Chemical Engineering Journal 219 (2013) 19–27

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Degradation of veterinary antibiotics by dielectric barrier discharge plasma

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HIGHLIGHTS

- The plasma method is very energy-efficient for degrading antibiotics.
- The degradation followed exponential decay with respect to the delivered energy.
- Each antibiotic substance shows a different degradability in the plasma reactor.

ARTICLE INFO

Article history:
Received 18 August 2012
Received in revised form 3 December 2012
Accepted 29 December 2012
Available online 11 January 2013

Keywords:
Veterinary antibiotics
Dielectric barrier discharge
Degradation
Wastewater

ABSTRACT

This work investigated the degradation of antibiotics in synthetically prepared wastewater by using dielectric barrier discharge (DBD) plasma. The veterinary antibiotics investigated include lincomycin, ciprofloxacin, enrofloxacin, chlortetracycline, oxytetracycline, sulfathiazole, sulfamethoxazole, sulfamethazine and trimethoprim. The effect of discharge power, initial concentration, working gas type (air or O_2) and working gas flow rate on the degradation was examined and discussed. The experimental results indicated that the antibiotics were easily degraded by the DBD plasma and the degradation rates were mainly governed by the amount of the delivered energy. The degradation of the antibiotics followed an exponential decay with respect to the delivered energy. Each antibiotic substance was found to show a different degradability. On the basis of an initial concentration of 5 mg L^{-1}, the energy requirements for 60% degradation efficiency were in the range of 0.26–1.49 kJ mg^{-1}, depending on the type of antibiotic substance, while those for 90% degradation efficiency ranged from 0.39 to 2.06 kJ mg^{-1}. The DBD process proposed in this work may be a promising method for effectively degrading veterinary antibiotics.

1. Introduction

Veterinary antibiotics are powerful drugs that prevent and fight bacterial infectious diseases of animals. Since prevention of disease transmission and enhancement of growth and feed efficiency are critical in modern animal husbandry, there has been widespread incorporation of antibiotics into feeds for livestock in many countries [1]. Even though estimates from different sources are not directly comparable, it is certain that there is considerable use of antibiotics in livestock farming. Releases of veterinary medicines to the environment occur both directly, for example through the treatment of animals on pasture, and indirectly, via the application of animal manure containing excreted products to land and once released to land, the veterinary medicines may leach to groundwater or be transported to surface waters in drainage waters and overland flow [2]. Such veterinary antibiotics may pose a risk to the environment as a new class of contaminants, and recently the potential hazard of residual antibiotics to the ecological system has been the subject of intense debate and research. In general, antibiotics have low biodegradability because they are biocidal substances. To arrest potential threat of antibiotics, misuse and abuse should be avoided, and in the long run, appropriate processes to effectively degrade the antibiotics need to be developed.

The degradation of antibiotics cannot be accomplished in the natural environment or biological treatment plants [3], and thus it is clear that chemical oxidation methods or advanced oxidation processes (AOPs) such as ozonation, photolysis, radiation and catalysis are necessary for the degradation of these pollutants; yet, there have so far been only a few studies reported in the literature. Bhakta and Munekage [4] investigated the degradation capacity of widely used trimethoprim and sulfamethoxazole antibiotics by employing ultraviolet (UV) light and TiO_2 in water phase, which revealed that the synergistic photocatalytic effects of the TiO_2 with UV leads to a rapid and higher degree of degradation of the antibiotics, compared to that of only UV photolysis.

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http://dx.doi.org/10.1016/j.cej.2012.12.079

Photodegradation of oxytetracycline, doxycycline and ciprofloxacin under UV irradiation and UV irradiation plus H_2O_2 was investigated by Yuan et al. [5]. They found that an increased toxic effect occurred in the UV direct photolysis with the decay of the antibiotics whereas in the UV/H_2O_2 process, the toxicity increased first, and then decreased to no measurable toxicity. Antibiotics with complicated chemical structure have many reaction sites that can be attacked by ozone, and ozonation can be proposed as a means for the abatement of antibiotics. Previous investigations by several authors have demonstrated that ozone is capable of attacking antibiotics of different classes [6,7]. According to Lange et al. [7], antibiotics can be fully eliminated from wastewater even at a low ozone dose and the rate of degradation reaction is fast. Balcioğlue and Ötker [3] compared ozonation process with O_3/H_2O_2 and O_3/UV (254 nm) processes, who found that the introduction of H_2O_2 did not enhance the treatment efficiency of enrofloxacin but the incorporation of UV light somewhat enhanced the degradation, implying that ozonation or photolytic ozonation processes seem to be promising methods for degrading antibiotics. More recently, various conventional techniques (biological processes, filtration, coagulation, flocculation and sedimentation), AOPs, adsorption, membrane processes and combined methods were evaluated and compared by Homem and Santos [8] who addressed that combined processes may the best solution for the treatment of effluents containing antibiotics. AOPs can be combined with bioremediation technologies for non-biodegradable wastewater treatment and reuse. Oller et al. [9] reviewed AOPs (as a pre-treatment or post-treatment stage) combined with bioremediation technologies, placing special emphasis on recent studies and large-scale combination schemes.

In this work, we applied dielectric barrier discharge (DBD) plasma to the degradation of antibiotics in aqueous phase. The DBD plasma has been widely used to generate ozone and remove air and water contaminants [10–14]. To evaluate the effectiveness of the plasma technology for the treatment of livestock wastewater containing antibiotics, nine common veterinary antibiotics including lincosamide group (lincomycin), quinolone group (enrofloxacin, ciprofloxacin), sulfonamide group (sulfathiazole, sulfamethoxazole, sulfamethazine, trimethoprim) and tetracycline group (chlortetracycline, oxytetracycline) were chosen. Previously, Magureanu et al. [13,14] studied the degradation of several pharmaceutical compounds such as β-lactam antibiotics (amoxicillin, oxacillin and ampicillin) and pentoxifylline by using a pulsed DBD plasma generated at gas–liquid interface. The remediation of soil contaminated by antibiotics using an atmospheric pressure DBD plasma was investigated by Lou et al. [15]. Their results suggest that plasma process might be of interest for the treatment of wastewater and soil containing recalcitrant pharmaceutical compounds. For the present work, a cylindrical DBD reactor consisting of a quartz tube and a concentric metal electrode was submerged in synthetically prepared wastewater. Dry air or O_2 was fed to the DBD reactor and reactive species generated from the DBD reactor was transferred to the wastewater through a ceramic gas diffuser. This paper reports that the antibiotics examined could be effectively degraded by using the DBD process. To the best of our knowledge, this is the first report covering the degradation of a wide range of antibiotics by using the plasma technology.

2. Experimental

2.1. Materials

The target antibiotics such as lincomycin, ciprofloxacin, enrofloxacin, chlortetracycline, oxytetracycline, sulfathiazole, sulfamethoxazole, sulfamethazine and trimethoprim were purchased from Dr. Ehrenstorfer GmbH (Germany). Fig. 1 presents the molecular structures of the antibiotic substances investigated in this work.

$^{13}C_3{}^{15}N$-ciprofloxacin (99%), $^{13}C_6$-sulfamethazine (90%), $^{13}C_6$-sulfamethoxazole (99%), $^{13}C_6$-thiabendazole (99%) and $^{13}C_3$-trimethoprim used as isotopic internal standards were supplied by Cambridge Isotope Laboratories (USA).

Methanol (HPLC grade), formic acid and hydrochloric acid were obtained from Fisher Scientific (USA), Wako (Japan) and Matsunoen (Japan), respectively. Milli-Q system (Millipore, USA) was used to produce ultrapure water.

Standard solutions of ciprofloxacin, enrofloxacin, chlortetracycline, oxytetracycline, lincomycin, sulfathiazole, sulfamethoxazole, sulfamethazine and trimethoprim were prepared by diluting with methanol to a concentration of 250 mg L^{-1}, which were kept in a refrigerator. Synthetic wastewater was made by dissolving a given amount of the aforementioned standard solutions in distilled water of which volume was 1000 mL. The initial antibiotic concentration was changed from 0.2 to 5.0 mg L^{-1}.

2.2. Apparatus and methods

Fig. 2 shows the DBD plasma reactor comprising a quartz tube (inner diameter: 22 mm; outer diameter: 25 mm), a coaxial stainless steel screw electrode (diameter: 7.7 mm) and a ceramic gas diffuser connected to the lower end. The DBD reactor was energized by applying 60 Hz alternating current (AC) high voltage to the stainless steel screw acting as the discharging electrode. The DBD plasma reactor was partly immersed in the synthetic wastewater that was connected to the ground electrode. Due to its electric conductivity, the synthetic wastewater effectively elongates the ground electrode to the surface of the quartz tube. Dry air or pure oxygen was fed to the DBD reactor from the top, and gas-phase reactive species formed there (mainly ozone) were transferred and dispersed into the wastewater through the ceramic gas diffuser. The upper end of the quartz tube is open, through which the dry air or oxygen enters the quartz tube. The volume of treated water was 1000 mL. The degradation of each antibiotic compound was separately investigated. The effective DBD reactor length corresponding to the submerged part was about 20 cm. The discharge power was changed in the range up to 8.9 W by changing the voltage applied to the DBD reactor.

2.3. Analyses and measurements

Liquid chromatography–electrospray ionization tandem mass spectrometry (LC–ESI-MS/MS) system equipped with an ACQUITY® TQ detector and a 1.7 m ACQUITY UPLC BEH C_{18} column (100 × 2.1 mm) (Waters, USA) was employed to analyze the antibiotic substances. The LC–ESI-MS/MS may provide the most promising method for analyzing the antibiotics at environmentally relevant levels. The limits of quantification for the antibiotics investigated are 2.07 (lincomycin), 4.84 (ciprofloxacin), 4.82 (enrofloxacin), 2.32 (chlortetracycline), 3.89 (oxytetracycline), 1.77 (sulfathiazole), 4.63 (sulfamethoxazole), 5.87 (sulfamethazine) and 2.88 ng mL^{-1} (trimethoprim), respectively. The mobile phase was prepared by 0.1% formic acid solution and methanol, and its flow rate was 0.2 mL min^{-1}. The temperature of the column was maintained at 30 °C. Details on the analytical condition are summarized in Table 1. The concentration of gaseous ozone generated by the DBD plasma reactor was analyzed by a photometric O_3 analyzer (Model 400E, Teledyne Instruments) after diluting the gas sample with dry air to less than detection limit.

The voltage applied to the DBD reactor was measured by a high voltage probe having an attenuation ratio of 1000:1 (P6015, Tektronix) and a digital oscilloscope (TDS 3032, Tektronix). The