Chemical Engineering Journal 271 (2015) 31–42

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Elucidation of the degradation pathways of sulfonamide antibiotics in a dielectric barrier discharge plasma system

Kil-Seong Kim [a], Sang Kyu Kam [b], Young Sun Mok [c,*]

[a] Environmental and Health Research Institute of Jeju Province, Jeju 690-700, Republic of Korea
[b] Department of Environmental Engineering, Jeju National University, Jeju 690-756, Republic of Korea
[c] Department of Chemical and Biological Engineering, Jeju National University, Jeju 690-756, Republic of Korea

HIGHLIGHTS

- The degradation behavior of several sulfonamide antibiotics were characterized.
- The intermediates and byproducts formed during the plasma treatment were identified.
- The degradation pathways of the antibiotics were proposed.

ARTICLE INFO

Article history:
Received 14 November 2014
Received in revised form 17 February 2015
Accepted 18 February 2015
Available online 24 February 2015

Keywords:
Plasma
Sulfonamide antibiotics
Degradation pathways

ABSTRACT

The degradation of sulfonamide antibiotics, such as sulfathiazole (STZ), sulfamethazine (SMT) and sulfamethoxazole (SMZ) in water was carried out with a nonthermal dielectric barrier discharge plasma reactor operating under dry air or oxygen. In order to understand the degradation pathways of the antibiotics, the plasma-treated aqueous antibiotic solutions were characterized by various techniques such as UV–visible spectroscopy, ion chromatography, liquid chromatography coupled to a tandem mass spectrometer (LC–MS/MS), pH and electrical conductivity measurements, and total organic carbon analysis. The degradation rates of the antibiotics investigated were found to be higher with pure oxygen than with dry air, and decreased in the order: SMT > STZ > SMZ. As the degradation proceeded, the characteristic absorption peaks gradually decreased and the solution pH and conductivity increased, indicating that the antibiotics were being mineralized. The ion chromatography identified both inorganic (SO_4^{2-}, NO_3^- and NH_4^+) and organic ions (acetate, formate and oxalate) as the stable degradation products. After 60-min plasma treatment with oxygen, the percentage of the S atoms transformed into SO_4^{2-} was in the range of 66.9–86.4%, depending upon the type of antibiotics, while of the percentage of the N atoms transformed into NH_4^+ and NO_3^- was in the range of 15.7–33.2%. The possible degradation pathways of the antibiotics were proposed from the identified intermediate products formed during the degradation, which elucidates that the hydroxylation of the ring structures in the antibiotic molecules initiates the degradation.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Antibiotics are pharmaceuticals used in a bid to cure or prevent diseases caused by microorganisms. Ever since Sir Alexander Fleming discovered penicillin in 1928, a large number of antibiotics have been discovered to-date, which has immense contribution in curing human diseases and in veterinary industries. In recent years, it has been reported that a variety of residual antibiotics was detected in the aquatic ecosystem due to misuse and improper disposal of the medicines, and has been regarded as emerging contaminants because of their latent risk and environmental persistence even at low concentrations [1–6]. Since most of the antibiotics are tolerant to biological degradation, conventional water treatment facilities adopting biological methods cannot effectively reduce their concentrations [7,8].

Among various antibiotics, sulfonamides, such as sulfathiazole (STZ), sulfamethazine (SMT) and sulfamethoxazole (SMZ) are frequently detected in the surface water because they are polar, highly water-soluble, and readily transported from one medium to another in the environment [8]. The ranges of concentrations reported in the literature for SMT, STZ and SMZ in surface water monitoring studies worldwide are 0–2.11 μg/L [9,10], 0–1.36 μg/L [10,11], and 0–0.48 μg/L [11–15], respectively. It is not possible

* Corresponding author. Tel.: +82 64 754 3682; fax: +82 64 755 3670.
E-mail address: smokie@jejunu.ac.kr (Y.S. Mok).

http://dx.doi.org/10.1016/j.cej.2015.02.073
1385-8947/© 2015 Elsevier B.V. All rights reserved.

to completely avoid such antibiotics entering the water environment through various routes, and thus an acceptable solution other than biological methods should be provided to tackle this important issue. Till now, several advanced oxidation technologies, including ozonation, ultraviolet (UV) photolysis, photocatalysis, and non-thermal plasma have been proposed to abate antibiotic compounds [16–20]. Even though the previous investigations showed that adoption of such processes can do much for reducing residual antibiotics, development of reliable technologies is still ongoing.

Homem and Santos [1] reviewed various abatement techniques available for the treatment of effluents containing antibiotics. In their review paper, they mentioned that combination of two or more processes seem to be the best solution. The degradation of trimethoprim and sulphamethoxazole antibiotics by using UV-photocatalysis was studied by Bhakta and Munekage [16] who showed that titanium oxide photocatalyst was able to degrade the antibiotics into simpler forms leaving no or less adverse impacts in the environment. More recently, the effectiveness of UV and UV/H_2O_2 process to degrade three antibiotics (oxytetracycline, doxycycline and ciprofloxacin) in natural water systems were investigated by Yuan et al. [21]. The antibiotics explored were fully detoxified after exposure to a given amount of energy, but their total organic carbon (TOC) removal was much less, indicating that the complete mineralization required much more energy. Lange et al. [22], Andreozzi et al. [23], Zheng et al. [24] and Ben et al. [25] proposed ozonation for the abatement of antibiotics. Their results revealed that the ozonation can be a cost-efficient technique for quickly eliminating the biological activity of antibiotics. Magureanu et al. [18,26] applied atmospheric-pressure dielectric barrier discharge (DBD) plasma to the oxidation of pentoxifylline and β-lactam antibiotics (amoxicillin, oxacillin and ampicillin) in water. They concluded that plasma treatment might be suitable for pre-treatment of wastewater containing recalcitrant pharmaceutical compounds. The application of DBD plasma to the treatment of antibiotics-contaminated soil was studied by Lou et al. [27], demonstrating that the DBD plasma can be a reasonable alternative to existing approach in the remediation of soil contaminated by antibiotics. They found that among various reactive species ozone played a major role in the degradation of antibiotics. Pulsed corona discharge plasma as a means for advanced oxidation has also been applied to the oxidation of aqueous pharmaceuticals [28,29]. The authors reported that this method is effective in the oxidation of pharmaceuticals and ultimate oxidation byproducts are low-molecular carboxylic acids. In the previous study [2], we applied DBD plasma operating underwater to the treatment of synthetic livestock wastewater, and evaluated the effectiveness of the plasma technology for the degradation of various antibiotics in aqueous phase. The experimental results revealed that the DBD plasma was a powerful means to degrade the antibiotics, and the degradability of each antibiotic substance differed from one another.

The objective of this work is to investigate the degradation characteristics of three antibiotics, including STZ, SMT and SMZ that belong to the sulfonamide group in a nonthermal DBD plasma reactor with dry air or oxygen as the working gas. The degradation products formed during the mineralization process were identified and analyzed to understand the degradation pathways. As well, temporal variations in pH, electrical conductivity, UV absorption pattern and TOC were monitored during the time course experiments.

2. Experimental

2.1. Materials and methods

The sulfonamide antibiotics investigated in this work are STZ (⩾98%), SMT (⩾99%) and SMZ (⩾98%), which were purchased from Fluka (USA). The molecular structures of these antibiotics with different substituents are shown in Fig. 1. The antibiotics were each dissolved in 1000 mL of distilled water to prepare synthetic antibiotic wastewater. The concentration was fixed at 50 mg L^{-1} throughout this work.

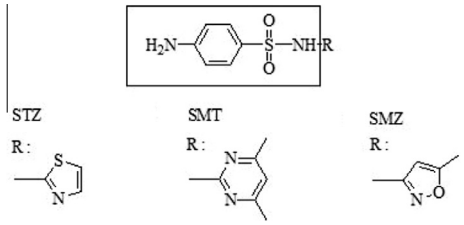

Fig. 1. Molecular structures of the antibiotics investigated.

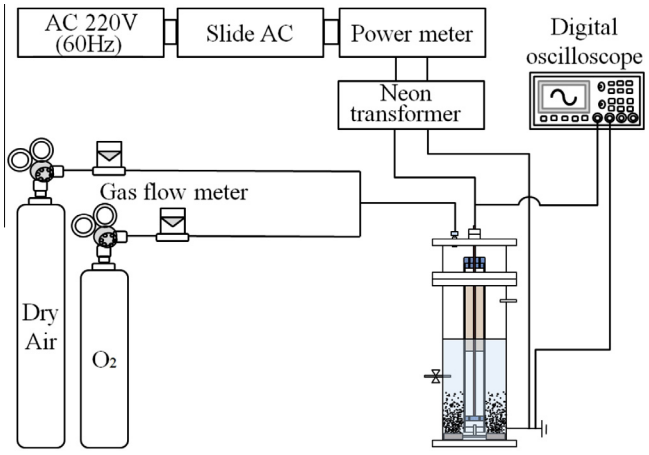

Fig. 2. Schematic diagram of the water treatment reactor.

The byproducts formed from the antibiotics, including nitrate, sulfate, ammonium, acetate, formate and oxalate, were analyzed by ion chromatography. The standard solutions for nitrate, sulfate and ammonium ions (1000 mg L^{-1}) were obtained from AccuStandard (USA), while those for acetate, formate and oxalate (1000 mg L^{-1}) from Alltech (USA). The standard solutions were diluted to suit the analytical purpose.

The mobile phase for liquid chromatography was prepared using methanol (HPLC grade, Fisher Scientific, USA), formic acid (>98%, Fluka, USA) and ammonium formate (>98%, Sigma–Aldrich, USA). The eluent for ion chromatography was prepared using methanesulfonic acid (⩾99.5%) purchased from Sigma–Aldrich (USA). Milli-Q system (Millipore, USA) was employed to make ultrapure water.

Fig. 2 describes the atmospheric-pressure DBD plasma reactor that operated underwater. It was made of a quartz tube (inner diameter: 22 mm; thickness: 1.5 mm) serving as a dielectric layer and a 7.7-mm-thick concentric stainless steel screw electrode to which alternating current (AC) high voltage at a fixed frequency of 60 Hz was connected. The vessel in which the aqueous antibiotic solution was contained was made of acrylic with an inner diameter of 90 mm. Dry air or pure oxygen (0.5 L min^{-1}) was supplied to the DBD reactor through the gas inlet on the top side of the reactor to create plasma. The voltage applied to the DBD plasma reactor was measured using a 1000:1 voltage probe (P6015, Tektronix) along with a digital oscilloscope (TDS3032, Tektronix), and the discharge power was determined by the Lissajous charge–voltage figure [30]. According to the Lissajous charge–voltage figure given in Supplementary material (Fig. S1), the discharge onset voltage (the

Download English Version:

https://daneshyari.com/en/article/146348

Download Persian Version:

https://daneshyari.com/article/146348

Daneshyari.com