Chemosphere 117 (2014) 506–514

Contents lists available at ScienceDirect

Chemosphere

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

Wire–cylinder dielectric barrier discharge induced degradation of aqueous atrazine

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HIGHLIGHTS

- A novel wire–cylinder DBD plasma reactor was designed for atrazine degradation.
- The novel wire–cylinder DBD plasma reactor show superior atrazine degradation rate.
- The degradation pathway of aqueous atrazine by DBD plasma reactor was proposed.

ARTICLE INFO

Article history:
Received 12 July 2014
Received in revised form 4 September 2014
Accepted 4 September 2014

Handling Editor: E. Brillas

Keywords:
Atrazine
Dielectric barrier discharge
Degradation intermediates
Degradation pathways

ABSTRACT

The wire–cylinder dielectric barrier discharge reactor was adopted for removal of aqueous atrazine. The effect of different parameters on the degradation efficiency of atrazine was investigated, and the degradation mechanism of atrazine was studied. The experimental results showed that when the discharge power was 50 W and the air flow rate was 140 L h^{-1}, 93.7% of atrazine was degraded after 18 min of discharge time. The concentrations of generated O_3 and H_2O_2 increased with increasing discharge time. The pH decreased from 6.80 to 2.50, 12.7% of TOC was removed after 18 min. The concentrations of generated Cl^- and NO_3^- increased significantly during the degradation process of atrazine, and the decreasing toxicity trend was observed for the treated atrazine solution. The degradation byproducts of atrazine were identified using liquid chromatography–time-of-flight mass spectrometry (LC–TOF-MS), which might be formed mainly in dechlorination hydroxylation, alkyl oxidation, dechlorination hydroxylation combined with alkyl oxidation and demethylation oxidation reactions.

1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is one of the most widely used pesticides in agriculture, primarily for the control broadleaf weeds in corn (Bianchi et al., 2006; Briceno et al., 2010; Andrus et al., 2013; Xu et al., 2013; Liu et al., 2014; Zhang et al., 2014). Atrazine is a kind of non-polar compounds, it is moderately retained by the polar soil colloids (El-Bestawy et al., 2013; Dalton et al., 2014), thus may be easily washed out from the root zone into groundwater, especially in the heavy rain (Ng and Clegg, 1997; Marchetti et al., 2013). Nowadays, the annual usage amount of atrazine increased from 70000 to 90000 tons. In the environment, atrazine is hard to be degraded and its half-life usually ranges from 21 d to over one year (Zhang et al., 2012). On account of its long half-life and high mobility in soil, atrazine and its metabolites have been found in surface water, soil and groundwater (Jablonowski et al., 2011), causing serious water pollution problems (Mudhoo and Garg, 2011).

Atrazine is harmful for human health. It can cause endocrine-disrupting effects even at a low concentration. At present, the common methods to remove atrazine are chemical dechlorination, biological processes, adsorption and advanced oxidation processes (AOPs) (Debasmita and Rajasimman, 2013). AOPs with their high efficiency characteristics have caused wide public concern. Nowadays, some AOPs are used to remove non-degradable organic substance. These AOPs include photocatalysis (Liu and Chiou, 2005; Liu et al., 2006), Fenton oxidation (Chan and Chu, 2005; Barros et al., 2006), ozonation (Wu et al., 2009), electrochemical degradation (Borràs et al., 2010; Samet et al., 2010; Oturan et al., 2012), and dielectric barrier discharge (DBD) plasma (Mahammadunnisa et al., 2013).

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http://dx.doi.org/10.1016/j.chemosphere.2014.09.031
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As one of the AOPs, DBD plasma has received great attention in the field of wastewater treatment (Rajkumar et al., 2007; Li et al., 2011). DBD is a typical non-equilibrium high-pressure gas discharge (Xue et al., 2008; Oliveira et al., 2014). The high degradation rate of organic substance during DBD treatment is caused by the physical and chemical conditions. Physical conditions include the shock waves and ultraviolet. Chemical conditions include some active substances such as $^{\cdot}O$, $^{\cdot}H$, $^{\cdot}OH$ radicals, O_3 and H_2O_2 generated by electrical discharge. Experimental investigation shows that these active species play an important role in the degradation of organic substance (Hu et al., 2013). As one of DBD plasma reactor, the wire–cylinder DBD plasma reactor has been used for NO, NO_x and SO_2 removal (Mok et al., 2000; Jiang et al., 2014). The wire–cylinder DBD plasma reactor allows a reduction of energy consumption and an increase in the treated air flow (Moscosa-Santillan et al., 2008). However, little attention has been paid on the use of wire–cylinder DBD plasma for water treatment.

The degradation behavior of aqueous atrazine by the wire–cylinder DBD plasma has not yet been studied and it is possibly different from that by other AOPs. In this research, atrazine was selected as the target organic contaminate to examine the degradation effect by wire–cylinder DBD plasma. The effect of input power, air flow rate, initial concentration and pH values on the degradation efficiency of atrazine was examined. In order to clarify the degradation pathway of atrazine by wire–cylinder DBD plasma, the changes of pH, TOC, Cl^-, NO_3^- and NH_4^+ were analyzed. Furthermore, the degradation intermediates of atrazine were indentified using liquid chromatography–time-of-flight mass spectrometry (LC–TOF-MS).

2. Experimental

2.1. Chemicals

Atrazine (97%) was purchased from Shandong Qiaochang Chemical Co., Ltd., China. Methanol was chromatographic grade. The other chemicals used in the experiment were all analytical grade.

2.2. DBD plasma reactor

The schematic diagram of wire–cylinder DBD plasma reactor is shown in Fig. 1. It mainly consisted of a high voltage power supply (CTP 2000K, Nanjing Suman Electronics Co., Ltd., China), a reactor with discharge zone and degradation zone. The range of discharge voltage was 0–30 kV, and the range of discharge frequency was 0–100 kHz. The copper electrode (120 mm in length and 5 mm in diameter) connected with high voltage power supply was located at the inner of the quartz glass tube A. And the quartz glass tube A was inserted into the quartz glass tube B. The length of quartz glass tube A and B was 160 mm. The diameter of quartz glass tube A was 6 mm, and the diameter of quartz glass tube B was 13 mm. The gap between the quartz glass A and B was 3.5 mm, which was the discharge zone. The air was pumped into the top of the discharge zone. A gas flowmeter (LZB-4, 16–160 L h^{-1}, Shanghai tianhu Co., Ltd., China) was used to control the air flow rate, which was connected with the pump by silicone tube. The quartz glass tube B was inserted into the organic glass container. And the cavity between quartz glass tube B and organic glass container was degradation zone. Eight air distribution needles located under the organic glass container were used to connect the discharge zone and degradation zone. A cooling jacket was equipped at the outer of the degradation zone. The height of organic glass container was 130 mm and the diameter was 50 mm.

2.3. Experiment methods

The experiment was carried out in the wire–cylinder DBD plasma. This organic glass container adopted the batch operation mode. And 150 mL of atrazine solution was degraded for each time. The degradation experiments were carried out at four factors of input power (30 W, 50 W, 80 W), air flow rate (60 L h^{-1}, 100 L h^{-1}, 140 L h^{-1}), initial concentration (5.80 mg L^{-1}, 11.90 mg L^{-1}, 30.10 mg L^{-1}) and initial pH values (3.30, 6.80, 10.30). At predetermined time interval of 3 min, 1 mL of liquid sample was taken out for analysis. Triplicates were performed for each experiment.

2.4. Analysis methods

The concentration of atrazine was determined using a high performance liquid chromatograph (HPLC, 1260 Infinity, Agilent, USA) equipped with an ultraviolet detector at wavelength of 220 nm and a C18 column (4.6 mm × 250 mm, 5 μm, Agilent, USA). The operating conditions of HPLC were as follows: methanol and water (V:V = 70:30) were used as mobile phase, the flow rate was 1.0 mL min^{-1}, the injection volume was 10 μL, and the column temperature was 30 °C. The degradation products of atrazine were

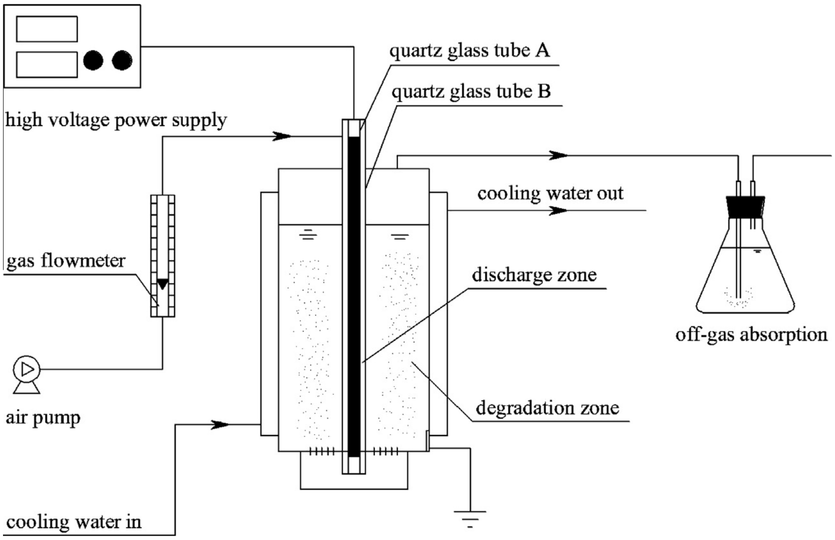

Fig. 1. Schematic diagram of wire–cylinder dielectric barrier discharge reactor.