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Research article

Evaluation of antibiotic oxytetracycline removal in water using a gas phase dielectric barrier discharge plasma

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ABSTRACT

Degradation of oxytetracycline (OTC), a primary member of antibiotics in water, was performed by a gas phase dielectric barrier discharge (GPDBD) plasma reactor. The influences of operation conditions including applied voltages, air bubbling rates, initial OTC concentrations and initial pH values on OTC abatement were investigated respectively. The results showed that the decontamination process can be fitted by first order kinetics, and the removal ratio and rate were affected obviously by those parameters. After 20 min of discharge treatment, approximately 93.4% of OTC was removed under the experimental conditions: applied voltage of 7.5 kV, air flow rate of 1.0 L/min, initial OTC concentration of 100 mg/L, and initial pH of 5.0. In addition, TOC and COD removal efficiency reached 43.0% and 73.7% at the original pH 9.3, respectively. Furthermore, the amounts of hydrogen peroxide and ozone in aqueous were quantitatively measured to evaluate their roles during antibiotic removal, and the main function of hydroxyl radicals was demonstrated by the radicals scavenger test. At last, the analyses of UV–Vis spectra and HPLC-MS were employed to study the OTC elimination mechanism, and the possible decomposition pathway was proposed based on the speculated intermediates.

1. Introduction

Antibiotics, a kind of most widely used pharmaceuticals and personal care products (PPCPs), have obtained grave concern in the field of emergent environmental pollution control (Moussavi et al., 2018; Pa Dzior et al., 2017). Many researchers reported that the concentration of antibiotics is not low in the effluent of sewage disposal plant, the reason may be that the design objective of antibiotics is to sterilize bacteria, so the traditional biological technique is ineffective to remove theses pollutants, which eventually lead to a few underlying and adverse effects on ecological balance and public health (Lucas et al., 2016). For antibiotic tetracyclines, oxytetracycline (OTC) is a key member, which is detected in various water bodies throughout the world (Ren et al., 2017; Gu et al., 2018). Some papers found that the residues of OTC not only can affect the biological activity of environmental organisms, but also disorder the normal function of human body (Gu and Karthikeyan, 2005; Watkinson et al., 2007). Herein, great attention has been given to the removal of OTC in water.

The research for degradation of OTC is concentrated on several physical and chemical methods, for instance, adsorption, membrane filtration, electrolysis, photocatalysis, as well as other advance oxidation processes (AOPs) (Acosta et al., 2016; Lu et al., 2017; Zhang et al., 2017a; Zhao et al., 2013; Liu et al., 2018a). However, the contaminants are just transferred to the solid phase and not decomposed completely in these physical approaches, which would result in secondary pollution (Wang et al., 2017a; Zhang et al., 2017b). In addition, some more toxic byproducts would generate during few chemical processes. Even though those techniques may be feasible to eliminate OTC, there are still plenty of rooms for improvement to realize the process for low cost, safe, rapid and easy in practice.

Non-thermal discharge plasma is a new way of AOPs, which can effectively degrade organic compounds in water and atmosphere (Li et al., 2016; Tang et al., 2013; Wang et al., 2018). Its action mechanism could be attributed to the large number of chemically oxidative species generated in plasma, for example, ozone (O_3), hydroxyl radical (·OH), and hydrogen peroxide (H_2O_2), and multiple physical effects such as high-energy electrons, strong field, shockwave, and ultraviolet radiation, which can decompose most organics fast and non-selectively (Mizuno, 2013; Jiang et al., 2018). So the merits of discharge plasma include high removal rate, good efficiency, and friendly for environment. The forms of discharge mainly have glow, corona, gliding arc, jet, and dielectric barrier discharge (DBD), and their productions are decided by the various configurations of discharge electrodes and power supplies (Tao et al., 2016; Tang et al., 2018). Among these plasma types, DBD plasma is extensively studied and developed since it can be produced heavily and stably by some simple electrode

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structures.

Nowadays, the obstacles to the practical application for DBD plasma are as follows (Jiang et al., 2014; Locke and Thagard, 2012): firstly, for typical gas phase, liquid phase and gas liquid phase discharge reactors, the discharge gap between high voltage electrode and ground electrode is usually only a few millimeters, limiting the reactor processing capacity for waste gas, water, and solid; secondly, the mass transfer and contact of chemically reactive species and target pollutants are confined by the reactor configuration; thirdly, if the discharge channel is enlarged for the increasing treatment ability, the supply power of the plasma reactor is put forward higher requirements on the discharge stability and energy conversion efficiency; fourthly, for the wastewater treatment, the generation state of DBD is often influenced by the water conductivity, electrode corrosion and system temperature elevation.

Hence, to overcome those shortcomings in DBD practical application, we develop a gas phase dielectric barrier discharge (GPDBD) reactor for wastewater treatment. Its characteristics are as follows: first, a large amount of reactive substances, including O_3, ·OH, and ·O radicals, could be produced in gaseous phase, and then quickly injected to the liquid phase in the shape of minute bubbles, enhancing the mass transfer and fully contacting with the objective pollutants; second, this continuous injection form can break through the limitation of plasma reactor scale, increasing treatment capacity of wastewater and reducing the demand of power supply; third, the treated wastewater is used as the ground electrode, so the discharge state is hardly affected by water conductivity; fourth, the discharge electrode is separated from water by dielectric, avoiding the electrode corrosion; fifth, the treated water can be utilized to cool high voltage electrode, preventing the overheating of electrode. To sum up, this GPDBD reactor might be a very promising technique to treat organic wastewater in practice (Zhang et al., 2017c; Wang et al., 2016a).

In this work, OTC was chosen as the model antibiotic due to its extensive application, high water solubility, highly poisonous, and biorefractory in environment. The target of this work was to evaluate the potential employment of the GPDBD system to degrade OTC in water. OTC removal efficiency was determined under different operation parameters, including applied voltages, air flow rates, initial OTC concentrations, and initial pH values. The roles of chemically oxidative species were assessed during OTC removal. The mineralization and degradation process was characterized by the analyses of TOC, COD, UV–Vis adsorption spectrogram, and High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS).

2. Experimental

2.1. Materials

OTC was of analytical reagent grade and purchased from Nanjing Duly Biotechnology Corporation, China. Other reagents applied in this work were analytical grade and employed as purchased. The simulated OTC wastewaters with different concentrations were prepared by adding various amount of solid sample into a certain volume of deionized water.

2.2. GPDBD reactor

The schematic drawing of the GPDBD system applied in this study is shown in Fig. 1a, which included an alternating current power source (6 kHz, CTP-2000K, Nanjing Suman Plasma), an electric monitoring unit that contained a Tektronix P6015A voltage probe, a Tektronix P6021 current probe, and a Rigol DS2102A oscilloscope, a gas supply part that consisted of an air pump and a rotor flow meter, and a plasma reactor. The reactor was a cylindrical quartz tube with 13 mm inner diameter, 1 mm wall thickness, and 300 mm height. A stainless steel spring with 13 mm outer diameter and 260 mm height, was applied as the high voltage (HV) terminal and tightly placed in the wall of that silica tube. A plexiglass cylinder with 80 mm inner diameter and 430 mm height was used as the reactor shell and filled with 900 mL OTC solution, and then the wastewater was applied as the ground electrode and grounded by an electric wire in the bottom of the reactor. The carrier gas was pumped into the liquid phase through the submerged tube after being dried by a self-prepared silica gel pipe. Reactive species were produced from the gas surface discharge area in the tube and injected to the solution by an aerator.

The representative voltage and current wave profiles received from the oscilloscope are presented in Fig. 1b. The Lissajous figure (Fig. 1c) was obtained by the measured high voltage and low voltage of a 60 μF capacitance, which was inserted between the ground electrode and earth. The calculated area of Lissajous figure was used to compute the discharge power of the GPDBD reactor by the following equation (Li et al., 2011):

$$P = f\int_{o}^{1} UIdt = fC\int_{0}^{1} U\frac{dU_c}{dt}dt = fC\oint UdU_c = fCS$$

where P (W) was the discharge power, U (V) was the peak voltage, I (A) was the current, f (Hz) was the discharge frequency, C was the measuring capacitance, Uc (V) was the voltage between the capacitance, S was the area of Lissajous figure.

OTC, and its TOC and COD removal efficiencies were calculated by the following equation, respectively:

$$\text{Removal } \% = \frac{C_0 - C_t}{C_0} \times 100\%$$

where the C_0 and C_t were the concentrations of target value at time 0 and t, respectively.

The energy efficiency (G, mg/kJ) was defined as the removed mass of OTC divided by discharge power:

$$G = \frac{m_{OTC}}{Pt}$$

where m_{OTC} (mg) was the amount of removed OTC, P (kW) was the discharge power, and t (s) was the treatment time.

2.3. Analysis methods

TOC values of the simulated OTC wastewater were determined by a total organic carbon analyzer (Shimadzu TOC-V). COD values were identified by the potassium dichromate standard method. H_2O_2 amounts were analyzed by potassium titanium (IV) oxalate method (Sellers, 1980; Li et al., 2018). O_3 concentrations were measured by iodometry method (Rakness et al., 2010). The determination of OTC and its elimination intermediates was performed by a HPLC-MS (Agilent 6460 Triple Quad LC/MS, USA) using an Agilent Eclipse XDB-C_{18} analytical reversed-phase column (150 × 4.6 mm, 3.5 μm) in the positive ion mode. The UV detector of HPLC was implemented at the wavelength of 354 nm, and the mobile phase was consisted of 0.1% acetic acid in H_2O and acetonitrile (84:16 v/v) at 0.2 mL/min flow rate.

3. Results and discussion

3.1. OTC removal in GPDBD

3.1.1. Effect of applied voltage

Fig. 1d illustrates the main process of OTC degradation by GPDBD system. The generation of ·OH, H_2O_2, and O_3 in discharge plasma is the critical step during the removal process. The first important factor impacts these active species production is the applied voltage of the reactor. Herein, the effect of discharge voltage on OTC degradation was investigated initially, and the result is shown in Fig. 2a. The other experimental parameters included air bubbling velocity 1.0 L/min, original pH 9.3 and initial OTC concentration 100 mg/L. It was found that OTC decomposition efficiency enhanced with applied voltage, and the