Environmental Sciences Europe

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Kinetic and mechanistic study of sulfadimidine photodegradation under simulated sunlight irradiation

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Abstract

Background: The extensive uses of sulfadimidine (SDMD) resulted in its presence in water bodies, and subsequent posed risks to eco-environment and human health. In this study, photodegradation of SDMD in water was studied under UV–Visible irradiation. The intermediates, degradation pathways of SDMD photodegradation and ecological risk of SDMD were investigated as well.

Results: SDMD was rapidly degraded under alkaline conditions. Nitrate ion enhanced SDMD degradation under UV–Vis irradiation, while dissolved organic matter and Fe(III) inhibited its decay, and bicarbonate ion did not exert any effect. The reactive species involved in the SDMD photodegradation was singlet oxygen. Four major transformation products were identified by high-performance liquid chromatography–mass spectrometry (HPLC–MS), and the photolytic pathway was also proposed. Photoinduced hydrolysis, desulfonation and photooxidation were the major photodegradation mechanisms for SDMD. Toxicity analysis with *Vibrio fischeri* showed an obvious decrease in toxicity of the reaction solution, from the initial inhibition rate of 38.5% to 0% after 150-min irradiation.

Conclusion: Initial pH and common water constituents influence the photo-degradation of SDMD under UV–Vis irradiation. Photodegradation of SDMD could reduce its ecological risk in the aqueous solution.

Keywords: Photodegradation, Sulfadimidine, Antibiotics, Intermediates, Toxicity

Background

The ubiquitous occurrence of pharmaceuticals and personal care products (PPCPs) in the environment has now been recognized as a new environmental problem and has aroused increasing concern on their fate and risks [1–5]. In the aquatic ecosystem, the majority of PPCPs tends to absorb light due to their structural characteristics containing functional groups like aromatic rings and heteroatoms, making them prone to undergo photolysis under UV–Vis irradiation [6–8]. Pharmaceuticals may be directly photodegraded, which are converted into excited states and subject to chemical transformation as a result

of photo-absorption [9]. Indirect photolysis is also an important photodegradation pattern for PPCPs, which happens because of the energy transference or reactions with transient reactive species in natural water arising from irradiation, including reactive oxygen species (ROS, for instance, ·OH and $^1O_2$) and triplet excited states of natural organic matter ($^3NOM*$) [8, 9].

In the aqueous environment, the water constituents (such as nitrate, bicarbonate, dissolved organic matter (DOM) and Fe(III)) are of great importance to the photochemical behavior of pollutants [10–12]. Nitrate can generate ·OH under light irradiation which is photoactive to the organic contaminants [10, 13–15]. Bicarbonate is documented to yield $CO_3^{-·}$ through reacting with ·OH, and it could also prohibit the photo-transformation of organic contaminants because of the ·OH scavenging [14–16]. DOM, as the major form of organic carbon existing in surface water, has dual effects on the

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photodegradation of organic compounds. It can accelerate the photooxidation by generating oxidants such as HOO/O_2^-, $\cdot OH$, $^1O_2$ and triplet excited-state DOM, and also can scavenge ROS or compete light absorption [11, 17, 18]. The photodegradation of organic compounds is accelerated by Fe(III) complexes by internal charge transfer to generate Fe(II) and hydroxyl radical, which could enhance the photodegradation and serve as the catalytic oxidant [10, 17, 19].

Sulfonamides belong to antibiotics which contain aromatic rings in their structure, with potential to absorb light and undergo photochemical degradation under irradiation [8, 20]. Many researchers have reported the photodegradation of sulfonamides, including sulfamethoxazole, sulfamethazine, and sulfadimethoxine in aqueous environment [16, 18, 21–24]. Albeit with similar structures, these antibiotics undertake different photodegradation behaviors [8, 21]. Sulfadimidine (SDMD) is a sulfonamide antibiotic which has long been used for prophylactic or therapeutic purposes in animal production [25]. Due to its high water solubility and mobility, SDMD has been widely detected in various environmental matrices, with concentrations up to 323 ng/L in water [25–27], up to 20 mg/kg in animal manure [26, 28] and 15 µg/kg in agriculture soils [26, 27]. The runoff concentration from manured plots could reach 680 µg/L with 1-day contact time [26, 28]. Generally, sorption and photodegradation processes governed sulfamethazine fate in freshwater–sediment microcosms [29], and the SDMD photodegradation have been studied in several studies [7, 30–32]. However, few studies have been solely conducted to investigate its photodegradation behaviors, and its photodegradaion products and mechanisms remained unclear. In this study, we investigated the photochemical degradation of SDMD in aqueous solution under UV–Vis irradiation. The experiments were conducted under different conditions including different pH values and different levels of water constituents. The degradation intermediates/products were identified by high-performance liquid chromatography–mass spectrometry (HPLC–MS), and tentative degradation pathways were proposed. Bioassay with *Vibrio fischeri* bacteria was carried out to test the acute toxicity variation of SDMD during its photodegradation process.

Materials and methods
Chemicals and materials
Sulfadimidine (purity > 99%) and humic acid sodium salt (HA) were purchased from Sigma Aldrich (St. Louis, MO, USA). Methanol and isopropanol (HPLC grade) were obtained from Tedia Company, Inc. All other analytical-grade chemicals were used without further purification.

Photodegradation experiments
A Hg lamp (300 W) and a xenon lamp (800 W, Institute of Electric Light Source, Beijing) placed in the cold trap were employed to simulate UV–Vis and sunlight irradiation. The photodegradation experiment was performed in the photochemical reactor system (XPA-7, Nanjing Xujiang Machinery Factory, Nanjing, China) with the main apparatus containing cylindrical quartz well for the UV irradiation ($\lambda > 200$ nm) and Pyrex well for the sunlight irradiation ($\lambda > 290$ nm). The light source irradiance spectra (Fig. 1) were measured by a fiber-optic spectrometer (Ocean Optics, USB2000-FLG), and the light intensities were measured with a full spectrum bright light power meter (CEL-NP2000, Beijing Zhongjiaojinyuan Technology Limited company) in the center of the solutions with 3.85 mW/cm^2 and 4 mW/cm^2 for the mercury and xenon lamp, respectively. The relatively stable photon flux (< 5%) confirmed the stable irradiance during the photodegradation experiment [33]. The SDMD absorption spectra (Additional file 1: Figure S1) under different pH condition were determined by UV–Vis spectrophotometer (Varian Cary 100).

The pH value of the solution was adjusted with HCl or NaOH.

Quartz tubes (60 mL) containing 50 mL of reaction solution ([SDMD]$_0$ = 10 mg/L) were placed in the photochemical reactor system and magnetically stirred. Two milliliters of reaction solution were sampled at specific time intervals. To explore the effects of pH and water compositions [nitrate, bicarbonate, humic acid (HA) and Fe(III)] on SDMD photodegradation, the reagents with serial and concentration gradient at specific pH were added to the reaction solutions. To examine the reactive species involved in SDMD photodegradation, scavenging experiments were performed using
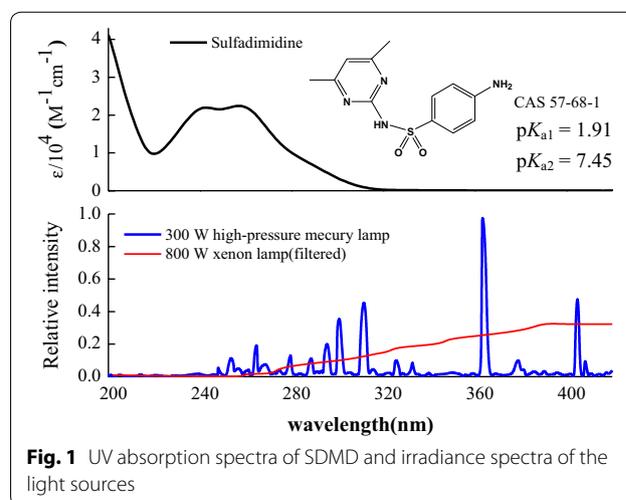

Fig. 1 UV absorption spectra of SDMD and irradiance spectra of the light sources

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isopropanol as the quencher of ·OH [34] and sodium azide (NaN₃) as the quencher of $^1O_2$ and ·OH [34, 35]. Dark control experiments were performed in the same procedures with quartz tubes wrapped with aluminum foils. Triplicate experiments were conducted for all conditions.

Products/intermediates analysis

An Agilent 1200 HPLC equipped with a diode array detector was employed to analyze SDMD concentrations, with the absorbance wavelength at 261 nm. Compounds were separated by an Agilent Zorbax Eclipse XDB-C18 column (100 mm × 2.1 mm, 3.5 μm). 30% methanol and 70% water with 0.1% formic acid were used as the mobile phases. The flow speed was maintained at 1.0 mL/min.

The photodegradation products were identified by LC–MS (Quest LCQ Duo, US) equipped with an electrospray ionization (ESI) source and operated in the positive ion mode (ESI+) with the mass ranging from 50–500 m/z. The LC separation was performed using an eclipse XDB-C18 column (150 mm × 2.1 mm, 5 μm) with a mobile phase of acetonitrile (A) and water (B) (with 0.1% formic acid) at a flow of 0.3 mL/min. The column temperature was kept at 40 °C, and the gradient was as follows: 0–5 min: 90% B; 5–7 min: 85% B; 7–11 min: 60% B; 11–15 min: 10% B; 15–25 min: 90% B. The capillary voltage and cone voltage were 3.5 kV and 25 V, respectively. The desolvation temperature was 350 °C and source temperature was 120 °C. The flow of sheath gas was 7 L/min.

Toxicity evolvement

The toxicity of SDMD solution during photodegradation was evaluated with the bioluminescence inhibition test using *Vibrio fischeri*. The test was conducted with Microtox Toxicity Analyzer (Model 500), with the initial SDMD concentration at 10 mg/L. The luminescence was determined after incubation at 15 °C for 15 min. The inhibition of luminescence compared to a toxic-free control gives the percentage of inhibition, and was calculated following the established protocol using the Microtox calculation program [36, 37]. Briefly, the decrease in bacterial luminescence (Γ, %) due to the addition of toxic chemicals can be determined with the equation [36, 37]:

$$\Gamma = 100 - \left(\frac{\mathrm{IT}_T}{\mathrm{IT}_0 \times \left(\mathrm{IC}_T / \mathrm{IC}_0 \right)} \right) \times 100,$$

where IC_0 and IT_0 are the luminescence of control and test sample at $t = 0$. IC_T and IT_T are luminescence values for control and test samples measured after T minutes of exposure.

Results and discussion

The comparative experiment showed that no observable loss of SDMD was found in dark control, indicating that the SDMD degradation other than photolysis was negligible. Results also showed that under simulated sunlight irradiation ($\lambda > 290$ nm), SDMD did not photodegrade due to the weak absorption of light at $\lambda > 290$ nm (Fig. 1), which was consistent with previous observation [38]. In contrast, SDMD could be quickly photodegraded under UV–Vis ($\lambda > 200$ nm) irradiation. In this study, 300-W high-pressure mercury lamp was used to explore the SDMD photodegradation in aqueous solution.

SDMD photodegradation at varying pH

Figure 2 illustrated the photodegradation of SDMD in solution at different pH values. It showed that within 150-min UV–Vis irradiation, SDMD was almost completely eliminated under alkaline conditions. Linear regression between $\ln(C_t/C_0)$ and time (t) indicated that photochemical reaction followed the pseudo-first-order kinetics ($R^2 > 0.98$). The degradation rate constant k, half-live ($t_{1/2}$) and R^2 are summarized in Additional file 1: Table S1. Results indicated that SDMD in the alkaline solution was photolyzed more quickly than in acidic environment. The highest k value was 0.0363 min^{-1} at pH 9, which was much greater than the maximum degradation rate of 0.0179 min^{-1} in acidic solution at pH 2. This is likely due to the speciation of SDMD under different pH values influencing the absorption of light wavelength (Additional file 1: Figure S1). The pK_{a1} and pK_{a2} values of SDMD were 1.95 and 7.45, respectively [39]; thus, substrate anions with high electron density surrounding the ring structure under alkaline condition were much more reactive for photochemical reaction than their neutral or protonated species [40, 41].
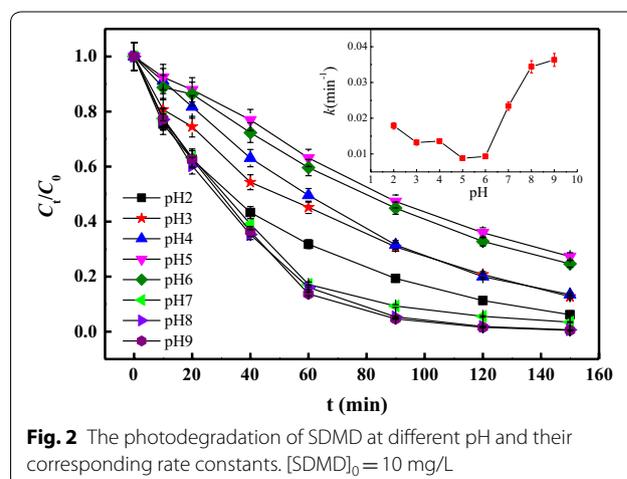

Fig. 2 The photodegradation of SDMD at different pH and their corresponding rate constants. [SDMD]₀ = 10 mg/L

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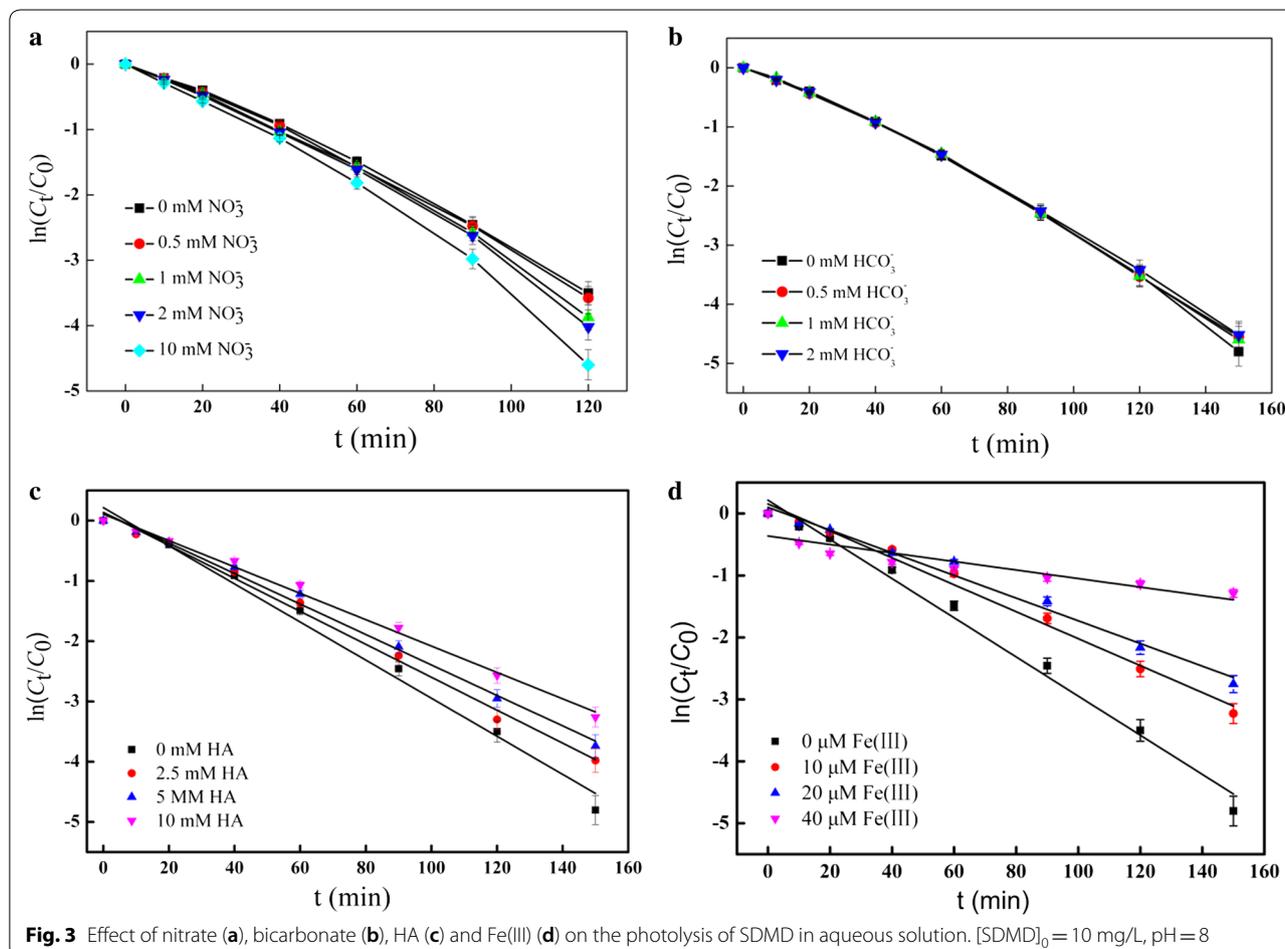### Influence of different constituents

Nitrate ion

The effect of NO_3^- on the SDMD photodegradation is illustrated in Fig. 3a. In natural water bodies, the level of nitrate ion generally ranges from 10^{-5} to 10^{-3} mol/L [12]. In this study, the addition of NO_3^- slightly accelerated the SDMD removal rate. The first-order rate constant k increased from 0.032 min^{-1} (without NO_3^-) to 0.037 min^{-1} (10 mmol/L NO_3^-). It has been reported that the ubiquitous nitrate ion in natural water is the main source for ·OH under irradiation, which will further induce the photodegradation of organic compounds [13, 42]. The results suggested that ·OH could result in SDMD photodegradation. Since SDMD was mainly degraded through direct photolysis, indirect photolysis induced by ·OH only played a minor role in SDMD removal. In view of the nonselectivity of ·OH to react with organic pollutants and high reactivity to sulfonamides [43], ·OH formed in natural sunlit waters might play important roles in the photodegradation of SDMD and other sulfonamides.

Bicarbonate ion

The effect of bicarbonate on SDMD photodegradation is shown in Fig. 3b, which suggested that the addition of bicarbonate did not exert any effect. Bicarbonate is also a ubiquitous ion in natural water, and its presence is of great importance to the photochemical reaction of organic compounds. Bicarbonate can cause approximately 10% of ·OH quenching as a radical scavenger [13], and it could also lead to the generation of carbonate radical ($·CO_3^-$). Compared with ·OH, $·CO_3^-$ is less reactive, and is conducive to the removal of easily oxidized substances in nature water [44, 45]. Due to the lower reactivity, $·CO_3^-$ in natural water was more steady than ·OH [14], and its effect on SDMD photodegradation was negligible.

Dissolved organic matter (DOM)

Figure 3c showed that SDMD photodegradation followed the pseudo-first-order kinetics in the presence of humic acid (HA), and HA had an inhibition impact on SDMD photolysis. As shown in Additional file 1: Figure S2, HA

Fig. 3 Effect of nitrate (**a**), bicarbonate (**b**), HA (**c**) and Fe(III) (**d**) on the photolysis of SDMD in aqueous solution. $[SDMD]_0 = 10$ mg/L, pH = 8

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has a wide light absorption range of 200–700 nm. HA could compete with SDMD to absorb short-wavelength UV light in the solution, resulting in the inhibition of SDMD photodegradation. Its scavenging ability toward ·OH might be another reason for the inhibition effect. As a photosensitizer, HA may be conducive to photodegradation [46–48], while this result showed the minor role of photosensitization played in SDMD photodegradation.

Iron (III)

Iron is the abundant element in natural water environment [19]. In this study, three concentrations of $FeCl_3$ (10 μmol/L, 20 μmol/L and 40 μmol/L) representing environmental levels were added into the reaction solution to evaluate its effect on SDMD photodegradation. As shown in Fig. 3d, the degradation of SDMD under UV–Vis irradiation was obviously decreased in the presence of Fe(III).

As reported that Fe(III) could enhance the sulfadimethoxine photodegradation [18], in this experiment a reversed trend was observed for SDMD. This was mainly related to the iron speciation. Under acidic condition, Fe^{3+}, $FeOH^{2+}$, and $FeSO_4^+$ were the main dissolved forms of Fe(III), which were photoactive for the removal of organic chemicals by the photo-generated ·OH [49]. Under neutral or alkaline conditions, dimeric and oligomeric Fe(III) compounds and Fe(III) colloids were the dominant forms. Fe(III) colloids like ferric oxyhydroxides tend to prevail over other iron species at pH 8 [49], which would absorb or scatter light, and finally lead to less light received by SDMD in aqueous solution.

Mechanisms of SDMD photodegradation

To determine which reactive oxygen species was involved in the SDMD photolysis, NaN_3, isopropanol and N_2 were individually added and introduced into the reaction system. It has been reported that NaN_3 quenches $^1O_2$ and isopropanol quenches ·OH or $O_2 \cdot^-$, while purging N_2 into the system can eliminate dissolved oxygen (DO) which is documented to quench the molecules from excited triplet state to unexcited state [50]. Results in Fig. 4 showed that the addition of NaN_3 inhibited SDMD degradation, suggesting that $^1O_2$ formed during photoreaction played an important role in SDMD photodegradation. Other ROS such as ·OH or $O_2 \cdot^-$ may be not the key radicals involved in the photolysis process.

Due to the high sensitivity, selectivity and efficiency, LC–MS has been widely used as a powerful tool in identifying and charactering drug metabolites [51]. Herein, the intermediates/products of SDMD photodegradation were identified with the retention time and LC/MS–ESI+ spectra. A total of eleven intermediates/products were identified, with detailed information in
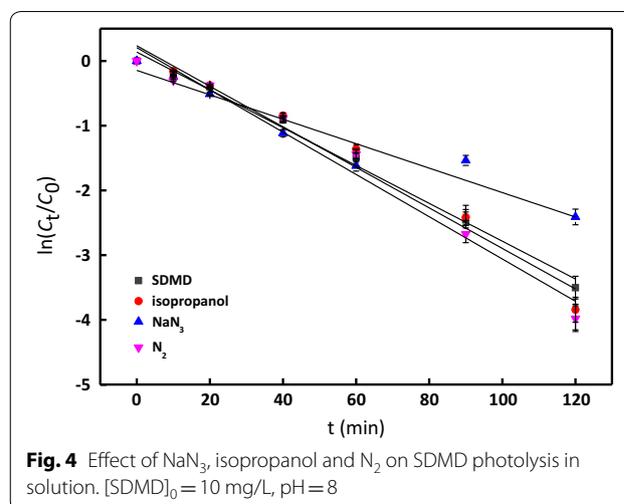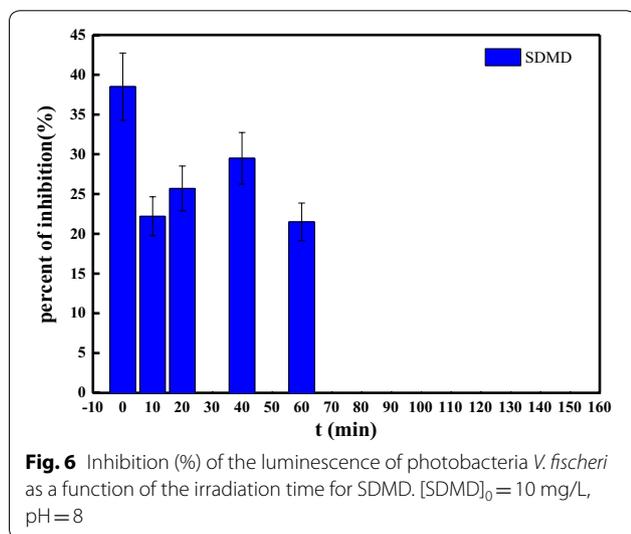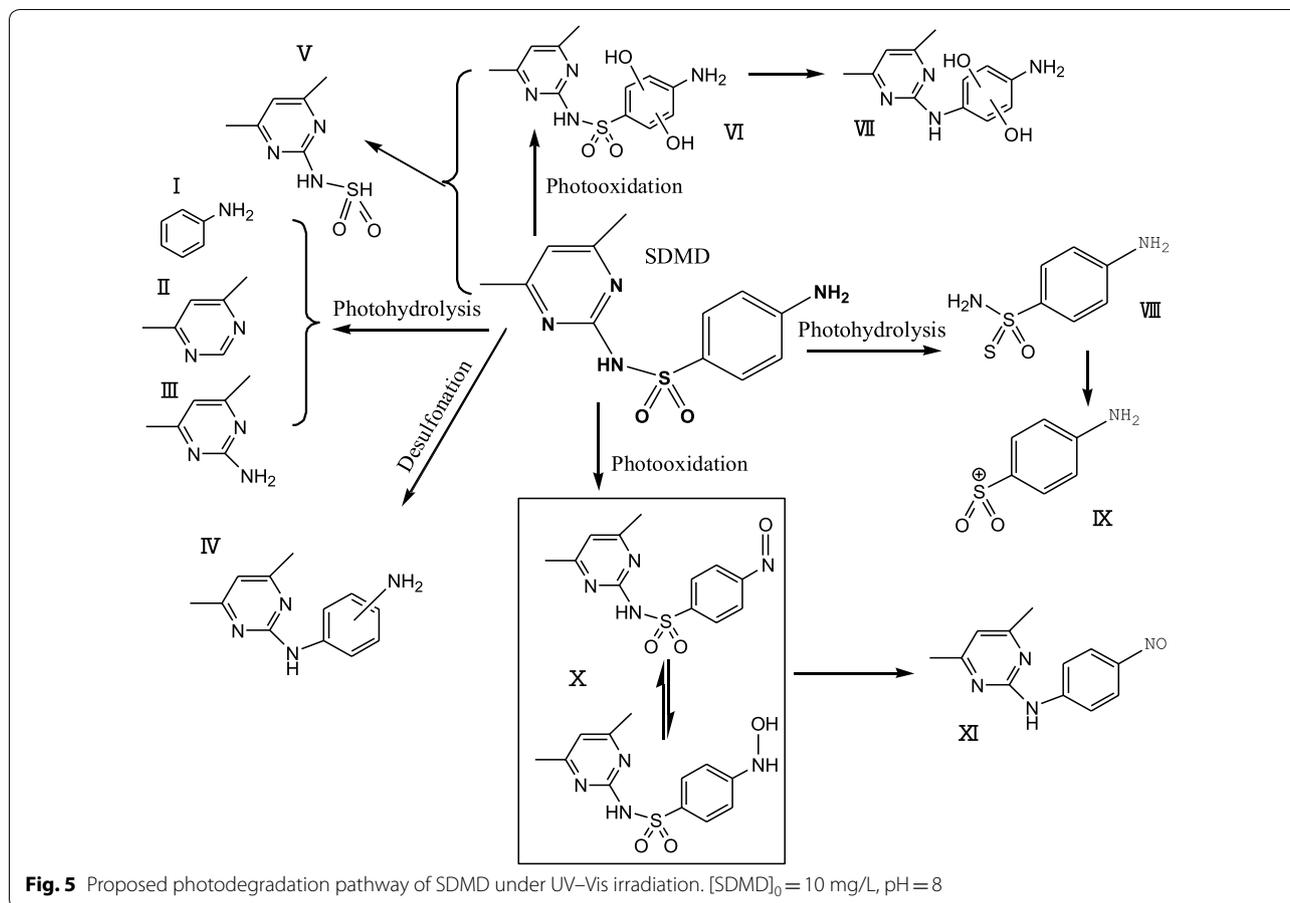

Fig. 4 Effect of NaN_3, isopropanol and N_2 on SDMD photolysis in solution. $[SDMD]_0 = 10$ mg/L, pH $= 8$

Additional file 1: Figures S3 and S4. To avoid unreliable analysis, these intermediates were compared to previous studies [8, 51]. Usually, the direct photodegradation products of sulfonamides arise from similar cleavage as shown in Additional file 1: Scheme S1, and cleavage at these positions are mainly involved in photohydrolysis and desulfonation processes [11, 20, 51–53]. As shown in Additional file 1: Figures S3 and S4, the direct photolysis of SDMD generated several photoproducts which were also observed by others [18, 51–53]. The direct cleavage processes generated products I, II, III, V and VIII, which have been reported in literatures [8, 51]. Desulfonylation is the other important direct pathway induced by excitation of SDMD to its triplet state to produce SO_2 extrusion product IV, which has been identified by previous studies [20, 21]. In addition, photooxidation was involved in SDMD photodegradation. Oxidation products where the m/z increased by 16 were identified to N-oxides (VI and X), and by 32 were identified to product VI. O-addition to the phenyl ring or addition to both rings, or the hydroxyl addition through reaction with HO· may result in the oxidation products [18]. The photoproducts may further undergo the desulfonylation process to produce SO_2 extrusion products VII and X. The SDMD photolysis pathways are proposed in Fig. 5.

Toxicity variation

As *V. fischeri* luminescent bacteria can demonstrate a great potential in ecotoxicological evaluation in comparison to other bioassays, it has been widely used for assessing the toxic effect in aquatic ecosystem [36, 37]. Figure 6 illustrated the toxicity evolvement of the photodegradation reaction solution under UV–Vis irradiation. Results showed that the initial inhibition percentage of SDMD (0 h of irradiation) to *V. fischeri* was 38.5%. With the reaction continued, the degradation intermediates

Fig. 5 Proposed photodegradation pathway of SDMD under UV–Vis irradiation. [SDMD]$_0$ = 10 mg/L, pH = 8

Fig. 6 Inhibition (%) of the luminescence of photobacteria *V. fischeri* as a function of the irradiation time for SDMD. [SDMD]$_0$ = 10 mg/L, pH = 8

showed decreased toxicity to *V. fischeri*. The inhibition disappeared after 90-min experiment. It should be noted that the inhibition percentage firstly decreased to 22.2% (10 min), then increased to 29.5% (40%) and finally decreased to 21.5% (60 min) and 0 ($\geq$ 90 min). This trend indicated the complex photodegradation pathways of SDMD, with some toxic intermediates produced and further transformed to more toxic compounds. Overall, the whole toxicity was eliminated after long-time photodegradation, and the risk of SDMD in natural environments was reduced when exposed to light irradiation. When utilizing UV light to remove SDMD and other antibiotics, the toxicity variation should be monitored, so that the optimum treatment time with low toxicological risk to ecology and human health could be determined.

Conclusions

The present work explored the photo-degradation of SDMD in aqueous solution. The SDMD photo-degradation under UV–Vis irradiation was pH dependent, with higher removal efficiencies under alkaline condition than acidic and neutral conditions. The common water constituents exerted different influence on the SDMD photolysis, depending on different reactive oxygen species involved. Results showed that $^1O_2$ was an important radical generated during the photolysis process. A total of

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eleven reaction intermediates/products were identified, which were less toxic toward *V. fischeri*, indicating that photodegradation played a positive role in diminishing the ecotoxicological risk of SDMD in natural water.

Additional file

Additional file 1: Figure S1. The absorption spectra of SDMD at different pH. **Figure S2.** UV–Vis spectrum of the HA. **Figure S3.** The total ion chromatogram for UV–Vis photodegradation of SDMD. **Figure S4.** MS spectra of the intermediates detected in the SDMD photodegradation solutions under the simulated light irradiation. **Scheme S1.** Potential direct photolysis cleavage sites [1]. **Table S1.** Rate constants (k), half-lives ($t_{1/2}$) and correlation coefficients (r^2) for the photodegradation of the SDMD under irradiation of UV–Vis at different pH.

Abbreviations
SDMD: sulfadimidine; HPLC–MS: high-performance liquid chromatography–mass spectrometry; PPCPs: pharmaceuticals and personal care products; ROS: reactive oxygen species; DOM: dissolved organic matter; ^{3}NOM*: triplet excited states of natural organic matter; HA: humic acid; ESI: electrospray ionization; DO: dissolved oxygen.

Authors' contributions
ZH, CG and JX involved in the experiments and manuscript writing, JL, Yan Zhang and Yuan Zhang were responsible for the data analysis and study designing. ZH and JX contributed to the manuscript correction. All authors read and approved the final manuscript.

Availability of data and materials
The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Competing interests
The authors declare that they have no competing interests.

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