Water Research 84 (2015) 127–135

Contents lists available at ScienceDirect

Water Research

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

Potential of pulsed corona discharges generated in water for the degradation of persistent pharmaceutical residues

Robert Banaschik [a], Petr Lukes [b], Helena Jablonowski [a], Malte U. Hammer [a], Klaus-Dieter Weltmann [a], Juergen F. Kolb [a, *]

[a] Leibniz Institute for Plasma Science and Technology e.V. (INP Greifswald), Felix-Hausdorff-Strasse 2, 17489 Greifswald, Germany
[b] Department of Pulse Plasma Systems, Institute of Plasma Physics AS CR, Za Slovankou 3, 182 00 Prague 8, Czech Republic

ARTICLE INFO

Article history:
Received 7 February 2015
Received in revised form
29 June 2015
Accepted 11 July 2015
Available online 15 July 2015

Keywords:
Advanced oxidation
Non-thermal plasma
Ethinylestradiol
Diclofenac
Phenol
Hydroxyl radicals

ABSTRACT

Anthropogenic pollutants and in particular pharmaceutical residues are a potential risk for potable water where they are found in increasing concentrations. Different environmental effects could already be linked to the presence of pharmaceuticals in surface waters even for low concentrations. Many pharmaceuticals withstand conventional water treatment technologies. Consequently, there is a need for new water purification techniques. Advanced oxidation processes (AOP), and especially plasmas with their ability to create reactive species directly in water, may offer a promising solution. We developed a plasma reactor with a coaxial geometry to generate large volume corona discharges directly in water and investigated the degradation of seven recalcitrant pharmaceuticals (carbamazepine, diatrizoate, diazepam, diclofenac, ibuprofen, 17α-ethinylestradiol, trimethoprim). For most substances we observed decomposition rates from 45% to 99% for treatment times of 15–66 min. Especially ethinylestradiol and diclofenac were readily decomposed. As an inherent advantage of the method, we found no acidification and only an insignificant increase in nitrate/nitrite concentrations below legal limits for the treatment. Studies on the basic plasma chemical processes for the model system of phenol showed that the degradation is primarily caused by hydroxyl radicals.

1. Introduction

Medical advances have always been going along with the development and increasing use of pharmaceuticals. Accordingly, IMS Health, a company that provides information for the US healthcare industry, reported a steady increase in dispensed prescriptions of 5.4% from 2008 to 2012 (Health, 2012). A further increase is expected due to continuing progress in pharmaceutical sciences together with an aging population, especially in industrialized countries. Most of the active compounds prescribed for treatment are in fact excreted from the body by the renal and biliary system (Jjemba, 2006). At the same time, a lot of these substances are essentially not biodegradable and withstand destruction in sewage treatment plants (STP) (Ternes et al., 2002; Stackelberg et al., 2004). As a result, increasing concentrations of pharmaceuticals are now a burden on the environment and a potential risk to drinking water supplies. A prominent example is the triiodinated X-ray contrast agent, diatrizoate, which resists oxidation by ozone even in combination with UV-irradiation (Ternes et al., 2003). However, in particular the concentrations of antiepileptic drugs (diazepam, carbamazepine), analgesics (ibuprofen, diclofenac) and hormones (ethinylestradiol) are of growing concern (Heberer, 2002). Ternes et al. reported among 32 common drugs, found in effluents of German sewage treatment plants, carbamazepine in concentrations of 6.3 μg/l and ibuprofen and diclofenac in concentrations of 3.4 μg/l and 2.1 μg/l, respectively (Ternes, 1998). Hormones (17α-ethinylestradiol) were detected in effluents from German sewage treatment plants in concentrations of 62 ng/l and in surface water of the Netherlands in concentrations as high as 47 ng/l (Stumpf et al., 1996; Belfroid et al., 1999).

The detected residual concentrations seem to be low in comparison to therapeutic dosages but have already been found to have verifiable environmental effects. Psychiatric drugs (benzodiazepines) were linked to changes in the behavior and feeding rate of perches in concentrations as low as 1.8 μg/l (Brodin et al., 2013). Fluoxetine, an antidepressant drug, may cause a decrease in

---

* Corresponding author.
E-mail address: juergen.kolb@inp-greifswald.de (J.F. Kolb).

http://dx.doi.org/10.1016/j.watres.2015.07.018
0043-1354/© 2015 Elsevier Ltd. All rights reserved.

reproduction rates of snails (*P. antipodarum*) at concentrations of 0.81 μg/l (Nentwig, 2007). Estrogens were reported to disrupt amphibian mating behavior in doses as low as 0.296 ng/l and further affect the gender distribution of fish populations (Hoffmann and Kloas, 2012; Purdom et al., 1994). High concentrations of analgesics were identified as the cause of vulture population decline in Pakistan (Oaks et al., 2004). Increasing concentrations of antibiotics in the environment could further be a factor in the proliferation of antibiotic resistant bacteria (Kümmerer, 2009a, 2009b).

Growing public concern is therefore understandable, particularly since the long term effect of many of these compounds that are continuously administered in low doses are difficult to predict. In response to the potential risk to our surface waters the European Commission (EC) has decided to add the pharmaceuticals diclofenac (analgesic drug), 17α-ethinylestradiol and 17β-estradiol (both hormones) to a watch list of emerging pollutants [Water Framework Directive, Directive 2008/105/EC, Decision (EU) 2015/495 of 20 March 2015] (Commission).

Established water treatment methods, such as filtration and biological degradation are apparently not sufficient to address the problem even when improved and combined with membrane bioreactors, nanofiltration, reverse osmosis filters or activated carbon filters (Foster et al., 2012, 2013; Poyatos et al., 2010). Therefore other approaches are now focusing on advanced oxidation processes (AOPs), i.e. the generation of highly reactive species. Of particular interest is the hydroxyl radical that has a much higher oxidation potential than ozone or chlorine. Interactions with target molecules are primarily diffusion controlled and eventually result in fragmentation of organic compounds and mineralization to CO_2 (Giri et al., 2010; Magureanu et al., 2015). The commonly exploited generation mechanisms for hydroxyl radicals are photochemical degradation of ozone and hydrogen peroxide by exposure to ultraviolet light (O_3 + UV, H_2O_2 + UV). The process can be improved by photo catalysts, e.g. titanium-dioxide (TiO_2), or iron (Fe^{2+}). Catalytic process by themselves (TiO_2 + UV) and other chemical oxidation mechanisms (O_3/H_2O_2, H_2O_2/Fe^{2+}) are also investigated (Poyatos et al., 2010). Although effective to some degree, all of these methods are associated with some problems on a larger scale. For example is ozone or hydrogen peroxide consumed and has to be supplied accordingly. Assuming the use of UV/H_2O_2 for the waste water treatment facility of Hamburg/Dradenau (410,958 m^3 waste water/d) hydrogen peroxide in concentrations between 0.2 mM and 5 mM would be required (Katsoyiannis et al., 2011; Vogna et al., 2004). This would correspond to a need for H_2O_2 of 2.8–70 tons per day. Hydrogen peroxide production is further associated with hazards due to its corrosive nature and the risk of explosions during storage and transport of large volumes. Furthermore photo catalysts that are suspended in water have to be removed again, since they have been found to be potentially toxic (Mantzavinos and Psillakis, 2004; Pintar et al., 2004). Another efficient method for the generation of hydroxyl radicals and other reactive species is offered by plasmas. Dielectric barrier discharges (DBD) that are generated outside the water but close to water are often employed for this purpose. However, species that are generated in the plasma have to diffuse into the liquid first and as a consequence this approach is most effective only for shallow water layers. Magureanu et al. investigated the decomposition of different pharmaceutical compounds that were dissolved in water in a coaxial DBD configuration with the plasma generated in air (Magureanu et al., 2010, 2011, 2013). Hijosa-Valsero et al. also investigated a coaxial DBD configuration for the removal of organic micro pollutants (Hijosa-Valsero et al., 2013) Krause et al. studied barrier electrodes (Krause et al., 2009) and Gerrity et al. investigated a pilot-scale unit of an “electrode-to-plate” configuration (Gerrity et al., 2010). Pulsed corona discharges are another method for the creation of plasma in air (Locke and Thagard, 2012). Panorel et al. used a pulsed corona discharge (PCD), created along horizontal wires for the degradation of pharmaceuticals with solutions that were dispersed and showered in jets, droplets and films into the electrode array (Panorel et al., 2012, 2013). Dobrin et al. used pulsed corona discharges in oxygen in an array of 15 copper wires for the degradation of diclofenac (Dobrin et al., 2013). Results on the degradation that were achieved with these respective systems for different pharmaceuticals are summarized in Table 1.

Methods using corona discharges generated in a gaseous atmosphere outside the liquid are likewise facing the problem of a necessary diffusion of reactive species into and throughout the liquid for the method to be effective. This problem is avoided by creating plasma directly in water. One possibility is the generation of spark discharges, generally in point-to-point or point-to-plane (needle-plate) geometries in small volumes. Associated research on degradation of organic compounds has primarily focused on discoloration of dyes and the decomposition of phenolic derivatives (Sugiarto and Sato, 2001; Sato, 2008; Lukes and Locke, 2005). A notable exception in scope is a pilot facility for the use of spark discharges for waste water treatment that was brought into operation by Chang and his co-workers (Yantsis et al., 2008).

A more energy efficient method is the generation of pulsed corona discharges directly in water. The energy required is generally about three orders of magnitude lower than that for spark discharges (Locke and Thagard, 2012). Sato et al. investigated a combination of streamer (i.e. corona) discharges and spark discharges in a point-to-plane geometry for the degradation of Rhodamine B (Sato, 2009). A similar setup was studied by Malik et al. for corona discharges in combination with plasma catalysts and ozone treatment for the discoloration of methylene blue (Malik et al., 2002). Lukes et al. used a hybrid gas–liquid electrical discharge reactor with corona discharges generated inside and outside the liquid for the degradation of phenol (Lukes and Locke, 2005; Lukes et al., 2004). Results of the different studies on the degradation efficacy and efficiency are again included in Table 1.

In comparison with spark discharges, corona discharges offer the advantage of generating them also in extended geometries. This has been shown for example by Malik et al. (2011, 2005). With the future implementation of the method of pulsed corona discharges generated in water in treatment facilities in mind, we have also focused on the investigation of discharges that are generated in an extended coaxial geometry directly in water. Here we are presenting results on the potential of the approach for the degradation of pharmaceuticals that have been found to have possible harmful environmental impact.

2. Materials and methods

2.1. Water treatment

Corona discharges were generated in a coaxial geometry, as shown in Fig. 1. A thin tungsten wire of 50 μm in diameter that was drawn along the center of a glass tube served as a high voltage electrode. The wire was replaced after each experiment to provide reproducible experimental conditions. The reactor had an inner diameter of 47 mm and a length between the acrylic plates of 138 mm, hence retaining a volume of 240 ml. A steel mesh was attached to the inner wall. The diameter of the openings in the mesh was 0.4 mm and the wire thickness 0.25 mm.

A mesh was chosen instead of a sheet metal electrode in order to permit optical access to the discharges. Streamers, as shown in Fig. 2, were generated along the entire length of the wire when positive high voltage pulses were applied from a 6-stage Marx-bank. The pulse generator had an erected capacitance of 12 nF