

Original article

Degradation of sulfadiazine antibiotics by water falling film dielectric barrier discharge



Shao-Peng Rong, Ya-Bing Sun*, Ze-Hua Zhao

State Key Laboratory of Pollution Control & Resources Reuse, School of the Environment, Nanjing University, Nanjing 210046, China

ARTICLE INFO

Article history:

Received 14 June 2013

Received in revised form 28 September 2013

Accepted 21 October 2013

Available online 23 November 2013

Keywords:

Sulfadiazine

Water falling film dielectric barrier discharge

Degradation efficiency

LC-MS

Degradation pathway

ABSTRACT

A new water falling film dielectric barrier discharge was applied to the degradation of sulfadiazine in the aqueous solution. The various parameters that affect the degradation of sulfadiazine and the proposed evolutionary process were investigated. The results indicated that the inner concentrations of 10 mg/L sulfadiazine can be all removed within 30 min. The optimum pH value was 9.10 and both strong acidic and alkaline solution conditions were not suitable for the degradation. The degradation of sulfadiazine can be enhanced by the addition of hydrogen radical scavengers, but be inhibited by adding hydroxyl radical scavengers. The water falling film dielectric barrier discharge was rather ineffective in mineralization, because of the intermediates were recalcitrant to be degraded. The existence of Fe^{2+} and CCl_4 in the liquid phase can promote the degradation and mineralization of sulfadiazine. It was found that the degradation of SDZ was enhanced by CCl_4 was mainly because of the increase of $\cdot\text{OH}$ due to the reaction of CCl_4 with $\cdot\text{H}$ that reduce the chances of their recombination with $\cdot\text{OH}$. Based on the 8 intermediate products identified by LC-MS, the proposed evolution of the degradation process was investigated.

© 2013 Ya-Bing Sun. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

1. Introduction

Antibiotics, which are used in animal husbandry for prevention and treatment of bacterial diseases, are an important class of water pollutants due to their large variety, high consumption, and persistence in the environment. The presence of low concentrations of antibiotics compounds and their transformation products has been detected in treated sewage water, clearly showing that some antibiotics products cannot be eliminated during wastewater treatment [1,2]. Sulfadiazine [SDZ, 4-amino-*N*-(2-pyrimidinyl) benzene sulfonamide], a potent antibacterial agent belonging to the sulfonamide class of antibiotics, is widely used as a veterinary and human medicine [3]. After administration to livestock, about 50% of SDZ is excreted through manure as is, and 30% is excreted as an acetyl conjugate [4]. Once SDZ and its metabolites is released to agricultural land, they may interact with different soil components, wash off into surface water, or leach into ground water, where it may enter the food chain and impact the environment and human health [5,6].

Recently, the degradation of SDZ in water by advanced oxidation processes (AOPs) has been investigated. Temesgen *et al.* have found that ozonation could be used to effectively

remove the sulfonamides from water [7]. Premasis Sukul *et al.* have studied the photolysis of SDZ and identified 6 photoproducts, establishing a tentative reaction pathway. His research also showed that photolysis of SDZ in aqueous solution under simulated sunlight followed first-order kinetics [8]. Carolina Baeza *et al.* have studied the transformation kinetics of SDZ in low-pressure UV photolysis and UV/ H_2O_2 advanced oxidation processes [9]. The removal of SDZ was also investigated in Fenton and photo-Fenton, TiO_2 photo catalysis, photochemical oxidation, and electro-oxidation. Promising results have been achieved using AOPs which are based on *in situ* generation of strong oxygen-based oxidizers: hydroxyl radicals, ozone, atomic oxygen, hydrogen peroxide, or per hydroxyl radicals, which promote destruction of the target pollutant until mineralization [10]. Plasma as one of the AOPs has been also investigated as a possible method for water treatment. Plasma generated in electrical discharges in liquid or at the gas-liquid interface leads to the formation of oxidizing species: radicals ($\text{H}\cdot$, $\text{O}\cdot$, $\text{HO}\cdot$) and molecules (H_2O_2 , O_3 , etc.) [11], which are effective for the removal of pollutants. The plasma can be created either directly in the liquid, or in the gas above the liquid, or, both in liquid and in gas. The removal of antibiotics compounds using plasma has been recently studied by several authors [12–14]. But to the authors' knowledge the degradation of SDZ by water falling film dielectric barrier discharge together with the study of the resulting degradation products and the proposed evolutionary process has not been investigated up to now.

* Corresponding author.

E-mail address: sybnju@163.com (Y.-B. Sun).

In this research, SDZ in aqueous solution was removed by water falling film dielectric barrier discharge. The factors affecting the degradation efficiency of SDZ were investigated, and the presences of radical scavengers on the reaction were also studied. At the same time, the 8 degradation intermediates were identified by LC–MS and the degradation mechanism and pathway of SDZ in water by falling film dielectric barrier discharge was focused.

2. Experimental

2.1. Chemicals

SDZ (analytical standard, purity grade, 99.9%), was purchased from Aladdin Inc. All the chemicals used in the analysis were high-performance liquid chromatography (HPLC) grade. Other chemicals were all analytical grade and used without further purification. H_2SO_4 and NaOH were used to adjust the pH value of the solution and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used as the source of Fe^{2+} .

2.2. Experimental process

The schematic diagram of the reactor is shown in Fig. 1. The cylinder reactor was comprised of a quartz tube with respective inner and outer diameters of 6 mm and 25 mm and a 5 mm aluminum rod which was inserted into the inner tube. The outer electrode was made of aluminum foil glued on the outside of the quartz tube with a length of 150 mm. The SDZ solution was circulated by a peristaltic pump with a flow rate of 50 mL/min and was made to flow as a film on the inner surface of the outer quartz tube. The air was naturally introduced into the reactor, not by any other aerodynamic devices. A pulsed high voltage source (Nanjing SuMan Electronics Co., Ltd., China) was applied to the two aluminum electrodes, which could be operated at an adjustable amplitude voltage. The space between the inner and outer quartz

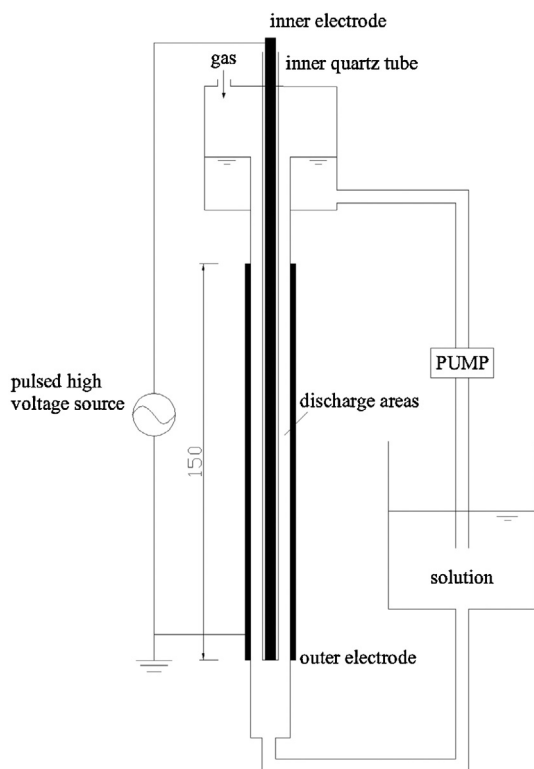


Fig. 1. Experimental setup.

tubes was the electrical discharge area. To operate the falling film reactor, water flowed down over the inner surface of outer quartz tube, making a thin dielectric film. Then, discharges occurred at the interface of the gas and the solution. For every experiment, 100 mL solutions were added into the reactor.

2.3. Analysis

An HPLC system (Agilent, USA, 1200 Series) equipped with a Thermo C18 column (4.6 mm \times 250 mm i.d., 5 μm , USA) and a multiple wavelength UV diode array detector was used to analyze the concentration of SDZ. The mobile phase consisted of 70% methanol and 30% water, the flow rate was 1.0 mL/min, and the injection volume was 20 μL . The column temperature was kept at 25 $^\circ\text{C}$ and a UV detector was set at 265 nm.

SDZ and its degradation products were analyzed by LC–MS (Agilent 1290 Infinity LC/6460 QQQ MS, USA) with an Agilent Eclipse XDB-C18 HPLC column (150 mm \times 2.1 mm i.d., 5 μm , Agilent, USA). The mobile phase was a mixture of 50% acetonitrile and 50% water with a flow rate of 0.2 mL/min. The capillary temperature was set to 200 $^\circ\text{C}$, the spray voltage was 4500 V, and the sheath gas flow rate was 18 arb. The spectra were acquired both in the negative ion scan mode and positive ion scan mode, over the m/z range from 50 to 600.

Total organic carbon (TOC) was determined on a Shimadzu 5000A TOC analyzer. The conductivity of the solution was measured by a DDS-11 AW conductivity meter. UV–vis absorption spectra of the SDZ solutions were measured by a UV-5600PC (Shanghai metash instruments Co., Ltd., China). The pH value of the solution was measured by a pH monitor (Shanghai Kangyi Instrument Co., Ltd., China, PHS-3B). The concentration of H_2O_2 was determined spectrophotometrically [15].

3. Results and discussion

3.1. The factors affecting the degradation efficiency of SDZ

The factors affecting the degradation efficiency of SDZ are shown in Fig. 2. The Fig. 2(a) shows the degradation of SDZ under different output power intensity. The output power has a significant effect on the active species production. The degradation efficiency of SDZ increased with increasing output power intensity. The maximum degradation efficiency of SDZ was 96% after 15 min under the condition of 150 W, while the degradation efficiencies were 87% and 94% in the case of 100 W and 120 W, respectively. As the output power increases, electrons gain more energy in the electric field and induce more ionization of oxygen and water molecules by collision [16], which increased the amount of the active species (HO^\bullet , O^\bullet , H^\bullet , H_2O_2 , O_3). Based on the above results, the degradation amount of SDZ was increased.

Most antibiotics have acidic and/or basic functionalities; their ionization state is controlled by both pH and their acid dissociation constant (pK_a) [17]. The pK_a of SDZ are: $\text{pK}_{a1} = 1.57$ and $\text{pK}_{a2} = 6.50$, which mean that SDZ has a neutral form at $1.57 < \text{pH} < 6.50$ and an anionic form at $\text{pH} > 6.50$. Fig. 2(b) shows the effect of the pH value on the degradation efficiency of SDZ and indicated that the degradation efficiency was the highest under weak alkaline conditions ($\text{pH} = 9.10$), where SDZ was in its anionic form. Researchers have reported that the major active species involved in the degradation of organic pollutants using gas discharge were HO^\bullet , O_3 and H_2O_2 , and under strongly alkaline conditions the generated HO^\bullet in the discharge reacted with carbonate ions immediately, which decreased the amount of HO^\bullet substantially [18], thus pH 11.04 is not suitable for the degradation of SDZ.

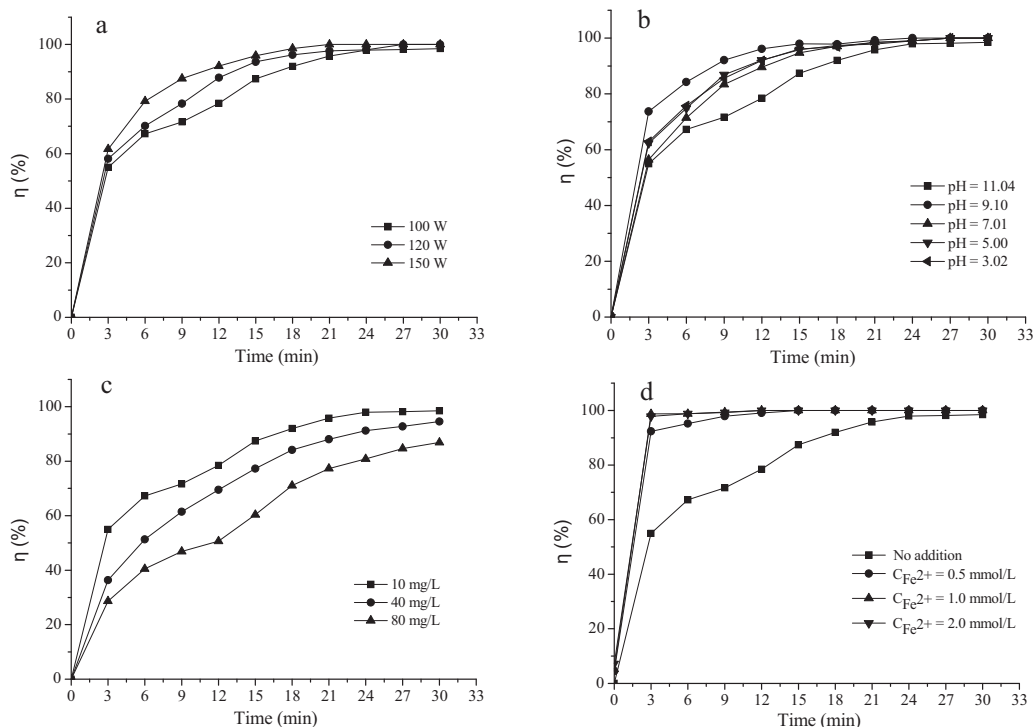


Fig. 2. The factors affecting the degradation efficiency of SDZ: (a) output power intensity ($C_0 = 10$ mg/L), (b) pH value ($C_0 = 10$ mg/L, output power = 100 W), (c) initial concentrations (output power = 100 W), (d) Fe^{2+} concentrations ($C_0 = 10$ mg/L, output power = 100 W).

As seen in Fig. 2(c), the degradation efficiency of SDZ decreases with increasing concentration. The SDZ and its intermediates are mainly oxidized by active species generated in discharge. When more SDZ is present in the solution, the active species are consumed not only in reactions with SDZ, but also in reactions with the intermediates. As such, when the inner concentration is higher, there is strong competition for reaction with the active species between SDZ and its intermediate products. In this case, the concentration of active species is probably not high enough to fully oxidize SDZ and its intermediates.

In the previous research, many researchers have found that the degradation efficiency of organic contaminants under the condition of pulsed discharge could be improved by the Fe^{2+} [19]. Fe^{2+} was added to the treated solution to increase the oxidizing power of generated H_2O_2 by the production of HO^\bullet from the Fenton reaction [20]:

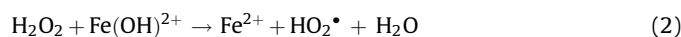


Fig. 2(d) shows the effect of adding different concentrations of Fe^{2+} on degradation efficiency of SDZ. It is shown in Fig. 2(d) that in the range of 0–1.0 mmol/L the degradation efficiency of SDZ increased with increasing Fe^{2+} concentration, which was contrary to the results from the range of 1.0–2.0 mmol/L. The lower enhancement of degradation efficiency at higher Fe^{2+} concentration could be explained by the competition between Fe^{2+} and the organic substance for HO^\bullet , with a reaction as follows [21]:



Excessive Fe^{2+} consumes HO^\bullet , reducing the amount available to react with SDZ, decreasing the degradation efficiency.

3.2. Change of pH values and conductivity

The variation of pH values of the solution during the treatment process is shown in Fig. 3 for all three initial pH values for SDZ. The pH value of the solution decreased rapidly during the first 3 min and then stayed around 1.40 for the last 15 min. The curves also show that the conductivity considerably increased linearly for all three initial pH values for SDZ, which means the ion concentration of the solution increased. The decrease of the pH value, accompanied by the increase of the conductivity, might be due to the formation of H_3O^+ ions and several special acidic substances such as nitric acid and nitrous acid during discharge [16]. Also, the formation of NO_3^- and NO_2^- from the dissolution of nitrogen oxides such as reactions (5)–(11) should be responsible for the decrease of the pH value and the increase of the conductivity. In

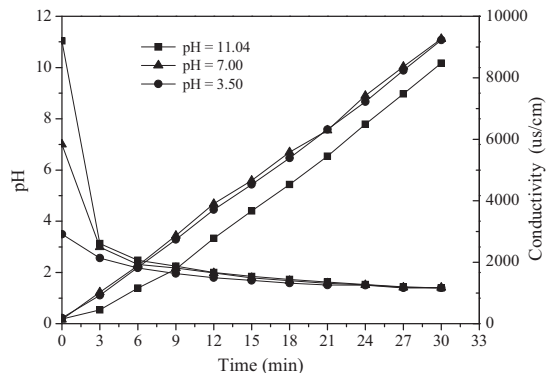
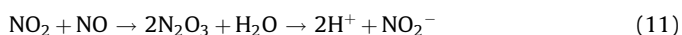


Fig. 3. The change of pH values and conductivity during the treatment ($C_0 = 10$ mg/L, output power = 100 W).

addition, the formation of H_2SO_4 formed from the degradation of SDZ decreases the pH value as discussed in the Section 3.5.



3.3. Effect of addition of radical scavengers

Fig. 4 shows the effect of adding different radical scavengers on the degradation efficiency of SDZ. Sodium carbonate, *iso*-propyl alcohol and *tert*-butyl alcohol are all hydroxyl radical scavengers, which could scavenge hydroxyl radicals in aqueous solution, and consume the amount of hydroxyl radical immediately [22]. The SDZ degradation efficiency was considerably reduced upon the addition of 150 mg/L sodium carbonate, 150 mg/L *iso*-propyl alcohol and 150 mg/L *tert*-butyl alcohol. With an addition of *iso*-propyl alcohol, the extent of degradation of SDZ decreased more drastically than from *tert*-butyl alcohol and sodium carbonate. The reaction rate constant (k) of *iso*-propyl alcohol, *tert*-butyl alcohol and sodium carbonate with hydroxyl radical are $1.9 \times 10^{10} \text{ mol L}^{-1} \text{ s}^{-1}$, $6.0 \times 10^8 \text{ mol L}^{-1} \text{ s}^{-1}$ and $3.9 \times 10^8 \text{ mol L}^{-1} \text{ s}^{-1}$, respectively [22], thus the reaction speed of *iso*-propyl alcohol with hydroxyl radical is highest, leading to the most severe decrease in the degradation of SDZ. In the presence of hydroxyl radical scavengers, the degradation efficiency was inhibited, but not completely, indicating that $\bullet\text{OH}$ played a primary role in the reaction, but not the only role.



In contrast with adding hydroxyl radical scavengers which considerably reduced degradation efficiency, Fig. 4 indicated that

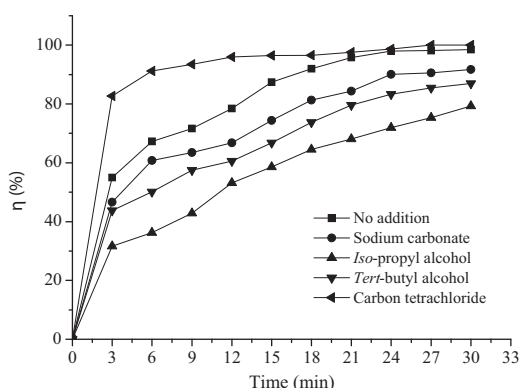


Fig. 4. Effect of addition of radical scavengers ($C_0 = 10 \text{ mg/L}$, output power = 100 W).

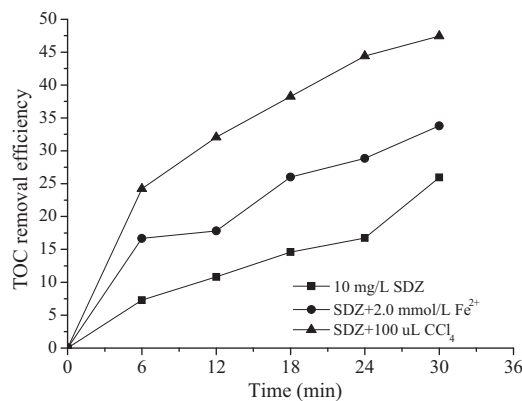


Fig. 5. Change of TOC removal ($C_0 = 10 \text{ mg/L}$, output power = 100 W).

the SDZ degradation efficiency was remarkably enhanced with CCl_4 addition. CCl_4 is one of the hydrogen radical scavengers which could react with hydrogen radical immediately. Reactions (12)–(15) indicate the enhancement mechanism of CCl_4 for the degradation of SDZ. Hydrogen radical in the system were scavenged with CCl_4 (reaction (15)), and reduce the chances of their recombination with hydroxyl radical (reaction (13)), thus increasing the concentration of hydroxyl radicals.

3.4. Change of TOC removal

The total concentration of organic pollutants in aqueous solution can be shown through the change of the TOC value, which could also reflect the mineralization rate of the pollutants in the solution. As shown in Fig. 5, only 25% TOC was removed at 30 min, indicating slower mineralization being obtained, while about 98% degradation efficiency of SDZ was achieved. It was obvious that only a small part of SDZ was mineralized. This may be explained by the generation of intermediates degrading from SDZ, which resist further degradation and react with hydroxyl radicals. The change in the UV–vis absorption spectra of SDZ solution during reaction processes has been shown in Fig. 6. After treatment, the absorbance at 265 nm shows a decrease, which indicated the degradation of SDZ molecules. However, the absorbance at around 200–250 nm shows an abrupt increase in contrast to that at 265 nm, which indicates that the formation amounts of intermediates increased with reaction times. This suggests that the mineralization of these intermediates is a much slower and difficult process.

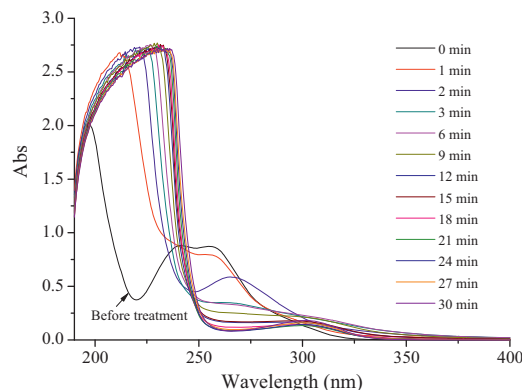
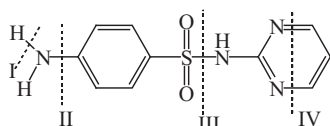


Fig. 6. UV–vis spectrum along with reaction time ($C_0 = 10 \text{ mg/L}$, output power = 100 W).

It is shown in Fig. 5 that the TOC removal rate increased in the presence of Fe^{2+} and CCl_4 , at the same reaction time the TOC removal rate increase to 33% and 47% from 25%. The enhancement of TOC removal rate in the presence of Fe^{2+} and CCl_4 could be attributed to the increase of hydroxyl radical. The increase of hydroxyl radical in the presence of Fe^{2+} was due to the reactions (1)–(3), and that in the presence of CCl_4 was due to the reactions (12)–(15), whose reason was similar to that of SDZ degradation efficiency in the presence of Fe^{2+} and CCl_4 .

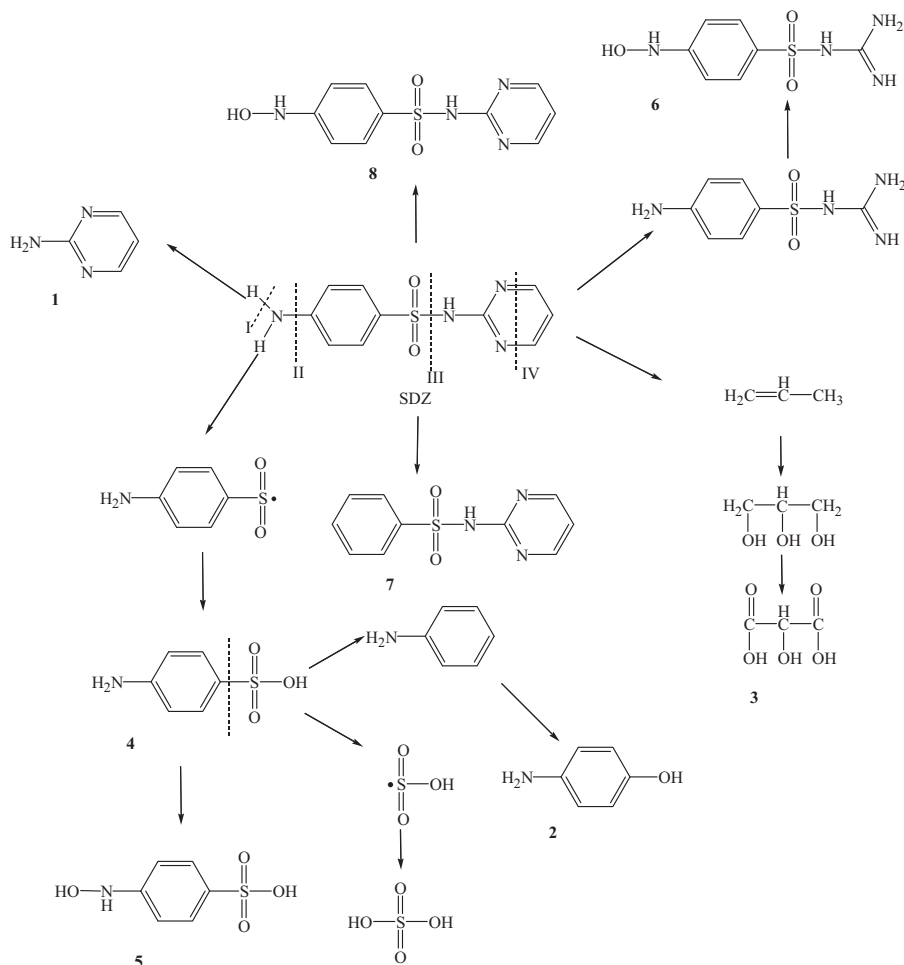
3.5. The proposed degradation pathway of SDZ

The extensive LC–MS has been successfully used for the identification of SDZ and its degradation intermediates by other researchers [8]. Based on the mass spectra, 8 intermediates of SDZ were detected, which in the Table 1. The identification of the structures corresponding to these fragments led to the degradation pathway during the reaction process depicted in Scheme 1. According to Boreen *et al.*, the potential cleavage sites of sulfonamides are as follows [23]:



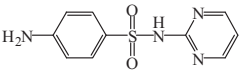
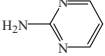


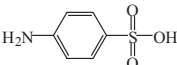
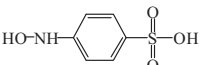
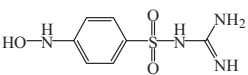
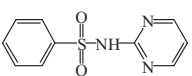
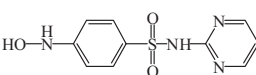
Many studies have shown that $\bullet\text{OH}$ radicals, which has strong electrophilic property and high redox potential, reacted with

most pollutants 10^6 – 10^9 times faster than that ozone [24,25], therefore the $\bullet\text{OH}$ radicals played an important role in the degradation process of SDZ in this study. The sites I to IV are all potential cleavage sites of sulfonamides that can easily be attacked by $\bullet\text{OH}$ radicals. As a result, the bond I was most likely to be attacked $\bullet\text{OH}$ radicals to produce new intermediates (compound 8). The degradation intermediate of compound 7 was mainly because of the breaking of bond II. The identification of 2-aminopyrimidine (compound 1) and sulfanilic acid (compound 4) suggested the cleavage of the III bond. Compound 5 was suggested as the oxidation products of compound 4 by the attack of $\bullet\text{OH}$ to the N–H. In addition, the observation of *p*-aminophenol (compound 2) was the product of compound 4 by breaking C–S. During the experiment process, the color of SDZ solution changed from clear to pale-yellow, this phenomenon indicated the presence of *p*-aminophenol, which is yellow in solution. The inorganic product sulfuric acid was also the products of compound 4 by the attack of $\bullet\text{OH}$, the formation of sulfuric acid may be responsible for the decrease of the pH value during reaction process. Guo *et al.* had used Gaussian 03 software to optimize the geometry structure of SDZ and found that the two bonds of N–C (cleavage sites of IV) in the pyrimidine ring were unstable and easily broken by large negative charges [26]. If the pyrimidine ring were attacked by big negative charges and other radicals, the pyrimidine would open, and then the produced radicals would be further oxidized by $\bullet\text{OH}$ radicals to form the new products compounds 3 and 6. The formation of a series of organic acids such as compound 3



Scheme 1. The degradation pathway of SDZ under plasma treatment.

Table 1
The degradation intermediates of SDZ.

Compd.	Main fragment (m/z)	Molecular formula	Molecular structure
SDZ	249	C ₁₀ H ₁₀ N ₄ O ₂ S	
1	97	C ₄ H ₅ N ₃	
2	109	C ₆ H ₇ NO	
3	118	C ₃ H ₄ O ₅	
4	172	C ₆ H ₇ NO ₃ S	
5	188	C ₆ H ₇ NO ₄ S	
6	225	C ₇ H ₁₀ N ₄ O ₃ S	
7	233	C ₁₀ H ₉ N ₃ O ₂ S	
8	264	C ₁₀ H ₁₀ N ₄ O ₃ S	

should also be responsible for the decrease of the pH value in Section 3.2, which was similar to that of sulfuric acid.

4. Conclusion

The water falling film dielectric barrier discharge was investigated with the aim of the removal of SDZ in water. The water falling film dielectric barrier discharge was very effective in the degradation of SDZ; the inner concentrations of 10 mg/L SDZ can be all removed within 30 min. The parameters that affect the degradation of SDZ such as output power intensity, pH value, inner concentration and Fe²⁺ were all strongly affected the SDZ degradation efficiency. The formation of H₃O⁺ ions, organic acids, NO₃⁻, NO₂⁻ and SO₄²⁻ led to the decrease of the pH value and the increase of conductivity. In the addition to hydroxyl radical scavengers, the degradation of SDZ was inhibited, indicating that •OH plays a primary role in the reaction. It was also found that the degradation of SDZ and the TOC removal was greatly enhanced by hydrogen radical scavenger CCl₄, which was due to the reaction of CCl₄ with •H that reduce the chances of their recombination with •OH. But, the results obtained with the change of TOC indicated that the intermediates were quite refractory to further mineralization, leading to ineffective mineralization. Based on the 8 intermediate products identified by LC-MS, the proposed degradation mechanism was investigated, and the degradation pathway of SDZ involved a series of hydroxylation, oxidative and opening of the ring processes. The •OH was the major active species and played an important role in the degradation of SDZ.

Acknowledgment

This research is supported by the State Key Laboratory of Pollution Control & Resources Reuse.

References

- [1] A.G. Trovo, S.A.S. Melo, R.F.P. Nogueira, Photodegradation of the pharmaceuticals amoxicillin, bezafibrate and paracetamol by the photo-Fenton process application to sewage treatment plant effluent, *J. Photochem. Photobiol. A: Chem.* 198 (2008) 215–220.
- [2] M.J. Benotti, B.D. Stanford, E.C. Wert, et al., Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water, *Water Res.* 43 (2009) 1513–1522.
- [3] A.B.A. Boxall, L.A. Fogg, P.A. Blackwell, et al., Veterinary medicines in the environment, *Rev. Environ. Contam.* 180 (2004) 1–91.
- [4] M. Lamshöft, P. Sukul, S. Zühlke, et al., Metabolism of 14C-sulfadiazine after administration to pigs, *Anal. Bioanal. Chem.* 388 (2007) 1733–1745.
- [5] P. Sukul, M. Spittler, Sulfonamides in the environment as veterinary drugs, *Rev. Environ. Contam. Toxicol.* 187 (2006) 67–101.
- [6] X.P. Hong, J.Y. Ma, Electrochemical study of sulfadiazine on a novel phthalocyanine-containing chemically modified electrode, *Chin. Chem. Lett.* 24 (2013) 329–331.
- [7] T. Garoma, S.K. Umamaheshwar, A. Mumper, Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation, *Chemosphere* 79 (2010) 814–820.
- [8] P. Sukul, M. Lamshöft, S. Zühlke, et al., Photolysis of 14C-sulfadiazine in water and manure, *Chemosphere* 71 (2008) 717–725.
- [9] C. Baeza, D.R.U. Knappe, Transformation kinetics of biochemically active compounds in low-pressure UV Photolysis and UV/H₂O₂ advanced oxidation processes, *Water Res.* 45 (2011) 4531–4543.
- [10] S. Esplugas, D.M. Bila, L.G.T. Krause, et al., Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents, *J. Hazard. Mater.* 149 (2007) 631–642.
- [11] P. Lukes, M. Clupek, V. Babick, et al., Generation of ozone by pulsed corona discharge over water surface in hybrid gas–liquid electrical discharge reactor, *J. Phys. D: Appl. Phys.* 38 (2005) 409–416.
- [12] D. Gerrity, B.D. Stanford, R.A. Trenholm, et al., An evaluation of a pilot-scale non-thermal plasma advanced oxidation process for trace organic compound degradation, *Water Res.* 44 (2010) 493–504.
- [13] H. Krause, B. Schweiger, J. Schuhmacher, et al., Degradation of the endocrine disrupting chemicals (EDCs) carbamazepine, clofibric acid, and iopromide by corona discharge over water, *Chemosphere* 75 (2009) 163–168.
- [14] M. Magureau, D. Piroi, N.B. Mandache, et al., Degradation of pharmaceutical compound pentoxifylline in water by non-thermal plasma treatment, *Water Res.* 44 (2010) 3445–3453.
- [15] C. Korman, D.W. Bahneman, M.R. Hoffman, et al., Photocatalytic production of H₂O₂ and organic peroxides in aqueous suspensions of TiO₂, ZnO, and desert sand, *Environ. Sci. Technol.* 22 (1988) 798–806.
- [16] Y. Zhang, M.H. Zhou, X.L. Hao, Degradation mechanisms of 4-chlorophenol in a novel gas–liquid hybrid discharge reactor by pulsed high voltage system with oxygen or nitrogen bubbling, *Chemosphere* 67 (2007) 702–711.
- [17] P. Sukul, M. Lamshöft, S. Zühlke, et al., Sorption and desorption of sulfadiazine in soil and soil-manure systems, *Chemosphere* 73 (2008) 1344–1350.
- [18] A.T. Sugiarto, T.M. Ohshima, T. Sato, et al., Oxidative decoloration of dyes by pulsed discharge plasma in water, *J. Electrostat.* 58 (2003) 135–145.
- [19] X.L. Hao, M.H. Zhou, Q. Xin, et al., Pulsed discharge plasma induced Fenton-like reactions for the enhancement of the degradation of 4-chlorophenol in water, *Chemosphere* 66 (2007) 2185–2192.
- [20] Y.F. Sun, J.J. Pignatello, Photochemical reactions involved in the total mineralization of 2, 4-D by Fe³⁺/H₂O₂/UV, *Environ. Sci. Technol.* 27 (1993) 304–310.
- [21] B.S. Lodha, S. Chaudhari, Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions, *J. Hazard. Mater.* 148 (2007) 459–466.
- [22] G.V. Buxton, C.L. Greenstock, W.P. Helman, et al., Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/O^{•-}) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [23] A.L. Boreen, X.A. Arnold, K. McNeill, Photochemical fate of sulfa drugs in the aquatic environment: sulfa drugs containing five-membered heterocyclic groups, *Environ. Sci. Technol.* 38 (2004) 3933–3940.
- [24] W.R. Haag, C.C. Yao, Rate constants of reaction of hydroxyl radicals with several drinking water contaminants, *Environ. Sci. Technol.* 26 (1992) 1005–1013.
- [25] C.C. Yao, W.R. Haag, Rate constants for direct reaction of ozone with several drinking water contaminants, *Water Res.* 25 (1991) 761–773.
- [26] Z.B. Guo, F. Zhou, Y.F. Zhao, et al., Gamma irradiation-induced sulfadiazine degradation and its removal mechanisms, *Chem. Eng. J.* 191 (2012) 256–262.