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Removal of atrazine in water by combination of activated carbon and dielectric barrier discharge

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HIGHLIGHTS

- Increasing input power with a factor 3.5 leads to deeper atrazine oxidation without significantly changing energy yield of atrazine removal.
- Chlorine containing oxidation by-products of first and later generations are detected with HPLC–MS analysis, in agreement with literature.
- Desorption analysis shows lower atrazine concentration and higher by-product concentration on activated carbon textile after plasma treatment.
- Comparison with plasma reactors described in literature for atrazine decomposition confirms relatively high energy efficiency of our reactor.

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ABSTRACT

Efficiency of modern wastewater treatment plants to remove or decompose persistent contaminants in low concentration is often insufficient to meet the demands imposed by governmental laws. Novel, efficient and cheap methods are required to address this global issue. We developed a new type of plasma reactor, in which atrazine decomposition by atmospheric dielectric barrier discharge (DBD) in dry air is combined with micropollutant adsorption on activated carbon textile and with extra bubbling of generated ozone. Investigation of reaction kinetics and by-product analysis shows that increasing input power with a factor 3.5 leads to deeper atrazine oxidation without significantly changing energy yield of atrazine removal. By-products of first and later generations are detected with HPLC–MS analysis in water and adsorbed on the activated carbon textile. Our reactor is compared in energy efficiency with reactors described in literature, showing that combination of plasma discharge with pollutant adsorption and ozone recycling is attractive for future applications of water treatment.

1. Introduction

Atrazine is one of the most widely used herbicides in agriculture, with an estimated annual usage amount in the late 1980s of 70000 tons [1]. This pollutant exhibits low biodegradability and high persistence in the environment with half-life ranging from 21 days to over one year [2]. Due to its high mobility in soil, atrazine and its metabolites are commonly found in ground water, surface water and drinking water supplies [3]. Atrazine has endocrine disruptive properties at relatively small concentrations and is considered to be hazardous to humans, animals and aquatic life. As a consequence, it has been banned in the European Union (EU) in 2004 [4], while most countries, including U.S. and China, continue its use on large scales. Its removal by modern wastewater treatment plants is often incomplete. Amongst the different proposed alternative water treatment methods, advanced oxidation processes (AOP) and in particular the use of low temperature plasma may prove to be a sustainable and efficient approach [5].

Electrical discharge in contact with water is an unconventional water treatment technique which generates highly reactive transitory oxidative species (OH, H_2O_2, O_3, atomic O, singlet O_2 and UV/VUV photons) in proximity of the water–gas interface. These

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plasma species react with a large group of organic compounds to form more oxidized intermediate products [6–7]. Amongst the generated species, both selective oxidants such as ozone and non-selective ones such as hydroxyl radicals play significant roles, causing a very complex chemistry. Hydroxyl radicals oxidize target pollutants with extremely high reaction rate, converting them into less complex intermediates or even fully mineralizing them to CO_2 and H_2O [8]. Nevertheless, this degradation process is likely to be impeded by competitive reactions due to its low selectivity [9]. Ozonation, on the other hand, has higher selectivity and stability but significantly lower reaction rate. In that perspective, water treatment with plasma discharge is an interesting and promising alternative to other AOPs, since it combines a wide spectrum of degradation processes with different oxidants. Moreover, it involves no extreme temperature increases [10], no external storage and addition of oxidants and no corresponding oxidant losses during transportation towards the solution under treatment. Despite the progress in this field, more research is required to further identify, more deeply understand and optimize the main oxidation mechanisms behind this process.

Amongst various plasma reactor configurations that have been investigated, AC powered dielectric barrier discharge over moving water film has been found to be both energy efficient and sustainable [11–13]. Bubnov et al. introduced this reactor type for the first time, where the internal electrode was covered with catalytic fabric [14]. This reactor concept is further optimized in our work by adding an adsorptive textile underneath the water surface and recycling the generated plasma gas by additionally bubbling it through the solution under treatment. Adsorption allows reaching higher local micropollutant concentration close to the active plasma region [15]. As a result, more collisions will take place between plasma species and micropollutants, increasing overall energy efficiency of the treatment process. Next to that, the plasma gas contains reactive species such as ozone and H_2O_2 that can further degrade organic compounds. Synergetic effect of plasma and ozone treatment is described already by Malik [16]. We have developed and tested a new reactor based on these two principles. In the first part of this work, kinetics and energy efficiency of atrazine decomposition in our reactor are investigated. In the second part, H_2O_2 and ozone generation is discussed and possible oxidation mechanisms are shortly explained. The last part of the paper deals with identification and investigation of atrazine oxidation by-products.

2. Experimental methods and materials

2.1. DBD water treatment reactor

The atrazine solution was treated with modulated AC dielectric barrier discharge (DBD) in contact with a falling water film and subsequent ozonation in a closed water circuit (Fig. 1a and b).

The discharge is generated in a plasma reactor chamber with cylindrical geometry. A stainless steel tube with outer diameter of 28 mm is placed inside a quartz glass tube with thickness of 1.5 mm. The stainless steel tube serves as grounded inner electrode and is covered by 2 layers of Zorflex® active carbon textile. The solution under treatment is pumped upwards through the stainless steel tube and subsequently flows downwards along the carbon textile. Plasma is generated in dry air over the carbon textile by applying a pulsed AC high voltage on the outer mesh electrode that covers the quartz glass tube. Next, the solution is pumped to a second chamber where the plasma generated ozone is bubbled through the solution bulk. The modulated AC high voltage is generated by a custom-made AC high voltage power supply triggered by a pulse generator model TGP110 Thurlby Thandar instruments. By pulsing the AC high voltage, gas and liquid temperature can be kept sufficiently low, in order to avoid excessive energy loss and ozone decomposition due to Joule heating. Temperature of the quartz glass tube after 20 min of continuous operation was determined with an infrared temperature probe to be 70 °C for AC voltage without modulation and 38 °C for used duty cycle of 14.3% at 25 W. Main parameters of the system are presented in Table 1 and the electrical characteristics are described in more detail in Section 2.2.

Table 1
The experimental parameters used in this work.

Experimental parameter	Value/description
Voltage amplitude	6.0–7.5 kV (low power), 7.5–8.0 kV (high power)
Input power	20-25 W (low power), 70–75 W (high power)
AC frequency	47.8 kHz
Modulation frequency	35.7 Hz
Duty cycle	14.3%
Treated volume	500 mL
Water flow rate	85.6 mL/min
Gas flow rate	0.33 SLM
Inter-electrode distance	1.75 mm
Dielectric barrier thickness	1.5 mm
Dielectric barrier material	Quartz
Discharge zone length	15.0 cm
Tube length for ozone transport	95 cm
Tube diameter for ozone transport	4.0 mm
Tube material for ozone transport	Teflon
Ozonation chamber inner diameter	44.5 mm
Solution height in ozonation chamber	25.7 cm
Initial atrazine concentration	30 μg/L
Initial conductivity	350 μS/cm
Initial pH	5.06

In our experiments, atrazine with an initial concentration of 30 μg/L was chosen as model micropollutant. Initial conductivity was set by addition of $NaH_2PO_4 \cdot 2H_2O$, in order to simulate a drinking water matrix. The solution was pumped through the system in a closed circuit with peristaltic pumps at a flow rate of 85.6 mL/min. Solution samples up to 50 mL are taken during the experiments for analysis by means of GC–MS, HPLC–MS and to measure H_2O_2 production.

Zorflex® textile type FM50K was provided by Chemviron Carbon. The double jersey knit structure, as shown in Fig. 1(c), provides a stretchable elastic fabric that does not shed or fray, which allows its use in many possible geometries. The textile has a surface density of 130 g/m^2 and a thickness of 0.5 mm. Zorflex® consists of 100% activated carbon, with a carbon tetrachloride activity of 55–70%ww. It is therefore fit for air and water filtration purposes. It has an extremely large surface area of more than 2000 m^2/g [17]. These features, in combination with the strong electrostatic forces within the cloth, make it highly efficient for pollutant adsorption.

2.2. Voltage, current and power

Voltage was measured with a Tektronix P6015HV probe and current was measured with a Pearson model 2877 current probe, both connected to a Tektronix S1200 oscilloscope. Voltage and current waveforms during reactor operation are presented in Fig. 2. After every time interval T_{on} of plasma generation, the input power is interrupted for a time T_{off}, giving a duty cycle of $T_{on}/(T_{on} + T_{off})$ = 14.3%. The distorted current sine indicates the formation of plasma discharge. Total input power P is determined by multiplying the duty cycle with the power during one period ΔT of the voltage sine:

$$P = \frac{0.143}{\Delta T} \int_{\Delta T} IV dt \quad (1)$$