_2$ [E$^0$ = 0.54 V] and I$^-$ [E$^0$ = 0.53 V] would be formed in the coexisting solution of H$_2$O$_2$ and KI in acidic condition. Besides, according to Milan et al [21], the intermediate oxide HIO [E$^0$=1.1-1.6 V] was also produced in the system to a large extent (equations (7) and (8)). Therefore, with the synergistic effect of I$_2$, I$^-$ and HIO, SD was degraded effectively. In addition, with UVA irradiation, the degradation of SD was further enhanced with 98.2% removal in UVA/H$_2$O$_2$/KI system.

\[
\Gamma + H_2O_2 + H^+ \rightarrow HIO + H_2O \tag{7}
\]

\[
HIO + \Gamma + H^+ \rightarrow I_2 + H_2O \tag{8}
\]

To validate the role of iodine on SD degradation, UV-Vis spectra in process of SD removal, both in H$_2$O$_2$/KI and UVA/H$_2$O$_2$/KI systems, were recorded. Figure 2 shows the UV-Vis spectra during SD degradation in H$_2$O$_2$/KI system. Obviously, A$^{}_{450\text{ nm}}$ and A$^{}_{460\text{ nm}}$ reduced as the reaction progress, and the maximum absorption less than 300 nm simultaneously moved left, indicating that SD was indeed degraded in H$_2$O$_2$/KI system and its degradation was closely connected to both I$_2$ and I$^-$. It should be noted that the variation trend of UV-Vis spectra as the reaction progress in UVA/H$_2$O$_2$/KI system was basically consistent with that in H$_2$O$_2$/KI system. Interestingly, it can be seen from figure 3 that UVA...
irradiation enhanced the consumption of I₂ (A460 nm decreased from 0.401 to 0.359 in 120 min) and affected I⁻ to some extent (A350 nm firstly decreased and then increased), and thus the degradation of SD was promoted. This may because that iodine radicals I⁻ [E° (I⁻/I) =1.33 V] and I₂·[E° (I₂/·I) =1.33 V] would be formed by the breakage of I-I covalent bond in both I₂ and I⁻ under UVA radiation (equations (4) and (5)) [17,18].

**Figure 2.** UV-Vis absorption spectra of sample as the reaction progress in H₂O₂/KI system.

**Figure 3.** Comparisons in absorbance at 460 nm and 350 nm in UVA/H₂O₂/KI and H₂O₂/KI systems with reaction time, respectively.

### 3.2. Identification of active species in UVA/H₂O₂/KI system

As shown in figure 4, the excess addition of methanol, the scavenger of HO⁻ radicals [15], had almost no influence on SD removal in UVA/H₂O₂/KI treatment, indicating that HO⁻ may not be the main active substance to the degradation of SD. As an inhibitor of both HO⁻ and iodine radicals (I⁻, I₂⁻) [22], methimazole (MMI) had obvious inhibitory effect on the SD removal. When the added concentration of MMI was 4.8 mmol.L⁻¹, SD removal was reduced from 98.2% to 82.8%, which was mostly equivalent to the removal (%) of SD obtained in H₂O₂/KI system. With the continous increase of MMI to 12.0 mmol.L⁻¹, the removal of SD was reduced to 66.7%. In addition, further increased MMI added concentration to 48.0 mmol.L⁻¹, SD degradation was completely inhibited in UVA/H₂O₂/KI system. Therefore, instead of HO⁻, iodine radicals (I⁻, I₂⁻) were the primary active substances for the degradation of SD in the UVA/H₂O₂/KI system.

**Figure 4.** Inhibition effect of methanol, methimazole (MMI) on SD degradation under UVA/H₂O₂/KI system.

### 3.3. Effecting factors

#### 3.3.1. The initial pH value

It is shown in figure 5 that the initial pH value of system has obvious effect
on SD removal in UVA/H$_2$O$_2$/KI system. When it was set 2.6, 3.2 and 4.3, SD removal was 75.1%, 98.2% and 95.8% respectively. Interestingly, 100% removal of SD in 120 min was obtained with the pH value of 6.3.

![Figure 5](image-url)  
**Figure 5.** Effect of initial pH value on SD degradation in UVA/H$_2$O$_2$/KI system.

As mentioned above, the degradation of SD in US/H$_2$O$_2$/KI system was closely related to the formation of molecular iodine and subsequent iodine radicals. For system initial pH value directly affects both stability and oxidation of hydrogen peroxide [23], and H$^+$ is the critical factor of the formation of molecular iodine in the system (equations (1) and (2)), lower pH value was more beneficial to the formation of I$_2$ and I$_3^-$ to some extent, which was verified by the results shown in both figures 6 and 7. Herein, at the beginning of SD photodegradation (0 min), the concentration of formed I$_3^-$ ($A_{350\text{ nm}}$) and I$_2$ ($A_{460\text{ nm}}$) decreased with the increase of initial pH value ranging from 2.6 to 6.2 (except for the condition of pH=4.3). As the initial pH value reduced from 2.6 to 3.2, it showed no obvious change in SD removal. With the increase of initial pH to 4.3, the oxidation ability of H$_2$O$_2$ relatively reduced, and thus I$_3^-$ and its photolysis may be dominant in the system (equations (3) and (5)). As a result, I$_2^-$ would be the main active substance for SD degradation due to the reaction shown in equation (9). In comparison, the oxidation activity of I$_2^-$ is lower than I- [17,18,24], which would hinder SD removal to some extent.

\[
\Gamma + I^\cdot \rightarrow I_2^\cdot.
\]  
(9)

With the initial pH value added to 6.2, the amount of I$_2$ and I$_3^-$ in the system was relatively low, but SD removal increased. This may be due to the fact that the oxidation ability of H$_2$O$_2$ in the neutral condition was weak, and it was likely to be oxidized by the intermediate oxide HIO mentioned above.
(equation (10)) [25]. Besides, the amount of both $I_2$ and $I_3^-$ in the system was minimum at the beginning of the reaction (figures 6 and 7), thus I$^-$ would be dominant in the system. According to Yeo et al [15], the complex $I_2\text{H}_2\text{O}^*$ would be produced by electron transfer of I$^-$ under UVA irradiation, which greatly promoted the formation of I$^-$, $I_2^*$ and $O_2^*$, and thus SD removal was enhanced (equations (11) - (14)).

$$H_2O_2 + HI\rightarrow I + H_2O + O_2 + H^+$$  \hspace{1cm} (10)

$$I^- + H_2O + h\nu \rightarrow I\text{H}_2\text{O}^-$$ \hspace{1cm} (11)

$$I\text{H}_2\text{O}^- \rightarrow (I, e^-) + H_2O$$ \hspace{1cm} (12)

$$(I, e^-) \rightarrow I^- + e^-_{aq}$$ \hspace{1cm} (13)

$$(I, e^-) + O_2 \rightarrow I^- + O_2^-$$ \hspace{1cm} (14)

### 3.3.2. KI added concentration

KI added concentration had an obvious effect on SD degradation in UVA/$H_2O_2$/KI system. Seen in figure 8, when KI added concentration was 0.2, 0.8 and 2.4 mmol.L$^{-1}$, SD removal was 78.1%, 89.3% and 98.2%, respectively. Further increased KI added concentration to 3.2 mmol.L$^{-1}$, SD removal had no obvious change.

![Figure 8](image)

**Figure 8.** Effect of KI added concentration on SD degradation under UVA/$H_2O_2$/KI system.

The influence of KI added concentration on the removal of SD was also connected to the generation of iodine and subsequent free radicals. Changes of UV-Vis spectra in both $A_{350}$ nm ($I_3^-$) and $A_{460}$ nm ($I_2$) during SD photodegradation in UVA/$H_2O_2$/KI system with different KI added concentrations were investigated to analyze these phenomena. Figures 9 and 10 show that the production of both $I_2$ and $I_3^-$ obviously increased with the increase of KI added concentration ranging from 0.2 to 3.2 mmol.L$^{-1}$ (0 min), resulting in enhancement of I$^-$ and $I_3^-$ would be boosted under UVA irradiation, and thus SD degradation significantly increased [13, 19]. It should be noted that the further increase of KI added concentration to 3.2 mmol.L$^{-1}$, SD removal seemed to be hindered to some extent, which may explained by the fact that overloading $I_2$ and $I_3^-$ formed in the system would generate a barrier between the covalent bond of I-I and the photons emitted by UVA irradiation to impede the production of iodine radicals.
3.3.3. \( \text{H}_2\text{O}_2 \) added concentration. \( \text{H}_2\text{O}_2 \) added concentration also had a significant effect on SD degradation in the proposed system. Seen from figure 11, when \( \text{H}_2\text{O}_2 \) added concentration increased ranging from 10.0 to 120.0 mmol.L\(^{-1} \), SD removal was 21.2 %, 85.7 % and 98.2 %, respectively. Further increased \( \text{H}_2\text{O}_2 \) added concentration to 180.0 mmol.L\(^{-1} \), SD removal did not change significantly (97.0%).

These phenomena could also be explained by the generation of molecular iodine and subsequent iodine radicals under UVA irradiation (figure 12). It should be noted that when the added concentration of \( \text{H}_2\text{O}_2 \) further increased to 180.0 mmol.L\(^{-1} \), greatly due to the reaction between the intermediate oxide HIO and the excess \( \text{H}_2\text{O}_2 \) (equation (10)), \( \text{I}_2^- \) would be the predominate, which limited SD degradation to some extent.

4. Conclusions
Research on degradation of organic and inorganic contaminants based on photocatalytic reaction is increasing, but the photocatalytic degradation of antibiotic drugs with molecular iodine as catalyst has not been reported. In our study, hydrogen peroxide and potassium iodide were used as the source of molecular iodine in acidic condition, and UVA/\( \text{H}_2\text{O}_2/\text{KI} \) system was proposed to degrade sulfadiazine (SD), a typical sort of sulfonamides. Results showed that UVA/\( \text{H}_2\text{O}_2/\text{KI} \) system obtained 98.2% removal of SD within 120 min under the following reaction condition: 0.04 mmol.L\(^{-1} \) SD initial concentration, 3.2 the initial pH value, 2.4 mmol.L\(^{-1} \) KI added concentration, and 120.0 mmol.L\(^{-1} \) \( \text{H}_2\text{O}_2 \) added concentration. Besides, instead of \( \text{HO}^- \), iodine radicals (\( \text{I}^- \) and \( \text{I}_2^- \)) were verified as the main substances to SD removal.
Currently, photocatalysts reported in most researches are expensive and difficult to synthesize. For I is a kind of common ions in water environment, and hydrogen peroxide is the recognized green oxidant with low price, UVA/H₂O₂/KI system we proposed has a certain practical significance on the removal of antibiotic drugs from water environment. In addition, the complexity of the reactions between H₂O₂ and I may cause a certain uncertainty and instability of the proposed system, so further researches on the identification, antibacterial and toxicity analysis of degradation products, as well as the degradation pathway are very important, on which are our next research focus.

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