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Acetamiprid removal in wastewater by the low-temperature plasma using dielectric barrier discharge

Shanping Li [a,b,*], Xiaolong Ma [a], Yanyan Jiang [a], Xiaohong Cao [a]

[a] School of Environmental Science and Engineering, Shandong University, 27 Shandananlu, Jinan 250100, China
[b] Shandong Key Laboratory of Water Pollution Control and Resource Reuse, Jinan 250100, China

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ABSTRACT

Degradation of acetamiprid in wastewater was studied in a dielectric barrier discharge (DBD) reactor. This reactor produces ultraviolet light and reactive species like ozone (O_3) can be used for the treatment of wastewater. We examined the factors that could affect the degradation process, including the discharge power, and the initial concentrations of acetamiprid, and O_3 which is generated by the DBD reactor. We also investigated the effect of adding $Na_2B_4O_7$ as a radical scavenger to probe the role of hydroxyl radical in the reaction. The results indicated that acetamiprid could be removed from aqueous solution effectively and hydroxyl radicals played an important role during the degradation by the low temperature plasma. The degradation process of acetamiprid fits the first-order kinetics. The degradation efficiency was 83.48 percent at 200 min when the discharge power was 170 W and the initial acetamiprid concentration was 50 mg/L. The removal efficiency of acetamiprid decreased with the increasing concentration of $Na_2B_4O_7$ because $B_4O_7^{2-}$ is an excellent radical scavenger that inhibited the generation of $^{\bullet}OH$ during the DBD process. The removal efficiency of acetamiprid improved in the presence of O_3. The main reason was that O_3 can oxidize certain organic compounds directly or indirectly by generating hydroxyl radicals. The degradation products of acetamiprid were characterized qualitatively and quantitatively using high performance liquid chromatography, mass spectrometry and UV–vis spectroscopy.

1. Introduction

Acetamiprid, a neonicotinoid insecticide, is a nitromethylene heterocyclic compound that has a relatively strong groundwater infiltration (Shi et al., 2013). Acetamiprid has been widely used in agriculture because of its good insecticidal effect, but it has also brought serious environmental problems at the same time (Li et al., 2010). Due to the high stability and solubility of acetamiprid in aqueous solution (Yang et al., 2013), the conventional technologies used for the purification of wastewater that contain acetamiprid are not effective (Kavitha and Palanivelu, 2005). Though on a large scale, many physico-chemical methods have been tested for the treatment of pesticide wastewater, in general, mineralization was not achieved. These methods may transfer the pollutant to another phase that resists the desired mineralization (Jansson et al., 2004).The degradation processes using microorganisms like bacteria are relatively slow and inefficient (Guo et al., 2005). Therefore, new techniques are needed for the removal of this kind of pollutant in wastewater.

In this challenging context, the development of new advanced oxidation processes (AOPs) is the subject of intense scientific activity at national and international levels (Molina et al., 2013). Among the different techniques, the "low-temperature plasma techniques" are very promising (Wei et al., 2014) because the resulting processes are simple, effective and easy for further technological transfer and do not require the use of other chemical agents (Gao et al., 2003; Grabowski et al., 2006). They have been widely used in research regarding catalyst treatment (Wang et al., 2004), surface treatment (Liu et al., 2004), volatile organic compound (VOC) degradation (He et al., 2005), and some other fields. The application of dielectric barrier discharge (DBD) technology in the degradation of organic wastewater has been developed in recent years (Mok and Jo, 2006; Sobczyk-Guzenda et al., 2013). The main merits of electrical discharge plasmas in environmental applications may be the in situ generation of strong oxidizing agents such as ozone (O_3) and hydroxyl radicals ($^{\bullet}OH$), which are highly effective for removing contaminants from polluted gas or water (Jiang et al., 2013; Kim 2004; Lukes et al., 2004).

At the beginning of dielectric barrier discharge, both physical and chemical processes happen (Bian et al., 2003). The detailed mechanisms are as follows:

(1) The role of high-energy electrons. When the discharge begins, high-energy electrons are formed (Zheng et al., 2004). High-

* Corresponding author. Fax: +86 0531 88362872.
E-mail address: lishanping@sdu.edu.cn (S. Li).

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energy electrons could react with water in 10^{-7} s and produce many radicals (Trofymenko and Shulga 2013; Zheng et al., 2004).

$$H_2O \overset{e}{\Longrightarrow} {}^{\bullet}OH + e^{-}{}_{ap} + {}^{\bullet}H + H_2O_2 + H_3O + H_2 \tag{1}$$

At the same time, the following reactions happen and $O^{\bullet}$ and O_3 are also formed (Feng et al., 2008):

$$O_2 \overset{e}{\Longrightarrow} 2{}^{\bullet}O \overset{H_2O}{\Longrightarrow} 2{}^{\bullet}OH \tag{2}$$

$$O_2 + O^{\bullet} \rightarrow O_3 \tag{3}$$

(2) The role of ozone. When the discharge begins, ozone is also formed. Ozone is of high solubility in water and reported to be an effective oxidant. Furthermore, it could remove pollutants by forming ${}^{\bullet}OH$ as follows (Umar et al., 2013; Wu et al., 2002):

$$O_3 \rightarrow O_2 + O^{\bullet} \tag{4}$$

$$O^{\bullet} + H^{+} + e \rightarrow {}^{\bullet}OH \text{ (in acid media)} \tag{5}$$

$$O_3 + H_2O_2 \rightarrow {}^{\bullet}OH + O_2 + HO_2^{\bullet} \tag{6}$$

$$O_3 + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + 2O_2 \tag{7}$$

(3) The role of UV light. The efficiency of producing ${}^{\bullet}OH$ in water only by UV light is very low. But the efficiency is relatively high in the presence of O_3 (Zhang et al., 2008):

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2 \tag{8}$$

$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH \tag{9}$$

Both e_{aq}^{-} and ${}^{\bullet}H$ are subject to be scavenged by dissolved oxygen in water and ${}^{\bullet}OH$ is the strongest oxidant among the radicals mentioned above (Mok et al., 2008). So, ${}^{\bullet}OH$ is the main radical that is responsible for the degradation of organic pollutants.

In the present work, acetamiprid was selected as the target pollutant to examine the degradation effect by dielectric barrier discharge (DBD). The degradation of acetamiprid by DBD has not previously been studied. The aim of the present work is to investigate the degradation behavior and the mechanism of degradation of acetamiprid in aqueous solution by DBD. Several factors affecting the degradation of acetamiprid were studied in detail.

2. Materials and methods

2.1. Experimental apparatus

As will be described below, the dielectric barrier discharge (DBD) reactor of the present investigation acted not only as a means to generate reactive species but also as a UV/visible lamp. Fig. 1a shows a diagram of the experimental DBD apparatus. It consisted of a reaction cell (DBD-50) and a power supply (CTP-2000 K) that could provide a steady voltage up to 250 V and current in the range 0–4 A. The reactor had a structure of a radial flow sedimentation tank (height 100 mm, inner diameter 100 mm and outer diameter 150 mm). Isolation medium was quartz glass (diameter 90 mm) and the high voltage electrode was located above the quartz glass. The ground electrode was placed in the center of the reactor. The power was supplied by an AC source, which could be operated at an adjustable amplitude voltage. The intensity of discharge in the reaction tank could be denoted by the input power, which was calculated from the average voltage and current of the AC power. The solution was circulated continuously by means of a pump (BT100–1L) connected in the inlet.

2.2. Chemicals and reagents

Acetamiprid was obtained from Shandong Pesticide Research Institute and used without further purification. The molecular structure of acetamiprid is shown in Fig. 2. All chemicals were of reagent grade with purity higher than 99 percent.

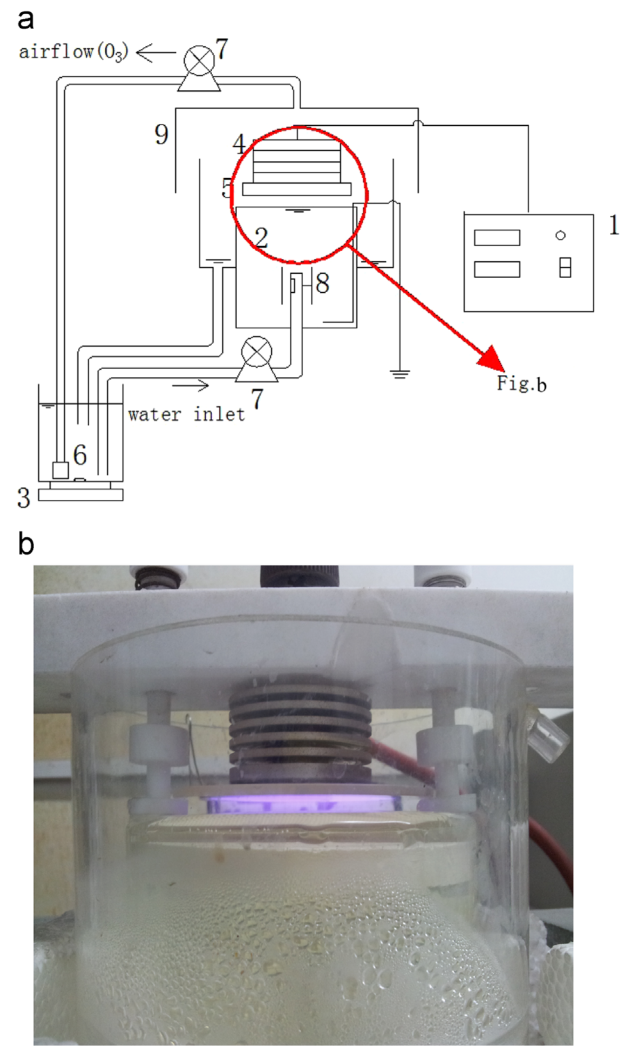

Fig. 1. (a) Diagram of the experimental DBD apparatus. (1. The AC high-voltage power; 2. reaction cell; 3. magnetic stirrer; 4. high voltage electrode; 5. quartz glass; 6. beaker; 7. peristaltic pump; 8. baffle; 9. gas collection hood). (b) Photograph of part of the experimental apparatus.

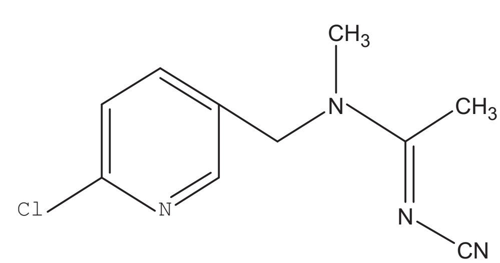

Fig. 2. Schematic diagram of acetamiprid molecular structure.

Acetamiprid solution (deionized water was used as solvent) was prepared as simulated wastewater solution.

2.3. Experimental content

In this study, acetamiprid was treated by dielectric barrier discharge (DBD). Different initial concentrations of acetamiprid and discharge powers were chosen to investigate their effect on the degradation of acetamiprid. The concentration of O_3 and the radical scavenger $Na_2B_4O_7$ were also adjusted to investigate their effects and to determine the mechanism of degradation of acetamiprid. The acetamiprid concentration was measured by UV–vis spectrophotometer and high performance liquid chromatography/mass spectrometer (HPLC–MS) (Krause et al., 2011). Finally,