Chinese Chemical Letters 25 (2014) 187–192

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Degradation of sulfadiazine antibiotics by water falling film dielectric barrier discharge

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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 $^{\bullet}OH$ due to the reaction of CCl_4 with $^{\bullet}H$ that reduce the chances of their recombination with $^{\bullet}OH$. Based on the 8 intermediate products identified by LC–MS, the proposed evolution of the degradation process was investigated.

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 ($H^{\bullet}$, $O^{\bullet}$, $HO^{\bullet}$) 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.

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http://dx.doi.org/10.1016/j.cclet.2013.11.003

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 $FeSO_4{\cdot}7H_2O$ 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 nm 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 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.

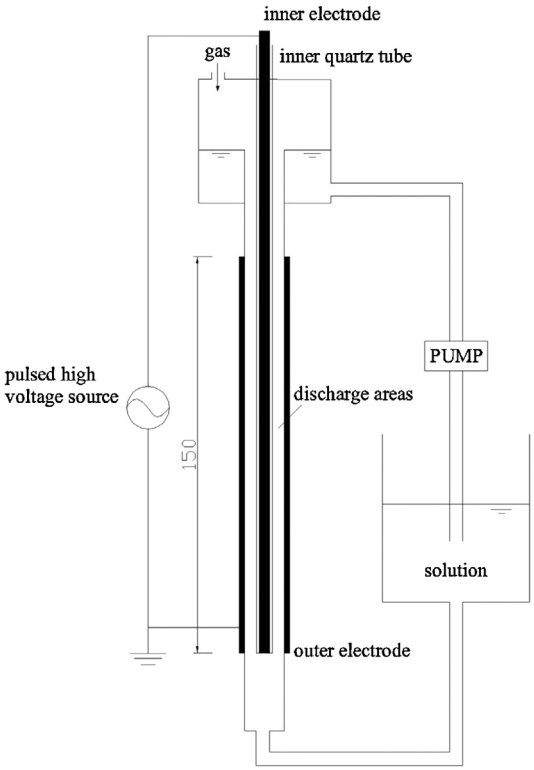

Fig. 1. Experimental setup.

2.3. Analysis

An HPLC system (Agilent, USA, 1200 Series) equipped with a Thermo C18 column (4.6 mm × 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 °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 × 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 °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: $pK_{a1} = 1.57$ and $pK_{a2} = 6.50$, which mean that SDZ has a neutral form at $1.57 < pH < 6.50$ and an anionic form at $pH > 6.50$. 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 (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.