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Application of dielectric barrier discharge plasma for degradation and pathways of dimethoate in aqueous solution

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ABSTRACT

Increasing concerns on environmental water quality have led to the development of effective techniques to remove or decompose water pollutants for health purposes. This paper reported dielectric barrier discharge (DBD) plasma-induced degradation and effects of degradation parameters and degradation pathways of dimethoate in aqueous solution. DBD parameters including discharge power and air-gap distance, dimethoate initial concentration, and radical intervention with radical promoters or scavenger were investigated for their effects on the degradation efficiency by determination of the remaining concentration of dimethoate in the treated solution using HPLC. In addition, identification of intermediates and products were explored using GC–MS, UV–VIS spectrometer and FT-IR techniques. The corresponding DBD plasma degradation pathways of dimethoate were also proposed. The result shows that the degradation efficiency is greater than 96% at the optimum degradation parameters: dimethoate initial concentration = 20 mg L^{-1}, applied power = 85 W, air-gap distance = 5 mm, and treatment time = 7 min. The degradation efficiency is clearly accelerated by adding radical promoters, but sharply decelerated in the presence of radical scavenger. These results have revealed a novel effective method for dimethoate degradation, demonstrated hydroxyl radical (·OH) playing an important role in the degradation pathways, and suggested potential application of DBD plasma for degradation of dimethoate in water.

1. Introduction

In the past decades, organophosphorus pesticides have been widely used as an alternative to organochlorine compounds for controlling pests and improving agricultural productivity. However, due to the extensive application and moderate persistence of organophosphorus pesticides, currently their residues accumulated in air, soil, food, surface water, and wastewater have been widely detected, and it has become a major environmental issue [1–4]. Therefore, increasing concerns on environmental water quality have led to the development of effective techniques to remove or decompose pesticide residues for health purposes.

Some Advanced Oxidation Process (AOPs) including Fenton oxidation [5,6], photocatalysis [7,8], ozonation [9], and electrochemical degradation [10] have been used to remove organophosphorus pesticide residues. However, these treatments still have limitations due to the lower removal efficiency and the formation of undesirable by-products. Plasma is an innovative medium that may rise to these challenges since it has been proven to be effective for the removal of organophosphorus pesticide molecules [11–15] by degradation and detoxication of the contaminants while producing no secondary pollutants during the process. In recent years, dielectric barrier discharge (DBD) plasma has become one of the most effective plasmas, and received a great deal of attention in the environmental protection field. It is stable and can be easily produced under ambient conditions to realize uniform micro-discharge with a large discharge area [16]. Electrical discharge of DBD applied upon water has been demonstrated to initiate a variety of physical and chemical conditions that can directly or indirectly cause organic compound degradation. Physical conditions include the formation of ultraviolet light and shock waves, and the magnitude of the contributions of these factors depends strongly upon the discharge parameters. Chemical conditions that occur in electrical discharges in water include the direct formation of reactive species such as ·OH, ·O, ·H radicals, H_2O_2, and O_3. Many hazardous organic compounds are readily attacked by excited species, free radicals, electrons, ions and/or UV photons generated in DBD to form certain small organic and inorganic molecules [17–19]. However, DBD degradation pathways are still not well understood.

Dimethoate has been widely used as a broad spectrum dithiophosphate pesticide in agricultural cultivations in the world. Over 20,000 tons of dimethoate was consumed in China last year; consequently, it was increasingly detected in surface water and wastewaters [4,20]. It is reported that exposure to dimethoate can cause certain abnormalities, such as benign and malignant

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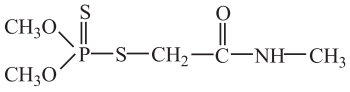
neoplasms of the liver, endocrine organs and lymphatic system, atrophy of the testes, chronic renal disease and parathyroid hyperplasia [21]. In addition, a recent report has also revealed that dimethoate can induce oxidative stress and DNA damage in rainbow trout [22]. So far, the degradation of dimethoate by DBD is still largely unreported, and the related degradation pathways need to be explored.

In this research, dimethoate was selected as the representative organophosphate pesticides. The dimethoate degradation behavior and pathways by DBD plasma treatment in aqueous solution were experimentally investigated. DBD parameters including applied power, air-gap distance, and other degradation parameters such as dimethoate initial concentration, the presence of radical promoters (hydrogen peroxide and ferrous ion) and radical scavenger (tertiary butanol) with different degradation efficiency were detected. In order to clarify the major DBD plasma degradation reactions as well as degradation pathways, the intermediates and products obtained during DBD plasma treatment were also analyzed. To the best of our knowledge, this work is the first research that investigates the DBD plasma degradation of dimethoate in aqueous solution with a reaction mechanism proposal. Therefore, this work is of great scientific significance both in the treatment of wastewater containing contaminants and in the applications of environmental protection.

2. Material and methods

2.1. Chemicals

Dimethoate (*O*,*O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate) has a molar mass of 229.3 g mol^{-1}, with the molecular formula of $C_5H_{12}NO_3PS_2$. The CAS registry number for dimethoate is 60-51-5 and the acute oral LD_{50} in rats is 387 mg kg^{-1}. The solubility of dimethoate in the water at room temperature is 39 g L^{-1} and the chemical structure of dimethoate is listed as follow



Dimethoate with 99% purity was obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China) and used as a standard to calibrate the concentration of dimethoate with 50% purity by standard curve method of HPLC. Commercial dimethoate with a purity of 50% purchased from the Wuhan Zhongxin Chemical Co. was employed for DBD plasma treatment. Stock working solution with accurate concentration of 2500 mg L^{-1} was prepared and calibrated by the 99% purity one for further dilution at desired working concentration series. It was stored avoiding exposure to light in the refrigerator at 4 °C, and made to ensure that no degradation occurred prior to the DBD plasma treatment. All samples were prepared using ultrapure water prepared by an Ultrapure Gradient water purification system (AXLC 1805). All other chemicals, purchased from Xi'an Chemical Co., were analytical grade and organic chemicals were redistilled before using.

2.2. DBD plasma reactor

Fig. 1 shows the schematic diagram of experimental apparatus employed in this work. The experimental apparatus consists of a high-frequency AC power supply and a DBD reactor. Power supply was supplied by Nanjing Suman Electronic Corporation, Ltd. with a

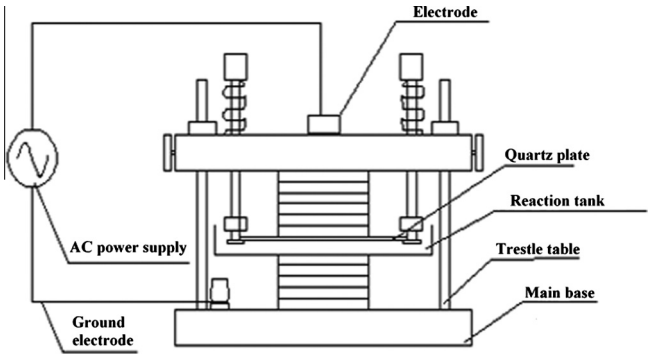


Fig. 1. Schematic diagram of the experimental apparatus.

frequency ranges of 5–35 kHz. The electrical power is calculated by the product of voltage (0–250 V) and current (0–1.2 A). The main part of the reactor used to treat the dimethoate solution is a reaction tank, which consisted of two parts. The upper part of the reaction tank is a quartz plate (110 mm × 1 mm) and the bottom part (150 mm × 2 mm × 10 mm) is a glass culture dish containing the contaminant solution. The reaction tank is put in the center of two stainless steel electrodes. The gap between the quartz plate and the water surface is filled with air. A large number of high-reactive species are generated in the discharging process, which facilitate the degradation of dimethoate solution.

2.3. Analysis methods

2.3.1. HPLC analysis

For each experiment, 40 mL dimethoate solution was added to the reaction tank, and taken from the reactor at regular intervals and analyzed immediately to avoid further reactions. The concentrations of dimethoate remained in the solution were measured using a Shimadzu LC-10A HPLC system with a 5-μm reversed phase C_{18} column (150 mm × 4.6 mm) and detected with a diode array UV detector, SPD-M10Avp. Methanol and an aqueous solution made by mixing ultrapure water with 0.25% acetic acid and 0.005% triethylamine were used as the mobile phase with a volume ratio of 40:60 (methanol to aqueous solution) and a flow rate of 0.8 mL min^{-1}. Identification and quantitative analysis were taken based on the peak retention times and UV spectra standard calibration. The detection wavelength was set at λ = 220 nm and the injection volume was 10 μL. Each sample was injected twice during HPLC analysis to monitor the reproducibility. The degradation percentage η_A was calculated by equation (1).

$$\eta_A = \frac{c_0 - c_t}{c_0} \times 100\% \quad (1)$$

where C_0 and C_t are the initial and final concentration of the dimethoate solution, respectively.

2.3.2. GC–MS analysis

The analysis of intermediates and products during DBD plasma degradation of dimethoate was performed using a Shimadzu gas chromatograph (2010 plus), equipped with an Rxi-5MS column (30 m × 0.25 mm × 0.25 μm), and the GC–MS column was operated under a programmed temperature mode in which an initial temperature of 50 °C was held for 3 min before ramping up to 280 °C at a rate of 10 °C min^{-1}, and the final temperature was held for 2 min. The injector, interface and ion source temperatures were set at 230, 250 and 200 °C, respectively. Helium was used as the carrier gas with a flow rate of 1 mL min^{-1}. A 1.0 μL sample was injected into GC–MS and their fragmentation ions and retention times were determined. Mass spectra was obtained by