Available online at www.sciencedirect.com

ScienceDirect

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

Decomposition of atrazine traces in water by combination of non-thermal electrical discharge and adsorption on nanofiber membrane

Patrick Vanraes [a,*], *Gert Willems* [a], *Nele Daels* [b,c], *Stijn W.H. Van Hulle* [c], *Karen De Clerck* [b], *Pieter Surmont* [d], *Frederic Lynen* [d], *Jeroen Vandamme* [e], *Jim Van Durme* [e], *Anton Nikiforov* [a,f], *Christophe Leys* [a]

[a] *Department of Applied Physics, Ghent University, Sint-Pietersnieuwstraat 41 B4, 9000 Ghent, Belgium*

[b] *Department of Textiles, Ghent University, Technologiepark 907, 9052 Zwijnaarde, Belgium*

[c] *Department of Industrial Biological Sciences, Ghent University, Graaf Karel de Goedelaan 5, 8500 Kortrijk, Belgium*

[d] *Separation Science Group, Department of Organic Chemistry, Universiteit Gent, Krijgslaan 281 S4-bis, 9000 Gent, Belgium*

[e] *Research Group Molecular Odor Chemistry, Department of Microbial and Molecular Systems (M2S), KU Leuven, Technology Campus, Gebroeders De Smetstraat 1, 9000 Ghent, Belgium*

[f] *Institute of Solution Chemistry RAS, Academicheskaya 1, 153012 Ivanovo, Russia*

ARTICLE INFO

Article history:
Received 1 June 2014
Received in revised form
2 November 2014
Accepted 8 November 2014
Available online xxx

Keywords:
Dielectric barrier discharge
Wastewater treatment
Advanced oxidation processes
Peroxone
Energy efficiency
Degradation by-products

ABSTRACT

In recent decades, several types of persistent substances are detected in the aquatic environment at very low concentrations. Unfortunately, conventional water treatment processes are not able to remove these micropollutants. As such, advanced treatment methods are required to meet both current and anticipated maximally allowed concentrations. Plasma discharge in contact with water is a promising new technology, since it produces a wide spectrum of oxidizing species. In this study, a new type of reactor is tested, in which decomposition by atmospheric pulsed direct barrier discharge (pDBD) plasma is combined with micropollutant adsorption on a nanofiber polyamide membrane. Atrazine is chosen as model micropollutant with an initial concentration of 30 μg/L. While the H_2O_2 and O_3 production in the reactor is not influenced by the presence of the membrane, there is a significant increase in atrazine decomposition when the membrane is added. With membrane, 85% atrazine removal can be obtained in comparison to only 61% removal without membrane, at the same experimental parameters. The by-products of atrazine decomposition identified by HPLC-MS are deethylatrazine and ammelide. Formation of these by-products is more pronounced when the membrane is added. These results indicate the synergetic effect of plasma discharge and pollutant adsorption, which is attractive for future applications of water treatment.

* *Corresponding author.*
E-mail address: patrick.vanraes@ugent.be (P. Vanraes).

http://dx.doi.org/10.1016/j.watres.2014.11.009
0043-1354/

1. Introduction

Throughout the EU, effluents of wastewater treatment plants deteriorate the chemical and biological status of surface waters (Schwarzenbach et al., 2006). New and largely unknown persistent substances, including pharmaceuticals, pesticides and compounds that disrupt the hormonal balance in humans, appear in the aquatic environment (Bolong et al., 2009; Ternes et al., 2004). In spite of their low concentrations, they have a high impact on water quality. The European Water Framework Directive is extending the scope of pollution control measures to protect surface water (EC, 2000). The recent report, 'European waters – assessment of status and pressures', published by the European Environment Agency (EEA, 2012), concludes that the actual ecological status with respect to persistent micropollutants is worse than desired. Due to the chemical properties of some pesticides and pharmaceuticals, their removal in wastewater treatment plants is often incomplete (Sunka, 2001; Bruggeman and Leys, 2009; Grymonpre et al., 2004). This causes micropollutants to find their way into natural water and eventually drinking water. Therefore, novel treatment technologies have to be developed if current and anticipated criteria for effluent and drinking water are to be met. Among the different advanced oxidation processes (AOP) that are under investigation, the use of low temperature plasma may prove to be a sustainable approach (UKWIR, 2009). Within the field of applied plasma science, electrical discharges in contact with water, in literature also referred to as "liquid plasmas", have received a lot of attention during the last decade (Sunka, 2001; Bruggeman and Leys, 2009), with water treatment as one of the main possible applications. Liquid plasma is a source of oxidizing species (OH, H_2O_2, O_3, atomic O, singlet O_2, and UV/VUV photons) that can initiate decomposition of organic pollutants dissolved in water (Grymonpre et al., 2004). Among various plasma reactor concepts that have been investigated (Nikiforov and Leys, 2006; Lukes et al., 2013; Sugiarto et al., 2003), pulsed power systems have been found to be the most efficient. By applying high voltage pulses, non-equilibrium plasmas with a relatively large active volume and a low gas temperature can be generated in the gas phase above liquid (Lukes et al., 2005).

Despite the progress that has been made in the engineering of liquid plasma systems, important research questions need to be answered to more deeply understand and optimize the oxidation mechanisms. First of all, up to now, only plasma initiated decomposition of a few very simple compounds have been studied in detail, e.g. phenol (Grabowski et al., 2006), sulfonol (Bobkova et al., 2012) and textile dyes (Benetoli et al., 2012). Moreover, when decomposition of common micropollutants in a plasma reactor is investigated, high concentrations in mg/L range are used for simplicity in many cases. Since their concentration in wastewater and natural water typically ranges up to μg/L only, more research is required that focusses on micropollutant removal in this lower range, as for example in the present study.

Secondly, degradation efficiency can be increased by enlarging the surface of the plasma–liquid interface by dispersion of micro-drops in the discharge (Locke and Thagard, 2009) or by forming a thin layer of liquid on one of the electrodes (Dojcinovic et al., 2011; Magureanu et al., 2008). The idea within this study is to further improve the latter concept with an additional step of adsorption of micropollutants on a nanofiber membrane placed on the electrode surface. The extremely high surface area of the nanofiber membrane, as described in Section 2.2, allows to reach higher micropollutant concentration at its surface, close to the active plasma region (Toth, 2002). There, reaction with active plasma species can take place and remove the micropollutants. This explains the expected synergy of plasma combined with pollutant adsorption.

In the present work, the pesticide atrazine is used as model micropollutant, since it is a good representative of persistent micropollution in water and stated in EU protocol as a dangerous pollutant. The applied concentration (30 μg/L) is one order of magnitude higher than the maximally allowed concentration in drinking water as defined by the United States Environmental Protection Agency (U.S. EPA, 2007), and the World Health Organization (WHO, 2008) and two orders of magnitude higher than the limit defined by the European Parliament and the Council (EC, 2006). In the first part of this work, the kinetics of H_2O_2 and O_3 production under plasma action is investigated, as they are well known to be responsible for atrazine oxidation in AOPs. The second part of the paper deals with investigation of atrazine removal by the combination of non-thermal plasma and adsorption on nanofiber membrane and investigation of the by-products of atrazine oxidation.

2. Materials and methods

2.1. DBD reactor for water treatment

The atrazine solution was treated in pulsed dielectric barrier discharge (pDBD) generated above the solution. The scheme of the setup is presented on Fig. 1. The discharge was generated in between the high voltage electrode (HV) covered by a layer of dielectric material with thickness of about 360 μm and a 0.3 mm thick water film formed on the surface of nanofiber membrane. The membrane was placed on the support made from porous Robu glass which was used to distribute water uniformly on the membrane surface. The distance between the HV electrode and water surface can be controlled with micro-screw. The radius of HV electrode is 11 mm and the radius of Robu porous glass is 20 mm. In the present study we used HV pulse duration of 400 ns in order to generate the discharge. The pulsed system was based on solid state switch technology from Behlke. The HV switch was connected to positive output of DC high voltage power supply IO BRANDENBURG. The main parameters of the system are presented in Table 1.

The voltage was measured with a Tektronix P6015 HV probe and the current was measured with a Pearson model 2877 current probe. The short duration of HV pulses is favorable to generate a uniform discharge and to keep the gas temperature low. In all our experiments the water temperature never exceeded 35 °C which means that the pDBD plasma has a low gas temperature and can be used for water treatment. The discharge was generated in dry air which is continuously

Please cite this article in press as: Vanraes, P., et al., Decomposition of atrazine traces in water by combination of non-thermal electrical discharge and adsorption on nanofiber membrane, Water Research (2014), http://dx.doi.org/10.1016/j.watres.2014.11.009