Acta Universitatis
Lappeenrantaensis
793

LAPPEENRANNAN TEKNILLINEN YLIOPISTO

Petri Ajo

# HYDROXYL RADICAL BEHAVIOR IN WATER TREATMENT WITH GAS-PHASE PULSED CORONA DISCHARGE

**LUT**
Lappeenranta
University of Technology

Petri Ajo

# HYDROXYL RADICAL BEHAVIOR IN WATER TREATMENT WITH GAS-PHASE PULSED CORONA DISCHARGE

A thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium of the Student Union House at Lappeenranta University of Technology, Lappeenranta, Finland on the 29th of March, 2018, at noon.

Acta Universitatis
Lappeenrantaensis 793

Supervisors Professor Marjatta Louhi-Kultanen
LUT School of Engineering Science
Lappeenranta University of Technology
Finland
School of Chemical Engineering
Aalto University
Finland

Professor Sergei Preis
Department of Materials and Environmental Technology
Tallinn University of Technology
Estonia

Associate Professor Eeva Jernström
LUT School of Engineering Science
Lappeenranta University of Technology

Reviewers Docent Wilfred Hoeben
Department of Electrical Engineering
Eindhoven University of Technology
Netherlands

Professor Sven-Uwe Geißen
Department of Environmental Technology
Berlin University of Technology
Germany

Opponent Docent Wilfred Hoeben
Department of Electrical Engineering
Eindhoven University of Technology
Netherlands

ISBN 978-952-335-212-4
ISBN 978-952-335-213-1 (PDF)
ISSN-L 1456-4491
ISSN 1456-4491

Lappeenrannan teknillinen yliopisto
Yliopistopaino 2018

# Abstract

**Petri Ajo**
**Hydroxyl radical behavior in water treatment with gas-phase pulsed corona discharge**
Lappeenranta 2018
45 pages
Acta Universitatis Lappeenrantaensis 793
Diss. Lappeenranta University of Technology
ISBN 978-952-335-212-4, ISBN 978-952-335-213-1 (PDF), ISSN-L 1456-4491, ISSN 1456-4491

In recent years, the problem of pharmaceutical residues in wastewaters accumulating in the environment has become of growing concern. Although some pharmaceutical compounds are easily biodegradable, many exhibit strong refractory character, rendering conventional biological wastewater treatment an incomplete enterprise. The application of gas-phase pulsed corona discharge (PCD) is one of the potential alternatives studied for the energy efficient oxidation of aqueous organic pollutants, and forms the subject of the present study. This thesis assesses the behavior of hydroxyl radicals (OH) in PCD water treatment. The process is also studied for application in removal of pharmaceutical residues from real wastewaters. It is seen that OH formation and utilization depends strongly on hydrodynamic conditions with the gas-liquid contact surface being a major variable for oxidation energy efficiency, which can be increased by increasing the contact surface area. Excessive volumetric flow rate, however, results in adverse effects due to disturbances in the plasma zone that unfavorably alter the net effect between radical oxidant formation and premature termination reactions. The optimum gas-liquid area increases with pulse frequency. Furthermore, it is shown that the OH radicals are only produced on the gas side of the gas-liquid interface, from where they dissolve through the phase boundary for reactive affinity with the aqueous pollutants; no plasma induced primary reactions take place in the liquid phase to form OH. The successful transfer through the phase boundary requires an atomic H scavenger in the gas phase to avoid undesirable recombination of the radicals, thus enabling the oxidant reactions with the dissolved species. In contrast with the liquid phase, the plasma-produced OH radicals remain effective in oxidation of gaseous species even in the absence of H scavenger, which is explained by the immediate phase affinity of the oxidant and the reactant. Harnessing the reactive oxygen species for the degradation of pharmaceutical compounds in municipally treated wastewater effluent, raw sewage of a hospital and biologically treated wastewater from a health institution showed high feasibility and energy efficiency of the process in non-selective destruction of a variety of pharmaceutical substances and their metabolites. The 'pharmaceutical content' of the wastewaters is substantially higher if transformation products are also considered, which leads to an inherent negative bias in the removal efficiency estimations due to the simultaneous reformation of the original parent substance during oxidation, for which the transformation products may act as precursors. On the other hand, this further emphasizes the importance of non-selective oxidation of products exhibiting biological activity.

Keywords: Non-thermal plasma, ozone, drugs, radical termination, temperature

# Acknowledgements

Science, the final frontier.

This work was carried out in School of Engineering Science at Lappeenranta University of Technology, Finland, between 2014 and 2017. I thank Fulbright Center Finland, Maa- ja vesitekniikan tuki ry and LUT Tukisäätiö for their generosity in funding my work. The work was partly funded by the EMIR project (Exploiting Municipal and Industrial Residues) financed by European Neighbourhood and Partnership Instrument (ENPI) Program, and the EPIC project (Efficient Treatment of Pharmaceutical Residues at Source) by the Finnish Funding Agency for Innovation, Tekes.

I also must thank the people who taught me into the ways here, starting from my Master's in 2013, and continuously made the experimental work possible. These would include Liisa Puro, Tuomas Nevalainen, Toni Väkiparta, the late Markku Maijanen and many more (must not list comprehensively, someone would be awkwardly forgotten). And Jakov, you I thank for making this research technically possible, and for the many, many fruitful argues! Oh, how many hard times I gave you all with wacky ideas. Such is science. I also thank my colleagues, reminiscing the countless hours spent in the coffee room storming over vexed scientific problems. Such is science, *at its best*, is it not? My supervisors, Marjatta and Eeva, I have to thank for their professional touch in holistic steering of the dissertation progress. Thank you, ladies, invaluable contribution. And thank you all my friends at LUT, Mohammad, Johanna, Alexander et al.

Now then, what really carved my scientific *figure* out of the formless lump of unrefined researcher matter was the guidance by Sergei, the jean-luc of this enterprise. With mystic intellectual brute force he always managed to take my tangled problems and bend them into a neat explanation of what I actually was talking about before I perplexed myself. Imagine, remarkable! Countless occasions, countless juicy debates. And Mr. Jones, the linguistic gentleman with whom I philosophized the arts of scientific expression: thank you, friend. Anyway, the last professional thanks I must dedicate to Michael R. Hoffmann and his group at California Institute of Technology, highlighting the role of Dr. A.J. Colussi, working with whom I morphed into the researcher I am, viewing science as an infinite array of interdisciplinary opportunities. Respect.

The personal properties required to reach the present milestone are a catalyst inherited from the heroes, my parents. And the source for the daily confidence, fueling an unflappable ambition, is my beautiful wife whose support has proved vital for any splendid enterprise I've plunged into, be it head first or uncoordinatedly sideways; anything is possible when you got your back covered. For the boyish tomfoolery and adventurous shenanigans that importantly took my mind off from work when needed, Antti of Tampere deserves a massive high five. Any decency I have gained, in turn, origins from becoming a father. Thus, I should also extend the rightful gratitude to Silja, Aleksi and Niklas, who forged me into a sort of grown-up. Peace and long life.

Petri Ajo / March 2018 / Lappeenranta, Finland

*To Teuras,*

*for long enough were black metal bands not dedicated*
*doctoral theses.*

# Contents

**Abstract**

**Acknowledgements**

**Contents**

**Publications**

# List of publications

This thesis is based on the following papers. The rights have been granted by publishers to include the papers in dissertation.

I. Ajo, P., Kornev, I., and Preis, S. (2015). Pulsed corona discharge in water treatment: the effect of hydrodynamic conditions on oxidation energy efficiency. *Industrial and Engineering Chemistry Research*, 54(30), pp. 7452-7458.
II. Ajo, P., Krzymyk, E., Preis, S., Kornev, I., Kronberg, L. and Louhi-Kultanen, M. (2016). Pulsed corona discharge oxidation of aqueous carbamazepine micropollutant. *Environmental Technology*, 37(16), pp. 2072-2081.
III. Ajo, P., Preis, S., Vornamo, T., Mänttäri, M., Kallioinen, M. and Louhi-Kultanen, M. (2018). Hospital wastewater treatment with pilot-scale pulsed corona discharge for removal of pharmaceutical residues. *Journal of Environmental Chemical Engineering*, 6, pp. 1569-1577.
IV. Ajo, P., Kornev, I. and Preis, S. (2017). Pulsed corona discharge induced hydroxyl radical transfer through the gas-liquid interface. *Scientific Reports*, 7, 16152.

# Author's contribution

Petri Ajo is the principal author in papers I – IV and responsible for the majority of experimental design and work in all papers. Ewelina Krzymyk conducted the chemical analyses in paper II. In paper III, Timo Vornamo conducted the membrane separation part of the experimental work.

# Nomenclature

## Latin alphabet

| | | |
|---|---|---|
| $A$ | specific gas-liquid contact area | m$^{-1}$ |
| $E$ | delivered pulse energy | kWh m$^{-3}$ |
| $f$ | pulse frequency | pps |
| $P$ | pulse power | W |
| $T$ | temperature | °C |
| $t$ | time | s, min |

## Abbreviations

| | |
|---|---|
| AOP | advanced oxidation process |
| BQM | 1-(2-benzaldehyde)-4-hydroquinazoline2-one |
| BQD | 1-(2-benzaldehyde)-4-hydro-quinazoline-2,4-dione |
| CAW | corona above water |
| CBZ | carbamazepine |
| DBD | dielectric barrier discharge |
| EC | electrolysis cell |
| FID | flame ionization detector |
| GC | gas chromatography |
| IC | ion chromatography |
| LC | liquid chromatography |
| MS | mass spectrometry |
| OA | oxalic acid |
| PCD | pulsed corona discharge |
| RCS | reactive chlorine species |
| ROS | reactive oxygen species |
| SWW | synthetic wastewater |
| TN | total nitrogen |
| TOC | total organic carbon |
| UF | ultrafiltration |
| UPLC | ultraperformance liquid chromatograph |
| WWTP | wastewater treatment plant |

# 1 Introduction

## 1.1 Background

Where high quality water is readily available in everyday life, water and water resources may, by some, if not many, intuitively be described with rather prosaic expressions; with limits to the devoted enthusiasm, perhaps to the extent of interest; or, more cynically, the colloquial water may simply be deemed with little or no special respect, in respect to the necessity of it, which conveniently follows the (modern?) human perception of taking for granted what is easily accessible, like the air that is inhaled, or the skin that covers the human body. Water, however, *is* a special substance, even exceptional (like many of the substances whose presence is taken for granted, following mere abundance). Water consumption is required by the human body, and it is used for hygienic purposes, food production, industrial raw material, coolant, hydrogen source; the list is infinitely long. Water has peculiar properties that enable life as we know it. It is at its highest density at around 4 °C, expands upon freezing and exhibits remarkable latent heat, and makes a universal solvent and mass transfer media, to name a few. For the unique properties, as well as its ubiquitous nature in our life, water will always be a topic for the works of scientific research.

Treatment of water is one of the global key infrastructural elements. Initially, the consumption of water, for whatever purpose, may require purification. Treatment is also often required before returning the water to the environment (usually by legislative means). These are self-explanatory perceptions of the need for water treatment.

Declining freshwater supplies are often perceived as potential triggers for future wars, which can be considered concerning primarily locations suffering from e.g. scarce water supplies, poor economy and hot climate. Research-wise, for the richer countries the growing concern has been more about the quality of the water supplies, instead of the quantity. This, however, is largely a matter of perspective, as quality and quantity of water are intrinsically connected by definition of how to measure the latter.

The quality of water can be measured by many parameters, chosen accordingly to a given perspective from which it is assessed. For a few decades now [1], the state of aquatic environments has received wide concern from the point of view of pollution by the daily consumed chemicals conveying intentional biological activity, such as personal care products and pharmaceutical compounds. These substances may enter the environment for example via manufacturing industry discharges [2-4], careless individual discarding of medicines and their packaging [3], or simply by human (or animal) consumption and excretion [3-5]. Pharmaceutical compounds may transform into metabolites in human body, or exit unchanged, resulting in a complex composition of wastewaters conveying an undetermined number of biologically active chemicals into the environment [1,6,7]. Evidently, the pharmaceutical residues and their metabolites are somewhat scattered and found in very low concentrations, which, unfortunately, may often still be enough to affect aquatic organisms [1].

Selective removal of low concentration target pollutants, especially in large scale applications treating large volumes, is a challenging engineering issue. A non-selective approach provides an intuitively better alternative, not only because small targets are difficult to aim at, but also because it is not feasible (or even possible) to detect and identify every single harmful constituent present. Since the degradation of organic compounds is generally an oxidation process, various advanced oxidation processes, AOPs, have been studied for the purpose of non-selective pollutant degradation [8,9]. After the definition by Glaze et al. in 1987 [10], water treatment processes utilizing hydroxyl radical (OH, a strong oxidant) are collectively referred to as AOPs. A brief overview and listing of AOP technologies is given in chapter 2 Advanced oxidation processes.

The AOP under scrutiny in the present study is an application of gas-phase pulsed corona discharge (PCD), a non-thermal plasma (NTP) process operating at ambient pressure. Due to the substantial differences, low pressure and thermal plasmas will be left out of discussion for brevity and focused analysis. While some variations of the practical PCD configuration do exist (see e.g. [8,11,12]), this study is focused on a system where a wire-plate electrode setup is established vertically with the treated water falling freely through the discharge zone. The primary OH radicals in PCD water treatment are formed from the water molecules in contact with the plasma that also forms ozone ($O_3$) from ambient oxygen [13]: these are the two main oxidants whose operation will be discussed in the following pages. (Note: henceforth, the present configuration is referred to as PCD and any other discussed configuration, even those producing pulsed corona, will be referred to with another name/abbreviation to make the distinction clear.)

Degradation of pharmaceutical compounds (paracetamol, ibuprofen, salicylic acid, indomethacin, β-estradiol) from water with PCD was previously studied by Panorel et al. in [14] using synthetic model solutions. The authors reported successful removal of the target pollutants at low energy consumption, yielding 20 to 150 g $kWh^{-1}$ drug removal under acidic conditions. The studies proved a highly effective process, although the focus was more on kinetics of the treatment and the experiments were conducted at concentrations of $\sim10^2$ mg $L^{-1}$ which is at least four orders of magnitude higher than the typical concentrations detected in wastewaters and aquatic environments ($\sim10^{-2}\ldots10^1$ µg $L^{-1}$ [5-7]). Several other methods, however, have been studied for real wastewaters, and examples with points of comparison will be discussed at the appropriate chapters. A comprehensive review on NTP induced degradation of aqueous pharmaceuticals was given by Magureanu et al. in [8].

For optimal operating conditions, knowing the effect of the process parameters on the behavior of the oxidants is crucial and enables the anticipation of the kind of reactions that are achievable in the given system. In PCD water treatment, the plasma induced formation of the hydroxyl radicals reacting with the dissolved species has earlier been established to occur at the gas-liquid interface [15] from high energy electron collisions with water molecules (Eqs. 1 [13] and 2 [16]):

$$\mathrm{H_2O} + e^- \rightarrow \mathrm{OH} + \mathrm{H} + e^- \tag{1}$$

$$\mathrm{H_2O^+} + e^- \rightarrow \mathrm{OH} + \mathrm{H} \tag{2}$$

It was also shown in [15] that increasing the gas-liquid (also plasma-liquid) contact surface area enhances the oxidation energy efficiency due to the increase in radical formation sites, a property with a certain maximum value beyond which the energy of a plasma pulse was considered to be the limiting factor, restraining further improvement. The authors also reported zero oxidation of aqueous phenol in PCD under $N_2$, which was suggested to be the result of prevailing recombination of the products in Eqs. (1-2) due to the absence of H scavenging by $O_2$.

The complete absence of reaction without $O_2$, however, promotes interest for this research, and its continuing mission to explore the OH radical formation at the interface. After all, the radical reactions have been reported effective even in natural waters without oxygen [17]. This phenomenon has not yet been attributed to other types of plasma water systems, most likely because there is no apparent practical need for substituting the air atmosphere with $N_2$ for water treatment purposes. In wider scope, the effect of gas composition for water treatment with various discharges has been studied, and the oxidation of aqueous organic compounds reported successful even in the absence of $O_2$ [18-22]. This suggests that these processes rely on various mechanisms with mutuality of limited extent; the discharge parameters that govern the scheme of available reactions may substantially vary even between different corona setups [13,23,24]. Studying the reactions under $N_2$, however, provides a convenient route for analyzing certain reactions, as will be discussed in the following.

## 1.2 Research motivation and objectives

The present study aimed to explain the conditions and parameters determining the efficiency of OH radical utilization for the oxidation of dissolved aqueous pollutants. It was considered that the key characteristics for the description of OH dynamics would be the hydrodynamic conditions and the gas-liquid interface, due to the previously recognized surface character of the radical activity. Therefore, in this thesis, the complex interrelation of the hydrodynamic conditions and the OH radical utilization will be given consideration by mapping and justifying optimal process conditions. The general suggestion that the radicals are formed at the gas-liquid interface will be further elaborated to produce a more specific description of the radical formation regime and explain premature radical termination conditions. These studies aim to provide better understanding to the heterogeneous PCD water treatment process, aiding process optimization and intensification design as well as the conceptualization of future studies and possible (and the recognition of the impossible) reaction schemes.

Furthermore, the research on PCD degradation of aqueous pharmaceuticals is extended to cover actual wastewaters with realistic concentrations, in order to study the feasibility of the process not relying on laboratory model solutions. The issue is initially approached by employing PCD as tertiary treatment for wastewater effluent from a local municipal wastewater treatment plant (WWTP). Next, considering that the low concentrations provide difficult conditions for high efficiency pollutant removal, the studies are extended to include wastewaters with characteristically more extensive pharmaceutical content, i.e. wastewaters from source points of higher pharmaceutical consumption. For these studies, PCD treatment was applied directly to institutional wastewaters from two locations, raw sewage from the first and biologically treated wastewater effluent from the other.

# 2 Advanced oxidation processes

The performance of different AOPs is largely determined by the formation and delivery of the desired oxidants, although by definition the OH-radical is considered the primary one, as mentioned above; operation at ambient temperature and pressure is a major characteristic asset for most AOPs. Several other oxidants, other reactive oxygen species (ROS) and reactive chlorine species (RCS), make essential characteristics for some of these processes as well. In essence, OH-radicals may even play a rather minor role in comparison to other oxidants in a given AOP, also often dependent on specific process conditions such as pH or the presence of certain radical scavenger species like carbonate ($CO_3^{2-}$) and bicarbonate ($HCO_3^-$) ions. In the case of ozonation, for example, the reaction routes promote OH-radical formation from ozone decomposition only at elevated pH range [25]. Still, conventional ozonation is quite often excluded from the list of AOPs, but sometimes included when coupled with some other technology (ultrasound, ultraviolet light, peroxides, catalysts etc.). Water treatment processes applying electrolysis may also result in OH radical having a role in the oxidation kinetics, although RCS are often regarded as the primary oxidants. For this reason, electrolysis is generally not discussed within the AOP context. Table 1 briefly lists some common oxidation technologies in water treatment research, including some, but not limiting to, commercially applied solutions (for comprehensive listing of various NTP based AOPs, see e.g. [8,26]).

Table 1: Common oxidation processes operating at ambient conditions. PCD refers to the configuration described in this thesis, another, perhaps more famous corona based method, is the corona above water (CAW); DBD refers to dielectric barrier discharge. The classification of some processes* as AOPs is not unambiguous; these processes are listed due to relevant similarity and high popularity in water research. Further combinations of the listed applications make popular topics and can be abundantly found in literature. Reference examples are reviews or early-work publications, except for [27] that is given particularly for the ROS discussion in electrolysis.

| *AOP* | *Primary oxidants* | *Description* | *Ref.* |
|---|---|---|---|
| Ozonation* | $O_3$, (OH) | Ozone gas sparging through the liquid solution, catalysts often used for promoting OH radical formation | [28] |
| Sonozone | OH, $O_3$ | Ozonation coupled with ultrasonic excitation | [29] |
| UV/$H_2O_2$ | $H_2O_2$, OH | Hydrogen peroxide dissociated into OH-radicals by UV irradiation | [30] |

| | | | |
|---|---|---|---|
| UV/$TiO_2$ | OH, $TiO_2$+ | Photocatalysis | [31] |
| Fenton | $H_2O_2$, HOO·, OH | ROS production from $H_2O_2$ via catalytic reactions with ferrous/ferric ions | [32] |
| Photo-Fenton | $H_2O_2$, HOO·, OH | Fenton coupled with UV irradiation | [30] |
| PCD | OH, $O_3$ | Treated solution showered through NTP volume | [15] |
| CAW | OH, $O_3$ | Treated solution flowing as a film below NTP volume | [33] |
| DBD | OH, $O_3$ | Pulsed or AC plasma distributed over insulator surface | [34] |
| Electrolysis* | $Cl_2$, HClO, $ClO^-$ | Immersed low voltage electrode pair driving current through the treated solution, various anode materials | [27] |

The examples presented in Table 1 reflect AOPs relying on the utilization of OH and other ROS, whereas in electrolysis the primary oxidants are RCS as mentioned above. In electrolysis, however, some ROS (like OH, $H_2O_2$, $O_3$, $\cdot O_2^-$) are also formed through electrochemical water splitting reactions [27,35], the process this how exhibiting similarity with AOPs.

In addition to the applicable oxidative species, the kinetics governing the efficient utilization of formed oxidants determine the overall effectiveness of the oxidation process. This is closely connected to optimizing the amount of produced oxidants for reactions with the organic pollutants; excess oxidants result in their useless decomposition, which reduces the efficiency for oxidant-pollutant reaction per resource input (energy or chemical) for producing the oxidant. There is some variance in the importance of this balance between different technologies. In $H_2O_2$ applications, for example, the amount of hydrogen peroxide is important to match an optimum that is determined by the pollutant concentration [36]. Similarly, in ozonation process where ozone gas is sparged through the treated solution, the dosage determines the efficiency: no reason in bubbling excess ozone through the water to waste exhaust. Somewhat in contrast, in PCD treatment where the most important reactions take place at the plasma-water interface, as explained in *Publication I* and [15], the amount of oxidants is less of an important variable since no chemicals are physically added to the process. The formed oxidants in PCD are created from the ambient oxygen and water molecules themselves, and for high efficiency, the optimization becomes more of a question on how to introduce the treated solution into the system.

Along the removal of organic compounds from water or wastewater, AOPs in many cases carry the parallel purpose of disinfection. This is often the target in drinking water purification, which sets certain limitations to the applied method. For example, electrolysis is not suitable since it requires the presence of electrolytes, chloride in particular, which in potable water may not be present in reasonable amounts for the purpose. AOPs since the early days of ozonation [37] have been acknowledged very suitable. The formation of harmful disinfection byproducts (DBPs), however, may be of concern also in these applications due to the strict requirements for drinking water (with regional discretion). The relevant DBPs in drinking water AOPs may typically be nitrate ($NO_3^-$) and nitrite ($NO_2^-$) [38], or, in the presence of bromide ($Br^-$), bromate ($BrO_3^-$) [39] and bromoform ($CHBr_3$, a trihalomethane) [40], both of which are known carcinogens [41]. The Br-based byproduct species in NTP water treatment processes is not a well-studied subject and out of the scope of the present study as well. Here, the products that can be considered DBPs consist only of $NO_x$ species, as will be discussed in the experimental section and results analysis.

Comparing different AOPs, PCD can be considered to have the following assets: insensitivity towards turbidity (in contrast to photochemical methods), no addition of chemicals (consider peroxide) and no special oxidant delivery system (e.g. $O_3$ sparging) since all oxidants are produced *in situ*, and high plasma-liquid contact surface area (compare to CAW and DBD). A generalizing comparison of the performance of different AOPs, however, is very challenging for the reasons mentioned above; evidently, the operating circumstances notably affect the AOP ranking. The assessment of PCD performance is often done by experimental PCD data comparison with literature values for other processes. The primary selected method for comparison has been ozonation for the similarity of the chemistry, and for ozonation representing a traditional, commercially wide-spread technology. For example, Preis et al. (2013) [15] observed 88 g $kWh^{-1}$ yield in aqueous phenol degradation in air and 140 g $kWh^{-1}$ in oxygen atmosphere using PCD, whereas the best result of the extensive data collected by Krichevskaya et al. (2011) [42] using ozonation was 63 g $kWh^{-1}$. Oxalic acid oxidation is given some figures and literature values for conventional ozonation in *Publications I* and *IV*, and chapter 4.1 Hydrodynamics of the present work. A brief comparison of a few technological approaches with experimental support is described in Appendix A.

# 3 Experimental methods

In this section, a general overview of the practical conducted research is given. More detailed descriptions of individual experimental operations can be found in the attributable articles, *Publications I-IV*. The following description is divided in two sections, starting with the studies on the phenomena related to OH radical utilization and the effect of hydrodynamic conditions, followed by the application in removal of pharmaceutical residues from synthetic solutions and real wastewaters. A pivotal parameter frequently occurring in this thesis will be energy dose, *E*, with the unit kWh $m^{-3}$ (1 kWh $m^{-3}$ = 3.6 kJ $L^{-1}$). This parameter indicates the nominal energy expense of the process as calculated by the discharge power multiplied with the treatment time over the treated volume. Yield (i.e. conversion efficiency) reports the amount of target substance transformed as a result of the oxidation process per the delivered pulse energy, i.e. presented in g $kWh^{-1}$.

## 3.1 Experimental system

Two separate PCD water treatment systems were used during the experimental studies. In *Publications I, II* and *IV* a reactor of 100 W nominal power was used and a larger scale 250 W reactor (nominal power) was used in *Publication III*. The reactors have individual water circulation systems and pulse generators, the smaller system including a flow-through setup enabling single-pass treatment of the solutions for minimal energy dose. The system concept is illustrated in Fig. 1. The experimental parameters for *Publications I-IV* are given in Table 2 with some technical characteristics referring to the elements in Fig. 1.

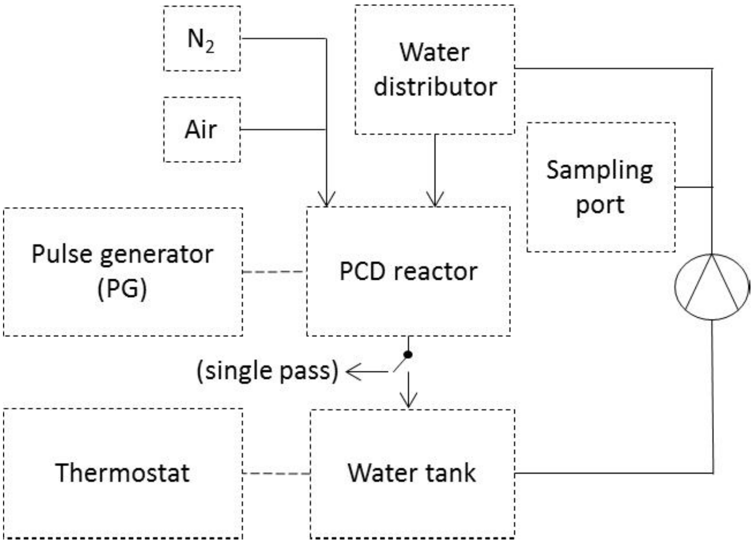


Figure 1: Experimental system concept.

Table 2: Experimental parameters. In *Publication II*: † ≡ batch; ‡ ≡ single-pass.

| **Publication** | **I** | **II** | **III** | **IV** |
|---|---|---|---|---|
| PG and PCD reactor | 100 W(0.12 J/pulse) | 100 W (0.12 J/pulse) | 250 W (0.3 J/pulse) | 100 W (0.12 J/pulse) |
| Applied power, W (frequency, pps) | 100 (833),<br>60 (500),<br>36 (300) | 100 (833)†‡,<br>60 (500)†,<br>24 (200)†,<br>6 (50)‡ | 250 (840)<br>30 (100) | 100 (833),<br>60 (500),<br>36 (300) |
| Operation | Batch | Batch †,<br>single-pass ‡ | Batch | Batch |
| Water distributor | Perforated plate | Perforated plate | Perforated plate | Atomizer array |
| Water volumes | 10 L | 10 L†, 15 L‡ | 50 L | 7 L, 10 L |
| Atmosphere | Air | Air | Air | Air, $N_2$ |
| Temperature | Ambient | Ambient | Ambient | 13, 20, 30 °C |
| Water solution | Synthetic binary | Synthetic binary and municipal WWTP effluent | Hospital wastewater, biologically treated effluent from a health institution | Synthetic, various |

In the present PCD devices, the corona discharges are produced by thyristor pulse generators with high-voltage transformers and magnetic compression stages shortening the pulse duration. This description with further information and detailed schematics of the electrical circuit can be found in [43], where the described configuration follows the same design. Both PCD reactors contain a vertical electrode configuration in a dielectric housing. Two grounded plate electrodes are set vertically with the high voltage wire anode passing between the plates multiple times in a parallel array. The PCD systems studied in the thesis are thus set to produce positive corona discharges only. The treated water can be either directed to a top chamber with a perforated bottom plate above the plasma reactor (*Publications I-III*), or sprayed into the plasma with a five-point atomizer nozzle array placed above and parallel to the high voltage wires (*Publication IV*). The 100-W and the 250-W reactors each have their own pulse generator matching with the reactor (detailed descriptions with illustrations of the overall setups are available in *Publications I-IV*). The specifications for the reactors and the generators are given in Table 3 below. The current and voltage information was gathered with an Agilent 54622D oscilloscope and the energy of an individual pulse produced as an integral product of voltage and current peak areas, measured with a Tektronix P6015 voltage probe and a Pearson 2878 current probe, respectively. Typical waveforms for the pulses can be found in *Publication I* for the 100-W device and in [15] for the 250-W device.

Table 3: Reactor and pulse generator specifications; the data for the 250-W system is derived from [15]. Data for 100-W reactor is also available in *Publication I*.

| **Power** | **100 W** | **250 W** |
|---|---|---|
| Plate electrode dimensions | 21 × 100 cm | 50 × 200 cm |
| Times the anode passes between the plates | 33 | 64 |
| Current in pulse peak | 180 A | 380-400 A |
| Voltage in pulse peak | 22 kV | 18-20 kV |
| Pulse length | 100 ns | 100 ns |
| Pulse energy | 0.12 J | 0.30-0.33 J |

## 3.2 Hydro- and OH radical dynamics

Studying the effect of flow conditions was done by altering the solution flow rate through the PCD reactor within the range of 1.73…5.04 L $\text{min}^{-1}$, corresponding to a spray density (the volumetric flow rate over channel cross-section) of 0.24…0.71 m $\text{s}^{-1}$. The experiments were conducted at pulse powers $P$ of 100, 60 and 36 W (corresponding to frequencies of 833, 500 and 300 pps, respectively). A linear correlation was established for the specific gas-liquid contact area $A$ (related to the treated volume) and the flow rate $q_v$ (Fig. 2) by the sulfite oxidation method described in [44]. The measurement is based on catalytic sulfite oxidation to sulfate by ambient molecular oxygen, a reaction whose rate is dependent on the contact surface area. The practical description and equations as applied in the present study are given in detail in *Publication I*. By this approach, an optimal contact area to pulse power ratio $A/P$ was investigated.

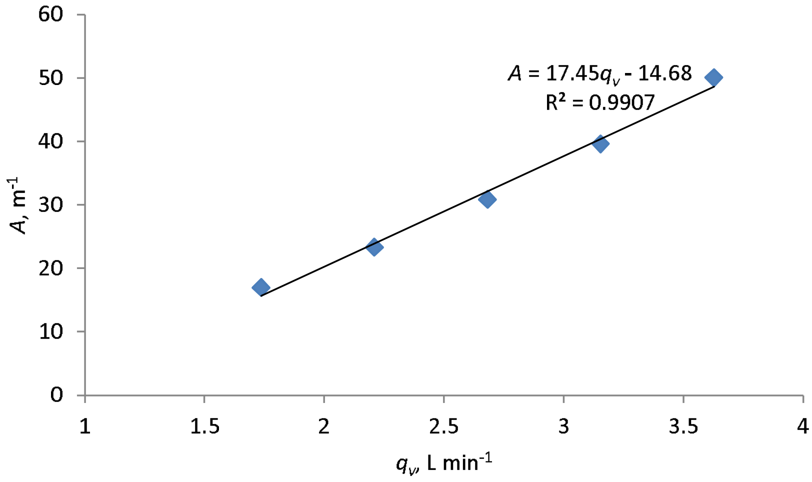


Figure 2: Specific gas-liquid contact surface area ($A$) dependence on water flow rate ($q_v$).

OH radical formation regime was studied under air and $N_2$ atmosphere, the motivation for the latter being the replacement of H scavenging species, i.e. molecular oxygen. The study was conducted by investigating gas phase and liquid phase reactions separately and the treated solution was introduced to the PCD reactor in aerosol form through an array of atomizer nozzles at 1.8 L min$^{-1}$, instead of the perforated plate that produces droplets and streams. OH radical activity in the absence of oxygen was monitored in the gas phase by analyzing the dissolved oxidation products of nitrogen ($NO_2^-$, $NO_3^-$) and acetone (acetate and formate) in the liquid phase (*Publication IV*). Indeed, it is worth noting that products analyzed from the gas phase would yield highly relevant and useful information, which, however, is beyond the scope of this thesis; analysis of the dissolved products was considered to meet the experimental purpose by demonstrating the desired reactions and their rate in comparison to the equivalent at changed process parameters. The dissolved $NO_x$ was monitored under air and $N_2$ at different pulse frequencies and operating temperatures to provide information for gas phase oxidation in the absence of molecular oxygen; the gaseous oxidation under these circumstances was confirmed with high concentration acetone (17%) in the liquid phase, exploiting the high volatility of the substance.

Temperature effect on OH radical utilization for the oxidation of aqueous organic compounds was studied in experiments with varying pulse frequencies and temperatures. To ascertain if plasma induced OH radicals are formed in the liquid phase in the absence of oxygen, potassium permanganate ($KMnO_4$) was used as an atomic H scavenger in the dissolved phase: if Eqs. (1-2) were valid in the liquid side of the interface as well, the atomic H as a product of those reactions would have a chance to react (half-reaction Eq. 3) with the permanganate via reduction to $MnO_2$ (half-reaction

Eq. 4), thus promoting OH radical reactions with other dissolved species, i.e. the probe compound, which would be seen in the analysis. Since ozone reactions are strongly temperature dependent, oxalic acid was used as a probe compound for its slow reactivity with ozone ($k \leq 4 \cdot 10^{-2}$ $M^{-1}$ $s^{-1}$ [28]), thus favoring reactions with the OH radical ($k = 5.3 \cdot 10^{6}$ $M^{-1}$ $s^{-1}$ [45]), and also for the excellent analytical simplicity.

$$\mathrm{H} \rightarrow \mathrm{H}^{+} + \mathrm{e}^{-} \tag{3}$$

$$\mathrm{Mn(VII)O_4}^{-} + 3\mathrm{e}^{-} \rightarrow \mathrm{Mn(IV)O_2}(s) \tag{4}$$

## 3.3 Wastewater treatment

The experiments with real wastewaters were conducted with two approaches: (i) to monitor a selected pharmaceutical substance and its transformation products during oxidation of binary solutions and real wastewater, and (ii) to study a more comprehensive range of pharmaceuticals in more concentrated wastewaters.

First (i), a selected pharmaceutical, anti-epileptic drug carbamazepine (CBZ), was experimented with in binary model solutions and spiked WWTP effluent. Oxidation was studied in these two parallel experimental series to inspect how the complex mixture of real wastewater affects the oxidation of a single pharmaceutical compound and its transformation products in very low concentrations (*Publication II*); the typical co-pollutants were previously observed to exhibit notable negative impact on the target pharmaceutical oxidation energy efficiency when operating at higher concentrations [14]. Here, the experiments were conducted in high concentrations also ($10^{2}$ mg $L^{-1}$), to observe the degradation in similar concentration range as the earlier PCD studies with different pharmaceuticals. Microconcentrations degradation was studied in batch mode and single-pass experiments, the latter meaning that the treated solution was only allowed to pass through the reactor once without circulation. This was done to test the effect of the minimum technically feasible energy dose (0.006 kWh $m^{-3}$) on CBZ oxidation, using minimum power (6 W) and maximum flow rate (~20 L $min^{-1}$) of the experimental system.

Second (ii), a total of 57 pharmaceutical substances were monitored in PCD treatment of wastewaters collected from two locations of likely elevated concentrations of pharmaceuticals (listed in Tab. 1 of *Publication III*). The first location was a central hospital in South-East Finland, from whose sewage the treated waters were derived, and the other a health institution with a biological wastewater treatment site whose effluent was used for the experiments. The hospital sewage was allowed to settle and filtered with a simple string filter (50 µm) to exclude most of the solid matter from the experimental volumes and PCD oxidation was coupled with ultrafiltration (UF) pre-treatment to investigate potential improvement in oxidation energy efficiency from working with clearer solution matrix. Health institutional wastewater effluent was treated as such. The details of the procedures for the studies involving real wastewaters are described in *Publications II* and *III*.

## 3.4 Analyses

Oxalic acid was analyzed using ion chromatography (IC, Dionex ICS-1100 with an AS22 column), permanganometric titration, and total organic carbon analysis (TOC, Shimadzu TOC L-series coupled with a total nitrogen analysis unit; *Publications I* and *IV*). $NO_x^-$ species were identified with IC and collectively quantified with total nitrogen (TN) analysis (*Publication IV*). Acetone oxidation products, acetate and formate, were identified with IC in *Publication IV*. Carbamazepine and its transformation product concentrations were analyzed with liquid chromatograph tandem mass spectrometry (LCMS/MS, Agilent Technologies 6460, Triple Quadruple), gas chromatograph mass spectrometry (GCMS, Agilent Technologies 7890A) and gas chromatography coupled with flame ionization detector (GC-FID, Agilent Technologies 6850) (*Publication II*). In *Publication III*, pharmaceutical content was analyzed by Eurofins Ltd. with ultra-performance liquid chromatograph coupled with tandem mass spectrometry (UPLC/MS/MS); wastewater characterization was done with several common methods explained in the publication. Details of the analyses are given in the attributable publications.

# 4 Results and discussion

## 4.1 Hydrodynamics

Oxalic acid oxidation energy efficiency was observed to be highly dependent on the gas-liquid contact area (Fig. 6 in *Publication I*), agreeing with the observations presented for phenol in [15]. The optimal area was established to linearly increase with pulse power, although in disproportion: the relative increase in optimal area is roughly a 3/5 fraction of the relative increase in power as observed within the experimental range (Fig. 8 in *Publication I*).

Increasing the contact surface area beyond the optimal value resulted in notable decrease at any pulse power, which is probably explained by overly disturbance of the plasma volume by airborne water, i.e. unfavorable distribution of discharge energy in the heterogeneous space geometry. Increasing liquid water volume in the interelectrode area results in decreasing portion of plasma volume, which may increase active species density and promote premature radical termination reactions, therefore decreasing the oxidation energy efficiency of dissolved species.

The observed maximum yield in oxalic acid oxidation was 5.4 (*Publication I*), and 8.6 g kWh$^{-1}$ when the water was introduced in aerosol form (*Publication IV*). The latter was obtained at the temperature of 13 °C; at 20 °C, which is close to the ambient temperature (20-22 °C) in *Publication I,* the maximum yield was 7.1 g kWh$^{-1}$. For reference, the maximum value for ozonation observed by Lagunova et al. (2012) [46] was 4.4 g kWh$^{-1}$. The significance of this difference comes from the initial concentration of oxalate, which was 60 mg L$^{-1}$ in PCD experiments and 900 mg L$^{-1}$ in ozonation. While the numeric result is in the same order of magnitude, the order of magnitude difference in initial concentration reveals the essentially higher efficiency of PCD (rate of binary reaction depends on concentrations of the reactants). Excessive filling of the interelectrode space with liquid water was not an issue in aerosol experiments as the liquid flow rate of 1.8 L min$^{-1}$ was near the minimum value used in the hydrodynamic studies (1.73 L min$^{-1}$) with the perforated plate as the water distributor.

The highest applied pulse frequency, 833 pps, was observed to yield consistently lower energy efficiency than as with frequencies of 500 and 300 pps: the two lower frequencies performed at similar efficiencies when the water was introduced into the reactor through the perforation, provided that the flow conditions were optimized for the given frequency (*Publication I*). This suggests that oxidation at the maximum frequency is somewhat diffusion controlled and that oxidation attributed to ozone reactions is no more improved with further decrease in frequency. Differences in efficiency between 500 and 300 pps were more pronounced when the water was sprayed into the system (*Publication IV),* although these experiments could be done only at fixed flow rate, not enabling optimization of flow conditions according to the applied frequency. It is possible that also with the sprinkler system, the differences between oxidation efficiencies at sub-maximum frequencies might have been narrowed with optimization of the hydrodynamic conditions. The results of *Publication IV*, however, serve to give more information on the OH radical dynamics, as is discussed in the designated chapter below.

The results from the two separate experimental series (*Publications I and IV*) together give intuitively reasonable insight into the practical design of the water distribution system in a PCD water treatment system. Finer droplets provide better oxidation efficiency considering the flow-through capacity, while excessive volumetric flow rate results in hindered performance. Although the efficiency generally decreases with increasing pulse frequency, the optimal conditions at higher frequency allow higher capacity as well, which leads to the optimal design trade-off being a question of preference over capacity and energy efficiency.

## 4.2 OH radical dynamics

Experiments under $N_2$ yielded zero oxidation of dissolved oxalic acid; by excluding liquid phase oxidation reactions with $N_2$ replacement of ambient molecular oxygen, the reactions in the gas phase could be focused on. $NO_x$ formation in the absence of oxygen was observed to linearly increase with pulse energy delivery, although at lower rate than under air plasma (Fig. 1 in *Publication IV*). Acetone oxidation confirmed OH radical formation and reactions in the gas phase under $N_2$, i.e. gaseous reactions Eqs. (1-2) with water vapor, as monitored by the increase in dissolved oxidation species, acetate and formate (Fig. 2 in *Publication IV*). Zero oxidation of the dissolved species, OA, was also observed regardless of the presence of permanganate as a liquid atomic H scavenger, which suggests that reactions in Eqs. (1-2) do not take place in the liquid phase in PCD. These results show that OH radical formation occurs only in the gas side of the interface, which means that plasma induced OH radicals are only effective for aqueous pollutant oxidation after transferring through the gas-liquid interface.

Temperature and pulse frequency showed consistent correlation with oxidation energy efficiency; the oxidation yield increased consistently along decrease in both parameters (Fig. 4 in *Publication IV)*. Since the decrease in pulse frequency results in prolonged treatment time at fixed energy dose (= constant amount of pulses distributed over a longer period), the thus improved yield is attributable to the role of ozone in the oxidation process, representing the slower reacting (longer living) species. It should be noted that the lifetime of OH radicals on water surface is ~2,7 µs [47] and 1-2 orders of magnitude longer in the gas phase [48], which is essentially shorter than the pulse intervals (1.2 ms at the highest frequency), meaning that OH radicals work only during and very shortly after a discharge pulse (pulse length maximum 0.1 µs, oscillogram in *Publication I*).

The effect of extended treatment time is more pronounced when transitioning from 833 to 500 pps than from 500 to 300 pps. It is concluded that since the oxidation efficiency is at similar range in lower frequencies and notably lower at the highest frequency (*Publication I*), ozone utilization is at 500 pps close to reasonable maximum; further extension in treatment time provides little improvement. The increase in yield from 833 to 500 pps in aerosol treatment exhibited little variance over the experimental temperature range (+2.32…2.61 g kWh$^{-1}$ at 13…30 °C; see Supplementary Discussions in *Publication IV*), while changing the temperature alone at 833 pps resulted in a nearly doubled yield on oxalate oxidation, from 2.20 to 4.06 g kWh$^{-1}$ at 30 to 13 °C. It should be borne in mind that higher frequency also favors the role of OH radicals by diminishing the role of ozone, as explained above. This notable effect by the temperature is by these observations largely attributed to OH radical utilization efficiency. (Note: formation rate of the OH radical can hardly be affected by varying the temperature over the experimental range because the high-energy electrons that fuel the reactions in Eqs. (1-2) exhibit three orders of magnitude higher temperature than the ionic and molecular species in the gas phase [49].)

The strong temperature dependence of OH radical efficiency in oxidation of the dissolved species suggests that the radical reactivity increases with temperature, which counter-intuitively decreases the efficiency via increasing amount of premature reactions before successful radical transfer into the liquid phase.

## 4.3 Removal of pharmaceuticals from wastewaters

### 4.3.1 Carbamazepine and transformation products

Initial experiments with high concentration CBZ removal resulted in up to 99.5-% removal at 3.0 kWh m$^{-3}$ discharge energy dose. Subsequent experiments were carried out at lower energy doses and shorter sampling intervals (0.03, 0.1, 0.6 kWh m$^{-3}$) for better observation of the degradation trend. The resulting yield was observed as high as 189 g kWh$^{-1}$, exceeding even that of indomethacin (120-150 g kWh$^{-1}$) that was the fastest degrading pharmaceutical in [14].

The experiments in microconcentrations were also conducted first using model solutions, ranging from 0.22 to 19.0 µg L$^{-1}$ in concentration. Operating at such low concentrations, increasing energy dose notably affected the removal yields over a wide magnitude range (0.008…0.5 g kWh$^{-1}$), making the parameter referential at best. It should be noted that naturally, very small changes in absolute concentrations when operating at µg L$^{-1}$ or ng L$^{-1}$ level result in notable relative changes, making accurate calculations and comparisons largely inessential, potentially even misleading.

A clear effect of the complex composition of the WWTP effluent on the oxidation efficiency was not observed. Perhaps in some contrast with the results presented by Panorel et al. [14], where co-pollutants resulted in substantial reduction of the efficiency, the simple explanation lies in the concentrations: differences in the kinetics between binary solutions and spiked wastewaters in the unselective PCD oxidation process remain largely undetected when operated at very low concentrations near the level of analytical quantification. Put in numbers, the singe-pass experiments with the binary solution at minimum power (6 W) resulted in up to 16-% reduction and at maximum power (100 W) up to 94-% reduction, with the energy doses of 0.006 and 0.1 kWh $m^{-3}$, respectively; from wastewater, a 61-% removal was achieved at 0.1 kWh $m^{-3}$. It should be noted that the flow rate in single-pass experiments was ~20 L $min^{-1}$, which exceeds substantially the beyond-optimal conditions (max ~5 L $min^{-1}$) observed in *Publication I*. This flowrate equals to a spray density of 2.80 m $s^{-1}$. Batch treatment i.e. circulation of the solution at more moderate flow rate was observed to give essentially better results from energy consumption point of view: up to 97-% CBZ reduction was observed at mere 0.3 kWh $m^{-3}$. By the dose of 3 kWh $m^{-3}$, 99.9% of the substance was oxidized. The efficiency presented here exceeds the previously published results available in literature, as discussed in more detail in *Publication II*.

Several known transformation products were detected during CBZ oxidation, the most frequently occurring compounds being 1-(2-benzaldehyde)-4-hydroquinazoline2-one (BQM) and 1-(2-benzaldehyde)-4-hydro-quinazoline-2,4-dione (BQD). A detailed list of the compounds is given in Supplementary Material of *Publication II*. All transformation products were oxidized during PCD treatment of the spiked WWTP effluent – although quantification of the reduction was not possible – reproducing the unselective nature of PCD oxidation. The concentrations of BQM were observed to increase with the oxidation of CBZ until CBZ was practically completely oxidized, after which the concentrations of the transformation product also decreased. Estimation of the rates of potentially simultaneous formation and degradation of BQM is not possible from these results.

Detailed comparison of the results with those found in literature is challenging due to substantial differences between the experimental conditions in different studies and the difficulties in kinetics estimation. Comparing oxidation at higher concentrations, the removal yields from a few different studies, the closest matches by initial concentrations found in literature, can be arranged in order of PCD > dielectric barrier corona [50] > ozonation [51] > sonozone [52], as listed in *Publication II*. Concerning microconcentrations, Gerrity et al. (2010) [53] studied a pilot-scale CAW reactor, achieving yields around an order of magnitude smaller than those reported with PCD in *Publication II*. It should be noted, however, that in these examples as well the conditions have been notably different, including initial concentrations, giving the comparison a tentative character.

### 4.3.2 Hospital and health institutional wastewaters

*Hospital wastewaters*

Treatment of hospital wastewaters showed highly non-selective oxidation of the monitored pharmaceutical content. A total of 27 pharmaceutical substances was detected in the raw hospital sewage, and during oxidation, progesterone and methylprednisolone appeared in consistently increasing concentrations, totaling 29 substances altogether (this increase in concentration, which was momentarily observed for ibuprofen as well, is further discussed below). The evolution of progesterone and methylprednisolone in wastewater oxidation has not been previously reported in literature. While the bulk of the pharmaceutical compounds occurred at concentration not higher than 28 µg $L^{-1}$ (ibuprofen), paracetamol and caffeine were substantially more abundant at 580 and 470 mg $L^{-1}$, respectively, which is explained by paracetamol being a common painkiller and caffeine a ubiquitous nervous stimulant, also found in daily products and refreshments. Considering the total pharmaceutical content, high power PCD (250 W) performed at essentially lower energy efficiency than low power (30 W). This is in accordance with the improving ozone utilization efficiency obtained by extended treatment time at fixed energy dose, as further elaborated in [15] and *Publication I*. Ultrafiltration pretreatment had modest effect on pharmaceuticals reduction and little on PCD oxidation efficiency. It can be considered from practical perspective that, as an additional unit process with characteristic requirement for maintenance, the UF pretreatment may be of excessive economic inconvenience.

The compounds exhibiting consistent or momentary increase in concentration during PCD oxidation can be attributed to the simultaneous reformation of the parent substance from the various metabolites and transformation products present in the wastewater. Similar evolution of CBZ was previously observed in biological wastewater treatment [6]. These results suggest that even a wide number of monitored pharmaceutical substances does not give a comprehensive picture of the process efficiency, nor on the actual pharmaceutical composition of the wastewater. Indeed, in [54], several metabolites were reported for ibuprofen in wastewater, the overall mass concentration exceeding that of the parent compound in a WWTP influent. The presence of transformation products therefore produces negative bias on the oxidation energy efficiency as the parent compound is reformed simultaneously with oxidative degradation. This also means that, given the non-selective character of PCD oxidation, the measurable overall process effectiveness would be substantially higher if all pharmaceuticals and their active transformation products were possible to include in the study. The removal of individual pharmaceutical compounds is tabulated and discussed in detail in *Publication III*.

Overall, these results indicate a very high effect of direct PCD treatment on raw hospital sewage, substantially reducing the pharmaceutical content of the waters entering to the public sewer network, to the municipal WWTP plants, and, eventually, the aquatic environments.

*Health institutional wastewaters*

A total of 17 pharmaceutical compounds were detected in the biologically treated wastewater effluent from the health institution, i.e. from the stream that is directly released into the environment. The compounds were not found in concentrations higher than 0.44 µg $L^{-1}$ (metoprolol), except for CBZ which occurred at 3.1 µg $L^{-1}$. All pharmaceuticals were completely oxidized (i.e. below level of detection) with 30 W PCD treatment at 0.5 kWh $m^{-3}$. Even 0.1 kWh $m^{-3}$ energy dose was enough for most substances, with only a few compounds showing some residual concentrations. Ultrafiltration pretreatment did not show useful character with these wastewaters. The detailed results are presented in *Publication III*. Experiments with the health institutional wastewaters suggest that PCD is a highly feasible practical solution as a tertiary treatment for polishing biologically treated wastewaters, essentially reducing the environmental load from residual pharmaceutical substances at a moderate energy requirement.

# 5 Conclusions

The increasing awareness and concern on pollution control and protection of aquatic environments raises interest in efficient and more effective water treatment systems. The public trend proceeds towards tighter regulations and better emissions control also for water treatment scenarios and effluent discharges. One of the popular topics in this field is the removal of refractory micropollutants from wastewater streams, such as pharmaceutical residues. A number of oxidation technologies have been studied for the purpose, pulsed corona discharge (PCD) as one of them and making the focus of the present study. Efficient application and further development of PCD water treatment requires understanding of the dynamics that govern the successful oxidant-pollutant reactions, which has not been previously studied in sufficient detail.

Ambient pressure gas-phase PCD for water treatment was studied in this thesis from the perspective of efficient utilization of OH radicals produced by the high temperature plasma electrons in contact with water molecules, and the practical application in removal of residual pharmaceutical substances in real wastewaters. The role of hydrodynamic conditions was established to affect the oxidation energy efficiency of aqueous components by OH radicals via the balance between increasing the plasma-liquid contact area and the partial replacement of the plasma volume by liquid water. An optimal water surface area was found connected to the applied pulse power (or frequency), and too high volumetric flow rate was observed to disturb the efficient discharge energy distribution on the gas-liquid interface where the formation of the effective OH radicals has earlier been reported to occur. The formation of OH radicals was then studied in more detail, revealing that in this kind of plasma configuration, the radical formation only takes place at the gas side of the interface and no plasma induced primary reactions in the liquid phase are able to produce the radicals. The oxidation of aqueous dissolved species by plasma induced OH radicals are therefore only the ones initiated by species formed in the gas phase and successfully dissolved into the liquid phase for reactive affinity with the target pollutants. This transfer through the interfacial boundary is highly temperature dependent as the reactivity of the radicals increases with temperature, which promotes premature radical termination reactions. For successful oxidation of the liquid solutes, an atomic H scavenger is also required in the gas phase for inhibiting H + OH recombination and thus enabling the radical transfer into the liquid phase; gas phase oxidation by the OH radical, on the contrary, does not require H scavenging species since there is no interfacial boundary crossing. Typically, gas-phase oxygen acts as the H scavenger.

The practical application in removal of pharmaceutical compounds from real wastewaters showed high feasibility by displaying high removal percentages of a wide range of pharmaceutical substances at feasible energy consumption, as applied to municipal WWTP effluent, raw hospital sewage and biologically treated wastewater effluent from a health institution. The transformation products of the pharmaceuticals were also oxidized in the non-selective process, as demonstrated from the removal of identified transformation products and the reformation of the original parent compounds during oxidation. Two compounds, progesterone and methylprednisolone, specifically displayed such behavior previously not attributed to these particular substances. The results also point out that any oxidation process studied for real wastewaters with unknown content of the transformation products of the given parent compounds may be subjected to negative bias for oxidation efficiency due to the unknown rate of the reformation reactions. The overall results implicate in a directly practical manner that the environmental load from pharmaceutical residues entering the aquatic systems through wastewater discharges could be well reduced with the application of the PCD technology, located either after the conventional biological wastewater treatment, or, for higher removal rates, directly after the point sources like hospitals and other health institutions. Indeed, treatment at the source would also reduce the incoming pharmaceutical load at municipal wastewater plants, likely reducing the concentrations in the sludge fraction from clarifier underflows as well as in the treated effluent. This would be beneficial for the subsequent sludge utilization opportunities.

Further research is recommended for studying the gas phase composition during PCD water treatment process and for the practical application of designing new chemical processes involving heterogeneous gas-liquid-plasma system, utilizing the presently obtained understanding on OH radical dynamics. For water treatment, further optimization of the hydrodynamic conditions should be concerned, involving experiments at higher flow rates using an atomizer configuration, i.e. varying the spray density similarly as in *Publication I* while incorporating very small droplet size as in *Publication IV*.

# References

[1] Halling-Sørensen B, Nors Nielsen S, Lanzky PF, Ingerslev F, Holten Lützhøft HC, Jørgensen SE. Occurrence, fate and effects of pharmaceutical substances in the environment - A review, *Chemosphere*, **1998**, 36, 357-93.

[2] Larsson DGJ. Pollution from drug manufacturing: Review and perspectives, *Philos Trans R Soc B Biol Sci*, **2014**, 19, 20130571.

[3] Sui Q, Cao X, Lu S, Zhao W, Qiu Z, Yu G. Occurrence, sources and fate of pharmaceuticals and personal care products in the groundwater: A review. *Emerg Contam*, **2015**, 1, 14-24.

[4] Chévre N. Pharmaceuticals in surface waters: Sources, behavior, ecological risk, and possible solutions. Case study of lake Geneva, Switzerland. WIREs Water, **2014**, 1, 6986.

[5] Ternes TA. Occurrence of drugs in German sewage treatment plants and rivers. *Water Res*, **1998**, 11, 3245-60.

[6] Vieno N, Tuhkanen T, Kronberg L. Elimination of pharmaceuticals in sewage treatment plants in Finland. *Water Res*, **2007**, 41, 1001-12.

[7] Tixier C, Singer HP, Oellers S, Müller SR. Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters. *Environ Sci Technol*, **2003**, 37, 1061-8.

[8] Magureanu M, Mandache NB, Parvulescu VI. Degradation of pharmaceutical compounds in water by non-thermal plasma treatment. *Water Res*, **2015**, 81, 124-36.

[9] Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ Int*, **2009**, 35, 402-17.

[10] Glaze WH, Kang J, Chapin DH. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone: Sci. Eng*. **1987**, 9, 335-52.

[11] Grabowski LR, van Veldhuizen EM, Pemen AJM, Rutgers WR. Corona above water reactor for systematic study of aqueous phenol degradation. *Plasma Chem Plasma Proc*, **2006**, 26, 3-17.

[12] Wang H, Li J, Quan X. Decoloration of azo dye by a multi-needle-to-plate highvoltage pulsed corona discharge system in water. *J Electrostat*, **2006**, 64, 416-21.

[13] Ono R, Oda T. Dynamics of ozone and OH radicals generated by pulsed corona discharge in humid-air flow reactor measured by laser spectroscopy. *J Appl Phys*, **2003** 93, 5876-82.

[14] Panorel I, Preis S, Kornev I, Hatakka H, Louhi-Kultanen M. Oxidation of aqueous pharmaceuticals by pulsed corona discharge. *Environ Technol*, **2013**, 34, 923-30.

[15] Preis S, Panorel I, Kornev I, Hatakka H, Kallas J. Pulsed corona discharge: The role of ozone and hydroxyl radical in aqueous pollutants oxidation. *Water Sci Technol*, **2013**, 68, 1536-42.

[16] Bruggeman P, Schram DC. On OH production in water containing atmospheric pressure plasmas. *Plasma Sources Sci Technol*, **2010**, 19, 045025.

[17]. Vaughan PP, Blough NV. Photochemical formation of hydroxyl radical by constituents of natural waters. *Environ Sci Technol*, **1998**, 32, 2947-53.

[18] Shen Y, Lei L, Zhang X, Zhou M, Zhang Y. Effect of various gases and chemical catalysts on phenol degradation pathways by pulsed electrical discharges. *J Haz Mater*, **2008**, 150, 713-22.

[19] Zhang Y, Zhou M, Hao X, Lei L. Degradation mechanisms of 4-chlorophenol in a novel gas–liquid hybrid discharge reactor by pulsed high voltage system with oxygen or nitrogen bubbling. *Chemosphere*, **2007**, 67, 702-11.

[20] Hayashi D, Hoeben W, Dooms G, van Veldhuizen E, Rutgers W, Kroesen G. Influence of gaseous atmosphere on corona-induced degradation of aqueous phenol. *J Phys D*, **2000**, 33, 2769.

[21] Chandana L, Manoj Kumar Reddy P, Subrahmanyam C. (2015) Atmospheric pressure non-thermal plasma jet for the degradation of methylene blue in aqueous medium. *Chem Eng J*, **2015**, 282, 116-22.

[22] Hsieh K, Wandell R, Bresch S, Locke B. Analysis of hydroxyl radical formation in a gas-liquid electrical discharge plasma reactor utilizing liquid and gaseous radical scavengers. *Plasma Proc Polym*, **2017**, 14, 1600171.

[23] Banaschik R, Lukes P, Jablonowski H, Hammer M, Weltmann K, Kolb J. Potential of pulsed corona discharges generated in water for the degradation of persistent pharmaceutical residues. *Water Res*, **2015**, 84, 127-35.

[24] Njatawidjaja E, Tri Sugiarto A, Ohshima T, Sato M. Decoloration of electrostatically atomized organic dye by the pulsed streamer corona discharge. *J Electrostat*, **2005**, 63, 353-9.

[25] Baird C. Free radical reactions in aqueous solutions: Examples from advanced oxidation processes for wastewater from the chemistry in airborne water droplets. *J Chem Educ*, **1997**, 7, 817.

[26] Malik M. Water purification by plasmas: Which reactors are most energy efficient? *Plasma Chem Plasma Proc*, **2010**, 30, 21-31.

[27] Jeong J, Kim J, Yoon J. The role of reactive oxygen species in the electrochemical inactivation of microorganisms. *Environ Sci Technol*, **2006**, 40, 611722.

[28] Hoigné J, Bader H. Rate constants of reactions of ozone with organic and inorganic compounds in water—II: Dissociating organic compounds. *Water Res*, **1983**, 17, 18594.

[29] Vecitis C, Lesko T, Colussi A, Hoffmann M. Sonolytic decomposition of aqueous bioxalate in the presence of ozone. *J Phys Chem A*, **2010**, 114, 4968-80.

[30] Pera-Titus M, García-Molina V, Baños MA, Giménez J, Esplugas S. Degradation of chlorophenols by means of advanced oxidation processes: A general review. *Appl Cat B Environ*, **2004**, 47, 219-56.

[31] Thiruvenkatachari R, Vigneswaran S, Moon IS. A review on UV/TiO2 photocatalytic oxidation process (journal review). *Kor J Chem Eng*, **2008**, 25, 64-72.

[32] Neyens E, Baeyens J. A review of classic fenton's peroxidation as an advanced oxidation technique. *J Haz Mater*, **2003**, 98, 33-50.

[33] Hayashi D, Hoeben W, Dooms G, van Veldhuizen E, Rutgers W, Kroesen G. Laser-induced fluorescence spectroscopy for phenol and intermediate products in aqueous solutions degraded by pulsed corona discharges above water. *Appl Opt*, **2001**, 40, 986-93.

[34] Kornev J. In: Electric discharge treatment of water containing organic substances. Korus 2003: 7th Korea-Russia international symposium on science and technology, vol 1 proceedings: Machine parts and materials processing; Ulsan, South Korea, **2003**, 221-6.

[35] Bergmann H, Koparal AT, Koparal AS, Ehrig F. The influence of products and byproducts obtained by drinking water electrolysis on microorganisms. *Microchem J*, **2008**, 89, 98-107.

[36] Ahmed B, Mohamed H, Limem E, Nasr B. Degradation and mineralization of organic pollutants contained in actual pulp and paper mill wastewaters by a UV/H2O2 process. *Ind Eng Chem Res*, **2009**, 48, 3370-9.

[37] Preis S. History of ozone synthesis and use for water treatment. In: Munter R, editor. Encyclopedia of Life Support Systems (EOLSS). Oxford, UK: Eolss Publishers; **2008**.

[38] Kornev I, Osokin G, Galanov A, Yavorovskiy N, Preis S. Formation of nitrite- and nitrate-ions in aqueous solutions treated with pulsed electric discharges. *Ozone: Sci Eng*, **2013**, 35, 22-30.

[39] von Gunten U, Hoigne J. Bromate formation during ozonization of bromidecontaining waters: Interaction of ozone and hydroxyl radical reactions. *Environ Sci Technol*, **1994**, 28, 1234-42.

[40] Cooper W, Amy G, Moore C, Zilca R. Bromoform formation in ozonated groundwater containing bromide and humic substances. *Ozone: Sci Eng*, **1986**, 8, 6375.

[41] Elshorbagy W, Abu-Qdais H, Elsheamy M. Simulation of THM species in water distribution systems. *Water Res*, **2000**, 34, 3431-9.

[42] Krichevskaya M, Klauson D, Portjanskaja E, Preis S. The cost evaluation of advanced oxidation processes in laboratory and pilot-scale experiments. *Ozone: Sci Eng*, **2011**, 33, 211-23.

[43] Kornev I, Saprykin F, Preis S. Stability and energy efficiency of pulsed corona discharge in treatment of dispersed high-conductivity aqueous solutions. *J Electrostat*, **2017**, 89, 42-50.

[44] Danckwerts PV. Gas-liquid reactions. McGraw-Hill Book Co.; **1970**.

[45] Sehested K, Getoff N, Schwoerer F, Markovic VM, Nielsen SO. Pulse radiolysis of oxalic acid and oxalates. *J Phys Chem*, **1971**, 75, 749-55.

[46] Lagunova YO, Seliverstov AF, Ershov BG, Basiev AG. Oxidative decomposition of oxalate ions in water solutions of concentrated ozone. *Atom Energ*, **2012**, 113, 1126.

[47] Attri P, Kim YH, Park DH, Park JH, Hong YJ, Uhm HS, et al. Generation mechanism of hydroxyl radical species and its lifetime prediction during the plasmainitiated ultraviolet (UV) photolysis. *Sci Rep*, **2015**, 5, 9332.

[48] Kanazawa S, Kawano H, Watanabe S, Furuki T, Akamine S, Ichiki R, Ohkubo T, Kocik M, Mizeraczyk J. Observation of OH radicals produced by pulsed discharges on the surface of a liquid. *Plasma Sourc Sci Technol*, **2011**, 20, 034010.

[49] Müller S, Zahn R. Air pollution control by non-thermal plasma. *Contrib Plasma Phys*, **2007**, 47, 520-9.

[50] Krause H, Schweiger B, Schuhmacher J, Scholl S, Steinfeld U. Degradation of the endocrine disrupting chemicals (EDCs) carbamazepine, clofibric acid, and iopromide by corona discharge over water. *Chemosphere*, **2009**, 75, 163-8.

[51] Palo P, Domínguez J, Sánchez-Martín J. Ozonation of a carbamazepine effluent. designing the operational parameters under economic considerations. *Water Air Soil Pollut*, **2012**, 223, 5999-6007.

[52] Naddeo V, Uyguner-Demirel CS, Prado M, Cesaro A, Belgiorno V, Ballesteros F. Enhanced ozonation of selected pharmaceuticals by sonolysis. *Environ Technol*, **2015**, 36, 1876-83.

[53] Gerrity D, Stanford BD, Trenholm RA, Snyder SA. An evaluation of a pilot-scale nonthermal plasma advanced oxidation process for trace organic compound degradation. *Water Res*, **2010**, 44, 493-504.

[54] Ferrando-Climent L, Collado N, Buttiglieri G, Gros M, Rodriguez-Roda I, Rodriguez-Mozaz S, et al. Comprehensive study of ibuprofen and its metabolites in activated sludge batch experiments and aquatic environment. *Sci Total Environ*, **2012**, 438, 404-13.

[55] OECD guidelines for the testing of chemicals, section 3. test no. 303. simulation test – aerobic sewage treatment – A: Activated sludge units; B: Biofilms. ISBN 9789264070424. **2001**.

[56] Chidambara Raj C, Li Quen H. Advanced oxidation processes for wastewater treatment: Optimization of UV/H2O2 process through a statistical technique. *Chem Eng Sci*, **2005**, 5305-11.

# Appendix: Brief comparison of select oxidation methods

When comparing different methods, it is important to apply optimal conditions for each process to enable fair comparison of results. The reports describing the methods in Table 1 show that in different studies, the ranking of different methods can vary even when the same processes and model compounds are used.

A preliminary practical comparison of PCD was also attempted with UV/$H_2O_2$ and electrolysis cell (EC) experiments using synthetic wastewater (SWW). Synthetic wastewater was selected instead of actual wastewater to ensure identic starting conditions in different experiments. The recipe for the SWW followed the OECD guidelines [55] and is presented in Table A1. TOC of the SWW is 105 mg $L^{-1}$ and COD correspondingly 279 mg $L^{-1}$.

**Table A1.** Composition of the OECD synthetic wastewater.

| *Constituent* | *Concentration, mg $L^{-1}$* |
|---|---|
| Peptone | 160 |
| Meat extract | 110 |
| Urea | 30 |
| $K_2HPO_4$ | 28 |
| NaCl | 7 |
| $CaCl_2$ | 3 |
| $Mg_2SO_4$ | 0.5 |

Since the processes were studied for oxidation efficiency, the comparison was done by measuring mineralization, in this case COD reduction, after 5 kWh $m^{-3}$ treatment. Each process was optimized for fair comparison. In UV/$H_2O_2$ experiments, pretreatment of the samples for residual peroxide destruction was done by adding sodium sulfite and cobalt catalyst with subsequent aeration. A hydrogen peroxide to TOC mass ratio of 10:1, suitable for this COD range, was selected according to the observations in [36]. The UV light source was a medium pressure UV lamp, emitting 2384 µW $cm^{-2}$ at 254 nm, immersed in the SWW-$H_2O_2$-solution with a 94.2 $cm^2$ contact area. Energy input was calculated using these values. For the EC, Ir/$TiO_2$ anodes paired with Hastelloy C-22 steel cathodes were used in a 3-anode 4-cathode stack with electrode dimensions of 23 mm x 53 mm. The optimal electrode surface to solution volume ratio was determined in preliminary experiments to be around 57 $m^{-1}$ and the optimal voltage difference to be 3.5 V. Energy input was calculated from the U-I raw data collected with the same potentiostat used for maintaining the voltage. In PCD experiments, the preliminary testing indicated slow reaction and therefore maximum pulse frequency of 840 pps was applied. Energy input was calculated from corresponding discharge power of 250 W.

This testing revealed very low COD reduction in all three processes in treatment of the OECD SWW. Since each process have proven highly efficient in other studies, it can be deduced that the solution matrix is not very prone to chemical oxidation. The average performance of each technology is presented in Fig. A1.

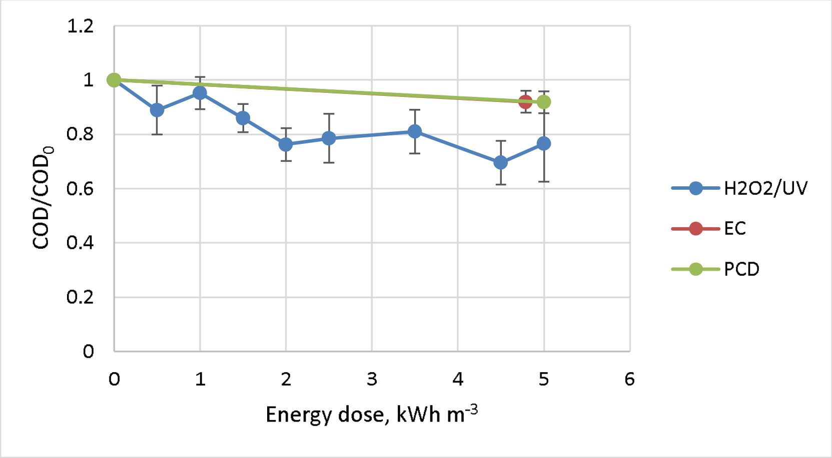


**Figure A1.** COD reduction of OECD SWW with different oxidation processes.

Figure A1 and the substantial error in UV/$H_2O_2$ samples reflect the difficulty in using COD as the probe for this kind of comparison. UV/$H_2O_2$ method gave the slightly better overall efficiency than the other two if mere energy efficiency is taken into account. This may be due to the high concentration peroxide presence. It, however, involves notable operating costs being the only process requiring the addition of a chemical, whereas the other two employ electricity only.

Another practical inconvenience was observed with EC, as the performance of the anode material was inconsistently decreasing basically after every run. It was observed that the anodes may be, however, regenerated by treating 30 mM pure NaCl solution at elevated voltage of 5 V. The regeneration by this method improved the performance in comparison of non-regenerated anodes at also very inconsistent rate (perhaps due to inconsistencies in the material), and provides a good topic for further investigations. Still, a regeneration step brings high inconvenience from practical perspective since frequent regeneration of the anodes in real installations is not feasible.

Upon experimenting, it became obvious that the most substantial assets of PCD in the group of AOPs include operational simplicity and general operation indifference towards wastewater composition, and freedom of maintenance as observed during this thesis work. No electrode corrosion has been observed after few years of experimenting. The process is also linear, and thus easily controlled to the desired extent of treatment; in contrast in UV/$H_2O_2$ for example, the most efficient way of operation (according to [56]) is introducing all the peroxide at once instead of continuous chemical input, making it nonlinear and more difficult to steer during process.

# Publication I

Ajo, P., Kornev, I. and Preis, S.

**Pulsed corona discharge in water treatment: the effect of hydrodynamic conditions on oxidation energy efficiency**

Reprinted with permission from
*Industrial and Engineering Chemistry Research*
Vol. 54, pp. 7452-7458, 2015

I&EC research
Industrial & Engineering Chemistry Research
Article
pubs.acs.org/IECR

# Pulsed Corona Discharge in Water Treatment: The Effect of Hydrodynamic Conditions on Oxidation Energy Efficiency

Petri Ajo,[†] Iakov Kornev,[‡] and Sergei Preis*[,§]

[†]School of Engineering Science, Lappeenranta University of Technology, Skinnarilankatu 34, 53850 Lappeenranta, Finland
[‡]Institute of High Technology Physics, Tomsk Polytechnic University, 2A Lenin Avenue, Tomsk 634050, Russia
[§]School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Center, Panyu District, Guangzhou, Guangdong Province 510006, P. R. China

**ABSTRACT:** Water treatment by gas-phase pulsed corona discharge (PCD) relies mainly on utilization of ozone and OH radicals as oxidizing agents. In a configuration where the treated solution is showered through the plasma zone, the gas−liquid contact surface is the primary OH-radical formation site and the interface in the mass transfer of ozone. Its significance to overall process efficiency is therefore notable. In this study, the effect of varying contact surface area at different discharge powers was investigated from the perspective of efficient utilization of the two prime oxidants in slow reaction with oxalate. It is seen that increasing the area of the contact surface improves OH-radical utilization up to the point where the pollutant oxidation efficiency abruptly decreases presumably because of unfavorable pulse energy distribution in the gas−liquid mixture. The existence of an optimal area for a given power has implications for future studies in the design of pulsed plasma applications for water treatment.

## INTRODUCTION

The global problem of declining fresh water supplies gives considerable significance to research on cost efficient water purification. The necessity for inexpensive and effective water treatment methods is self-explanatory; markets for cost efficient and effective water purification technologies are worldwide. Contemporary challenges bear a universal character and include the following:

- High energy consumption and secondary pollution are not admissible, from neither an economic nor an environmental perspective.
- Recalcitrant compounds endure biological oxidation, and conventional tertiary treatment is often insufficient.
- More powerful treatment for recalcitrant pollutants should be economically viable.
- Trends of increasingly strict regulation set new requirements for water treatment.

Overcoming the economic deficiencies and adverse environmental consequences of traditional water treatment methods would clearly yield great benefits. The degradation of recalcitrant compounds is of particular interest, since they tend to accumulate in the environment.[1]

As conventional treatment is often insufficient for effective removal of refractory substances from wastewater, more effective measures are required.[2] The mechanism of degradation of organic pollutants is generally based on oxidation, and thus utilization of highly reactive oxidants is clearly a promising and relevant field of research. The most powerful feasible oxidant is the hydroxyl radical, and water treatment methods that generate and exploit this radical are collectively referred to as advanced oxidation processes (AOPs).[3]

One group of AOPs comprises treatment approaches applying electric discharge, an area that during the past decade has been the subject of increasing research interest. The underlying principle in water treatment with electric discharge is the production and utilization of short-living oxidative species in situ, namely, ozone and hydroxyl radicals, thus improving the energy efficiency of oxidation. A number of studies have indicated that the application of gas-phase PCD in a configuration where the treated solution is showered through the plasma zone is both effective and efficient in degradation of organic pollutants in water.[4−10] Particular benefits of gas-phase PCD treatment are its superior energy efficiency over other methods[10] and that the system is operated in ambient conditions with no additional chemicals included in the process.

A number of process phenomena have been studied in PCD treatment of water, such as the formation of nitrites and nitrates[11] and oxidant roles and kinetics.[12−15] Preis et al. (2013)[15] indicated that in PCD treatment, hydroxyl radicals are formed in the gas−liquid interface and reported that the increase in contact surface area enhanced the oxidation efficiency of aqueous phenol. It was also observed that a maximum efficiency was reached at some point, after which the efficiency remained constant regardless of any subsequent increase in the contact surface area. It was implied that the factor restraining further efficiency enhancement was the discharge power.

So far, the research on physical and chemical interactions of nonthermal plasma and liquid surfaces involves considerable field of uncharted phenomena.[16,17] Identification of optimal operating parameters is also of major importance in commercialization of the technology. For the present study, it was hypothesized that there may be a generally applicable

**Received:** May 24, 2015
**Revised:** July 10, 2015
**Accepted:** July 14, 2015

ACS Publications

DOI: 10.1021/acs.iecr.5b01915

optimal contact surface area for a fixed discharge power, i.e., an optimum area to power ratio for the process. Thereby, the objective of the work was to establish the dependence of the oxidation rate on the treatment power and specific gas−liquid contact area exposed to the plasma zone.

## ■ MATERIALS AND METHODS

**Chemicals.** Oxalic acid was chosen as the probe compound for its simple molecular construction and minimizing competitive reactions of intermediate products. Oxalate is a well-known refractory compound and only slowly oxidized, which was anticipated to facilitate observing changes in the process when treatment parameters were altered. The oxidation via hydroxyl radical attack is also therefore emphasized over reactions with ozone. The oxidation experiments were conducted with 10 L oxalic acid solutions with initial concentration of 60 mg $L^{-1}$. The oxalic acid used in solutions preparation was of minimum 98% purity, by VWR International (Leuven, Belgium). Initial pH of the treated solutions was 3.5, decreasing to around 3.0 during treatment with minor deviations. All experiments were performed in ambient conditions, and the treated solutions were prepared with tap water. Otherwise, for example in analysis and stock solution preparation, Millipore water was used.

**Analysis.** Oxalate concentrations were analyzed by either permanganometric titration[18] or ionic chromatography (IC) using a Dionex ICS-1100 ionic chromatograph by Thermo Scientific, USA. For the IC analyses, a Dionex AS22 column was used with a simple isocratic carbonate/bicarbonate eluent. In this study, no particular differentiation is made between the three protonation states of the compound, and hence oxalic acid $(COOH)_2$, bioxalate $(COOH)(COO)^-$, and oxalate $(COO)_2^{2-}$ are conclusively referred to as oxalate. Gas-phase ozone concentration inside the reactor was measured by iodometric titration of a fixed volume gas sample.[19]

**Experimental Equipment.** The experimental system is a closed circulation batch process, as schematically illustrated in Figure 1, consisting of a PCD reactor with matching pulse generator and a water circulation system. The plasma reactor is a transparent acrylic chamber with two grounded vertical plate electrodes curtaining the inside of the front and back of the reactor. Between the plates, a set of parallel high voltage (HV) wire electrodes is suspended between two adjustable metal rods, shown as HV conductor in Figure 1. The HV electrode wire is 0.5 mm in diameter and positioned in the middle of the plates 17 mm from each. The grounded plates are 210 mm in width and 1 m in height, giving a total plasma volume of $7.14 \times 10^{-3}$ $m^3$. The pulse parameters were determined with an Agilent 54622D oscilloscope: the pulse generator produces pulses with 0.12 J energy of a single pulse at 22 kV and 180 A in the amplitude peak at about 100 ns duration, which corresponds to an average energy density of 16.8 J $m^{-3}$ in the plasma volume. Calculation of the energy of a single pulse was made using a well-known equation

$$W_p = \int_0^{T_p} U(t)\, I(t)\, dt \tag{1}$$

where $U(t)$ and $I(t)$ are waveforms of voltage and current and $T_p$ is the duration of the voltage pulse. Integration of voltage and current waveforms was done numerically using MathCAD software package.

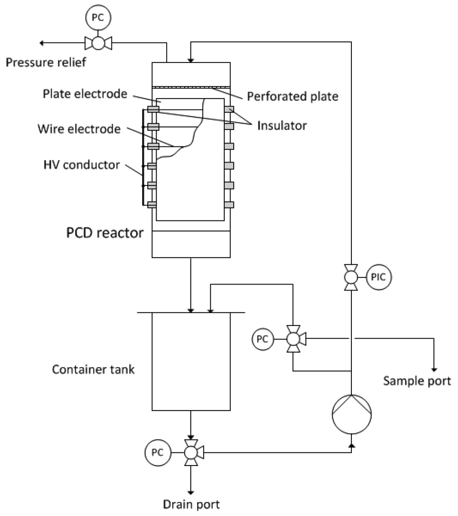


**Figure 1.** Schematic diagram of the experimental system.

The generator operates at various pulse repetition frequencies and corresponding discharge powers ranging from 50 to 833 pulses per second (pps) at 6−100 W of discharge power, respectively. The discharge power refers to the total energy delivered per time unit, that is, frequency times the energy of a single pulse. Below the reactor is a container tank from which the treated water is pumped to a chamber above the electrode compartment. The bottom of the chamber is perforated to shower the water evenly to the plasma zone between the grounded plates. Figure 2 shows a typical voltage and current oscillogram.

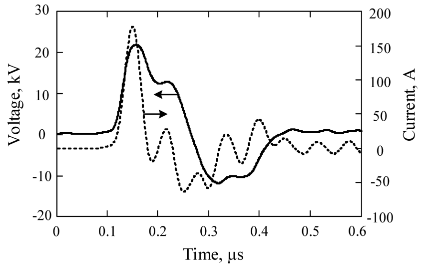


**Figure 2.** Voltage (solid) and current (dotted) of a pulse.

**Contact Surface Measurement.** As the experimental setup is batch type, the gas−liquid contact surface was adjusted by regulating the flow rate in the system at fixed treatment times. The ratio of contact surface and flow rate was shown to be linear with the classical method of sulfite oxidation by aerial oxygen with cobalt sulfate catalyzing the reaction.[20] With the cobalt sulfate catalyst added, 0.1 M sodium sulfite solution was circulated in the system resulting in steady, flow rate dependent $SO_3^{2-} \rightarrow SO_4^{2-}$ oxidation rate. The decreasing sulfite concentration was determined by iodometric reverse titration, using sodium thiosulfate titrant. The amount of oxygen absorbed by the sulfite solution was then calculated according to eq 2.

Table 1. Applied Gas−Liquid Contact Surface Relative to Applied Power, $A/P$ Ratios

| | $A/P$ ($m^{-1}$ $W^{-1}$) for contact surface area ($m^{-1}$) of | | | | | | |
|---|---|---|---|---|---|---|---|
| power (W) | 15.7 ± 0.5 | 32.1 ± 0.5 | 40.4 ± 0.5 | 48.6 ± 0.5 | 56.8 ± 1.0 | 65.1 ± 1.5 | 73.4 ± 1.5 |
| 36 | 0.43 | 0.89 | 1.12 | 1.35 | | 1.81 | |
| 60 | 0.26 | 0.54 | | 0.81 | 0.95 | 1.09 | |
| 100 | 0.16 | 0.32 | | 0.49 | | 0.65 | 0.73 |

$$M_{O_2} = \frac{\Delta N_{Na_2SO_3} V_L}{4\Delta t} \tag{2}$$

where $V_L$ is the total volume of liquid circulating in the system, $\Delta t$ is the time interval in which the decrease in sulfite concentration was observed, and factor 4 transforms the number of sulfite equivalents to moles of oxygen. The mass transfer eq 3 was used to derive the values for the contact surface area $F$ at different flow conditions.

$$M_{O_2} = KF\,\Delta C\,\Delta t \tag{3}$$

where $K$ is the mass transfer coefficient and $\Delta C$ is the mass transfer driving force, both of which are considered constant. The gas−liquid contact surface was subsequently estimated upon the knowledge of the contact surface in the tank and oxygen absorption rate when water was not circulated in the reactor. This was done through a pair of simultaneous equations for eq 3, where $M_{O_2}$, $F$, and $\Delta t$ all have two values: one for system flow with reactor circulation (on) and one without (off).

$$M_{O_2\,on} = KF_{on}\,\Delta C\,\Delta t_{on} \tag{4}$$

$$M_{O_2\,off} = KF_{off}\,\Delta C\,\Delta t_{off} \tag{5}$$

The gas−liquid contact surface ($F_{on}$) is thereafter calculable from eqs 4 and 5, since all other remaining quantities are either measured or calculated during procedure; $K$ and $\Delta C$ will be reduced out of the equations as constant.

For measuring the gas−liquid contact surface in the plasma zone, the approach produces minor error in the absolute calculated values; the area exposed to the plasma zone was determined by subtracting the gas−liquid surface area in the container tank from the surface area of complete circulation through the system. Although there can be assumed a small positive bias in the surface values resulting from the water droplets and jets in the reactor above and below the plasma zone, its contribution is considered insignificant in view of results comparability between altering flow conditions. The relative height of the free falling zone above and below plasma is altogether 0.23 m, which comprises 19% of the total free falling length and remains unchanged between experiments, thus allowing reliable comparison of results.

**Oxidation Experiments.** The experiments were conducted at three different pulse frequencies of 300, 500, and 833 pps corresponding to treatment powers of 36, 60, and 100 W, respectively. The treated aqueous solution was circulated at flow rates ranging from 1.73 to 5.04 L $min^{-1}$. The experimental parameters are presented in Table 1. All experiments were duplicated. The goal was to establish a $m^{-1}$ $W^{-1}$ value for the optimal area to power ratio (henceforth referred to as $A/P$ ratio).

The experiments were conducted in ambient conditions at room temperature of 20−22 °C. The container tank (Figure 1) was supplied with a thermostat, which was, however, never required: the raise in temperature did not exceed 2 °C for the time of treatment. Atmospheric composition was not specifically controlled; all experiments were initiated with gas phase content equivalent to ambient air.

Since the oxalic acid solution exiting the plasma zone is expected to contain a reduced concentration of the target compound in comparison to the solution in the container tank, the concentration in the system may be considered heterogeneous during treatment. Therefore, prior to sampling, the solution was allowed to mix by circulating it in the system with the reactor unpowered. Mixing times were set individually for different flow rates to allow full circulation through the system and thus proper mixing with minimized concentration gradients.

## ■ RESULTS AND DISCUSSION

**Contact Surface Impact.** Comparison of the PCD performance at different $A/P$ ratios is done from the perspective of energy efficiency, expressed in the form of oxidation rate as a function of delivered energy and calculated for the delivered energy dose of 10 kW h $m^{-3}$, for which oxalate degradation was observed to be linear. The corresponding treatment times at powers of 100, 60, and 36 W were 60, 100, and 167 min, respectively. The rate is represented by the absolute slope value $|k|$ of relative oxalate concentration decreasing versus the delivered energy as shown in Figures 3, 4, and 5. The values represent the average of duplicated experiments with the deviation of data in parallel experiments around 5%.

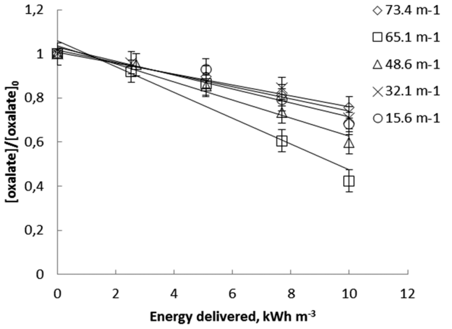


Figure 3. Oxidation of oxalic acid at 100 W with varying contact surface area ($m^{-1}$).

From Figures 3−5, higher oxidation efficiency can be observed at lower frequencies attributed to the prolonged ozone exposure at longer treatment times. Absolute values of the slopes were obtained to arrange the results for illustration; the highest value of $|k|$ is produced from the highest degradation rate. The value of $|k|$ at different $A/P$ ratios is

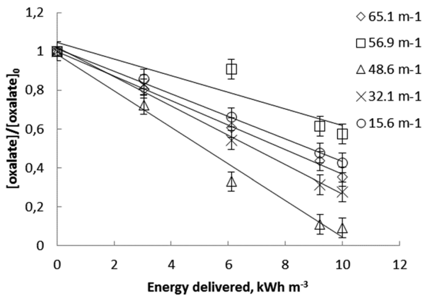


**Figure 4.** Oxidation of oxalic acid at 60 W with varying contact surface area ($m^{-1}$).

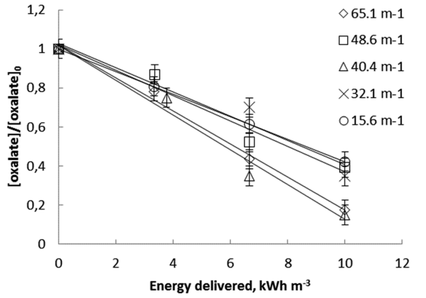


**Figure 5.** Oxidation of oxalic acid at 36 W with varying contact surface area ($m^{-1}$).

presented in Figure 6, where each data point represents the efficiency of a complete process of 10 kW h $m^{-3}$ from repeated experiments.

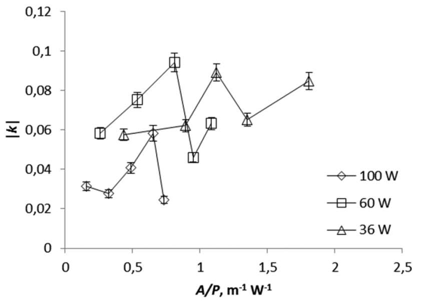


**Figure 6.** Degradation rate dependence on $A/P$ ratio at 10 kW h $m^{-3}$ delivered energy.

In Figure 6, an optimum peak with subsequent decrease is a characteristic of each curve. The degradation rates at 100 W, however, are consistently lower than at smaller power. Since the $|k|$ value is presented as a function of delivered energy, the lower average rates may indicate that at 100 W the reaction is somewhat diffusion controlled and a notable portion of OH radicals are consumed in useless decay reactions in possible instant lack of the target pollutant with limited diffusion rate. Furthermore, the contribution of ozone may influence the oxidation rates if for lower power, i.e., longer treatment time, the ozone yield responds better to demand by reactions with oxalate. At 100 W, a bigger portion of produced ozone, as well, is thus consumed in reactions of useless decomposing directly influencing the energy efficiency.

To investigate the role of ozone in the $A/P$ range of optimal and decreased efficiencies, gaseous ozone concentration was measured at corresponding gas—liquid contact areas at different powers. Ozone concentration was noted as being slightly higher with increasing power at the point of 5 kW h $m^{-3}$ energy delivered, although it stabilized at the end of the treatment (10 kW h $m^{-3}$) to closely match the values at lower powers with minor deviance between measurements at different contact surface areas (Figure 7).

The oxidation efficiency undergoes a noticeable decrease at greater than optimal $A/P$ ratio. The decrease occurs at varying flow rates (contact areas) corresponding to the applied power, which implies that the decrease is the result of unfavorable development in the interaction between the gas—liquid interface and the plasma environment. The abrupt decrease in efficiency is thus postulated as resulting from a decrease in OH formation rate or increased useless decomposition/recombination. The magnitude of the decrease and the minor deviations in gaseous ozone concentration also support the hypothesis of the OH radical being responsible rather than ozone, because of the low reactivity of oxalate with molecular ozone ($k \leq 4 \times 10^{-2}$ $M^{-1}$ $s^{-1}$).[21] The decreased overall efficiency with treatment power at 100 W further supports the idea that with surplus ozone, increased area should enhance ozone absorption and inherently increase efficiency, not cause it to decrease. In addition, gas phase ozone concentration was observed to be practically insensitive toward changes in $A/P$ ratio, whether measured at regions of optimal or decreased efficiency (Figure 7).

The observed decrease in oxidation efficiency originates from conditions of the water flow rather than changes in the pulse parameters; the pulse oscillograms were unaffected by the changes in flow rate at all pulse repetition frequencies. The increase in gas—liquid contact surface is considered to result from increasing number of airborne droplets rather than varying droplet size, which is supported by the linear correlation of gas—liquid contact area and volumetric flow rate. Shorter residence time from faster flow rate may also be excluded, since the residence time only depends on the free fall velocity determined by the hydrostatic pressure in the top chamber, which did not considerably change among experiments (data not shown). In practice, the arising variables at different flow rates are thus the average distance between droplets and the total volume of resident water in the plasma zone. Increasing amount of airborne water in the reactor, i.e., decreased gaseous volume in the plasma, may alter the discharge energy distribution in the heterogeneous medium. A probable outcome that would also explain the decreased efficiency is that the energy of a pulse is redistributed in streamers at increased water flow rates, which may be the result of reduced gaseous volume, shorter discharge propagation gaps, or more concentrated electric field in the altering heterogeneous space geometry. The density of active species may increase, thus pronouncing undesirable recombination reactions. Therefore, at the point of decreased efficiency, it may be considered that a local critical point is achieved in the volume of resident water in the plasma zone.

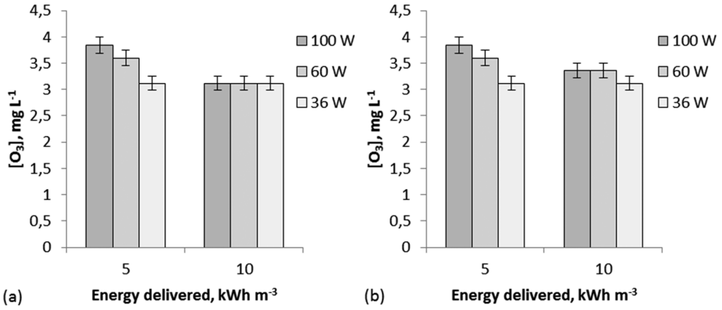


**Figure 7.** Gas phase ozone concentrations in experiments at contact surface areas corresponding to (a) optimal and (b) decreased efficiency.

In Figure 6, the degradation efficiency at 36 and 60 W pulsed powers can be observed to improve again after the decrease, when the contact area is further increased. This increase in efficiency may be explained, similarly as below the optimum $A/P$ ratio, by the increased gas–liquid contact area that still promotes reactions between the oxidants and the oxalate molecules. At 100 W, the peak in efficiency was observed at the technically maximum feasible $A/P$ ratio and the following suspected increase, judged from the results at lower power, is thereby left out of data range.

The optimal $A/P$ ratio (value at the peak) increases with decreasing treatment power (Figure 6). The gas–liquid interface areas corresponding to the values at the peaks can be further presented as a function of pulse frequency, as illustrated in Figure 8. One should keep in mind that the experimental points in Figure 8 present a summarized data from 30 experimental series covering the analytical data from 150 sampling points.

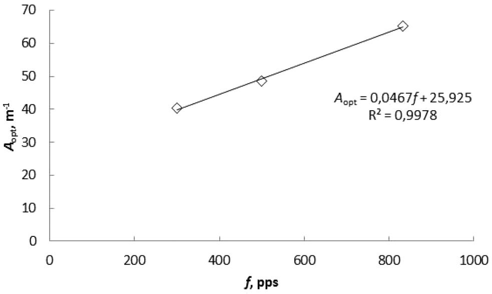


**Figure 8.** Optimal gas–liquid interface area ($A_{opt}$) dependent on the pulse frequency ($f$).

From Figure 8 one can see the value for optimal contact surface area increasing linearly, but not proportionally, with increasing pulse frequency. The optimal contact area increases approximately at a ratio of 3:5 to the increase in frequency. The disproportionate growth may be explained by the fact that a single pulse is identic with another regardless of the frequency: increasing frequency does not change the effect of a single pulse on the water surface, but it produces a linear compensation by increasing the amount of energy input per contact surface during the lifetime of a droplet. Further compensation from increasing frequency may arise from the enhanced diffusion due to the turbulence on the water surface, or the ionic wind, caused by the HV pulses.[6,22,23] This also explains why the specific area for the decreased efficiency is not fixed but dependent on the $A/P$ ratio. In other words, the linearity is suggested to be the result of increasing need for energy along increasing contact surface, yet the growth is disproportionate because a single pulse has a fixed energy and thus the increase in frequency has to be greater than the increase in area.

**Oxidation Efficiency Compared to Conventional Ozonation.** The energy efficiency of PCD was reported substantially surpassing conventional ozonation for rapidly reacting phenol,[15] pharmaceuticals,[10,24] and moderately reacting humic substances.[25] Ozonation of aqueous oxalate is a slow process, in which oxidation takes place in the solution saturated with ozone, thus making the energy consumption dependent on the concentrations of aqueous ozone and oxalate and the rate of replenishing reacted dissolved ozone. Two cases of oxalate ozonation were described earlier.[26,27] Lagunova et al.[26] show that oxalate oxidation from its concentration of 900 mg $L^{-1}$ to about 25 mg $L^{-1}$ at the ozone gas-phase concentration of 150 mg $L^{-1}$ took about 150 min at 20 °C and pH 9.9, making the oxidation rate 0.05 mg $L^{-1}$ $s^{-1}$, i.e., $5.6 \times 10^{-7}$ M $s^{-1}$. Ozone stoichiometric consumption in the second order reaction comprises 0.027 mg $L^{-1}$ $s^{-1}$. At the given concentration of gaseous ozone and its solubility equilibrium factor 0.32 at 20 °C,[27] the flow of ozone-containing gas should be provided at its minimum of 0.56 mL $s^{-1}$. The authors used the gas flow rate 2 mL $s^{-1}$, which seems to be reasonable for the reliable maintenance of ozone concentration. Energy consumption of ozone generators comprises no less than 15 kW h $kg^{-1}$ $O_3$ when using oxygen, which is doubled when using air.[28] This makes the practical energy efficiency of oxalate oxidation 4.4 g $kW^{-1}$ $h^{-1}$ under conditions of the experiment using oxygen and 2.2 g $kW^{-1}$ $h^{-1}$ with air.

Preis et al.[27] oxidized aqueous oxalate at pH 9.5–10.5 at its concentration of 1314 mg $L^{-1}$ and ozone aqueous concentration of 10 mg/L at 20 °C. The apparent second-order reaction rate constant was determined as 0.36 $M^{-1}$ $s^{-1}$, corresponding to the oxalate oxidation rate of $1.095 \times 10^{-6}$ M $s^{-1}$ or 0.099 mg $L^{-1}$ $s^{-1}$, showing similarity in oxidation rate with Lagunova et al.[26] The aqueous ozone concentration was maintained with the gas supply containing about 30 mg $L^{-1}$ of ozone in amount of 100 mL $min^{-1}$, which made practical ozone supply of 0.05 mg $L^{-1}$ $s^{-1}$. Under the conditions of air used for ozone synthesis, the energy efficiency for oxalate oxidation is

2.2 g $kW^{-1}$ $h^{-1}$, which practically reproduces the result obtained in ref 26.

The current research showed the degradation of oxalate in PCD treatment from 60 mg $L^{-1}$ for 90% with the pulsed power of 36 and 60 W with the 10 kW h $m^{-3}$ delivered energy (Figures 4 and 5). This makes the oxidation efficiency about 5.4 g $kW^{-1}$ $h^{-1}$; for the 100 W oxidation the highest efficiency of 3.6 g $kW^{-1}$ $h^{-1}$ was observed. These numbers should be doubled if oxygen is used.[15] The obtained numbers are similar to the ones in conventional ozonation but at the oxalate concentration an order of magnitude smaller in PCD experiments. Oxidation of oxalate takes place mostly because of radical oxidation, since the gas-phase concentration of ozone was not exceeding 3.8 mg $L^{-1}$ (Figure 7), which gives a reason to expect aqueous ozone concentration below 1.2 mg $L^{-1}$ following the aqueous solubility equilibrium factor.[27] In fact, multiple attempts of the authors to measure aqueous oxidants iodometrically at the exit point of the reactor showed numbers corresponding to ozone concentration below 1 mg $L^{-1}$. This makes the expected oxalate oxidation rate with ozone as small as $5.8 \times 10^{-4}$ mg $L^{-1}s^{-1}$ at its maximum, whereas degradation of oxalate was observed as big as $1 \times 10^{-2}$, $9 \times 10^{-3}$, and $5.4 \times 10^{-3}$ mg $L^{-1}s^{-1}$ at the 100, 60 and 36 W discharge power, respectively, i.e., minimum an order of magnitude faster.

## CONCLUSIONS

The oxidation efficiency of pulsed corona discharge (PCD) at different gas−liquid interface areas and treatment powers was investigated using slowly oxidized oxalic acid as a target compound. Experiments were carried out with a batch-type PCD system with contact area and treatment power adjusted respectively by altering flow rate and pulse repetition frequency.

The optimal contact area was established to increase linearly with increasing discharge power, which indicates enhanced OH-radical utilization in the pollutant oxidation. However, the relative increase in optimal area is approximately a $^3/_5$ fraction of the relative increase in power, which may be a useful estimation in the design of plasma treatment configurations.

The optimum area was also found to be followed by a notable decrease in oxidation efficiency when the contact area was further increased beyond optimum. The energy efficiency of the oxidation process was logically observed to continue to increase after the decrease when the contact area was further increased, since the increasing contact surface area alone is a process-enhancing factor.

The predominant role of hydroxyl radical by minimum of an order of magnitude surpassing ozone in oxalate PCD oxidation was observed. Pulsed corona discharge treatment appears to be a substantially more energy efficient means than conventional ozonation, showing comparable oxidation rate and the energy efficiency at an order of magnitude lower concentration of oxalate.

For acquiring a comprehensive model on the complex effect of the gas−liquid contact surface and the water volume in the plasma zone, further research is needed employing wider range of relative water content in the gas−liquid mixture. By the present results, it can be suggested that for the slow oxidation the process should benefit from increased gas−liquid contact area if the water content in the plasma zone remains reasonable, i.e., not exceeding the optimum contact surface area and volume.

## AUTHOR INFORMATION

### Corresponding Author

*Phone: +8618802094344. E-mail: prsergei@scut.edu.cn.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This study was conducted as part of the EMIR project (Exploiting Municipal and Industrial Residues), led by Lappeenranta University of Technology (LUT) and financed by European Neighbourhood and Partnership Instrument (ENPI) Program, South-East Finland—Russia Cross-Boundary Co-Operation 2007−2014. Furthermore, the authors acknowledge financial support provided by the IAWTC (International Advanced Water Technologies Centre) project.

## REFERENCES

(1) Önder, E.; Koparal, A. S.; Öğütveren, Ü. B. Electrochemical Treatment of Aqueous Oxalic Acid Solution by Using Solid Polymer Electrolyte (SPE) Reactor. *Chem. Eng. J.* **2009**, *147*, 122.

(2) Ternes, T. A. (1998) Occurrence of Drugs in German Sewage Treatment Plants and Rivers. *Water Res.* **1998**, *32*, 3245.

(3) Glaze, W. H.; Kang, J.; Chapin, D. H. The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. *Ozone: Sci. Eng.* **1987**, *9*, 335.

(4) Njatawidjaja, E.; Tri Sugiarto, A.; Ohshima, T.; Sato, M. Decoloration of Electrostatically Atomized Organic Dye by the Pulsed Streamer Corona Discharge. *J. Electrost.* **2005**, *63*, 353.

(5) Pokryvailo, A.; Wolf, M.; Yankelevich, Y.; Wald, S.; Grabowski, L.; van Veldhuizen, E.; Rutgers, W.; Reiser, M.; Glocker, B.; Eckhardt, T.; Kempenaers, P.; Welleman, A. High-Power Pulsed Corona for Treatment of Pollutants in Heterogeneous Media. *IEEE Trans. Plasma Sci.* **2006**, *34*, 1731.

(6) Grabowski, L. R.; van Veldhuizen, E. M.; Pemen, A. J. M.; Rutgers, W. R. Corona Above Water Reactor for Systematic Study of Aqueous Phenol Degradation. *Plasma Chem. Plasma Process.* **2006**, *26*, 3.

(7) Gerrity, D.; Stanford, B. D.; Trenholm, R. A.; Snyder, S. A. An Evaluation of a Pilot-Scale Nonthermal Plasma Advanced Oxidation Process for Trace Organic Compound Degradation. *Water Res.* **2010**, *44*, 493−504.

(8) Joubert, V.; Cheype, C.; Bonnet, J.; Packan, D.; Garnier, J.-P.; Teissié, J.; Blanckaert, V. Inactivation of Bacillus Subtilis var. Niger of Both Spore and Vegetative Forms by Means of Corona Discharges Applied in Water. *Water Res.* **2013**, *47*, 1381.

(9) Dobrin, D.; Bradu, C.; Magureanu, M.; Mandache, N. B.; Parvulescu, V. I. Degradation of Diclofenac in Water Using a Pulsed Corona Discharge. *Chem. Eng. J.* **2013**, *234*, 389.

(10) Panorel, I. C.; Preis, S.; Kornev, I.; Hatakka, H.; Louhi-Kultanen, M. Oxidation of Aqueous Paracetamol by Pulsed Corona Discharge. *Ozone: Sci. Eng.* **2013**, *35*, 116−24.

(11) Kornev, I.; Osokin, G.; Galanov, A.; Yavorovskiy, N.; Preis, S. Formation of Nitrite- and Nitrate-Ions in Aqueous Solutions Treated with Pulsed Electric Discharges. *Ozone: Sci. Eng.* **2013**, *35*, 22−30.

(12) Hayashi, D.; Hoeben, W.; Dooms, G.; van Veldhuizen, E.; Rutgers, W.; Kroesen, G. Influence of Gaseous Atmosphere on Corona-Induced Degradation of Aqueous Phenol. *J. Phys. D: Appl. Phys.* **2000**, *33*, 2769.

(13) Hoeben, W.; van Veldhuizen, E.; Rutgers, W.; Cramers, C.; Kroesen, G. The Degradation of Aqueous Phenol Solutions by Pulsed Positive Corona Discharges. *Plasma Sources Sci. Technol.* **2000**, *9*, 361.

(14) Ono, R.; Oda, T. Dynamics of Ozone and OH Radicals Generated by Pulsed Corona Discharge in Humid-Air Flow Reactor Measured by Laser Spectroscopy. *J. Appl. Phys.* **2003**, *93*, 5876.

(15) Preis, S.; Panorel, I.; Kornev, I.; Hatakka, H.; Kallas, J. Pulsed Corona Discharge: the Role of Ozone and Hydroxyl Radical in Aqueous Pollutants Oxidation. *Water Sci. Technol.* **2013**, *68*, 1536.

(16) Bruggeman, P.; Leys, C. Non-Thermal Plasmas In and In Contact with Liquids. *J. Phys. D: Appl. Phys.* **2009**, *42*, 053001.

(17) Meichsner, J., Schmidt, M., Schneider, R., Wagner, H., Eds. *Nonthermal Plasma Chemistry and Physics*, 1st ed.; CRC Press, Boca Raton, FL, 2002.

(18) Pohloudeck-Fabini, R.; Beyrich, T. *Organische Analyse unter Besonderer Berücksichtigung von Arzneistoffen*; Akademische Verlagsgesellschaft Geest & Portig K.-G.: Leipzig, Germany, 1975.

(19) Chemicals Used for Treatment of Water Intended for Human Consumption. Ozone. SFS-EN 1278; Finnish Standards Association: Helsinki, Finland, 2010.

(20) Danckwerts, P. V. *Gas-Liquid Reactions*; McGraw-Hill Book Co.: New York, 1970.

(21) Hoigné, J.; Bader, H. Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water—II: Dissociating Organic Compounds. *Water Res.* **1983**, *17*, 185.

(22) Ohyama, R.; Inoue, K.; Chang, J. Schlieren Optical Visualization for Transient EHD Induced Flow in a Stratified Dielectric Liquid under Gas-Phase AC Corona Discharges. *J. Phys. D: Appl. Phys.* **2007**, *40*, 573.

(23) Ognier, S.; Iya-sou, D.; Fourmond, C.; Cavadias, S. Analysis of Mechanisms at the Plasma-Liquid Interface in a Gas-Liquid Discharge Reactor Used for Treatment of Polluted Water. *Plasma Chem. Plasma Process.* **2009**, *29*, 261.

(24) Panorel, I. C.; Preis, S.; Kornev, I.; Hatakka, H.; Louhi-Kultanen, M. Oxidation of Aqueous Pharmaceuticals by Pulsed Corona Discharge. *Environ. Technol.* **2013**, *34*, 923.

(25) Panorel, I. C.; Kornev, I.; Hatakka, H.; Preis, S. Pulsed Corona Discharge for Degradation of Aqueous Humic Substances. *Water Sci. Technol.: Water Supply* **2011**, *11*, 238.

(26) Lagunova, Yu. O.; Seliverstov, A. F.; Ershov, B. G.; Basiev, A. G. Oxidative Decomposition of Oxalate Ions in Water Solutions of Concentrated Ozone. *At. Energy* **2012**, *113*, 112 (Translated from *At. Energ.* **2012**, *113* (No. 2), 93−95).

(27) Preis, S.; Munter, R.; Siirde, E. Kinetic Description of Industrial Wastewater Ozonation Processes. *Ozone: Sci. Eng.* **1988**, *10*, 379−392.

(28) Katsoyiannis, I. A.; Canonica, S.; von Gunten, U. Efficiency and Energy Requirements for the Transformation of Organic Micropollutants by Ozone, $O_3/H_2O_2$ and $UV/H_2O_2$. *Water Res.* **2011**, *45*, 3811.

DOI: 10.1021/acs.iecr.5b01915
*Ind. Eng. Chem. Res.* XXXX, XXX, XXX−XXX

# Publication II

Ajo, P., Krzymyk, E., Preis, S., Kornev, I., Kronberg, L. and Louhi-Kultanen, M.
**Pulsed corona discharge oxidation of aqueous carbamazepine micropollutant**

Reprinted with permission from
*Environmental Technology*
Vol. 37, pp. 2072-2081, 2016

ENVIRONMENTAL TECHNOLOGY, 2016
VOL. 37, NO. 16, 2072–2081
http://dx.doi.org/10.1080/09593330.2016.1141236

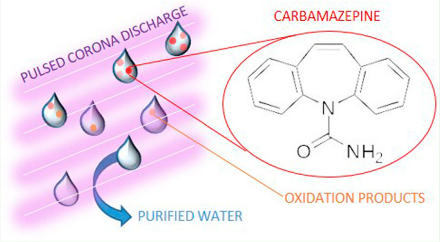
# Pulsed corona discharge oxidation of aqueous carbamazepine micropollutant

Petri Ajo[a], Ewelina Krzymyk[b], Sergei Preis[c], Iakov Kornev[d], Leif Kronberg[b] and Marjatta Louhi-Kultanen[a]

[a]Thermal Unit Operations/Separation Technology, School of Engineering Science, Lappeenranta University of Technology, Lappeenranta, Finland; [b]Laboratory of Organic Chemistry, Åbo Akademi University, Turku, Finland; [c]School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Center, Panyu District, Guangzhou, Guangdong Province, People's Republic of China; [d]Institute of Non-Destructive Testing, Tomsk Polytechnic University, Tomsk, Russia

**ABSTRACT**

The anti-epileptic drug carbamazepine (CBZ) receives growing attention due to slow biodegradation and inherent accumulation in the aquatic environment. The application of a gas-phase pulsed corona discharge (PCD) was investigated to remove CBZ from synthetic solutions and spiked wastewater effluent from a municipal wastewater treatment facility. The treated water was showered between high voltage (HV) wires and grounded plate electrodes, to which ultra-short HV pulses were applied. CBZ was readily oxidized and 1-(2-benzaldehyde)-4-hydroquinazoline-2-one (BQM) and 1-(2-benzaldehyde)-4-hydro-quinazoline-2,4-dione (BQD) were identified as the most abundant primary transformation products, which, contrary to CBZ ozonation data available in the literature, were further easily oxidized with PCD: BQM and BQD attributed to only a minor portion of the target compound oxidized. In concentrations commonly found in wastewater treatment plant effluents (around 5 μg $L^{-1}$), up to 97% reduction in CBZ concentration was achieved at mere 0.3 kW h $m^{-3}$ energy consumption, and over 99.9% was removed at 1 kW h $m^{-3}$. The PCD application proved to be efficient in the removal of both the parent substance and its known transformation products, even with the competing reactions in the complex composition of wastewater.



**ARTICLE HISTORY**
Received 20 November 2015
Accepted 7 January 2016

**KEYWORDS**
Transformation products; wastewater; ozone; hydroxyl radical; non-thermal plasma

## Introduction

Declining freshwater supplies are of growing general concern in regions facing scarcity of pure water. Global environmental awareness accentuates the need for research and development of cost-effective and energy-efficient water treatment technologies. Traditional wastewater treatment relies mainly on mechanical removal of solids and biological degradation of organics, which has little effect on dissolved non-biodegradable compounds. Typically, wastewater treatment plants (WWTPs) may employ UV, ozone or chlorine for tertiary treatment of effluent streams. These methods suffer from one or more general deficiencies, such as high cost, generation of harmful byproducts, low efficiency or considerable maintenance requirements. Conventional methods are also quite often insufficient in removing recalcitrant organic compounds, which underlines the need for more effective and environmentally friendly methods.[1,2]

One environmentally significant group of refractory organics is pharmaceuticals and their metabolites. Aqueous pharmaceuticals may originate from sewage through incomplete metabolism or direct disposal, or, for example, from industrial effluents. Pharmaceutical compounds in natural water bodies are apt for accumulation due to their slow or non-biodegradability, which,

**CONTACT** Petri Ajo ✉ petri.ajo@lut.fi Thermal Unit Operations/Separation Technology, School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland

Supplemental data for this article can be accessed at doi:10.1080/09593330.2016.1141236

taking into account their original purpose, poses environmental problems difficult to estimate. Pharmaceutical substances in the environment can be classified in three groups: general toxicants, antibiotics and endocrine disrupters, the last one referring to chemicals that may disturb hormonal functions.[3] A number of scientific reports disclose the occurrence of various pharmaceuticals in the effluent streams of WWTPs and various water bodies in the environment.[1,2,4–7] This occurrence has also been brought to general attention by public discussion. The requirements of wastewater and drinking water treatment in the future are currently one of the crucial global topics concerning water purification policies.

A pharmaceutical that has lately received considerable attention in scientific research is the anti-epileptic drug carbamazepine (CBZ). The substance is only slowly degraded in biological and chemical processes in the aquatic environment and found to a notable extent therein due to the relatively high dosing levels.[8–10] Over 30 metabolites and various transformation products of CBZ have been identified [11] and CBZ concentrations in wastewater treatment effluents have been reported as high as 6.3 μg $L^{-1}$.[1] Kosjek et al. [9] concluded several advanced oxidation processes (AOPs), including ozonation, as efficient means for CBZ removal. However, they emphasized that the transformation products in the process may be more resilient than the original product and that these transformation products should not be ignored when the overall effectiveness of a given method is assessed.

Since oxidation is in many cases an efficient method for the degradation of organic compounds in water, various AOPs have been developed for the purpose. The conjunction between AOPs is the production and utilization of hydroxyl radical, which is a highly reactive oxidant.[12] Among these, a popular research branch is the application of electric discharges in water treatment, wherein the organic pollutants are generally removed via the simultaneous production *in situ* of both hydroxyl radicals and ozone. One of the most effective applications of electric discharge in water treatment is the gas-phase pulsed corona discharge (PCD) with the vertical wire–plate electrode configuration, where hydroxyl radicals are formed at the gas–liquid interface of the water, and ozone is produced from the oxygen molecules in the surrounding gas phase.[13,14] This configuration is essentially different from that of other corona discharge applications that have been used for the oxidation of aqueous organics with CBZ among them. For example, earlier attempts showed successful corona-induced oxidation of CBZ,[15] although the applied techniques of dielectric barrier high-frequency corona discharge are attributed with inherent excessive energy consumption at high risk of discharge destabilization. Current research deals with the technology wherein these problems are solved by the application of ultra-short discharge pulses, further discussed in Experimental System. Weakly ionized plasma of PCD is an efficient source of active oxidant species, which are utilized *in situ*. Due to the use of short pulses, PCD can exist in humid air with water droplets without transformation into thermal spark or arc discharges. The main assets of this PCD technology are the absence of added chemicals, operation at ambient conditions, low maintenance requirements and high energy efficiency.[16] To date, the research on PCD oxidation of aqueous pharmaceuticals has mainly focused on process efficiency at concentrations of few tens to few hundred mg $L^{-1}$, which is above the concentration range of micropollutants typical in wastewaters by the factor of minimum $10^4$.

As the reaction rate in the oxidation of target pollutants depends on the concentration of the reactant, the rate that determines the efficiency in PCD removal of an aqueous compound decreases with decreasing concentration. Therefore, the process efficiency in the removal of pollutants in microconcentrations deserves attention. In the present study, the process efficiency of PCD in the removal of aqueous CBZ was investigated at concentrations characteristic to WWTP effluents, and the identification and detection of transformation products were included therein, although mineralization of CBZ was studied at elevated concentrations for analytical convenience.

## Materials and methods

### Chemicals

CBZ used in the experiments was of 99% purity by Acros Organics (CA, USA). CBZ used in the analysis (purity grade > 99%) was purchased from Sigma-Aldrich and the internal standard CBZ-$D_8$ from Toronto Research Chemicals (New York, ON). All other chemicals (e.g. solvents) were of the highest grade commercially available. Stock solutions (1 mg $mL^{-1}$) and working solutions for analysis were prepared in methanol (J.T. Baker) and stored at −20°C. Liquid chromatography (LC) eluents were prepared with MilliQ water.

### Wastewater

The treated wastewater used in the experiments was collected from the effluent stream of Toikansuo WWTP, a municipal plant collectively treating local wastewaters in Lappeenranta, Finland, at a daily average volume of 16,000 $m^3$. Around 10% of the wastewater volume entering the plant originates from industrial sources.[17] The plant employs typical treatment processes: screening and grit removal, coagulation with ferric sulphate and calcium oxide, primary clarification, aerobic biological treatment and secondary clarification. The samples were collected from the effluent streams of secondary clarifiers and mixed prior to experiments. Chemical oxygen demand (COD) and total suspended solids (TSS) values for the collected effluent samples averaged 58 and 24 mg $L^{-1}$, respectively.[18] pH of the mixed effluent samples was 7.2. To each wastewater experiment, CBZ was added to increase the initially unknown concentration by 5 µg $L^{-1}$ to ensure CBZ presence.

## Experimental system

The experimental PCD system consists of three primary elements: pulse generator, plasma reactor and water circulation system. The pulse generator is of non-commercial construction and configured to produce high voltage (HV) pulses at frequencies of 50–833 pulses per second (pps). Corresponding linearly to selected pulse frequency, the nominal power of the generator varies from 6 to 100 W. The amplitude of voltage pulses was 22 kV, and voltage pulse duration was 120 ns. Pulse parameters and generator properties were previously discussed more in detail by the authors in [19]. The reactor is a dielectric compartment including two grounded plate electrodes with a set of HV wire electrodes positioned parallel between the plates. Above the electrodes is a water distribution chamber with a perforated bottom plate, allowing the circulating water to shower through the plasma zone, that is, the interelectrode volume. The electrode compartment, providing the free falling length through the plasma zone, is 1 m in height. Under the reactor is a container tank for up to 15 L aqueous solutions, from which treated water is pumped to the distribution chamber atop the reactor. For batch experiments with closed atmosphere and a sealed container tank, the sampling port is located on a feedback line between the pump and the tank. When the system is operated in single-pass mode, sampling can be done directly from the output stream under the reactor. The reactor is illustrated in Figure 1.

## Experimental procedures

The first experiments were conducted at high concentrations of CBZ (81–141 mg $L^{-1}$) for facilitating transformation product identification and preliminarily observing of process efficiency. Working near the solubility of CBZ (125–189 mg $L^{-1}$ at 20–25°C [20–22]), the high-concentration solutions were prepared directly to the treated volume. The solutions were mixed carefully and filtered prior to treatment using a Büchner funnel and flask with a 150 mm Whatman 1 filter paper. Filtration was used to ensure the removal of any undissolved CBZ that might corrupt the oxidation results in case of dissolution during treatment.

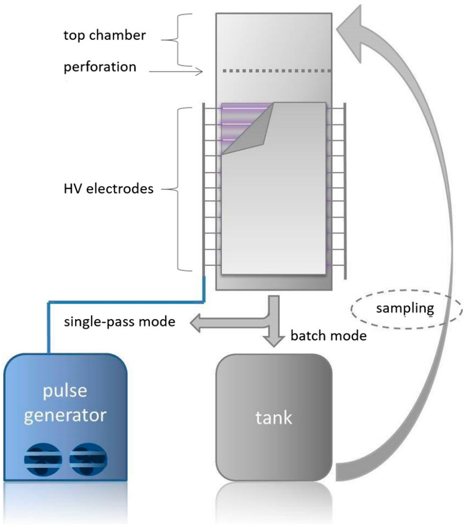


**Figure 1.** Schematic illustration of the experimental system.

For the CBZ experiments in microconcentrations (0.22–19 µg $L^{-1}$), stock solutions of 75 mg $L^{-1}$ were prepared prior to each experimental series; the experiments were initiated by circulating the predetermined volume of water or wastewater in the system and injecting the CBZ from the stock solution into the stream. For each experiment with aqueous solution at CBZ microconcentrations, the whole experimental system was carefully rinsed with deionized water. The treatment was carried out in two modes: batch treatment and single-pass mode. The batch mode enabled sequential sampling and thus comparison of treatment time and energy dose effects, whereas the single-pass mode was employed to simulate an operating scenario where the water would pass the reactor only once for economic convenience. In the batch mode, energy efficiency generally increases with decreasing pulse frequency due to prolonged ozone exposure at fixed energy dose, an effect that in the single-pass mode is discarded due to the short water residence time in the reactor. The volume of the treated solutions was 10 L for batch experiments and 15 L for continuous single-pass experiments. An additional 5-L volume for single-pass treatment was added for extending the process overall duration to give more time for practical operations of treatment and sampling.

Sampling in the batch experiments was initiated by taking a zero sample after a few minutes of solution circulation through the system. The oxidation process, that is, PCD treatment, was started subsequently by switching on the reactor. Sampling during the process was done by switching off the pulse generator after predetermined time or energy dose intervals, and by allowing sufficient time for full solution circulation through the system in order to enable proper mixing prior to sampling. This was done since the concentration in the system can be considered heterogeneous when the pulse generator is on; the solution upstream from the reactor contains higher pollutant concentrations than in downstream between the reactor and the container tank.

In single-pass experiments, water circulation started in the batch mode and the zero samples were taken prior to treatment, similarly as in batch experiments. Subsequently, recirculation from the reactor to the container tank was cut out and redirected out of the system, making the process mode quasi-continuous. The pulse generator was switched on simultaneously with mode switching, which started the single-pass oxidation process. The samples of the treated solutions were taken directly downstream from the reactor by collecting the flow in its complete cross section. The times taken to fill the sample bottles were measured and the collected samples were weighed for accurate flow rate determination and energy dose calculations against known reactor power. Taking into account the briefness of the single-pass experiments, this was considered more precise than reading the flow meter upstream from the pumping unit because the volume flux through the reactor was not perfectly uniform.

Suitable treatment times and energy doses were preliminarily estimated by the molecular structure of CBZ and its reactivity with ozone ($k_{CBZ+O3} = 3 \times 10^5$ M$^{-1}$ s$^{-1}$ [23]) and hydroxyl radical ($k_{CBZ+OH} = 8.8 \times 10^9$ M$^{-1}$ s$^{-1}$ [24]), and these parameters were adjusted for sequential experiments along obtaining results. The experimental parameters at different concentrations of CBZ are presented in Table 1. The treatment times corresponding to the energy doses and discharge powers varied from single-pass (20 L min$^{-1}$) to 2 h circulation, the latter being a particularly extended experiment for the high dose of 21 kWh m$^{-3}$ that was applied for investigating the mineralization by PCD, that is, the ultimate oxidation to carbon dioxide.

## Analytical methods

### Sample preparation for quantification of synthetic CBZ solution

For sample preparation, 100 µL of a solution of an internal standard CBZ-D$_8$ at a concentration of 100 µg mL$^{-1}$ was added to pure water in a row of dilutions. The solutions were injected directly into the liquid chromatography-tandem mass spectrometry (LC–MS/MS) system without additional treatment. In the experiments with the initial concentration of CBZ-D$_8$ around 100 mg L$^{-1}$, the samples were diluted 1/1000 with 0.5% acetic acid in MilliQ water prior to analysis. Accuracy of the method was evaluated in triplicated tests.

### Sample preparation for identification of CBZ transformation products

Prior to the gas chromatograph mass spectrometry (GC–MS), GC–flame ionization detector (FID) and LC–MS/MS analyses, the samples were filtered through grade GF-C microfibre glass filters with a diameter of 55 mm (Whatman, Buckinghamshire, UK). The filters were prewashed with hexane, acetone, methanol and MilliQ water. CBZ was extracted from the filtered aqueous sample (50 mL) by the use of an Oasis® HLB reversed-phase sorbent 3 cc (60 mg) (Waters, Corp., Milford, MA, USA). The extraction was performed at a basic pH adjusted to 10 with 2 M NaOH. The solid phase extraction (SPE) cartridges were pre-conditioned with 5 × 2 mL of methanol and 3 × 2 mL MilliQ water (pH 10) and then dried under nitrogen. After sample loading, the solid phase was dried under nitrogen and the adsorbed compounds were eluted with 2 × 2 mL of acetonitrile. The extract was evaporated to dryness under nitrogen and finally, the residue was dissolved in 1 mL dichloromethane.

### LC–MS/MS

The analysis of transformation products of CBZ in wastewater samples was performed by LC–MS/MS (Agilent Technologies 6460, Triple Quadruple) equipped with an electrospray ionization interface. The analysis was conducted in positive mode, using multiple-reaction monitoring. For chromatographic separation, an Eclipse plus C$_{18}$ column (2.1 × 5 mm, 1.8 µm) was used (Agilent Technology, USA). The flow rate was 550 µL min$^{-1}$ and water with 0.5% acetic acid and acetonitrile with 0.5% acetic acid were eluents A and B, respectively. The gradient applied was as follows: 0–1.10 min, 80% B; 1.10–2.5 min, 5% B. The injection volume was 5 µL. The source parameters were as follows: capillary voltage of 4.0 kV, gas temperature 225°C, gas flow 13 L min$^{-1}$, nebulizer 40 psi, sheath gas heater 200°C and sheath gas flow 12 L min$^{-1}$. A 5-point calibration curve (1–500 ng mL$^{-\mathbf{1}}$) of the target compound was used for quantification.

For analysing the transformation product in wastewater samples, the applied gradient was as follows: 0–0.5 min, 5% B; 0.5–5 min, 5–90% B; 5.5 min, 90% B; 5.5–6 min, 90–5% B; 6–7 min, 5% B. The Agilent Mass Hunter workstation software was used for data collection and analysis.

**Table 1.** Applied values for experimental parameters (WW = Wastewater).

| Water/WW + CBZ (initial concentration) | Discharge power, W (frequency, pps) | Maximum energy dose, kWh $m^{-3}$ | Time, min | Process mode |
|---|---|---|---|---|
| CBZ: | 100 (833) | 5 and 21 | 30 and 120 | Batch |
| (81–141 mg $L^{-1}$) | 60 (500) | 6 | 60 | Batch |
| | 6 (50) | 0.6 | 6 | Batch |
| CBZ: | 6 (50) | 0.006 | n.a. | Single-pass |
| (0.22–19 μg $L^{-1}$) | 100 (833) | 0.1 | n.a. | Single-pass |
| | 24 (200) | 1 | 25 | Batch |
| WW + CBZ: | 100 (833) | 0.1 | n.a. | Single-pass |
| (3.41–9.27 μg $L^{-1}$) | 24 (200) | 3 | 75 | Batch |

### *GC–MS*

The characterization of transformation products was also performed by GC–MS analysis by the use of an Agilent Technologies 7890A gas chromatograph with a 5875C Series inert XL EI/CI MSD Triple-Axis Detector (GC–MS). One microlitre samples were injected (splitless) using an injector 7683B Series (Agilent Technology). For the separation, a HP-5 MS column was used with helium as the carrier gas at the flow rate of 1 mL $min^{-1}$. The GC temperature programme was as follows: 2 min at 140°C increased to 300°C at 9°C $min^{-1}$ and held for 2 min. The total runtime was 21.7 min.

### *GC–FID*

A rough estimation of the concentrations of transformation products in synthetic solution samples was achieved using an Agilent Technology 6850 Series gas chromatograph with FID). One microlitre of sample was injected in an HP-1 Methyl Siloxane capillary column, with hydrogen as the carrier gas (flow rate 1 mL $min^{-1}$). The temperature gradient was as follows: 2 min at 140°C, an increase to 300°C at 9°C $min^{-1}$ followed by a hold time of 2 min. The total runtime was 21.7 min.

### *TOC*

The analyser used for the determination of total organic carbon (TOC) content was a Shimadzu TOC-L series analyser that applies catalytic oxidation at 680°C.

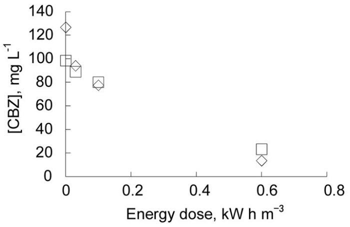


**Figure 2.** PCD oxidation with initial CBZ concentrations of 99 and 127 mg $L^{-3}$ at 6 W discharge power.

## Results and discussion

### *CBZ degradation in PCD treatment*

### *High concentrations*

Preliminary testing in the saturation range of aqueous solutions showed that CBZ is readily oxidized with PCD: CBZ was in practice completely oxidized with PCD treatment at 3 kW h $m^{-3}$ energy dose, inducing 99% degradation from 81 mg $L^{-1}$ initial concentration and 99.5% degradation from 141 mg $L^{-1}$ initial concentration, indicating the applied energy dose as excessive. Subsequent experiments were carried out with lower energy dose and shorter sampling intervals at 0, 0.03, 0.1 and 0.6 kWh $m^{-3}$, with initial concentrations of 99 and 127 mg $L^{-1}$. These results are shown in Figure 2. While the high reactivity of OH-radical enables many reaction routes, the rapid disappearance of CBZ is most probably attributed to the cleavage of the carbon double bond between the two phenolic rings in the molecule structure, which also is the initial reaction in the formation of the primary oxidation products.[8] Calculation of the CBZ oxidation energy efficiency, defined as the amount of compound removed with the delivery of the energy unit, gives for the reaction operated in air, dependent on the CBZ concentration, from 125 to 189 g $kW^{-1}$ $h^{-1}$, which is a result exceeding the one of, for example, rapidly reacting indomethacin.[16] The efficiency result obtained by Krause et al. [15] in high-frequency (30 kHz) dielectric barrier corona over a thin layer of treated solution at CBZ concentration of 0.1 mM (23.6 mg $L^{-1}$) with boron-doped diamond counter-electrode is about 71 and 28 g $kW^{-1}$ $h^{-1}$ for 50% and 90% degradation, respectively. For further comparison, Palo et al. [25] studied CBZ ozonation in the range of aqueous concentrations from 6 to 16 mg $L^{-1}$, that is, an order of magnitude smaller than that in the present research, observing approximately 0.3–0.5 g CBZ oxidized with 1 g of ozone, which gives, at the ozone synthesis energy efficiency of minimum 15 kW h $kg^{-1}$ $O_3$ in oxygen, from 19 to 33 g $kW^{-1}$ $h^{-1}$. These numbers have to be reduced twofold when air is used in ozone generators.[26] Naddeo et al. [27] oxidized aqueous CBZ at its initial concentration of 10 mg $L^{-1}$ in

**Table 2.** Oxidation of aqueous CBZ in different studies.

| Treatment method | [CBZ]$_0$, mg L$^{-1}$ | Reduction (%) | Yield, g kW$^{-1}$ h$^{-1}$ | Reference |
|---|---|---|---|---|
| PCD | 99, 127 | 76, 89 | 125, 189 | This work |
| Dielectric barrier corona | 23.6 | 50, 90 | 71, 28 | [13] |
| Ozonation | 6, 16 | ~100 | ~19, ~33 | [23] |
| Ozone + ultrasound | 10 | 56 | <1 | [25] |

ultrasound-enhanced ozonation showing the oxidation efficiency as low as 0.53 mg g$^{-1}$ O$_3$, operating apparently with the ozone supply exceeding consumption. Corresponding energy efficiency makes 0.036 and 0.018 g kW$^{-1}$ h$^{-1}$ in oxygen and air, respectively. Summary of this comparison is presented in Table 2.

Although rapid chemical oxidation of the target substance was observed, TOC analysis revealed that the transformation products are collectively more refractory, which is in good agreement with earlier findings.[9] The transformation products of CBZ have, however, been reported to be more biodegradable than the parent compound,[28] making them less prone for accumulation in the environment.

Contradicting the effective oxidation of the target compound and the primary products, the treatment was unsuccessful in mineralization of TOC in the high-concentration CBZ solutions, contrary to the previous success in TOC removal from solutions with other pharmaceuticals.[12] Negligible TOC removal may indicate notable radical scavenging by the transformation products with possibly some contribution by the slight hydrophobicity of CBZ regarding the surface character of hydroxyl radical activity in the process.[13] A satisfying explanation for the ineffective mineralization of concentrated CBZ solutions requires further research on the behaviour of the transformation products at the air–water interface.

### *Microconcentrations*

The single-pass experiments with a minimum power input of 0.006 kWh m$^{-3}$ at a minimum pulse frequency of 50 pps induced modest CBZ removal of 6–16% from 17 to 19 µg L$^{-1}$ initial concentration, thus showing the efficiency of CBZ oxidation around 0.3–0.5 g kW$^{-1}$ h$^{-1}$. At lower starting concentration (0.83–2.21 µg L$^{-1}$) and increased energy input of 0.1 kWh m$^{-3}$ at the discharge power of 100 W and constant flow-through rate of 20 L min$^{-1}$, the removal was enhanced resulting in 79–94% reduction in CBZ concentration, although the oxidation efficiency at this low concentrations and extended removal rate ranged between 0.008 and 0.017 g kW$^{-1}$ h$^{-1}$. The deviation in repeated experiments is likely to result from the scattered initial CBZ concentrations and, probably, non-uniform instant gas–liquid contact surface acquiring a substantial role in rapid changes at a single passage of treated flow through the reactor, that is, the free fall through the plasma zone. Higher energy dose, 0.16 kW h m$^{-3}$, supplied in a batch experiment with the initial CBZ concentrations from 0.22 to 0.5 µg L$^{\mathbf{-1}}$ resulted in bringing the CBZ concentration below the limit of quantification (LOD = 0.04 ng L$^{-1}$, LOQ = 0.2 ng L$^{-1}$), making the oxidation efficiency as low as 0.0014–0.0031 g kW$^{-1}$ h$^{-1}$. The results of the synthetic solutions for CBZ in microconcentrations are presented in Table 3.

The comparison of the observed efficiency results in microconcentration range with conventional ozonation did not seem to give a clear picture; data from various authors differ dramatically. For example, ozonation of spiked Rhine river water resulted in complete elimination of 0.5 µg L$^{\mathbf{-1}}$ of CBZ with the dose of ozone of ≥0.3 mg L$^{-1}$,[8] making the oxidation efficiency maximum of 0.056 g kW$^{-1}$ h$^{-1}$ in air, although removal of 236 µg L$^{-1}$ of CBZ from spiked Zurich lake water with an ozone dose of 1 mg L$^{-1}$ results in 7.9 g kW$^{-1}$ h$^{-1}$ in air. The review given by Liang et al. [29] shows a wide spectrum of CBZ contents of 10–300 ng L$^{-1}$ levels and ozone dosages from 0.5 to 8.2 mg L$^{-1}$, making the oxidation efficiency not exceeding 0.01 g kW$^{-1}$ h$^{-1}$ in air. Sometimes the applied ozone doses were not measured with only the residual dissolved ozone concentrations determined. Precise assessment of energy efficiency

**Table 3.** Removal of CBZ (%) in experiments with microconcentrations.

| Energy dose, kWh m$^{-3}$ | 0 | 0.006 | 0.1 | 0.16 | |
|---|---|---|---|---|---|
| Power (frequency), W (pps) | | 6 (50) | 100 (833) | 24 (200) | Process mode |
| [CBZ], µg L$^{-1}$ (% removal) | 19 | 16 (16%) | | | Single-pass |
| | 17 | 15 (11%) | | | Single-pass |
| | 2.21 | | 0.47 (79%) | | Single-pass |
| | 0.83 | | 0.05 (94%) | | Single-pass |
| | 0.50 | | | <LOQ | Batch |
| | 0.22 | | | <LOQ | Batch |

under the circumstances is therefore not very practical for ozone being mostly used for various parallel purposes, such as bacterial control, colour removal and oxidation of other organic compounds in mixtures. Similarly, corona discharge applied to micropollutant removal fulfils various parallel tasks in respect to CBZ degradation. For example, in a previous study by Gerrity et al.,[30] CBZ was oxidized in WWTP effluent from 219 ng $L^{-1}$, achieving 72% reduction in a corona-above-water (commonly referred to as CAW) reactor at 0.7 kW h $m^{-3}$ energy dose, thus demonstrating an efficiency of $2.25 \times 10^{-4}$ g $kW^{-1}$ $h^{-1}$. This number is an order of magnitude lower than the one observed in the present research in WWTP effluent waters, as discussed in the next section.

### WWTP effluent treatment

The initial CBZ concentrations in the spiked WWTP effluent waters were from 3.4 to 9.3 µg $L^{-1}$. The experiments showed promising efficiency from a practical perspective, removing up to 61% of the substance in single-pass treatment with an energy consumption of 0.1 kWh $m^{-3}$, which shows efficiency of a similar magnitude as with that of CBZ solutions prepared in clean water – up to 0.057 g $kW^{-1}$ $h^{-1}$.

For practical convenience, the batch experiments were conducted at lower pulse repetition frequency (200 pps) than the single-pass experiments (833 pps), which may also enhance the process energy efficiency due to notably longer treatment time and inherently prolonged ozone exposure between pulses.[13] However, it should be noted that in the case of wastewater, it is likely that the produced ozone is well consumed in reactions with the organic contents of the solution, thus attenuating the beneficial effect of lower pulse frequency. The results from the batch experiments are presented in Figure 3.

From Figure 3, it can be seen that the PCD treatment is able to substantially reduce CBZ concentrations in treated wastewaters with high energy efficiency. Up to 97% removal was achieved with mere 0.3 kW h $m^{-3}$ (the light grey bar) energy delivery with an oxidation efficiency of 0.019 g $kW^{-1}$ $h^{-1}$, and up to 99.9% removal at 3 kW h $m^{-3}$. In essence, the results obtained from the treatment of wastewater containing CBZ indicate that the studied PCD system has realistic and technically feasible potential in notable reduction of pharmaceutical load introduced to the environment through WWTP effluent streams. It should be stressed that in addition to the successful reduction of the target substance concentration, other harmful organics and microorganisms present in the wastewater are subjected to the oxidation process as well. For comparison, Vogna et al. [31] oxidized aqueous CBZ with UV/$H_2O_2$ and reported effective and fast removal from 1.9 mg $L^{-1}$ initial CBZ concentration, with $H_2O_2$ concentration an order of magnitude higher than that of CBZ, although the removal rate fell to practically zero when 4 mg $L^{-1}$ of humic acids was present, presumably due to the OH-radical scavenging effect of humic substances. Obviously, the presence of organic pollutants in biologically treated wastewater did not obstruct PCD oxidation of CBZ in the WWTP effluent, although the energy consumption somewhat increased. This observation fits well to the concept of the surface character of oxidation with abundant OH-radicals.[13]

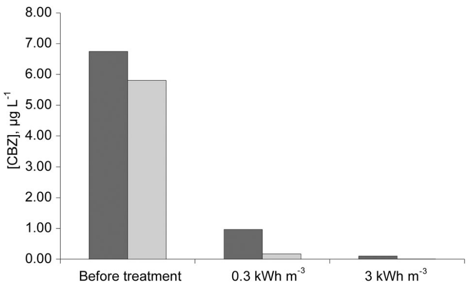


**Figure 3.** Parallel runs (dark and light grey) of batch treatment of WWTP effluent spiked with CBZ at 24 W discharge power.

## Transformation products

### Identification of transformation products in synthetic solutions

In the LC–MS chromatograms of the CBZ synthetic solutions PCD-treated at 0.1 and 0.3 kW h $m^{-3}$, masses corresponding to 1-(2-benzaldehyde)-4-hydroquinazoline-2-one (BQM) and 1-(2-benzaldehyde)-4-hydro-quinazoline-2,4-dione (BQD) could be observed. The molecular construction of these products is described and

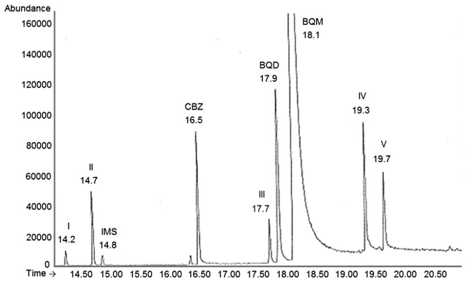


**Figure 4.** GC–MS ion chromatogram of a CBZ solution with initial concentration of 127 mg $L^{-1}$ treated with an energy dose of 0.3 kWh $m^{-3}$.

illustrated, for example, by McDowell et al.[8] However in the GC–MS chromatograms, nine ion peaks were observed. One of the peaks represented CBZ (retention time 16.5 min) and five others were assigned to CBZ transformation products (Figure 4). The molecular ions of these products were observed at *m/z* 207 (I), 225 (II), 252 (III), 266 (BQD) and 250 (BQM). The recorded mass spectra compared to previously published results on CBZ transformation products allowed the identification of acridine-9-carbaldehyde (I), hydroxyl-acridine-9-carbaldehyde (II), 10,11-dihydro-CBZ 10,11-epoxide (III), and BQM (Supporting Information, Table S1). The peak at 14.8 min exhibiting a molecular ion at *m/z* 193 was identified as iminostilbene (IMS), a thermal degradation product of CBZ formed in the heated GC injector liner.[9] Two additional product peaks were observed at 19.3 and 19.7 min (IV, V). The mass spectra of these indicated molecular ions at *m/z* 308 and 290, respectively, although the structure of the compounds remained unknown. The GC–MS spectrum of synthetic CBZ solution treated with 0.3 kWh $m^{-3}$ energy dose is presented in Figure 4.

## Quantification of transformation products in synthetic solutions

Exact quantification of the transformation products of CBZ was not feasible due to the absence of authentic standards; instead, an estimation of the quantities was performed by GC–FID, assuming an equal detector response for CBZ and the transformation products. The results of this quantification enabled a comparison of transformation product yield against delivered energy dose as well as an overall estimation of product formation and degradation during the process. The two primary products, BQM and BQD, were observed from the first sample at 0.03 kWh $m^{-3}$ at minimal concentrations. The concentration of dominating BQM increased to comprise about 24% and 16% of totally transformed CBZ from initial concentrations of 81 and 141 mg $L^{-1}$, respectively, while BQD concentration never grew above 3% of the transformed CBZ concentration. The change in CBZ and BQM presence during treatment is presented in Figure 5. The data indicate an increase in BQM content until CBZ depletion, after which the concentration is reduced because no further BQM formation can occur and oxidation is facilitated by the absence of competing oxidant reactions with the parent compound. Less than 3% of CBZ was transformed to the other five transformation products and all identified transformation products accounted for only about 29% of the original concentration of CBZ; transformation products that do not show up in the GC–FID chromatograms must have been formed, constituting the majority of the transformation products.

Since CBZ degradation is substantially faster than primary product formation (BQM and BQD), PCD treatment proved to be effective against both the parent compound and the identified transformation products. Moreover, prompt further oxidation of primary transformation products was also previously observed in PCD oxidation of phenol [13] and certain painkillers of phenolic structure,[16] therein explained by the surface character of the reaction of pollutants with abundant OH-radicals.

## Transformation products in spiked wastewater samples

In the wastewater samples spiked with $\sim$5 μg $\mathbf{L^{-1}}$ CBZ and treated with any of the applied energy dose, no by-products could be detected in GC analysis. However, in the LC–MS chromatograms of both treated and untreated samples of CBZ-spiked wastewater effluent, the peaks representing various forms of CBZ were observed. In the untreated sample, CBZ and the main human metabolites of CBZ,[32] 2-hydroxy-CBZ, and 3-

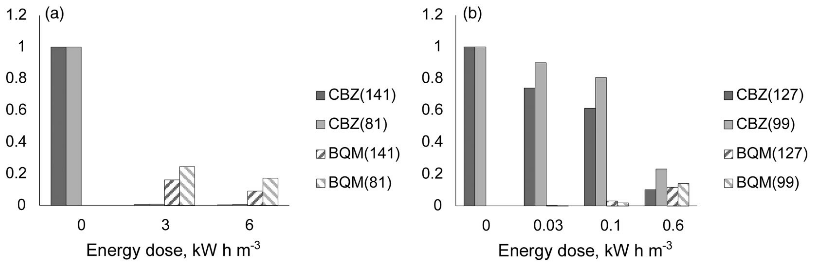


**Figure 5.** PCD treatment of CBZ solutions at high (a) and low energy dose (b). Legend brackets indicate the initial CBZ concentrations in mg $L^{-1}$; identical value for BQM and CBZ indicates same experiment. BQM concentrations represent estimations based on the assumption of equal GC-FID detector response.

hydroxy-CBZ, were observed. In the chromatograms of the treated sample, additional peaks representing BQM, BQD and hydroxy-acridine-9-carbaldehyde were present. Further small peaks could be observed that were due to 1-hydroxy-CBZ, 4-hydroxy-CBZ and acridine-9-carbaldehyde. The peak areas of the 2-hydroxy-CBZ and 3-hydroxy-CBZ in the chromatogram of the treated wastewater sample were about 95% smaller than those of the untreated wastewater, which shows that also these compounds were essentially affected by the treatment. The peak areas of all observed compounds decreased at increasing energy dose, indicating high efficiency in the removal of transformation products as well as the parent compound. Further information on the identified products in treated wastewater is presented in Supporting Information Table S2.

## Conclusions

Gas-phase PCD was proven to be efficient in the removal of aqueous CBZ from both synthetic solutions and CBZ-containing effluent wastewater. The energy efficiency surpasses that of conventional ozonation at higher CBZ concentrations. In microconcentrations, both the parent compound and the more refractory transformation products were successfully degraded from the effluent wastewater at an acceptable energy consumption; up to 97% reduction in CBZ concentration was achieved at 0.3 kW h $m^{-3}$ from the initial concentration of 5.8 μg $L^{-1}$, suggesting the present PCD system to be a considerable option for, for example, the tertiary treatment of municipal wastewaters for reducing pharmaceutical load to the environment. The formation of CBZ transformation products, found in previous research on conventional ozonation, was expectedly observed in the process. However, in contrast to the earlier studies reporting practically stoichiometric formation of transformation products that are difficult to efficiently remove by ozonation, PCD resulted in fast degrading of intermediates, which is explained by the surface character of oxidation with a massive attack of OH-radicals produced at the gas–liquid interface.

## Acknowledgements

The authors would like to thank help from Ms Riitta Moisio at Lappeenrannan Energia for granting the possibility to gather the effluent samples.

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Funding

This work was supported by the European Neighbourhood and Partnership Instrument Program (ENPI) under EMIR project (Exploiting Municipal and Industrial Residues) and the IAWTC (International Advanced Water Technologies Centre) Project.

## References

[1] Ternes TA. Occurrence of drugs in German sewage treatment plants and rivers. Water Res. 1998;11:3245–3260.
[2] Vieno N, Tuhkanen T, Kronberg L. Elimination of pharmaceuticals in sewage treatment plants in Finland. Water Res. 2007;41:1001–1012.
[3] Jørgensen SE, Halling-Sørensen B. Drugs in the environment. Chemosphere. 2000;40:691–699.
[4] Lee YM, Oleszkiewicz JA, Cicek N, et al. Endocrine disrupting chemicals (EDC) in municipal wastewater treatment: a need for mass balance. Environ Technol. 2004;25:635–645.
[5] Halling-Sørensen B, Nors Nielsen S, Lanzky PF, et al. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. Chemosphere. 1998;36:357–393.
[6] Andreozzi R, Marotta R, Paxéus N. Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere. 2003;50:1319–1330.
[7] Tixier C, Singer HP, Oellers S, et al. Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters. Environ Sci Technol. 2003;37:1061–1068.
[8] McDowell DC, Huber MM, Wagner M, et al. Ozonation of carbamazepine in drinking water: identification and kinetic study of major oxidation products. Environ Sci Technol. 2005;39:8014–8022.
[9] Kosjek T, Andersen HR, Kompare B, et al. Fate of carbamazepine during water treatment. Environ Sci Technol. 2009;43:6256–6261.
[10] Loos R, Locoro G, Comero S, et al. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Res. 2010;44:4115–4126.
[11] Bahlmann A, Brack W, Schneider RJ, et al. Carbamazepine and its metabolites in wastewater: analytical pitfalls and occurrence in Germany and Portugal. Water Res. 2014;57:104–114.
[12] Glaze WH, Kang J, Chapin DH. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone: Sci Eng. 1987;9:335–352.
[13] Preis S, Panorel I, Kornev I, et al. Pulsed corona discharge: the role of ozone and hydroxyl radical in aqueous pollutants oxidation. Water Sci Technol. 2013;68:1536–1542.
[14] Panorel I, Kaijanen L, Kornev I, et al. Pulsed corona discharge oxidation of aqueous lignin: decomposition and aldehydes formation. Environ Technol. 2013;35:171–176.
[15] Krause H, Schweiger B, Schuhmacher J, et al. Degradation of the endocrine disrupting chemicals (EDCs) carbamazepine, clorofibric acid, and iopromide by corona discharge over water. Chemosphere. 2009;75:163–168.

[16] Panorel I, Preis S, Kornev I, et al. Oxidation of aqueous pharmaceuticals by pulsed corona discharge. Environ Technol. 2013;34:923–930.

[17] Kankaanpää A, Ariniemi K, Heinonen M, et al. Use of illicit stimulant drugs in Finland: a wastewater study in ten major cities. Sci Total Environ. 2014;487:696–702.

[18] Ympäristölupahakemus Hyväristönmäelle rakennettavalle uudelle jätevedenpuhdistamolle [Application for the environmental permit for a new wastewater treatment plant to be built in Hyväristönmäki]. Lappeenranta (Finland): Pöyry Finland Oy; 2014.

[19] Ajo P, Kornev I, Preis S. Pulsed corona discharge in water treatment: the effect of hydrodynamic conditions on oxidation energy efficiency. Ind Eng Chem Res. 2015;54:7452–7458.

[20] Borisover M, Sela M, Chefetz B. Enhancement effect of water associated with natural organic matter (NOM) on organic compound–NOM interactions: a case study with carbamazepine. Chemosphere. 2011;82:1454–1460.

[21] Deng J, Shao Y, Gao N, et al. Degradation of the antiepileptic drug carbamazepine upon different UV-based advanced oxidation processes in water. Chem Eng J. 2013;222:150–158.

[22] Shayanfar A, Velaga S, Jouyban A. Solubility of carbamazepine, nicotinamide and carbamazepine–nicotinamide cocrystal in ethanol–water mixtures. Fluid Phase Equilib. 2014;15:97–105.

[23] von Sonntag C, von Gunten U. Chemistry of ozone in water and wastewater treatment: from basic principles to applications. London: IWA Publishing; 2012.

[24] Huber MM, Canonica S, Park G, et al. Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. Environ Sci Technol. 2003;37:1016–1024.

[25] Palo P, Domínguez J, Sánchez-Martín J. Ozonation of a carbamazepine effluent. Designing the operational parameters under economic considerations. Water Air Soil Poll. 2012;223:5999–6007.

[26] Katsoyiannis IA, Canonica S, von Gunten U. Efficiency and energy requirements for the transformation of organic micropollutants by ozone, $O_3/H_2O_2$ and UV/$H_2O_2$. Water Res. 2011;45:3811–3822.

[27] Naddeo V, Uyguner-Demirel CS, Prado M, et al. Enhanced ozonation of selected pharmaceuticals by sonolysis. Environ Technol. 2015;36:1876–1883.

[28] Keen OS, Baik S, Linden KG, et al. Enhanced biodegradation of carbamazepine after UV/$H_2O_2$ advanced oxidation. Environ Sci Technol. 2012;46:6222–6227.

[29] Liang S, Maceiko S, Takeguchi W, et al. Bench-scale ozonation for removing constituents of emerging concern. J Am Water Works Ass. 2014;106:E350–E361.

[30] Gerrity D, Stanford BD, Trenholm RA, et al. An evaluation of a pilot-scale nonthermal plasma advanced oxidation process for trace organic compound degradation. Water Res. 2010;44:493–504.

[31] Vogna D, Marotta R, Andreozzi R, et al. Kinetic and chemical assessment of the UV/$H_2O_2$ treatment of antiepileptic drug carbamazepine. Chemosphere. 2004;54:497–505.

[32] Miao XS, Metcalfe CD. Determination of carbamazepine and its metabolites in aqueous samples using liquid chromatography-electrospray tandem mass spectrometry. Anal chem. 2003;75:3731–3738.

# Publication III

Ajo, P., Vornamo, T., Preis, S., Kallioinen, M., Mänttäri, M., Louhi-Kultanen, M.
**Hospital wastewater treatment with pilot-scale pulsed corona discharge for removal of pharmaceutical residues**

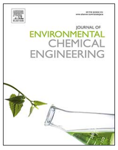
Reprinted with permission from
*Journal of Environmental Chemical Engineering*
Vol. 6, pp. 1569-1577, 2018

Journal of Environmental Chemical Engineering 6 (2018) 1569–1577

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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



# Hospital wastewater treatment with pilot-scale pulsed corona discharge for removal of pharmaceutical residues

Petri Ajo[a,*], Sergei Preis[b], Timo Vornamo[a], Mika Mänttäri[a], Mari Kallioinen[a], Marjatta Louhi-Kultanen[a,c]

[a] *School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, 53851 Lappeenranta, Finland*
[b] *Department of Materials and Environmental Technology, Tallinn University of Technology, Ehitajate Tee 5, 19086 Tallinn, Estonia*
[c] *School of Chemical Engineering, Aalto University, P.O. Box 16100, 00076 Aalto, Finland*

## ARTICLE INFO

*Keywords:*
Non-thermal plasma
Micropollutant
Drug
Hydroxyl radical
Ozone

## ABSTRACT

In recent years, accumulation of pharmaceutical compounds in the environment has been an issue of growing concern. Conventional wastewater treatment has limited effectiveness with many pharmaceuticals at concentrations of ppb or ppt scale. An intuitive solution would be to treat the pharmaceuticals-contaminated wastewaters at the source sites before dilution in sewer networks. Health institutions with concentrated drug consumption provide logical point sources for pharmaceuticals entering the sewage. This paper describes the pilot-scale removal of a wide range of pharmaceuticals from real wastewaters via gas-phase pulsed corona discharge oxidation. The process was studied for raw sewage from a public hospital and for biologically treated wastewater of a health-care institute. The non-selective oxidation of the observed pharmaceuticals (32 compounds) was effective at reasonable energy cost: 87-% reduction in residual pharmaceuticals (excluding biodegradable caffeine) from raw sewage was attained with 1 kWh $m^{-3}$ from the raw sewage and 100% removal was achieved for biologically treated wastewater at only 0.5 kWh $m^{-3}$. The impact for affected aquatic environments upon the present solution would be a dramatically reduced load of pharmaceutical accumulation.

## 1. Introduction

Medicinal compounds pose a threat to aquatic environments due to their biological activity. The issue has received wide scientific and public media attention in recent years [1,2]. A structural challenge in addressing this problem comes not only from the persistence commonly exhibited by such substances, but also from the very low concentrations at which they occur. These two factors make the removal of pharmaceutical residues in conventional wastewater treatment plants essentially insufficient with rare exceptions, e.g. ibuprofen, a common non-steroidal anti-inflammatory drug, exhibiting significant biological transformation [3]. In fact, biological water treatment process may even increase the amount of certain pharmaceuticals due to enzymatic reformation of metabolites, reproducing the original parent compounds, which has been observed for example for the anti-epileptic carbamazepine [4] and certain hormones.

Natural and synthetic hormones present in the sanitary fraction of wastewaters mainly enter wastewater treatment plants (WWTPs) in largely non-estrogenic form, excreted primarily as a variety of inactive glucoronide or sulfonide conjugates. During the sewage process, however, these inactive compounds are readily transformed into potentially more harmful ones [5]. This transformation seemingly happens due to the large amounts of β-glucuronidase enzyme produced by the fecal bacteria *Escherichia coli* [6]. Similar outcomes might presumably be attributable to other pharmaceuticals as well. Pharmaceutical metabolites and treatment byproducts therefore add to this widely recognized problem.

A potential way to tackle the inconvenience of low concentrations is to process the waters immediately at source points. In practice, this means health-care institutions, with wastewaters containing pharmaceutical contents higher than typical influent at a municipal WWTPs. Treatment before dilution into the public sewage would provide higher concentrations of pharmaceuticals abated in, for example, oxidation reactions, adsorption or reverse osmosis membrane filtration. The last two methods are known, however, together with high operating expenses, for their ability to only redistribute pollutants forming concentrated wastes that require further handling [7].

Various oxidation processes have been widely explored, frequently employing electrochemical methods [8], UV-light in photocatalytic oxidation [9–11], including various reactive oxygen species like ozone

---

[*] Corresponding author.
*E-mail address:* petri.ajo@lut.fi (P. Ajo).

https://doi.org/10.1016/j.jece.2018.02.007
Received 25 November 2017; Received in revised form 15 January 2018; Accepted 8 February 2018

($O_3$) [12] and hydrogen peroxide ($H_2O_2$) [13], or shorter living intermediates like hydroxyl (OH) radicals, atomic oxygen $O(^3P)$ and singlet oxygen $O_2$ ($^1\Delta_g$) [14,15]. The shorter lifetime for the latter group is attributed to their extreme reactivity, which translates as higher oxidation potential. These radical species are desirable in oxidative treatments, collectively known as advanced oxidation processes (AOPs) [16]. Ozonation is one of the most facile and common AOPs; its high price unfortunately restricting its use to rich countries. Ozonation or other AOPs, however, are not commonly assigned for pharmaceuticals destruction at point sources, despite the apparent public awareness of the problem. The natural explanation is of monetary and regulatory disposition; without legislative pressure, the motivation to invest in these solutions remains insufficient.

Many laboratory-scale systems have been developed in efforts to overcome the high cost of ozonation, a variety of non-thermal plasma (NTP) applications among them. Water treatment with NTP can be considered chemically similar to ozonation since these processes include ozone formation from ambient oxygen and OH-radical production from water molecules, which is also a part of ozone-water reaction kinetics. The most energy-efficient NTP for water treatment has been the gas-phase pulsed corona discharge (PCD), which in the context is usually produced in a wire-plate electrode system in which nano- to microsecond scale high voltage pulses are directed to a metal wire, whose high curvature profile then allows the discharge to initiate and propagate towards the grounded plates [17–20]. The high efficiency of such configuration is based on the non-equilibrium state of ions and free gaseous electrons in the plasma, which means highly energized electrons and excited but low energy molecular or atomic species, resulting in low or negligible heat losses in the overall process. A comprehensive review on pharmaceuticals degradation with NTP applications was reported by Magureanu et al. in [19] and Banaschik et al. in [21], highlighting fast target removal, increased biodegradability and comparable energy costs to other AOPs.

In this study, we examine a pilot-scale PCD unit for reduction of pharmaceuticals content in wastewater before discharge into the public sewage network. The objective is to investigate the feasibility and effectiveness of a PCD water treatment application at point sources with elevated pharmaceutical concentrations. Treatment prior to wastewater discharge to public sewage networks not only holds the potential of higher removal efficiency but also the eventual reduction of sludge contaminants as well, since the overall pharmaceutical content entering the sewage network will be decreased. The PCD is also coupled with ultrafiltration (UF) to investigate whether membrane separation pretreatment would increase PCD efficiency. Earlier, the effectiveness of PCD in oxidation of aqueous carbamazepine in municipal wastewater as well as identified transformation products of the parent compound were shown [22]; this research extends coverage to a wide range of pharmaceuticals in different wastewaters. Wastewaters from two sources in South and South-East Finland were used: raw wastewater from a hospital and effluent from an active sludge wastewater treatment plant of a health institute. Having more extensive pharmaceutical content, the hospital waters receive more detailed discussion, whereas the health institutional wastewater effluent may be considered, for example, as a supporting extension of this investigation.

## 2. Materials and methods

### 2.1. Wastewater sources

### 2.1.1. Etelä-Karjala Central Hospital

Etelä-Karjala Central Hospital is a public hospital located in Lappeenranta, Finland, and one of the 16 central hospitals in the country. The hospital works as a comprehensive centralized care unit for South Karelia Social and Health Care District. Annual sewage flow rate data is unfortunately not available. The hospital wastewater samples were pumped from a collective sewer line of the hospital downstream of an oil trap before being discharged into the public sewage network. The piloting was carried out in two sets, for both of which a volume of 1.0 $m^3$ of sewage was separately collected with a tank truck and kept dark and cool through storage. Experiments were conducted and samples delivered for analysis within 48 h of zero sampling. With the first set (Batch 1), the raw sewage containing suspended solids was allowed to settle in the container for 20 h, after which 350 L was pumped off the top to another container. All the experimental batches were then collected from this volume. From the sewage collected for the second experimental set (Batch 2), a similar initial volume was extracted into a different container through a string wound filter cartridge with a 50 μm filter ratio, after only 3 h settling.

### 2.1.2. Rinnekoti Foundation

Rinnekoti Foundation in Espoo, Finland, is a center producing healthcare and social inclusion services for people with intellectual or developmental disorders. The institute has its own wastewater treatment plant applying an active sludge process, including denitrification-nitrification steps and chemical phosphorus precipitation. In 2015, the annual treated volume was 114,484 $m^3$ [23]. The plant influent is mainly domestic wastewater collected from the Rinnekoti Foundation facilities, consisting of the daily wastewaters of approximately one thousand people. The wastewater samples from Rinnekoti Foundation were pumped from the effluent stream of the institutional wastewater treatment plant. A total of 1.0 $m^3$ of the treated wastewater was pumped with a submersible pump to a storage container, from which batches of required volume were extracted for the experiments with similar procedures as with the hospital waters. No settling was necessary with the biologically treated wastewaters. Before collecting the zero sample and experimental batches, the water was mixed by circulating the complete volume inside the container for 2 h using the submersible pump. No other pretreatment was applied.

### 2.2. Analyses

Pharmaceutical concentrations were analyzed by Eurofins Scientific Finland Ltd applying modified EPA methods 1694 and 539 and solid phase extraction. The analysis covered a total of 57 pharmaceutical compounds listed in Table 1. These compounds include clofibric acid, which is more of an active metabolite of etofibrate, etofyllinclofibrate and clofibrate, than a pharmaceutically applied substance [24].

Total organic carbon (TOC) was measured with a Shimadzu TOC L-series analyzer, which applies catalytic combustion at 680 °C. Chemical oxygen demand (COD) was analyzed using potassium dichromate analysis kits and a Hach DR/2000 spectrophotometer. Color and turbidity was measured with a HACH DR/2010- spectrophotometer, at 465 nm and 860 nm, respectively. UV measurements at 254 nm were made using a Jasco V-670 UV-VIS-NIR spectrophotometer. pH was measured with Metrohm 744 pH meter and conductivity with Knick Konduktometer 703.

### 2.3. Experimental setup

### 2.3.1. Plasma treatment system and procedure

The PCD system consists of a high voltage pulse generator, a gas-phase corona discharge reactor and a water circulation system. The PCD reactor is of vertical configuration wherein the treated water is allowed a free fall, showering through the NTP. The flow is arranged through a top chamber with a perforated bottom plate with 1-mm orifices. The pulse generator can be adjusted to deliver pulses with a stepwise frequency range from 100 to 840 Hz, which correlates linearly to a nominal power range of 30 to 250 W due to each pulse delivering the energy of 0.3 J. In these experiments, the maximum and the minimum power outputs were used in order to observe the difference between oxidation energy efficiency over maximum available power range. The reactor configuration was coupled with a water circulation

**Table 1**
The monitored pharmaceuticals and their limit of quantification (LQ). The analytical error at LQ is 30%. [a] = antibiotics, [b] = steroids, [c] = hormones, [d] = NSAID. Analysis was done using ultra-performance liquid chromatograph coupled with tandem mass spectroscopy (UPLC/MS/MS).

| Substance | LQ, µg/L | Substance | LQ, µg/L | Substance | LQ, µg/L | Substance | LQ, µg/L |
|---|---|---|---|---|---|---|---|
| 17α-ethinylestradiol[bc] | 0.001 | Enalapril | 0.01 | Metoprolol | 0.02 | Progesterone[bc] | 0.001 |
| 17β-estradiol[bc] | 0.005 | Entacapone | 0.01 | Iopromide | 0.01 | Propranolol | 0.01 |
| Atenol | 0.005 | Estriol[bc] | 0.005 | Ketoconazole | 0.01 | Salbutamol | 0.02 |
| Beclometasone | 0.005 | Estrone[bc] | 0.005 | Ketoprofen | 0.005 | Simvastatin | 0.05 |
| Bezafibrate | 0.005 | Felodipine | 0.05 | Methotrexate | 0.01 | Sotalol | 0.01 |
| Bisoprolol | 0.01 | Fenbendazole | 0.005 | Methylprednisolone | 0.02 | Sulfamethoxazole[a] | 0.01 |
| Caffeine | 0.01 | Flubendazole | 0.005 | Metoprolol | 0.005 | Terbutaline | 0.01 |
| Carbamazepine | 0.005 | Fluoxetine | 0.01 | Metronidazole[a] | 0.02 | Testosterone[bc] | 0.001 |
| Ciprofloxacin[a] | 0.01 | Furosemide | 0.05 | Naproxen | 0.01 | Tetracycline[a] | 0.001 |
| Citalopram | 0.01 | Gemfibrozil | 0.01 | Norethindrone[c] | 0.02 | Trimethoprim[a] | 0.01 |
| Clenbuterol | 0.005 | Hydrochlorothiazide | 0.05 | Norfloxacin[a] | 0.05 | Tylosin[a] | 0.02 |
| Clofibric acid | 0.05 | Hydrocortisone[bc] | 0.01 | Ofloxacin[a] | 0.05 | Warfarin | 0.005 |
| Cyclophosphamide | 0.005 | Ibuprofen[d] | 0.05 | Oxytetracycline[a] | 0.05 | | |
| Diclofenac[d] | 0.005 | Ifosfamide | 0.02 | Paracetamol | 0.05 | | |
| Doxycycline[a] | 0.02 | Iopamidol | 0.02 | Paroxetine | 0.005 | | |

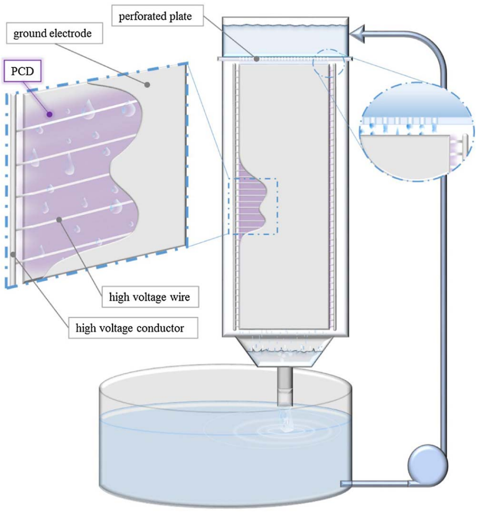


**Fig. 1.** Experimental PCD configuration for treatment of 50-L batches (not in scale).

system including a tank for 50 L batches. The system is illustrated in Fig. 1. Further details and technical description are presented in our previous publication [25] where the gas-phase ozone concentration in the reactor was also measured, comprising around $5\,mg\,L^{-1}$ in air atmosphere, and negligible amounts of oxidants, below $1\,mg\,L^{-1}$, were iodometrically measured in the treated water, which was a binary model solution with notably lower amount of oxidant consuming species than in the presently studied sewage.

During experiments, the water was circulated at $15\,L\,min^{-1}$ and prior to each sampling the treated volume was allowed to mix by circulating through the system for 5 min with the plasma off. In Batch 1 experiments with hospital wastewater, the treatment at 30 W was applied for 0.1 and $0.5\,kWh\,m^{-3}$ of pulse energy delivered, and at 250 W for 0.5 and $1.0\,kWh\,m^{-3}$. For Batch 2, the 30 W treatment was extended to $1.0\,kWh\,m^{-3}$ following the observed results with Batch 1, to meet better purification results. The energy efficiency of target pollutant oxidation, $g\,kWh^{-1}$, was calculated as described elsewhere [18,19] in respect to the removal data.

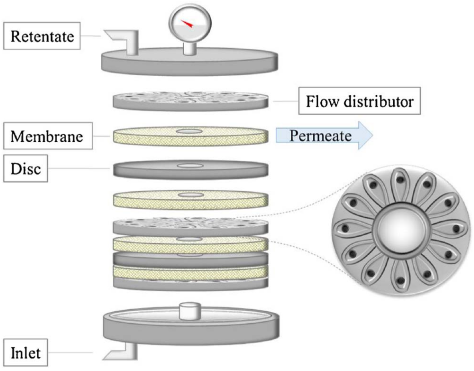


**Fig. 2.** Membrane filtration system (not in scale).

### 2.3.2. Membrane pretreatment system and procedures

The membrane filtrations were made using an Alfa Laval DSS LabStak® M20-filtration system (Fig. 2), designed for plate-and-frame operations with $0.036–0.72\,m^2$ membrane areas. Each permeate flow is collected separately from the permeate plate that holds a similar membrane on each side, one plate holding a membrane area $0.036\,m^2$. The permeate plates are separated with a plate that distributes the feed flow from the first permeate plate to the next one.

Ultrafiltration of the hospital waters was carried out with UC030 Microdyn-Nadir membranes with an area of $0.144\,m^2$ at 2.0–3.5 bar. In the experiments with Rinnekoti waters, the same membrane with an area of $0.108\,m^2$ was used at the pressure of 2.0–2.2 bar. In both cases the cross flow velocity was about $0.7\,m\,s^{-1}$.

## 3. Results and discussion

### 3.1. Hospital wastewaters

Analysis revealed a total of 27 pharmaceuticals in the untreated hospital wastewaters, plus progesterone and methylprednisolone that only occurred in the course of treatment. The two batches of hospital wastewater sported similar pharmaceutical content with minor exceptions: salbutamol ($0.88\,\mu g\,L^{-1}$), atenol ($2.3\,\mu g\,L^{-1}$) and warfarin ($0.082\,\mu g\,L^{-1}$) were only observed in Batch 1 and entacapone ($1.1\,\mu g\,L^{-1}$) and propranolol ($0.21\,\mu g\,L^{-1}$) only found in Batch 2. The pharmaceutical content of the wastewater was heavily reduced in PCD

**Table 2**
Direct PCD treatment on observed pharmaceutical residues in hospital wastewater Batch 2, complete removal of pollutants (100%) manifests concentrations reduced below LQ.

| Power<br>Energy, kWh m$^{-3}$<br>Substance, $\mu$g L$^{-1}$ | Raw | 30 W<br>0.1<br>PCD | Removal | 30 W<br>0.5<br>PCD | Removal | 30 W<br>1.0<br>PCD | Removal | 250 W<br>0.5<br>PCD | Removal | 250 W<br>1.0<br>PCD | Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bisoprolol | 0.84 | 0.6 | 29% | 0.17 | 80% | < 0.10 | 100% | 0.5 | 40% | 0.35 | 58% |
| Caffeine | 470 | 450 | 4% | 420 | 11% | 380 | 19% | 480 | −2% | 480 | −2% |
| Carbamazepine | 0.35 | 0.25 | 29% | < 0.05 | 100% | < 0.05 | 100% | 0.21 | 40% | 0.088 | 75% |
| Ciprofloxacin | 13 | 8.6 | 34% | 4.1 | 68% | 0.85 | 93% | 7.2 | 45% | 5.4 | 58% |
| Citalopram | 0.23 | 0.17 | 26% | < 0.10 | 100% | < 0.10 | 100% | 0.14 | 39% | < 0.10 | 100% |
| Diclofenac | 0.6 | 0.42 | 30% | < 0.05 | 100% | < 0.05 | 100% | 0.26 | 57% | 0.083 | 86% |
| Doxycycline | 2 | 1.2 | 40% | < 0.20 | 100% | < 0.20 | 100% | 0.81 | 60% | 0.32 | 84% |
| Enalapril | 0.31 | 0.26 | 16% | 0.23 | 26% | 0.19 | 39% | 0.27 | 13% | 0.25 | 19% |
| Entacapone | 1.1 | 0.26 | 76% | < 0.10 | 100% | < 0.10 | 100% | 0.18 | 84% | < 0.10 | 100% |
| Estriol | 0.91 | 1.1 | −21% | < 0.05 | 100% | < 0.05 | 100% | 0.49 | 46% | 0.2 | 78% |
| Estrone | 0.1 | 0.065 | 35% | < 0.05 | 100% | < 0.05 | 100% | < 0.050 | 100% | < 0.05 | 100% |
| Furosemide | 11 | 4.7 | 57% | < 0.50 | 100% | < 0.50 | 100% | 2.6 | 76% | < 0.50 | 100% |
| Hydrochlorothiazide | 4.2 | 4.8 | −14% | 4 | 5% | 2.2 | 48% | 5.4 | −29% | 4.3 | −2% |
| Hydrocortisone | 0.45 | 0.33 | 27% | 0.43 | 4% | 0.35 | 22% | 0.37 | 18% | 0.37 | 18% |
| Ibuprofen | 28 | 34 | −21% | 24 | 14% | 14 | 50% | 43 | −54% | 26 | 7% |
| Metoprolol | 0.37 | 0.33 | 11% | 0.18 | 51% | < 0.05 | 100% | 0.33 | 11% | 0.26 | 30% |
| Metronidazole | 8.9 | 6.6 | 26% | 7.8 | 12% | 7.3 | 18% | 8.1 | 9% | 8.4 | 6% |
| Naproxen | 1.1 | 0.78 | 29% | < 0.10 | 100% | < 0.10 | 100% | 0.69 | 37% | 0.5 | 55% |
| Ofloxacin | 16 | 11 | 31% | 2.2 | 86% | < 0.50 | 100% | 9.4 | 41% | 5.7 | 64% |
| Paracetamol | 580 | 420 | 28% | 70 | 88% | 63 | 89% | 260 | 55% | 130 | 78% |
| Propranolol | 0.21 | 0.1 | 52% | < 0.10 | 100% | < 0.10 | 100% | < 0.10 | 100% | < 0.10 | 100% |
| Sulfamethoxazole | 5.8 | 2.7 | 53% | < 0.10 | 100% | < 0.10 | 100% | 0.25 | 96% | < 0.10 | 100% |
| Tetracycline | 1.6 | 0.83 | 48% | 0.15 | 91% | 0.14 | 91% | 0.59 | 63% | 0.23 | 86% |
| Trimethoprim | 1.2 | 0.92 | 23% | 0.061 | 95% | < 0.01 | 100% | 0.73 | 39% | 0.31 | 74% |

**Table 3**
UF and UF + PCD (30 W) effect on observed pharmaceutical residues in hospital wastewater Batch 2, complete removal of pollutants (100%) manifests concentrations reduced below LQ.

| Energy, kWh m$^{-3}$ | Raw | UF | Removal | 0.1 | Removal | 0.5 | Removal | 1.0 | Removal |
|---|---|---|---|---|---|---|---|---|---|
| Substance, $\mu$g L$^{-1}$ | | | | UF + PCD | | UF + PCD | | UF + PCD | |
| Bisoprolol | 0.84 | 0.74 | 12% | 0.58 | 31% | < 0.10 | 100% | < 0.10 | 100% |
| Caffeine | 470 | 440 | 6% | 510 | −9% | 410 | 13% | 300 | 36% |
| Carbamazepine | 0.35 | 0.33 | 6% | 0.28 | 20% | < 0.05 | 100% | < 0.05 | 100% |
| Ciprofloxacin | 13 | 8.3 | 36% | 2.6 | 80% | 2 | 85% | < 0.50 | 100% |
| Citalopram | 0.23 | 0.18 | 22% | < 0.10 | 100% | < 0.10 | 100% | < 0.10 | 100% |
| Diclofenac | 0.6 | 0.68 | −13% | 0.37 | 38% | < 0.05 | 100% | < 0.05 | 100% |
| Doxycycline | 2 | 1.3 | 35% | < 0.20 | 100% | < 0.20 | 100% | < 0.20 | 100% |
| Enalapril | 0.31 | 0.21 | 32% | 0.2 | 35% | 0.14 | 55% | < 0.10 | 100% |
| Entacapone | 1.1 | 0.67 | 39% | 0.19 | 83% | < 0.10 | 100% | < 0.10 | 100% |
| Estriol | 0.91 | 0.65 | 29% | 0.61 | 33% | < 0.05 | 100% | < 0.05 | 100% |
| Estrone | 0.1 | 0.076 | 24% | < 0.050 | 100% | < 0.05 | 100% | < 0.05 | 100% |
| Furosemide | 11 | 7.3 | 34% | 4.2 | 62% | < 0.50 | 100% | < 0.50 | 100% |
| Hydrochlorothiazide | 4.2 | 4.2 | 0% | 3.8 | 10% | 2.2 | 48% | 0.58 | 86% |
| Hydrocortisone | 0.45 | 0.42 | 7% | 0.42 | 7% | 0.35 | 22% | 0.26 | 42% |
| Ibuprofen | 28 | 27 | 4% | 25 | 11% | 26 | 7% | 16 | 43% |
| Metoprolol | 0.37 | 0.37 | 0% | 0.37 | 0% | 0.097 | 74% | < 0.05 | 100% |
| Metronidazole | 8.9 | 8.2 | 8% | 8.5 | 4% | 7.3 | 18% | 5.7 | 36% |
| Naproxen | 1.1 | 1.2 | −9% | 0.92 | 16% | < 0.10 | 100% | < 0.10 | 100% |
| Ofloxacin | 16 | 12 | 25% | 3.7 | 77% | < 0.50 | 100% | < 0.50 | 100% |
| Paracetamol | 580 | 560 | 3% | 400 | 31% | 58 | 90% | 41 | 93% |
| Propranolol | 0.21 | 0.16 | 24% | 0.11 | 48% | < 0.10 | 100% | < 0.10 | 100% |
| Sulfamethoxazole | 5.8 | 4.8 | 17% | 0.42 | 93% | < 0.10 | 100% | < 0.10 | 100% |
| Tetracycline | 1.6 | 1.5 | 6% | 0.14 | 91% | < 0.10 | 100% | < 0.10 | 100% |
| Trimethoprim | 1.2 | 1.2 | 0% | 0.95 | 21% | 0.01 | 99% | < 0.01 | 100% |

treatment, with some deviation in the removal yield as further discussed below. Progesterone, methylprednisolone and ibuprofen exhibited interesting growth in concentration in the course of oxidation, ibuprofen so only momentarily. Tables 2 and 3 present pharmaceuticals removal from hospital waters for Batch 2, which exhibited a tendency for higher initial concentrations of most of the substances and for which the low power PCD treatment was sustained longer. Results for Batch 1 are included for reference in Supplementary information Table 1, and the discussion henceforth considers the presented results of Batch 2 unless specifically noted otherwise. Progesterone and methylprednisolone are presented and their occurrence discussed individually in 3.1.2 as they were not present in the untreated water and only occurred as oxidation products. In the following, the results are collectively tabulated and certain peculiarities are separately considered in chapters 3.1.1 to 3.1.3 for deeper scrutinizing; undetected monitored substances are excluded from further presentation.

Tables 2 and 3 show that ibuprofen, a common pain killer and NSAID, increases momentarily in concentration in certain PCD experiments (similar observations in Batch 1). Fast oxidation of the substance in the same process at higher concentrations in model solutions was reported earlier [18], suggesting that the slow reduction of ibuprofen in the present case probably overlapped with reformation from oxidation of metabolites. This would suggest that the actual removal rates cannot be accurately estimated in the context of real wastewaters without negative bias from simultaneous reformation. The suggestion that ibuprofen indeed is reforming from transformation products is supported by Ferrando-Climet et al. [26], where a number of ibuprofen metabolites were identified in WWTP influent totaling substantially more abundant than the parent substance.

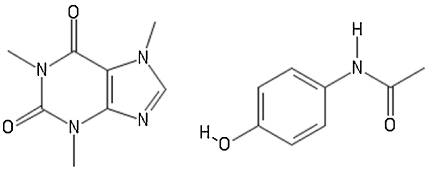
### 3.1.1. Paracetamol and caffeine

Paracetamol and caffeine were distinguished with two to three orders of magnitude higher concentrations than the other monitored substances. Paracetamol, abundant as common painkiller, was reduced by 93% with UF + PCD at 30. Direct PCD treatment achieved 89-% reduction at best, corresponding to a yield of 517 mg $kWh^{-1}$. For reference, Panorel et al. reported 40 times higher yield of 20 g $kWh^{-1}$ for paracetamol, with the same process in a binary model solution at two orders of magnitude higher initial concentration [18]. Although vaguely comparable in light of the experimental concentration difference, the similar response emphasizes the non-selective character of PCD treatment in successful operation with clean water solutions and wastewater. The results support previous findings on PCD treatment of municipal wastewater effluent [22].

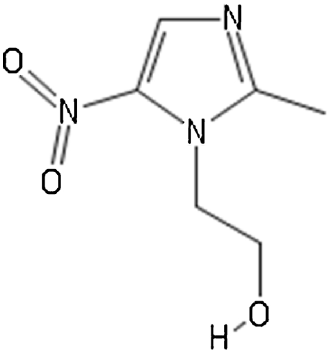
Caffeine, a nervous stimulant [27], is a ubiquitous ingredient in common refreshments and naturally present in over 60 plants [28]. Caffeine proved more resilient to oxidation than paracetamol which could be anticipated due to the strong molecular structure with concise nitrogen bonding and ketone groups: the vacancy available for the OH-radical or ozone attack, the C═N bond, is characterized by relatively high energy of 615 kJ $mol^{-1}$. Beltrán et al. [29] stated that caffeine is oxidized predominantly with OH-radicals and refractory to oxidation with molecular ozone. Siqueira Souza and Amaral Féris [30], Broséus et al. [31] and Ganzenko et al. [32] confirmed these observations in various AOPs with hard mineralization. A series of publications reported caffeine being oxidized more effectively in combination of ozone with catalysts and photocatalytic oxidation [33–36]. Analogously, dielectric barrier discharge (DBD) exhibited efficiency improved by a goethite catalyst [37]. Rosal et al. [38] disclosed a mechanism of caffeine ozonation with both ozone and OH-radicals indicating rather low second-order reaction rate constant ranging from 0.25 to 1.05 $M^{-1} s^{-1}$ and increasing with pH from 3 to 10, i.e. at improving OH-radical contribution in oxidation; the reaction rate constant for OH-radical formation in the reaction of ozone with OH-ion is 70 $M^{-1} s^{-1}$ [39]. In comparison, the phenyl moiety in paracetamol (Scheme 1) assumes facile oxidation [40]. The poor removal efficiency of caffeine, however, conveniently proposes little disappointment due to its biodegradability: it is reported to degrade at 94% average efficiency in conventional WWTPs [41], ranging even above 99% [42].

### 3.1.2. Antibiotics

Antibiotics can be largely unaffected in conventional WWTPs [43] and pose a special and generally recognized problem for potent development of bacterial resistance [44,45]. Removal in active sludge processes may be largely attributed to sorption in the sludge [46], which does not remove the problem. Concise and multi-reference description of accumulated antibiotics in the environment is given in [47]. In this study, doxycycline, metronidazole, ofloxacin, ciprofloxacin, sulfamethoxazole, tetracycline and trimethoprim were found in the hospital wastewaters at concentrations ranging from 1.2 to 13 μg $L^{-1}$. The best result was achieved with the UF + PCD (30 W) process at 1.0 kWh $m^{-3}$ where all the antibiotics were completely oxidized, except metronidazole (36-% reduction), which proved highly resilient to oxidation. The refractory nature of metronidazole is a characteristic of the concise molecular construction with two amines in the cycle and a nitro group (Scheme 2). Mota et al. [48] described oxidation of metronidazole with ozone starting from the high-energy C═N bond adjacent to the nitro-group analogously to the caffeine primary oxidation act. Previous studies showed refractory character of metronidazole towards oxidation with ozone, being improved with catalytic aid of activated carbons [49] and in combination with photocatalysis [50]. Considering the overall antibiotics oxidation result, improvement from ultrafiltration pretreatment was pronounced at lower energy doses: by 32, 11 and 5% higher total antibiotics removal at 0.1, 0.5 and 1.0 kWh $m^{-3}$, respectively.



**Scheme 1.** Molecular structures of caffeine (left) and paracetamol (right). The refractory nature of caffeine is obvious from the strong N- and O-bonding.



**Scheme 2.** Molecular structure of metronidazole.

### 3.1.3. Pharmaceuticals appearing during PCD oxidation

Progesterone and methylprednisolone, both steroidal hormones sharing structural similarity, appeared only during PCD oxidation of the hospital wastewaters and consistently increased in concentration throughout the pulsed energy delivery. The observed increase is an apparent recurrence: the result of oxidation of metabolites, e.g. cysteine conjugates [51], transforming back to the parent compound. Neither of the substances were observed in samples prior to treatment. The recurrence phenomenon resembles biological oxidation of carbamazepine metabolites in wastewater treatment transforming back into carbamazepine [4], although be it noted that carbamazepine concentrations only decreased in PCD-oxidation both in the present study and in [22]. A decreasing concentration was not observed for either substance within the extent of the experiments, suggesting the concentrations of the precursors exceed that of the observed parent compound maxima. Since degradation of organic compounds is generally an oxidation process, the observed formation of progesterone and methylprednisolone during PCD treatment proposes a possibility of these reactions taking place in common WWTPs as well, similarly as reported for carbamazepine. Besides, even though progesterone and methylprednisolone were observed to actually increase in the process, it should be noted that these are oxidation products and therefore assumable intermediate products in naturally occurring degradation pathways as well.

Progesterone, initially below the level of detection, was also not observed at the lowest energy dose of 0.1 kWh $m^{-3}$, which, as noted above, was well sufficient for effective reduction of many of the monitored substances. At low treatment power, the first occurrence was at 0.5 kWh $m^{-3}$ and at full power the concentration was measurable only at the end at 1 kWh $m^{-3}$. Here, a maximum progesterone concentration after PCD treatment was measured as 0.072 μg $L^{-1}$ at 30 W pulse power, while at 250 W the amounts remained at 0.017-0.021 μg $L^{-1}$, approximately four times lower at eight times higher pulse power. The disproportion between the rates and applied powers would suggest ozone has a notable role in the reactions [25]. The maximum value corresponds to a progesterone yield of 72 μg $kWh^{-1}$. The well-known metabolite, allopregnanolone, is suggested as a probable candidate for the main progesterone precursor in the oxidative conditions, having a hydroxyl group prone for oxidation by the abundant hydroxyl radicals. A comprehensive list of identified and theoretical metabolites of progesterone can be found in the article by Stanczyk [52]. Similar to testosterone, Fabreqat et al. [51] reported cysteine conjugates as progesterone metabolites. Since progesterone was not found from the first treated samples, regardless of plasma power, it is suggested that there may be multiple reaction steps until the parent compound is reformed, which could infer that the presence of metabolites changed beyond allopregnanolone that is still relatively similar with the parent compound. The development of progesterone concentrations in direct PCD treatment of the hospital waters is presented in Fig. 3. Peculiarly, no progesterone was observed in ultrafiltered and subsequent PCD samples, which may indicate adsorption properties in sedimentary material; indeed, Sangster et al. [53] described different progesterone spiked sediment materials resulting in essentially varied effects upon fish population in the given environment. The destruction of pharmaceutical metabolites is of equal importance with the destruction of the parent compounds, as, for example, the suggested precursor allopregnanonole is also highly bioactive [54].

Methylprednisolone concentration increased in both ultrafiltered and unfiltered hospital waters subjected to oxidation. A peak concentration of 1.4 μg $L^{-1}$ was recorded for methylprednisolone with the maximum energy dose at 30 W pulse power, which corresponds to a yield of 1400 μg $kWh^{-1}$. A comprehensive collection of 15 methylprednisolone metabolites was reported by Pozo et al. [55], proposing a list of precursor candidates whose oxidation would result in reformation of the parent compound. The most probable of these candidates would be the products of one-step reduction, which was suggested to occur at the keto moiety of the aliphatic carbon chain of the molecule. Methylprednisolone concentrations in PCD treated hospital waters are presented in Fig. 4.

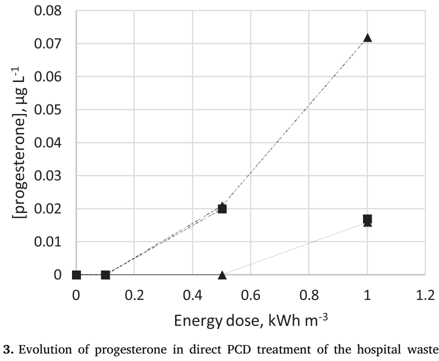


**Fig. 3.** Evolution of progesterone in direct PCD treatment of the hospital wastewater Batches 1 and 2: ■ = Batch 1; ▲ = Batch 2; solid line = 250 W PCD; dashed line = 30 W PCD.

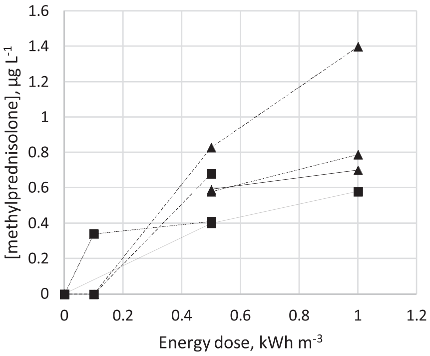


**Fig. 4.** Evolution of methylprednisolone in PCD treatment of hospital wastewater batches 1 and 2 with and without ultrafiltration: ■ = Batch 1; ▲ = Batch 2; solid line = 250 W PCD; dashed line = 30 W PCD; frequently dashed line = ultrafiltration and 30 W PCD.

### *3.1.4. Total pharmaceutical compound removal*

The mass-based occurrence of total detected pharmaceuticals amounted to 1148 μg $L^{-1}$, 678 μg $L^{-1}$ without caffeine and 98 μg $L^{-1}$ without caffeine and paracetamol, the two individual substances thus constituting a substantial 91% of the total pharmaceutical mass. Calculations for maximum reduction achieved from these values with UF, PCD and their combination are presented in Table 4.

Regardless of the noticeable removal of pharmaceuticals with UF, up to 17% if the reduction of other than caffeine and paracetamol is considered, contribution of preliminary UF to the sum effect with PCD was modest. The results propose the overall pharmaceuticals removal fitting to 9% difference whether UF is used as pretreatment before PCD or not −68% and 59% of total pharmaceuticals removed at 30 W applied power at PCD energy input of 1.0 kWh $m^{-3}$ with and without preliminary UF, respectively. The effect of preliminary UF was even smaller for pharmaceuticals considered with caffeine and caffeine together with paracetamol subtracted, 4% and 2%, respectively. This implies that as a combined unit process, UF pretreatment had very modest effect on the overall efficiency of PCD oxidation. Comparing a noticeable difference of the UF effect observed for antibiotics (see 3.1.2), an attractive solution for cutting the environmental load by pharmaceuticals with antibiotics deserves special emphasis in further research in PCD combination with UF.

The rate of PCD energy delivery expectedly makes a difference showing substantially positive effect at low pulse repetition frequency, i.e. smaller applied power explained by the contribution of ozone to the oxidation effect at longer treatment times (Table 4). The trade-off, however, involves longer time required at more energy-effective low-power treatment.

### *3.1.5. Wastewater characterization*

The effect of membrane processes was expectedly more pronounced

**Table 4**
Total pharmaceutical occurrence and maximum removal rate at PCD energy 1.0 kWh $m^{-3.}$

| | Content, μg $L^{-1}$ | *Removal (%)* | | | |
|---|---|---|---|---|---|
| | | UF | UF + PCD 30 W | PCD 30 W | PCD 250 W |
| Total | 1148.27 | 6 | 68 | 59 | 42 |
| w/o caffeine | 678.27 | 5 | 91 | 87 | 73 |
| w/o caffeine and paracetamol | 98.27 | 17 | 77 | 75 | 46 |

on other characteristics of the wastewater, TOC (30%), COD (37%), UV-absorption (20%) and color. Ultrafiltration alone resulted in 69-% reduction in turbidity and 63-% reduction in color; combined with PCD oxidation these results were 87% for both parameters. For comparison, PCD alone reduced turbidity by 47% and color by 58% via oxidative bleaching. A mild increase in conductivity can be observed during PCD treatment, which is likely a result of nitrate formation during the process from ambient nitrogen [56]. These results are presented in Supplementary information Table 2 with other characteristic parameters.

### *3.1.6. Maintenance*

Clogging of the perforation through which the water is introduced into the plasma reactor might be the most potential problem, and be it noted that in this work, settling (and string filtration for Batch 2) of the raw hospital sewage likely aided this cause. Yet, no maintenance requirements have been recognized by the authors, considering the reactor configuration designed for water treatment, or the pulse generator supplying the high voltage power. Membrane fouling, however, is a well-recognized characteristic. Here, in any membrane separation process the permeate flow immediately decreased from initial condition. Nonetheless, in each case permeability settled to a certain level during filtration and the membranes were restored to original permeability with post-process washing using commercial P3-Ultrasil 110 detergent by Ecolab. Membrane performance data is presented in more detail in Supplementary information Fig. 1.

## *3.2. Health institutional wastewaters*

A total of 17 of the monitored pharmaceutical substances were found in the biologically treated wastewater effluent of Rinnekoti Foundation. Of these, carbamazepine, a widely used antiepileptic substance, occurred at a concentration an order of magnitude higher than any other observed substance, which may be explained by the institutional provision of services for the inhabitants with physical disorders. Additionally, ibuprofen was observed only at 0.082 μg $L^{-1}$ in the first treated sample of the 250 W direct PCD experiment, at 0.5 kWh $m^{-3}$ energy delivered. This momentary appearance aligns similarly with the hospital waters, the briefly occurring low concentration disappearing along further treatment (introduced here, ibuprofen is omitted from the following tables for conciseness). Direct PCD and combined UF + PCD results in pharmaceuticals removal are presented in Tables 5 and 6, respectively.

All the studied pharmaceuticals, including hydrochlorothiazide and metronidazole (initial concentrations close to LQ), were substantially reduced with PCD at the minimum energy dose (250 W–0.5 kWh $m^{-3}$; 30 W–0.1 kWh $m^{-3}$) and completely disappeared at maximum (250 W–1 kWh $m^{-3}$; 30 W–0.5 kWh $m^{-3}$). This would suggest that biologically treated wastewater enables a more targeted oxidation process, i.e. less oxidants consumed in unwanted reactions than in the complex matrix of untreated sewage. The total pharmaceutical content is also lower in the biologically treated wastewater than in the untreated hospital sewage. In addition, albeit from different sources, the biodegradability of caffeine was apparent from the concentrations of the untreated hospital sewage and the biologically treated Rinnekoti effluent, demonstrating four orders of magnitude difference.

The results with Rinnekoti waters clearly show that the present PCD configuration can, in a realistic case, be effective as a tertiary treatment process for polishing wastewaters from medicinal pollutants before discharge into the environment. The total mass concentration of the detected pharmaceuticals in the effluent amounted to 6.286 μg $L^{-1}$, which was practically completely removed with direct PCD treatment at 0.5 kWh $m^{-3}$, yielding 12.6 mg $kWh^{-1}$ total drug removal. For perspective, for the annual reported flow through the plant this would correspond to an annual energy consumption of 57 242 kWh, which at a rounded estimate of electricity price of 0.1 € $kWh^{-1}$ and pulse generator efficiency of 67% [18] would result in a cost of €8543. Specific energy dose of 0.1 kWh $m^{-3}$, at which 91-% reduction of total pharmaceuticals was achieved (97% w/UF + PCD), gives an annual cost of €1709. The annual volume discharge with the observed concentrations would give a total of 720 g pharmaceuticals discharged to the aquatic environment, which gives an impression of relatively high cost versus absolute pharmaceuticals reduction. It should be stressed, however, that the estimated yields only consider the monitored substances, and do not include the non-selectively affected compounds of medicinal or any other origin, including the pharmaceuticals transformed beyond detection while retaining biological activity. This demonstration well describes the challenges intrinsic in chemical micropollutant abatement, the cost profile exponentially increasing with removal of decreasing concentrations. As presented, however, notable results are feasible at acceptable cost range.

## 4. Conclusions

A pilot-scale pulsed corona discharge (PCD) plasma was applied to oxidize micro-concentrations of pharmaceuticals in wastewaters collected at point sources. The PCD process was tested for both untreated

**Table 5**

Direct PCD treatment on observed pharmaceutical residues in biologically treated health institutional wastewater effluent, complete removal of pollutants (100%) manifests concentrations reduced below LQ.

| Power<br>Energy, kWh $m^{-3}$<br>Substance, μg $L^{-1}$ | Raw | 30 W<br>0.1<br>PCD | Removal | 30 W<br>0.5<br>PCD | Removal | 250 W<br>0.5<br>PCD | Removal | 250 W<br>1.0<br>PCD | Removal |
|---|---|---|---|---|---|---|---|---|---|
| Bisoprolol | 0.18 | 0.038 | 79% | < 0.010 | 100% | 0.022 | 88% | < 0.010 | 100% |
| Caffeine | 0.012 | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Carbamazepine | 3.1 | 0.013 | 100% | < 0.005 | 100% | 0.011 | 100% | < 0.005 | 100% |
| Citalopram | 0.26 | 0.048 | 82% | < 0.010 | 100% | 0.028 | 89% | < 0.010 | 100% |
| Diclofenac | 0.33 | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% |
| Fluoxetine | 0.068 | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Furosemide | 0.29 | < 0.050 | 100% | < 0.050 | 100% | < 0.050 | 100% | < 0.050 | 100% |
| Hydrochlorothiazide | 0.83 | 0.32 | 61% | < 0.050 | 100% | 0.14 | 83% | < 0.050 | 100% |
| Ketoprofen | 0.022 | 0.009 | 59% | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% |
| Metoprolol | 0.44 | 0.13 | 70% | < 0.005 | 100% | 0.066 | 85% | < 0.005 | 100% |
| Metronidazole | 0.059 | 0.034 | 42% | < 0.020 | 100% | < 0.020 | 100% | < 0.020 | 100% |
| Naproxen | 0.082 | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Propranolol | 0.23 | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Salbutamol | 0.2 | < 0.020 | 100% | < 0.020 | 100% | < 0.020 | 100% | < 0.020 | 100% |
| Sotalol | 0.14 | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Trimethoprim | 0.036 | < 0.001 | 100% | < 0.001 | 100% | < 0.001 | 100% | < 0.001 | 100% |
| Warfarin | 0.007 | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% |

**Table 6**
UF and UF + PCD effect on observed pharmaceutical residues in biologically treated health institutional wastewater effluent, complete removal of pollutants (100%) manifests concentrations reduced below LQ.

| Power<br>Energy, kWh $m^{-3}$<br>Substance, µg $L^{-1}$ | Raw | UF | Removal | 30 W<br>0.1<br>UF + PCD | Removal | 30 W<br>0.5<br>UF + PCD | Removal | 250 W<br>0.5<br>UF + PCD | Removal | 250 W<br>1.0<br>UF + PCD | Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bisoprolol | 0.18 | 0.17 | 6% | 0.021 | 88% | < 0.010 | 100% | 0.017 | 91% | < 0.010 | 100% |
| Caffeine | 0.012 | 0.013 | −8% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Carbamazepine | 3.1 | 2.9 | 6% | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% |
| Citalopram | 0.26 | 0.22 | 15% | < 0.010 | 100% | < 0.010 | 100% | 0.011 | 96% | < 0.010 | 100% |
| Diclofenac | 0.33 | 0.32 | 3% | 0.012 | 96% | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% |
| Fluoxetine | 0.068 | 0.023 | 66% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Furosemide | 0.29 | 0.3 | −3% | < 0.050 | 100% | < 0.050 | 100% | < 0.050 | 100% | < 0.050 | 100% |
| Hydrochlorothiazide | 0.83 | 0.58 | 30% | 0.07 | 92% | < 0.050 | 100% | 0.065 | 92% | < 0.050 | 100% |
| Ketoprofen | 0.022 | 0.016 | 27% | 0.006 | 73% | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% |
| Metoprolol | 0.44 | 0.43 | 2% | 0.076 | 83% | < 0.005 | 100% | 0.052 | 88% | < 0.005 | 100% |
| Metronidazole | 0.059 | 0.064 | −8% | 0.028 | 53% | < 0.020 | 100% | < 0.020 | 100% | < 0.020 | 100% |
| Naproxen | 0.082 | 0.12 | −46% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Propranolol | 0.23 | 0.19 | 17% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Salbutamol | 0.2 | 0.18 | 10% | < 0.020 | 100% | < 0.020 | 100% | < 0.020 | 100% | < 0.020 | 100% |
| Sotalol | 0.14 | 0.16 | −14% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% | < 0.010 | 100% |
| Trimethoprim | 0.036 | 0.033 | 8% | < 0.001 | 100% | < 0.001 | 100% | < 0.001 | 100% | < 0.001 | 100% |
| Warfarin | 0.007 | 0.008 | −14% | < 0.001 | 100% | < 0.005 | 100% | < 0.005 | 100% | < 0.005 | 100% |

sewage of a public hospital and for biologically treated wastewater effluent of a healthcare institute. In the hospital wastewaters, almost all of twenty-nine detected pharmaceuticals were readily oxidized: caffeine, hydrochlorothiazide and metronidazole exhibited strong resilience. Caffeine and paracetamol occurred in two to three orders of magnitude higher concentration than other pharmaceuticals. Of these, caffeine is readily biodegradable, which was emphasized by four orders of magnitude lower initial concentration in the biologically treated effluent.

The oxidation process was coupled with 30 kDa ultrafiltration pretreatment to investigate the effect of the separation process on oxidation energy efficiency of the PCD: UF had little effect on total pharmaceuticals content, excluding caffeine, in hospital waters (5-% reduction), improving the total result of UF + PCD by 4% when compared to sole PCD at 1 kWh $m^{-3}$ energy consumption. The oxidation resulted in 90-% reduction from the UF permeate concentration, which is only a 3-% improvement compared to oxidation of the raw sewage.

Reformation of progesterone and methylprednisolone was observed during the oxidation process; a phenomenon that has been observed for a few other pharmaceuticals earlier, where metabolites oxidize back to the parent compound. Similar behavior was observed for ibuprofen.

With the biologically treated wastewater effluent, a substantial effect in micropollutant removal was seen already at 0.1 kWh $m^{-3}$, and at 0.5 kWh $m^{-3}$ all the seventeen observed pharmaceuticals were oxidized below the limit of quantification. The result was more polished than as with the raw hospital wastewater sewage, due to the essentially lower concentrations of competing non-medical pollutants. The PCD efficiency in the raw sewage, however, is of emphasized importance as the volumes requiring treatment at such point source will obviously remain smaller and concentrations higher than those compiled at the influent of wastewater treatment sites. The non-selective pharmaceuticals reduction process will be inherently more efficient at locations of higher concentrations, leading to substantially reduced pharmaceutical load to the environment at the end of the pipe.

The capital cost assessment for the PCD treatment is unavailable currently for the absence of this technology at the market so far, the technology is developing at its piloting stage. Oxidative treatment, however, is a more final solution for micropollutants than e.g. adsorption redistributing the pollution for further handling of hazardous solid wastes.

## Funding

This study was conducted as part of the EPIC project (Efficient Treatment of Pharmaceutical Residues at Source) by the Finnish Funding Agency for Innovation, Tekes. S. Preis acknowledges funding from the Estonian Ministry of Education and Research, Project IUT 1-7 and Institutional Development Program of TUT for 2016-2022, Project 2014-2020.4.01.16-0032 financed by the EU Regional Development Fund.

## Declarations of interest

None.

## Acknowledgements

The authors would like to express their gratitude to Mr. Tuomas Nevalainen for his invaluable contribution in practical arrangements of the studies.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jece.2018.02.007.

## References

[1] I.T. Carvalho, L. Santos, Antibiotics in the aquatic environments: a review of the European scenario, Environ. Int. 94 (2016) 736–757.
[2] E. Prichard, E.F. Granek, Effects of pharmaceuticals and personal care products on marine organisms: from single-species studies to an ecosystem-based approach, Environ. Sci. Pollut. Res. Int. 23 (2016) 22365–22384.
[3] A. Joss, E. Keller, A.C. Alder, A. Göbel, C.S. McArdell, T. Ternes, H. Siegrist, Removal of pharmaceuticals and fragrances in biological wastewater treatment, Water Res. 39 (2005) 3139–3152.
[4] N. Vieno, T. Tuhkanen, L. Kronberg, Elimination of pharmaceuticals in sewage treatment plants in Finland, Water Res. 41 (2007) 1001–1012.
[5] A.C. Johnson, J.P. Sumpter, Removal of endocrine-disrupting chemicals in activated sludge treatment works, Environ. Sci. Technol. 35 (2001) 4697–4703.
[6] G. D'Ascenzo, A. Di Corcia, A. Gentili, R. Mancini, R. Mastropasqua, M. Nazzari, R. Samperi, Fate of natural estrogen conjugates in municipal sewage transport and treatment facilities, Sci. Total Environ. 302 (2003) 199–209.
[7] A. Talib, T.O. Randhir, Managing emerging contaminants: status, impacts and watershed-wide strategies, Expo Health 8 (2006) 143–158.
[8] L. Feng, E.D. van Hullebusch, M.A. Rodrigo, G. Esposito, M.A. Oturan, Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review, Chem. Eng. J. 228 (2013) 944–964.

[9] D. Kanakaraju, B.D. Glass, M. Oelgemöeller, Heterogeneous photocatalysis for pharmaceutical wastewater treatment, in: E. Lichtfouse, J. Schwarzbauer, D. Robert (Eds.), Green Materials for Energy, Products and Depollution, 3rd ed., Springer, Netherlands, 2013, pp. 69–133.

[10] T. Karpova, S. Preis, J. Kallas, Selective photocatalytic oxidation of steroid estrogens in water treatment: urea as co-pollutant, J. Hazard. Mater. 146 (2007) 465–471.

[11] A. Di Paola, E. García-Lopéz, G. Marcì, L. Palmisano, A survey of photocatalytic materials for environmental remediation, J. Hazard. Mater. 211 (2012) 3–29.

[12] J. Gomes, R. Costa, R.M. Quinta-Ferreira, R.C. Martins, Application of ozonation for pharmaceuticals and personal care products removal from water, Sci. Total Environ. 586 (2017) 265–283.

[13] A.D. Bokare, W. Choi, Review of iron-free fenton-like systems for activating $H_2O_2$ in advanced oxidation processes, J. Hazard. Mater. 275 (2014) 121–135.

[14] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402–417.

[15] D. Fatta-Kassinos, M.I. Vasquez, K. Kümmerer, Transformation products of pharmaceuticals in surface waters and wastewater formed during photolysis and advanced oxidation processes −degradation, elucidation of byproducts and assessment of their biological potency, Chemosphere 85 (2011) 693–709.

[16] W.H. Glaze, J. Kang, D.H. Chapin, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, Ozone: Sci. Eng. 9 (1987) 335–352.

[17] D. Gerrity, B.D. Stanford, R.A. Trenholm, S.A. Snyder, An evaluation of a pilot-scale nonthermal plasma advanced oxidation process for trace organic compound degradation, Water Res. 44 (2010) 493–504.

[18] I. Panorel, S. Preis, I. Kornev, H. Hatakka, M. Louhi-Kultanen, Oxidation of aqueous pharmaceuticals by pulsed corona discharge, Environ. Technol. 34 (2013) 923–930.

[19] M. Magureanu, N.B. Mandache, V.I. Parvulescu, Degradation of pharmaceutical compounds in water by non-thermal plasma treatment, Water Res. 81 (2015) 124–136.

[20] W.F.L.M. Hoeben, E.M. van Veldhuizen, W.R. Rutgers, G.M.W. Kroesen, Gas phase corona discharges for oxidation of phenol in an aqueous solution, J. Phys. D: Appl. Phys. 32 (1999) L133–L137.

[21] R. Banaschik, P. Lukes, H. Jablonowski, M.U. Hammer, K.D. Weltmann, J.F. Kolb, Potential of pulsed corona discharges generated in water for the degradation of persistent pharmaceutical residues, Water Res. 84 (2015) 127–135.

[22] P. Ajo P, E. Krzymyk, S. Preis, I. Kornev, L. Kronberg, M. Louhi-Kultanen, Pulsed corona discharge oxidation of aqueous carbamazepine micropollutant, Environ. Technol. 37 (2016) 2072–2081.

[23] J. Männynsalo, The Wastewater Treatment Plant of Rinnekoti Foundation, Espoo, Annual Summary of Operations and Emissions Monitoring 2015 (Finnish), The Water Protection Association of the River Vantaa and Helsinki Region, 2016.

[24] M. Stumpf, T.A. Ternes, R.D. Wilken, S.V. Rodrigues, W. Baumann, Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil, Sci. Total Environ. 225 (1999) 135–141.

[25] S. Preis, I. Panorel, I. Kornev, H. Hatakka, J. Kallas, Pulsed corona discharge: the role of ozone and hydroxyl radical in aqueous pollutants oxidation, Water Sci. Technol. 68 (2013) 1536–1542.

[26] L. Ferrando-Climent, N. Collado, G. Buttiglieri, M. Gros, I. Rodriguez-Roda, S. Rodriguez-Mozaz, D. Barceló, Comprehensive study of ibuprofen and its metabolites in activated sludge batch experiments and aquatic environment, Sci. Total Environ. 438 (2012) 404–413.

[27] A. Nehlig, J. Daval, G. Debry, Caffeine and the central nervous system: mechanisms of action, biochemical, metabolic and psychostimulant effects, Brain Res. Rev. 17 (1992) 139–170.

[28] J.J. Barone, H.R. Roberts, Caffeine consumption, Food Chem. Toxicol. 34 (1996) 119–129.

[29] F.J. Beltrán, Application of ozone involving advanced oxidation processes to remove some pharmaceutical compounds from urban wastewaters, Ozone: Sci. Eng. 34 (2012) 3–15.

[30] F. Siqueira Souza, L. Amaral Féris, Degradation of caffeine by advanced oxidative processes: $O_3$ and $O_3$/UV, Ozone: Sci. Eng. 37 (2015) 379–384.

[31] R. Broséus, S. Vincent, K. Aboulfadl, A. Daneshvar, S. Sauvé, B. Barbeau, M. Prévost, Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment, Water Res. 43 (2009) 4707–4717.

[32] O. Ganzenko, N. Oturan, D. Huguenot, E.D. van Hullebusch, G. Esposito, M.A. Oturan, Removal of psychoactive pharmaceutical caffeine from water by electro-Fenton process using BDD anode: effects of operating parameters on removal efficiency, Sep. Purif. Technol. 156 (2015) 987–995.

[33] Á. Encinas, F.J. Rivas, F.J. Beltrán, A. Oropesa, Combination of black-light photocatalysis and ozonation for emerging contaminants degradation in secondary effluents, Chem. Eng. Technol. 36 (2013) 492–499.

[34] A. Espejo, A. Aguinaco, A.M. Amat, F.J. Beltrán, Some ozone advanced oxidation processes to improve the biological removal of selected pharmaceutical contaminants from urban wastewater, J. Environ. Sci. Health A 49 (2014) 410–421.

[35] G. Márquez, E.M. Rodríguez, F.J. Beltrán, P.M. Álvarez, Solar photocatalytic ozonation of a mixture of pharmaceutical compounds in water, Chemosphere 113 (2014) 71–78.

[36] D.H. Quiñones, P.M. Álvarez, A. Rey, S. Contreras, F.J. Beltrán, Application of solar photocatalytic ozonation for the degradation of emerging contaminants in water in a pilot plant, Chem. Eng. J. 260 (2015) 399–410.

[37] J. Wang, Y. Sun, H. Jiang, J. Feng, Removal of caffeine from water by combining dielectric barrier discharge (DBD) plasma with goethite, J. Saudi Chem. Soc. 21 (2017) 545–557.

[38] R. Rosal, A. Rodríguez, J.A. Perdigón-Melón, A. Petre, E. García-Calvo, M.J. Gómez, A. Agüera, A.R. Fernández-Alba, Degradation of caffeine and identification of the transformation products generated by ozonation, Chemosphere 74 (2009) 825–831.

[39] J. Staehelin, J. Hoigne, Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, Environ. Sci. Technol. 16 (1982) 676–681.

[40] I. Panorel, S. Preis, I. Kornev, H. Hatakka, M. Louhi-Kultanen, Oxidation of aqueous paracetamol by pulsed corona discharge, Ozone: Sci. Eng. 35 (2013) 116–124.

[41] T. Bruton, A. Alboloushi, B. de la Garza, B.O. Kim, R.U. Halden, Fate of caffeine in the environment and ecotoxicological considerations, Contaminants of Emerging Concern in the Environment: Ecological and Human Health Considerations, American Chemical Society, 2010, pp. 257–273.

[42] K. Arola, H. Hatakka, M. Mänttäri, M. Kallioinen, Novel process concept alternatives for improved removal of micropollutants in wastewater treatment, Sep. Purif. Technol. 186 (2017) 333–341.

[43] T. Heberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, Toxicol. Lett. 131 (2002) 5–17.

[44] S. Kim, P. Eichhorn, J.N. Jensen, A.S. Weber, D.S. Aga, Removal of antibiotics in wastewater: effect of hydraulic and solid retention times on the fate of tetracycline in the activated sludge process, Environ. Sci. Technol. 39 (2005) 5816–5823.

[45] S. Holzbauer, T. Chiller, Antimicrobial resistance in bacteria of animal origin, Emerg. Infect. Dis. 12 (2006) 1180–1181.

[46] P. Verlicchi, E. Zambello, Pharmaceuticals and personal care products in untreated and treated sewage sludge: occurrence and environmental risk in the case of application on soil — a critical review, Sci. Total Environ. 538 (2015) 750–767.

[47] D. Klauson, J. Babkina, K. Stepanova, M. Krichevskaya, S. Preis, Aqueous photocatalytic oxidation of amoxicillin, Catal. Today 151 (2010) 39–45.

[48] A.J. Mota, G. Prados-Joya, D. Arráez-Román, M. Sánchez-Polo, R. Robles, M.Á. Ferro-García, J. Rivera-Utrilla, A convenient antibiotic indicator in the ozone treatment of wastewaters. An experimental and theoretical study, New J. Chem. 34 (2010) 2205–2212.

[49] M. Sánchez-Polo, J. Rivera-Utrilla, G. Prados-Joya, M.Á. Ferro-García, I. Bautista-Toledo, Removal of pharmaceutical compounds nitroimidazoles, from waters by using the ozone/carbon system, Water Res. 42 (2008) 4163–4171.

[50] A. Khataee, M. Kıranşan, S. Karaca, M. Sheydaei, Photocatalytic ozonation of metronidazole by synthesized zinc oxide nanoparticles immobilized on montmorillonite, J. Taiwan Inst. Chem. Eng. 74 (2017) 196–204.

[51] A. Fabregat, A. Kotronoulas, J. Marcos, J. Joglar, I. Alfonso, J. Segura, R. Ventura, O.J. Pozo, Detection, synthesis and characterization of metabolites of steroid hormones conjugated with cysteine, Steroids 78 (2013) 327–336.

[52] F.Z. Stanczyk, All progestins are not created equal, Steroids 68 (2003) 879–890.

[53] J.L. Sangster, J.M. Ali, D.D. Snow, A.S. Kolok, S.L. Bartelt-Hunt, Bioavailability and fate of sediment-associated progesterone in aquatic systems, Environ. Sci. Technol. 50 (2016) 4027–4036.

[54] D. Belelli, M.B. Bolger, K.W. Gee, Anticonvulsant profile of the progesterone metabolite 5α-pregnan-3α-ol-20-one, Eur. J. Pharmacol. 166 (1989) (1989) 325–329.

[55] O.J. Pozo, J. Marcos, X. Matabosch, R. Ventura, J. Segura, Using complementary mass spectrometric approaches for the determination of methylprednisolone metabolites in human urine, Rapid Commun. Mass Spectrom. 26 (2012) 541–553.

[56] I. Kornev, G. Osokin, A. Galanov, N. Yavorovskiy, S. Preis, Formation of nitrite- and nitrate-ions in aqueous solutions treated with pulsed electric discharges, Ozone: Sci. Eng. 35 (2013) 22–30.

# Publication IV

Ajo, P., Kornev, I., Preis, S.
**Pulsed Corona Discharge Induced Hydroxyl Radical Transfer Through the Gas-Liquid Interface**

*Scientific Reports*
Vol. 7, article number 16152, 2017

www.nature.com/scientificreports

SCIENTIFIC REPORTS

OPEN

# Pulsed Corona Discharge Induced Hydroxyl Radical Transfer Through the Gas-Liquid Interface

Received: 1 September 2017
Accepted: 9 November 2017

Petri Ajo[1], Iakov Kornev[2] & Sergei Preis[2]

**The highly energetic electrons in non-thermal plasma generated by gas phase pulsed corona discharge (PCD) produce hydroxyl (OH) radicals via collision reactions with water molecules. Previous work has established that OH radicals are formed at the plasma-liquid interface, making it an important location for the oxidation of aqueous pollutants. Here, by contacting water as aerosol with PCD plasma, it is shown that OH radicals are produced on the gas side of the interface, and not in the liquid phase. It is also demonstrated that the gas-liquid interfacial boundary poses a barrier for the OH radicals, one they need to cross for reactive affinity with dissolved components, and that this process requires a gaseous atomic H scavenger. For gaseous oxidation, a scavenger, oxygen in common cases, is an advantage but not a requirement. OH radical efficiency in liquid phase reactions is strongly temperature dependent as radical termination reaction rates increase with temperature.**

Atmospheric pressure non-thermal plasma technologies have been an on-going focus of research in water treatment over the last two decades. The most common laboratory-scale studies have included investigation of dielectric barrier discharge (DBD) and pulsed corona discharge (PCD), the latter forming the subject of discussion in this paper. Plasma treatment of water is chemically similar with traditional ozonation, as several oxidants are formed in plasma reactions from oxygen and water, including ozone $O_3$, hydroxyl radical OH, hydrogen peroxide $H_2O_2$, atomic oxygen $O(^3P)$ and singlet oxygen $O_2(^1\Delta_g)$. Of these, $O_3$ and OH are specially recognized as the major oxidants in plasma water treatment[1–5]. The latter is largely produced via inelastic electron collisions with water as in Eq. (1)[3]:

$$H_2O + e^- \rightarrow OH + H + e^- \quad (1)$$

For water treatment purposes, the gas-liquid interface where the OH radicals are formed is a crucial environment and the plasma-liquid contact surface area thus makes an important variable[4–6]. In earlier work, a vertical PCD reactor in which the treated solution is allowed to shower through a perforated plate positioned above the plasma zone was employed to generate a large plasma-liquid contact surface area[6]. Increasing this contact surface improves the oxidation energy efficiency mainly due to the enhanced action of superficial OH radicals[4,6]. Although OH radical activity at the plasma-liquid interface is evident, it is extinguished in complete absence of $O_2$[4]. So far this property, however, seems only observed with the present configuration; several other types of non-thermal plasmas applied in oxidation of aqueous organic compounds seem to have effect also in the absence of molecular $O_2$[7–11], suggesting that these processes include various mechanisms. The occurrence of such reports is understandably limited as in most water treatment studies the gas phase contains air for practical reasons, and thus $O_2$ at least as a partial constituent. Oxidation for example under Ar has shown similar efficiency with air[11], but papers describing oxidation under pure nitrogen plasma are scarce. More importantly, these reports tend to describe plasma discharge types that substantially differ from our PCD configuration.

It should be noted that here, the absence of $O_2$ does not suggest that Eq. (1) would be invalid under these circumstances. Instead, it is proposed in[4] that the atomic hydrogen H (a product in Eq. (1)) recombines with the OH radical in the absence of $O_2$, which is a strong H scavenger following Eq. (2)[5].

$$H + O_2 + M \rightarrow HO_2 + M \quad (2)$$

[1]School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, 53851, Lappeenranta, Finland. [2]School of Advanced Manufacturing Technologies, Tomsk Polytechnic University, 2A Lenina Ave., 634028, Tomsk, Russia. Correspondence and requests for materials should be addressed to P.A. (email: petri.ajo@lut.fi)

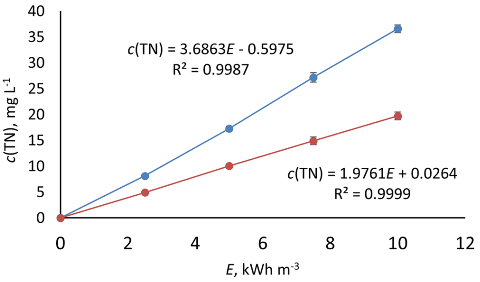


**Figure 1.** Average dissolved TN evolution in air (blue) and nitrogen (red) atmosphere during PCD oxidation. The experiments were conducted at 13, 20 and 30 °C and at pulse frequencies of 300, 500 and 833 pps. *E* = specific plasma energy dose.

In other words, OH radicals are not able to react with the dissolved species if H is not scavenged. It is, however, interesting to consider why OH radicals in this case are completely unreactive in the liquid phase without $O_2$, while they can be effective even in anaerobic natural waters[12]. In the present study, we address this problem by suggesting that OH radicals are formed only from water vapor and their transfer through the gas-liquid interface is the decisive process for successful oxidation of dissolved components. We arrive at this conclusion by describing: (i) OH radical oxidation of gaseous nitrogen and acetone without ambient $O_2$; (ii) zero oxidation of oxalic acid (OA) in the liquid phase in the absence of $O_2$; and (iii) demonstrating the temperature dependence of the possibility of the OH radical diffusing unreacted through the interface under air plasma. These observations provide essential information for the conceptualization of new PCD-based OH radical processes by enabling mapping of the kind of redox reactions that are achievable.

## Results and Discussion

Ambient plasma is known to result in oxidation of $N_2$, producing dissolved $NO_x$ in water treatment applications. In this study, the experiments showed temperature and pulse frequency as having no effect on the yield of $NO_x$ (per energy dose), measured as aqueous total nitrogen (TN). Since water vapor pressure increases with temperature, it would be reasonable to assume that the density of gaseous OH radicals would correlate with it. The observed temperature independence of $N_2$ oxidation is therefore very interesting, as it does not display any correlation to water vapor pressure, which at 13…30 °C ranges from 1.51 to 4.25 kPa.

In agreement with previous studies[13,14], the indifference towards pulse frequency indicates that only short-lived species present during and shortly after the pulses contributed to $NO_x$ formation (OH radical lifetime on water surface is ~2.7 μs[15], 1–2 orders of magnitude longer above the surface[5]). Under $N_2$, however, the TN formation rate at 1.98 g $kWh^{-1}$ was almost half that in air, 3.69 g $kWh^{-1}$. It should be noted that the yield in air is over twice the TN 1.77 g $kWh^{-1}$ calculated from $NO_3^-$ formation presented in[14], which is probably due to the water being introduced in aerosol form, rather than the previously applied showering approach, substantially increasing the gas-liquid contact area (see Experimental Methods). The dissolved TN evolution observed under $N_2$, i.e. in the absence of $O_2$, suggests OH radical induced oxidation taking place in the gas phase because simultaneously there was zero oxidation in the liquid phase, as will be discussed below. The difference in formation rates under air and $N_2$ indicates that nitrogen oxidation is supported by oxygen, which acts as a strong atomic H scavenger and contributes to the formation of strong oxidants. The evolution of TN concentration under air and $N_2$ is presented in Fig. 1. Since variation in the process parameters (temperature and pulse frequency) had no effect on TN formation rate against delivered energy, the values presented are averages of all experiments under a given atmosphere.

In agreement with previous findings[14], the dissolved TN in treatment under air was found to consist only of $NO_3^-$. Without oxygen, also $NO_2^-$ was identified, which may simply be explained by the absence of $O_3$ since dissolved $O_3$ readily oxidizes $NO_2^-$, producing mainly $NO_3^-$ and $O_2(^1\Delta_g)$[16].

The gas phase oxidation was confirmed with concentrated acetone solutions (17%); acetone oxidation under $N_2$ resulted in notable accumulation of dissolved oxidation products, acetic[17] and formic acid[18], during the treatment. The IC detector response for acetate and formate showed an increase consistent with delivered energy dose. Some inaccuracy of the acetate and formate concentrations may occur due to the partial overlapping of the chromatogram peaks (the chromatograms are presented in Supplementary Discussion 1). The evolution of the oxidation products, however, confirm the gas phase formation of OH radicals, whereas with the dissolved probe compound (OA), there was no indication of liquid phase OH radical activity under $N_2$ atmosphere (discussed further below). It should be noted that under these conditions, the presence of lower oxidation state $NO_x$ may enhance the OH induced oxidation process via secondary reactions[19], the extent of which may provide excellent topics for further research. The ion chromatograms of the acetone oxidation products with $NO_2^-$ and $NO_3^-$ are presented in Fig. 2.

Temperature and pulse frequency displayed consistent correlation with OA oxidation energy efficiency in the experiments conducted under air, the reaction rates exhibiting kinetic profile change from zero to first order along the decrease in both parameters from the highest to the lowest applied values, as can be seen in Fig. 3.

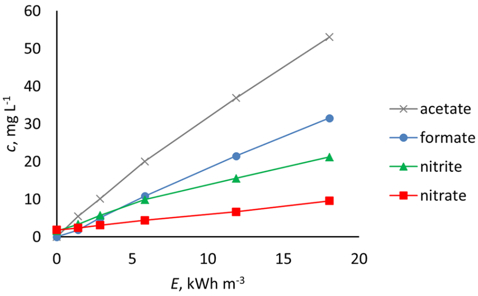


**Figure 2.** Oxidation product evolution in oxidation of 17% aqueous acetone under $N_2$.

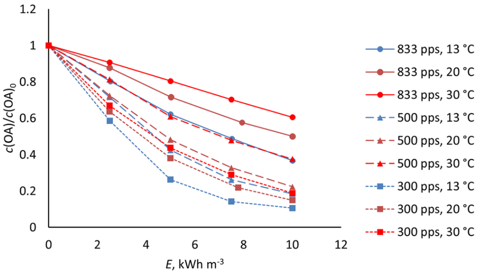


**Figure 3.** Oxalic acid oxidation at different temperatures and PCD pulse frequencies from initial concentration of 60 mg $L^{-1}$. $E$ = specific plasma energy dose.

The oxidation efficiency at 300 and 500 pps is at similar range while distinctly lower at 833 pps. The difference stems mainly from the role of $O_3$[6]. At equal energy doses, the amount of pulses and thus the amount of OH from Eq. (1) can be considered constant: the role of $O_3$ can then be considered from the difference in treatment times at different frequencies. The OA oxidation yield at 833 pps is almost halved from 13 to 30 °C, while its improvement when changing to 500 pps, attributable to longer treatment time, varies very little at any temperature, which emphasizes the temperature dependence of OH radical in the oxidation of the dissolved species (calculations in Supplementary Discussion 2).

By taking the reaction rates from the 0…5 kWh $m^{-3}$, wherein the degradation is practically linear in all cases (see Fig. 3), the frequency dependent decelerations of the OA oxidation rates caused by temperature increase can be directly visualized (Fig. 4).

Given the very low reactivity of $O_3$ and OA at low pH, the magnitude of the temperature effect seen in Fig. 4 - strong even at high pulse frequency - is largely attributed to OH radicals. For reference, at similar concentrations and pH, aqueous OA reduction by $O_3$ alone was reported in[20,21] as a maximum of ~10% for 30…60 min treatment. The applied $O_3$ concentration ranged from similar[20] to an order of magnitude higher[21] compared to our process[7]. Since formation of OH radicals is induced by electrons with ~3 orders of magnitude higher temperature than that of ions and molecules[22], the rate of it cannot practically be dependent on the gas temperature range in the current experiments. It can be therefore concluded that high temperature increases OH radical activity instead, which, however, results in decreasing the oxidation rates of dissolved components due to promotion of premature radical termination reactions. Several possibilities for these reactions are described in[23,24].

Under $N_2$, TOC remained unchanged i.e. zero oxidation for OA was observed at any combination of pulse frequency and applied temperature. The result is in agreement with earlier research, where even phenol remained unoxidized in PCD treatment without molecular oxygen[4]. The liquid phase OH radical formation testing by using $KMnO_4$ as an atomic H scavenger also yielded zero oxidation of OA, further demonstrating that no OH radicals are formed in the liquid phase, and that the radicals must therefore come from the gas side of the interface. During the treatment, the permanganate was gradually reduced to $Mn(IV)O_2$, which is an inevitable development due to the $NO_x$ formation. This development is presented in Supplementary Discussion 3. These findings extend and are supported by the report of Kanazawa *et al.*[5], where gas-phase OH radical formation and its dissolution into liquid phase are discussed and OH lifetime on water surface found to be substantially shorter than in humid air.

In summary, via simple experiments with a PCD plasma water treatment system under air and $N_2$, we have showed that although OH radicals are active also in the liquid phase, in the present kind of plasma-water interaction they are formed in the gas phase only (i.e. from water vapor), and that the gas-liquid interface is a major

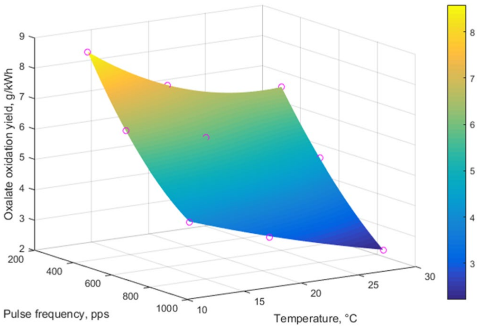


**Figure 4.** Oxalic acid reaction yield dependence on temperature and pulse frequency (zero order reaction 0…5 kWh $m^{-3}$).

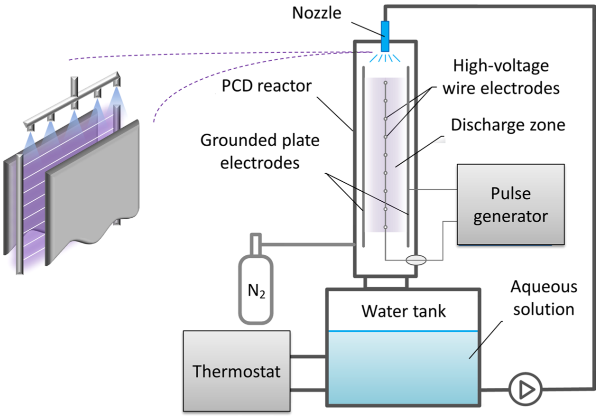


**Figure 5.** Top section of the PCD reactor with the atomizer array spraying the water into the plasma zone and a schematic illustration of the experimental configuration. The latter depicts a reactor view parallel to the electrodes.

barrier for the efficient utilization of the radicals in oxidation of aqueous compounds. The absence of atomic H scavengers in the gas phase promotes OH recombination with H, which is too fast for OH radicals to cross the gas-liquid interface boundary unreacted. Liquid-phase H scavenging does not enable OH induced oxidation, suggesting that no radicals are produced on the liquid side. In the absence of gaseous H scavengers, oxidation by OH still occurs in the gas phase because the radicals do not need to cross an interfacial boundary. Temperature increases OH radical reactivity, which hinders oxidation energy efficiency of dissolved compounds by promoting premature reactions, i.e. reactions occurring prior to successful transfer through the interface.

## Methods

The PCD reactor used is a vertical wire-plate configuration with a pulse generator adjustable to deliver identical pulses (22 kV and 180 A peak amplitude) at 50 to 833 pulses per second (pps) at corresponding nominal power of 6 to 100 W (0.12 J per pulse). Water was sprayed from above into direct contact with the plasma, using five axial-flow full cone atomizer nozzles, at volumetric flow rate of 1.8 L $min^{-1}$. Below the reactor is a tank holding the treated solution, a jacketed vessel coupled with a thermostat for adjusting the operating temperature. For experiments under $N_2$, oxygen absence was confirmed by measuring gas composition in the water tank head-space, using an oxygen analyzer (based on paramagnetic susceptibility measurements). The practical concept is illustrated in Fig. 5. A more detailed technical description of the PCD system (excluding the atomizer setup) and a pulse oscillogram can be found in our previous publication[6].

Oxalic acid (OA) concentrations were measured by analyzing the total organic carbon (TOC) concentrations (applying catalytic combustion at 680 °C) coupled with a total nitrogen (TN) unit for simultaneous TN analysis. Since OA has no organic oxidation products, i.e. is directly oxidized to $CO_2$, TOC corresponds directly to OA concentration. Similarly, in the experiments under air, TN value can be used to determine $NO_3$ concentrations since PCD yields no other dissolved $NO_x$ species under air, as mentioned above. Acetone oxidation products, formate and acetate, were observed using an ion chromatograph (IC) with an anion column. In the experiments under $N_2$ atmosphere, IC was also used to identify any presence of $NO_2^-$.

For the OH reactions with dissolved components, OA at 60 mg $L^{-1}$ (pH ~3.4) was used as the organic probe compound for favoring OH radical over $O_3$ reactions, following the low reactivity of OA with ozone ($k \leq 4 \cdot 10^{-2}\,M^{-1}\,s^{-1}$[25] at pH 5–6; for the reaction with OH $k = 5.3 \cdot 10^{6}\,M^{-1}\,s^{-1}$[26]), emphasized under acidic conditions. The experiments were conducted in 10 L batches and sampling was done at 2.5 kWh $m^{-3}$ intervals of discharge energy per treated water volume until 10 kWh $m^{-3}$. The experiments were carried out at three pulse frequencies, 300, 500 and 833 pps: due to the identic pulses, increasing frequency at fixed energy doses results in reduced treatment time, lower frequency therefore giving the longer living species, like $O_3$, more time to react with the probe compound. The experiments were conducted at temperatures of 13, 20 and 30 °C.

For the experiments under $N_2$, the system was flushed with $N_2$ until all oxygen was replaced. For these experiments, the treated solution was also degassed before introduction into the tank and kept running through the system under $N_2$ atmosphere for 40 minutes before starting the experiment to ensure negligible dissolved oxygen. $N_2$ inflow was kept at 7 L $min^{-1}$ throughout the experiments to ensure zero oxygen intake from ambient air. To ascertain whether OH radical formation in the liquid phase occurs, potassium permanganate KMn(VII)$O_4$ (0.1 mM) was used in a separate experiment as an atomic H scavenger in the dissolved phase. For any reaction following Eq. (1), the permanganate would not be oxidized by OH but instead serve as an oxidant for atomic H. Under $N_2$, thus scavenged atomic H in the liquid phase would enable OH radical reactions with OA. To exclude oxalate oxidation by permanganate, sodium oxalate was in this case used at neutral pH and at the lowest applied temperature of 13 °C, under which conditions permanganate is not reactive with oxalate.

Gas phase oxidation under $N_2$ was studied with a 17% acetone solution, exploiting the high volatility of the substance. Run under $N_2$ atmosphere, acetone was used to demonstrate organic species oxidation in the gas phase by OH radicals from water vapor, in the absence of $O_2$. The experimenting was conducted at 833 pps and 20 °C and acetone solution volume was reduced to 7 L for convenience, and the process overall duration was extended to 18.03 kWh $m^{-3}$ of delivered energy to highlight the observable effects.

**Data Availability.** The datasets generated during the current study are available from the corresponding author on reasonable request.

## References

1. Dobrin, D., Bradu, C., Magureanu, M., Mandache, N. B. & Parvulescu, V. I. Degradation of diclofenac in water using a pulsed corona discharge. *Chem. Eng. J.* **234**, 389–396 (2013).
2. Grabowski, L. R., van Veldhuizen, E. M., Pemen, A. J. M. & Rutgers, W. R. Corona above water reactor for systematic study of aqueous phenol degradation. *Plasma Chem. Plasma Process.* **26**, 3–17 (2006).
3. Ono, R. & Oda, T. Dynamics of ozone and OH radicals generated by pulsed corona discharge in humid-air flow reactor measured by laser spectroscopy. *J. Appl. Phys.* **93**, 5876–5882 (2003).
4. Preis, S., Panorel, I., Kornev, I., Hatakka, H. & Kallas, J. Pulsed corona discharge: the role of ozone and hydroxyl radical in aqueous pollutants oxidation. *Water Sci. Technol.* **68**, 1536–1542 (2013).
5. Kanazawa, S. *et al.* Observation of OH radicals produced by pulsed discharges on the surface of a liquid. *Plasma Sources Sci. Technol.* **20**, 034010 (2011).
6. Ajo, P., Kornev, I. & Preis, S. Pulsed corona discharge in water treatment: the effect of hydrodynamic conditions on oxidation energy efficiency. *Ind. Eng. Chem. Res.* **54**, 7452–7458 (2015).
7. Shen, Y., Lei, L., Zhang, X., Zhou, M. & Zhang, Y. Effect of various gases and chemical catalysts on phenol degradation pathways by pulsed electrical discharges. *J. Haz. Mat.* **150**, 713–722 (2008).
8. Zhang, Y., Zhou, M., Hao, X. & Lei, L. Degradation mechanisms of 4-chlorophenol in a novel gas–liquid hybrid discharge reactor by pulsed high voltage system with oxygen or nitrogen bubbling. *Chemosphere* **67**, 702–711 (2007).
9. Chandana, L., Reddy P, M. K. & Subrahmanyam, C. Atmospheric pressure non-thermal plasma jet for the degradation of methylene blue in aqueous medium. *Chem. Eng. J.* **282**, 116–122 (2015).
10. Hsieh, K. C., Wandell, R. J., Bresch, S. & Locke, B. R. Analysis of hydroxyl radical formation in a gas-liquid electrical discharge plasma reactor utilizing liquid and gaseous radical scavengers. *Plasma Process. Polym.* **14**, 1600171 (2017).
11. Hayashi, D. *et al.* Influence of gaseous atmosphere on corona-induced degradation of aqueous phenol. *J. Phys. D Appl. Phys.* **33**, 2769 (2000).
12. Vaughan, P. P. & Blough, N. V. Photochemical formation of hydroxyl radical by constituents of natural waters. *Environ. Sci. Technol.* **32**, 2947–2953 (1998).
13. Preis, S., Panorel, I., Llauger Coll, S. & Kornev, I. Formation of nitrates in aqueous solutions treated with pulsed corona discharge: the impact of organic pollutants. *Ozone: Sci. Eng.* **36**, 94–99 (2014).
14. Kornev, I., Osokin, G., Galanov, A., Yavorovskiy, N. & Preis, S. Formation of nitrite- and nitrate-ions in aqueous solutions treated with pulsed electric discharges. *Ozone: Sci. Eng.* **35**, 22–30 (2103).
15. Attri, P. *et al.* Generation mechanism of hydroxyl radical species and its lifetime prediction during the plasma-initiated ultraviolet (UV) photolysis. *Sci. Rep.* **5**, 9332 (2015).
16. Naumov, S., Mark, G., Jarocki, A. & von Sonntag, C. The reactions of nitrite ion with ozone in aqueous solution – new experimental data and quantum-chemical considerations. *Ozone: Sci. Eng.* **32**, 430–434 (2010).
17. Schaefer, T., Schindelka, J., Hoffmann, D. & Herrmann, H. Laboratory kinetic and mechanistic studies on the OH-initiated oxidation of acetone in aqueous solution. *J Phys Chem A.* **116**, 6317–6326 (2012).
18. Xu, W., Raftery, D. & Francisco, J. S. Effect of irradiation sources and oxygen concentration on the photocatalytic oxidation of 2-propanol and acetone studied by *in situ* FTIR. *J Phys Chem B.* **107**, 4537–4544 (2003).
19. Richards-Henderson, N., Goldstein, A. H. & Wilson, K. R. Large enhancement in the heterogeneous oxidation rate of organic aerosols by hydroxyl radicals in the presence of nitric oxide. *J Phys Chem Lett.* **6**, 4451–4455 (2015).
20. Huang, Y. *et al.* Removal of aqueous oxalic acid by heterogeneous catalytic ozonation with $MnO_x$/sewage sludge-derived activated carbon as catalysts. *Sci. Total Environ.* **575**, 50–57 (2017).

21. Jeirani, Z. & Soltan, J. Improved formulation of Fe-MCM-41 for catalytic ozonation of aqueous oxalic acid. *Chem. Eng. J.* **307**, 756–765 (2017).
22. Müller, S. & Zahn, R. Air pollution control by non-thermal plasma. *Contrib. Plasma Phys.* **47**, 520–529 (2007).
23. Ono, R. & Oda, T. Measurement of gas temperature and OH density in the afterglow of pulsed positive corona discharge. *J. Phys. D.* **41**, 035204 (2008).
24. Joshi, A. A., Locke, B. R., Arce, P. & Finney, W. C. Formation of hydroxyl radicals, hydrogen peroxide and aqueous electrons by pulsed streamer corona discharge in aqueous solution. *J. Haz. Mat.* **41**, 3–30 (1995).
25. Hoigné, J. & Bader, H. Rate constants of reactions of ozone with organic and inorganic compounds in water—II: dissociating organic compounds. *Water Res.* **17**, 185–194 (1983).
26. Getoff, N., Schwörer, F., Markovic, V. M., Sehested, K. & Nielsen, S. O. Pulse radiolysis of oxalic acid and oxalates. *J. Phys. Chem.* **75**, 749–755 (1971).

## Author Contributions

P.A. conducted the experimental part and wrote the body of the manuscript. I.K. and S.P. participated in the results analysis and experimental design, and writing the final version of the paper. All authors reviewed the manuscript.

## Additional Information

**Supplementary information** accompanies this paper at https://doi.org/10.1038/s41598-017-16333-1.

**Competing Interests:** The authors declare that they have no competing interests.

## ACTA UNIVERSITATIS LAPPEENRANTAENSIS

**754.** HUOTARI, PONTUS. Strategic interaction in platform-based markets: An agent-based simulation approach. 2017. Diss.

**755.** QU, BIN. Water chemistry and greenhouse gases emissions in the rivers of the "Third Pole" / Water Tower of Asia". 2017. Diss.

**756.** KARHU, PÄIVI. Cognitive ambidexterity: Examination of the cognitive dimension in decision-making dualities. 2017. Diss.

**757.** AGAFONOVA, OXANA. A numerical study of forest influences on the atmospheric boundary layer and wind turbines. 2017. Diss.

**758.** AZAM, RAHAMATHUNNISA MUHAMMAD. The study of chromium nitride coating by asymmetric bipolar pulsed DC reactive magnetron sputtering. 2017. Diss.

**759.** AHI, MOHAMADALI. Foreign market entry mode decision-making: Insights from real options reasoning. 2017. Diss.

**760.** AL HAMDI, ABDULLAH. Synthesis and comparison of the photocatalytic activities of antimony, iodide and rare earth metals on SnO2 for the photodegradation of phenol and its intermediates under UV, solar and visible light irradiations. 2017. Diss.

**761.** KAUTTO, JESSE. Evaluation of two pulping-based biorefinery concepts. 2017. Diss.

**762.** AFZALIFAR, ALI. Modelling nucleating flows of steam. 2017. Diss.

**763.** VANNINEN, HEINI. Micromultinationals - antecedents, processes and outcomes of the multinationalization of small- and medium-sized firms. 2017. Diss.

**764.** DEVIATKIN, IVAN. The role of waste pretreatment on the environmental sustainability of waste management. 2017. Diss.

**765.** TOGHYANI, AMIR. Effect of temperature on the shaping process of an extruded wood-plastic composite (WPC) profile in a novel post-production process. 2017. Diss.

**766.** LAAKKONEN, JUSSI. An approach for distinct information privacy risk assessment. 2017. Diss.

**767.** KASURINEN, HELI. Identifying the opportunities to develop holistically sustainable bioenergy business. 2017. Diss.

**768.** KESKISAARI, ANNA. The impact of recycled raw materials on the properties of wood-plastic composites. 2017. Diss.

**769.** JUKKA, MINNA. Perceptions of international buyer-supplier relational exchange. 2017. Diss.

**770.** BAYGILDINA, ELVIRA. Thermal load analysis and monitoring of doubly-fed wind power converters in low wind speed conditions. 2017. Diss.

**771.** STADE, SAM. Examination of the compaction of ultrafiltration membranes with ultrasonic time-domain reflectometry. 2017. Diss.

**772.** KOZLOVA, MARIIA. Analyzing the effects of a renewable energy support mechanism on investments under uncertainty: case of Russia. 2017. Diss.

**773.** KURAMA, ONESFOLE. Similarity based classification methods with different aggregation operators. 2017. Diss.

**774.** LYYTIKÄINEN, KATJA. Removal of xylan from birch kraft pulps and the effect of its removal on fiber properties, colloidal interactions and retention in papermaking. 2017. Diss.

**775.** GAFUROV, SALIMZHAN. Theoretical and experimental analysis of dynamic loading of a two-stage aircraft engine fuel pump and methods for its decreasing. 2017. Diss.

**776.** KULESHOV, DMITRII. Modelling the operation of short-term electricity market in Russia. 2017. Diss.

**777.** SAARI, JUSSI. Improving the effectiveness and profitability of thermal conversion of biomass. 2017. Diss.

**778.** ZHAO, FEIPING. Cross-linked chitosan and β-cyclodextrin as functional adsorbents in water treatment. 2017. Diss.

**779.** KORHONEN, ILKKA. Mobile sensor for measurements inside combustion chamber – preliminary study. 2017. Diss.

**780.** SIKIÖ, PÄIVI. Dynamical tree models for high Reynolds number turbulence applied in fluid-solid systems of 1D-space and time. 2017. Diss.

**781.** ROMANENKO, ALEKSEI. Study of inverter-induced bearing damage monitoring in variable-speed-driven motor systems. 2017. Diss.

**782.** SIPILÄ, JENNI. The many faces of ambivalence in the decision-making process. 2017. Diss.

**783.** HAN, MEI. Hydrodynamics and mass transfer in airlift bioreactors; experimental and numerical simulation analysis. 2017. Diss.

**784.** ESCALANTE, JOHN BRUZZO. Dynamic simulation of cross-country skiing. 2017. Diss.

**785.** NOKKA, JARKKO. Energy efficiency analyses of hybrid non-road mobile machinery by real-time virtual prototyping. 2018. Diss.

**786.** VUORIO, ANNA. Opportunity-specific entrepreneurial intentions in sustainable entrepreneurship. 2018. Diss.

**787.** PULKKINEN, AKI. Towards a better understanding of activity and selectivity trends involving K and O adsorption on selected metal surfaces. 2017. Diss.

**788.** ZHAO, WENLONG. Reliability based research on design, analysis and control of the remote handling maintenance system for fusion reactor. 2018. Diss.

**789.** IAKOVLEVA, EVGENIA. Novel sorbents from low-cost materials for water treatment. 2018. Diss.

**790.** KEDZIORA, DAMIAN. Service offshoring industry: systems engineering approach to its transitional challenges. 2018. Diss.

**791.** WU, JING. Soft computing methods for performance improvement of EAMA robot in fusion reactor application. 2018. Diss.

**792.** VOSTATEK, PAVEL. Blood vessel segmentation in the analysis of retinal and diaphragm images. 2018. Diss.

Acta Universitatis
Lappeenrantaensis
793

LUT
Lappeenranta
University of Technology

ISBN 978-952-335-212-4
ISBN 978-952-335-213-1 (PDF)
ISSN-L 1456-4491
ISSN 1456-4491
Lappeenranta 2018