



Alexander Sokolov

**PULSED CORONA DISCHARGE FOR WASTEWATER
TREATMENT AND MODIFICATION OF ORGANIC
MATERIALS**



Alexander Sokolov

PULSED CORONA DISCHARGE FOR WASTEWATER TREATMENT AND MODIFICATION OF ORGANIC MATERIALS

Dissertation for the degree of Doctor of Science (Technology), to be presented with due permission for public examination and criticism in the Auditorium 1318 at Lappeenranta-Lahti University of Technology LUT, Lappeenranta, Finland on the 2nd of July, 2019, at noon.

Acta Universitatis
Lappeenrantaensis 860

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

Dr. Eeva Jernström
LUT School of Engineering Science
Lappeenranta-Lahti University of Technology LUT
Finland

Reviewers Professor Cristina Paradisi
Department of Chemical Sciences
University of Padova
Italy

Professor Orlando J. Rojas
Department of Bioproducts and Biosystems
Aalto University
Finland

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

ISBN 978-952-335-390-9
ISBN 978-952-335-391-6 (PDF)
ISSN-L 1456-4491
ISSN 1456-4491

Lappeenranta-Lahti University of Technology LUT
LUT University Press 2019

Abstract

Alexander Sokolov

Pulsed corona discharge for wastewater treatment and modification of organic materials

Lappeenranta 2019

72 pages

Acta Universitatis Lappeenrantaensis 860

Diss. Lappeenranta-Lahti University of Technology LUT

ISBN 978-952-335-390-9, ISBN 978-952-335-391-6 (PDF), ISSN-L 1456-4491, ISSN 1456-4491

Sustainable development is one of the most important questions in the contemporary world. Wastewater treatment and the search for renewable sources of organic products are essential, not only in the future but also for present generations. The existing conventional methods used for wastewater treatment are not able to meet these challenges. There is an urgent need to develop new technologies. Advanced oxidation processes (AOPs), based on hydroxyl radical oxidation, are considered as an alternative. Gas-phase pulsed corona discharge (PCD) is one the AOPs, wherein active oxidants species, mainly OH radicals and ozone, are generated in situ from oxygen and water. This thesis is focused on research about the implementation of cold plasma technology, specifically PCD, for wastewater treatment and the modification of organic compounds.

Such a relative new threat for water usage as pharmaceuticals were the main target compounds for investigation. Pharmaceutical compounds are present in natural waters and their concentration is continuously growing as most of them, especially antibiotics, are not biodegradable and can pass through treatment facilities without degradation. Additionally, the applicability of PCD technology for thiosulfate abatement was studied. Thiosulfates are considered a potential replacement of hazardous cyanides in the leaching process of high-value metals. There are a lot of studies about it; however, water's purification from thiosulfates remains unexplored.

In order to remove pollutants from water in an efficient and environmentally safe manner, it is necessary to investigate the behaviour of the target compounds in the field of cold plasma. For this purpose, the formation of oxidation by-products and the degradation kinetics of target compounds were studied. The study took into account such parameters as pH, the initial concentration of the studied components, gas-phase composition, the water flow rate and the pulse repetition frequency. Particular attention was paid to the effect of the temperature of the treated solution on the oxidation process. Most of the studies about the implementation of electrical discharges for wastewater treatment have been done at ambient temperature, and experiments at lower or elevated temperatures have not been reported in the related literature.

Furthermore, a great number of studies reported in the literature are focused on research wherein only one component is dissolved in water, and aqueous solution systems with several components are little studied. Therefore, one of the objectives of this thesis was

to investigate the effect of the multicomponent system on the oxidation process. Energy efficiency was the main evaluation parameter of PCD performance.

In order to extend the potential application of cold plasma technology as a technology for the formation of value-added products, the thesis also includes a study about the treatment of lignin by PCD and its influence on lignin structure. Aldehyde formation was observed during the treatment and it was found that PCD considerably altered lignin structure and made it polymeric or oligomeric with a high number of carboxyl or carbonyl groups.

Most of the oxidation reactions of the studied pharmaceuticals can be described by an exponential function while the thiosulfate concentration decreases at a constant rate over time. Experiments with different temperatures have shown that temperature has no effect on reaction order. An elevated temperature of 50 °C significantly decreased the energy efficiency and reaction speed compared to 20 °C. No differences in oxidation efficiencies were observed between the results obtained at room temperature and at 10 °C. Increased pulse-repetition frequency significantly accelerates the oxidation process; however, the energy efficiency becomes lower at a higher frequency, except for the thiosulfate reactions. An atmosphere with a high oxygen content accelerates the oxidation process and contributes to less energy consumption. A low oxygen content leads to milder oxidation conditions and, along with a higher initial concentration of lignin, it is preferable for the conversion of lignin into aldehydes. The sulfamethizole reaction is not sensitive to pH changes while, in the case of other studied pharmaceuticals, pH has a significant impact. All the intermediates detected during the oxidation process were degraded by the end of the treatment, and the qualitative composition of oxidation by-products does not depend on whether the system is single- or multicomponent.

Keywords: wastewater treatment, non-thermal plasma, electrical discharge, advanced oxidation processes, pharmaceuticals, lignin, hydroxyl radicals, ozone, kinetic, energy efficiency, temperature.

Acknowledgements

The research documented in this thesis was carried out in the School of Engineering Science of Lappeenranta-Lahti University of Technology LUT. Part of the study was carried out within the framework of the Exploiting Municipal and Industrial Residues (EMIR) project. I would like to acknowledge the financial support received from Maa- ja vesitekniikan tuki ry, LUT Doctoral School, the Graduate School in Chemical Engineering and the Finnish Foundation for Technology Promotion (TES).

First of all, I would like to express my thanks to my supervisors, Marjatta Louhi-Kultanen and Eeva Jernström, for valuable guidance and support during my doctoral study. I would also like to express my gratitude to Sergei Preis, who acted as my supervisor at the beginning of my journey.

There are a lot of people without whom my research would not have been accomplished. Thanks to our analytical team, led by Liisa Puro (Liisa, your strict safety rules are going to stay with me forever), and thanks to Anne Martinen, Judy Hyvönen and Mari Toitturi, they were always ready to help with administrative formalities. I want to send my appreciation to Markku Maijanen for his help and assistance with experimental set-ups at earlier stages of my work. I appreciate Petri Ajo – his activity and passion for science did not let me stop and helped me to reach the final goal.

I want to thank all the students I taught and with whom I worked in the laboratory. I really hope I managed to teach them something useful because I learned a lot from them.

Some of the experiments were carried out at the University of Tor Vergata, Rome, Italy, within the framework of the COST Action FP 1105 programme. I want to thank all the people I had an opportunity to work with during my visit to Italy, in particular I would like to thank Claudia Crestini and Heiko Lange for their hospitality and fruitful cooperation.

I want to thank my colleagues from Åbo Akademi University, Matilda Kråkström, Patrik Eklund and Lucas Lagerquist, for their contribution to my work.

Special thanks go to Peter Jones who helped me to convert my broken scientific English into proper and understandable language.

Some special words of gratitude go to my friends: Sergey V., Mikhail S., Polina B., Alexander S., Ludmila S., Nikita U., Maria U., Pavel P., Maria P., Dmitry S. and Marina A.. Thank you for the endless motivation that you always gave to me (I know people usually call it *trolling*, but I prefer the word *motivation*). I am really happy that life gave me an opportunity to be with all of you. I am sure we are going to keep in touch no matter where we are now and where we are going to be in the future.

A PhD is a big and difficult project, but a more difficult project was the project of raising me. Mom and Dad, despite all the difficulties, you managed to make me the man I am today. I am deeply grateful to you.

Nobody has been more important to me in the pursuit of this research than my lovely wife, Ekaterina. She is The Woman who has always supported me and she will stand by me in the future, I am sure. Thank you, Katya for your love.

A handwritten signature in blue ink, appearing to read 'Alex Sokolov', with a large, stylized initial 'A'.

Alexander Sokolov
July 2019, Lappeenranta, Finland

Посвящается моим родителям

*Соколову Герману Дмитриевичу
Соколовой Ирине Александровне*

*This work is dedicated to my parents
Sokolov German Dmitrievich
Sokolova Irina Alexandrovna*

Contents

Abstract

Acknowledgements

Contents

List of publications	11
Nomenclature	13
1 Introduction	15
1.1 Background	15
1.2 Problem statement	17
1.3 Objectives	17
1.4 Outline of the thesis	18
2 Electrical discharge for wastewater treatment	19
2.1 Corona discharge reactors	19
2.2 Reaction mechanisms and physical processes	21
2.2.1 Formation of molecular and radical species.	21
2.2.2 UV light and shockwave	23
2.3 Factors affecting process efficiency	23
2.3.1 Reactor design	23
2.3.2 Energy input	24
2.3.3 pH and conductivity	24
2.3.4 Temperature	25
2.3.5 Target compound	25
3 Materials and methods	27
3.1 Materials	27
3.2 Experimental setup	27
3.3 Analytical part	29
3.4 Experimental procedure	30
3.5 Energy efficiency	32
3.6 Reaction kinetics	33
4 Results and discussion	35
4.1 Kinetics	35
4.2 Energy efficiency	41
4.3 Temperature effect	47
4.4 Multicomponent system.	49
4.5 Oxidation by-products	50
4.6 Lignin modification	55

5 Conclusions	59
References	61
Appendix A: Figures. Concentration vs delivered energy	69
Publications	

List of publications

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

- I. Sokolov, A., Kråkström, M., Eklund, P., Kronberg, L., and Louhi-Kultanen, M. (2018). Abatement of amoxicillin and doxycycline in binary and ternary aqueous solutions by gas-phase pulsed corona discharge oxidation. *Chemical Engineering Journal*, 334, pp. 673–681.
- II. Sokolov, A., and Louhi-Kultanen, M. (2018). Behaviour of aqueous sulfamethizole solution and temperature effects in cold plasma oxidation treatment. *Scientific Reports*, 8, 8734.
- III. Sokolov, A., Lagerquist, L., Eklund P., and Louhi-Kultanen, M. (2018). Non-thermal gas-phase pulsed corona discharge for lignin modification. *Chemical Engineering and Processing: Process Intensification*, 126, pp. 141–149.

The author's contribution

Alexander Sokolov is the principal and corresponding author in Publications I–III, responsible for the greater number of the experiments and calculations. Matilda Kråkström conducted the analyses of transformation by-products in Publications I and II. In Publication III Lucas Lagerquist carried out some of the lignin analyses.

Nomenclature

Symbols

C	reactant concentration	ppm, mg/L
E	delivered energy dose	Wh/m ³
f	pulse-repetition frequency	pulses per secon (pps)
k_1	first-order reaction rate constant	min ⁻¹
k_2	second-order reaction rate constant	m ³ J ⁻¹ , L
m	mass	kg
P	discharge power	W
R	compound removal	%
T	temperature of the liquid phase	°C
T_p	pulse duration	ns
t	treatment time	min
$t_{1/2}$	half-life treatment time	min
V_{pl}	total plasma volume	m ³
V	volume of treated liquid	m/s
W_p	single pulse energy	J
ε	energy efficiency	g/kWh
$\varepsilon_{1/2}$	half-life energy efficiency	g/kWh
ε_{final}	final energy efficiency	g/kWh

Abbreviations

AMX	amoxicillin
AMX-C1	OH amoxicillin
AMX-C2	amoxicillin penicilloic acid
AOP	advanced oxidation processes
BLN	birch lignin
DXC	doxycycline
DXC-C1	OH doxycycline
DXC-C2	2-OH doxycycline
GPC	gel permeation chromatography
HPLC	high-performance liquid chromatography
HPSEC	high-performance size exclusion liquid chromatography
HSQC	heteronuclear single-quantum coherence
HV	high voltage
MAA	meglumine acridonacetate
NMR	nuclear magnetic resonance
PCD	pulsed corona discharge
PDBD	pulsed dielectric barrier discharge
RQ	risk quotient
SMX	sulfamethizole

1 Introduction

1.1 Background

Green chemistry and energy, recovering, biorefining, water purification and sustainable development are the key fields of research and investments these days and they will be in the future. In this regard, it is very important to make every effort to work in these fields. The purification of wastewater is becoming more and more important nowadays. Industrialisation, as well as the significant increase in population, leads to increases in disposal pollutants entering water bodies. Conventional methods used for wastewater treatment are not able to effectively remove many classes of pollutants, especially refractory and toxic compounds, such as pharmaceuticals, especially antibiotics [1, 2]. Ozonation has high removal efficiency regarding any organics, including pharmaceuticals [3]. However, ozonation remains an expensive method and this makes it economically unviable [4].

Using advanced oxidation processes (AOP) as an alternative to these methods is attracting more and more of the attention of researchers. The production of hydroxyl radicals in a sufficient amount for the chemical oxidation of organics and inorganics contaminants under ambient conditions is the main feature of advanced oxidation processes [5]. AOPs implemented for wastewater treatment usually include the Fenton process, UV radiation, hydrogen peroxide oxidation, photochemical and electrochemical oxidation, and the combination of these methods. One of the main advantages of AOPs is the suitability of these processes for water purification that involves direct human contact, for example, house wastewater reuse.

Electrical plasma technology is one of the AOPs, and the implementation of this technology for wastewater treatment is of great interest due to its environmental integrity, high degree of water purification and its energy efficiency. This technology combines several chemical and physical processes: the generation of oxidising species and the formation of shockwaves, electrohydraulic cavitation and ultraviolet light [6–8].

Plasma can be generated by various types of electrical discharges generated either directly in water or above the water surface. Consequently, a large variety of reactors and electrode configurations have been used. Several studies were made on the degradation of organic pollutants by corona discharges [7–9]. Some other studies involving ultra-short, gas-phase pulsed corona discharge (PCD) and pulsed dielectric barrier discharge (PDBD) [10, 11] effectively showed the generation of OH radicals in humid gas and concluded that these processes are a viable means of oxidising air pollutants. It is known that PDBD shows lower efficiency in the oxidation of refractory and toxic compounds compared to PCD. In the PCD method, the discharge is generated in the gas space between non-insulated electrodes. The absence of insulation makes the voltage applied to the electrodes work on the formation of active oxidative species in the inter-electrode gap

instead of charging the insulation. This makes the PCD method a very competitive technique among the AOPs for water treatment.

The oxidation of organics is a difficult and multi-stage process and can lead to the formation of by-products which are more toxic than parent compounds. For example, the ozone doses used in traditional ozonation are not enough for the removal of these products [12, 13]. However, the appearance of intermediates during oxidation offers opportunities for the formation of value-added products from waste. In this respect, one of the most interesting compounds is lignin. Lignin is one of the most abundant polymers, extracted by a cooking process in the pulp industry and mainly used for energy recover via burning. Lignin is a polymeric compound consisting of phenolpropane structural units and has the potential to become a raw material for the production of various products (phenolic substances and aromatic aldehydes). Attempts to form aldehydes from lignin using PCD have been made earlier, but the lignin-to-aldehydes conversion rate was insignificant [17]. It is still unknown what happens to the lignin's structure in the field of plasma. The knowledge about structural changes to lignin in the field of cold plasma will help to optimise the conversion of lignin into a value-added product.

The range of PCD implementation is not limited to organic oxidation. The scope of the current study also includes unpublished material about the oxidation of an aqueous solution of thiosulfate. A lot of research has been made regarding the implementation of thiosulfate leaching instead of hazardous cyanide leaching [18,19]. However, the presence of thiosulfates in water is not acceptable as it leads to the corrosion of sewer pipes, eutrophication, silting and hydrogen sulphide formation [20]. The removal of thiosulfates from water has received less attention from scientists. Sulphur compounds are usually removed by oxidation (chemical or biological oxidation). There are some studies about the oxidation of sulphur compounds in the presence of catalysts. However, these catalysts are poisonous and hazardous, and their complete recovery after treatment is essential [21]. Photo-oxidation has also been studied, but in the absence of catalysts, the process requires high energy consumption. That is not economically suitable for a large continuous wastewater treatment process [13]. Thiosulfate oxidation by ozone can solve the problem. Oxidation with ozone is rapid, and the complete decomposition of thiosulfate can be reached without undesirable by-products. However, ozonation remains expensive; the high cost of ozone limits the application of ozonation.

Oxidation by PCD is also rapid, and no by-products are expected at the end of the treatment. PCD technology is superior to ozonation due to the higher energy efficiency and lower capital investment cost. However, oxidation of thiosulfates by PCD is an unknown process – nobody has tried it before. The objective of this research question is to investigate the possibility of the implementation of PCD for thiosulfate oxidation and the optimisation of the experiment conditions in order to increase energy efficiency.

1.2 Problem statement

It is well known that pharmaceuticals are present in natural water and their concentration is steadily growing, especially in recent years [22]. Increasing the concentration is conditioned by three main factors: (i) the rapid growth of the global consumption of pharmaceutical compounds [23], (ii) the absence of legislation specifically addressing the discharge of wastewaters containing pharmaceuticals into water bodies [24] and (iii) the incapability of existing municipal wastewater treatment facilities to effectively remove medical drugs from water, especially refractory compounds such as antibiotics, and as a result, the accumulation of these compounds in water bodies [1, 2].

The greater number of studies related to pharmaceutical abatement from water by AOPs are carried out with a single compound while the multicomponent system, as well as the effect of one compound on another, is not studied comprehensively. The question of how the temperature affects oxidation in the field of cold plasma also remains largely unanswered. Mainly, when referring to AOPs and especially to AOPs based on electric discharges, it is assumed that the treatment process proceeds at the ambient temperature of water. In the laboratory scale it is usually around 20 °C, but in real conditions the initial temperature of water can vary from 0 °C to 50 °C, for instance due to seasonal variations or in industrial processes.

Based on previous research, the PCD method proved to be an efficient method for the abatement of not only organic compounds but also various inorganic compounds. The removal of thiosulfates from water has received less attention from scientists, and there were no attempts to implement an electrical discharge technology in the purification of water from thiosulfates.

Experiments have also showed that PCD can be used for the formation of value-added products from waste, specifically the formation of aldehydes from lignin. However, the mechanism of conducting the oxidation process by PCD remains uninvestigated.

1.3 Objectives

The main objective of the thesis is to extend the potential application of cold plasma technology, specifically gas-phase PCD, by addressing the following research questions:

- What is the behaviour of pharmaceuticals in the cold plasma field?
- Does the water temperature have any effect on the oxidation process?
- How does the presence of more than one pharmaceutical compound in the water influence the oxidation process in the PCD reactor?
- What happens to the lignin structure during oxidation by PCD? Can this technology be implemented for lignin's conversion into aldehydes?
- Can we use PCD to remove thiosulfates from water?

1.4 Outline of the thesis

This thesis consists of three international publications in peer-reviewed journals and unpublished earlier material. The thesis comprises three main chapters. Chapter 2 provides the basic knowledge about using electrical technology as an AOP for wastewater treatment. This chapter describes the types of reactors and the main reaction mechanisms and processes, as well as the main factors influencing the processes. Chapter 2 mainly focuses on corona discharge reactors since a corona discharge reactor was used in this work. Chapter 3 presents the description of the experimental set-up, experimental procedure and analysis, as well as ways of calculating the main process evaluation parameters. Chapter 4 provides and discusses the results from all the experiments.

2 Electrical discharge for wastewater treatment

As was mentioned earlier, the conventional water treatment systems are not able to efficiently remove contamination, especially emerging contaminants. In regard to this, AOPs are attracting more and more attention. Over the last past few years, the pattern of the implementation of plasma technology caused by electric discharges has been subjected to considerable scrutiny.

The plasma technology implemented for water treatment includes different chemical and physical processes, such as the formation of oxidising species, UV light, shock waves and electrohydraulic cavitation [6–8]. Therefore, it is possible to say that plasma technology for wastewater treatment combines several AOPs.

Traditionally plasma methods can be divided into two groups: thermal plasma and non-thermal plasma methods, also named as cold plasma [8]. Non-thermal plasma is a plasma which is not in thermodynamic equilibrium and formed with less delivered energy while thermal plasma is associated with high electrical energy. In the case of thermal plasma, a high flux of heat is created, and it can be used for the remediation of the most recalcitrant waste. However, the non-thermal plasma is a more common technology for wastewater treatment due to the low energy consumption, and safer and more reliable operation [25].

2.1 Corona discharge reactors

A corona discharge itself is a relatively low power electrical discharge that occurs at near atmospheric pressure. The typical geometry of a corona discharge reactor has two electrodes: one is flat or has small curvature, the other is an electrode with high curvature. In such a configuration, a uniform electric field is generated on the curved electrode and induces a high potential gradient, therefore the corona inception voltage is reduced. The form of corona discharge depends on the polarity of the field and configuration of the electrodes. In the case of a negative corona, in the point-plate electrode configuration, discharges start with the Trichel pulse corona and proceed to a pulseless corona and spark discharge as the applied voltage increases. For a positive corona in the same electrode configuration, the initial form of discharge is the burst pulse corona, followed by the streamer corona, glow corona and spark discharge as the applying voltage increases. If the wire-plate configuration is in use, a negative corona discharge may have the form of a general, rapidly moving glow or it may be concentrated into small, active “tufts” or “beads”. A positive corona discharge may take the form of a streamer moving away from the electrode or it can appear as a tight sheath around the electrode [26].

Pulsed corona reactors equipped with a pulsed electric generator create a sharp high voltage pulse with a micro- or nanosecond range-duration time. Contrary to the pulsed electrical corona, a DC corona can continuously generate radical species, but on the other hand, it is significantly affected by water conductivity and the energy consumption is higher. Among all the configurations of pulsed corona reactors, the point-plate

configuration is the most studied. Usually, such a configuration includes a needle [27] or a set of needles as high voltage electrodes [28], placed some distance from a grounded plate. There are a lot of options for the electrodes' location. For example, either both electrodes can be immersed in treated water or one electrode can be installed above the water. In the first case, oxidative species are generated in liquid and directly interact with target compounds. However, according to Locke and Thagard, mass and heat transport in the liquid has a low rate and leads to a sharp gradient in temperature and concentration between the bulk solution and plasma zone. Only around 10 % of the formed radicals spread into the bulk solution to react with target compounds [29]. Jiang et al. reported the same difficulties in the case of the configuration, wherein a high voltage needle electrode is located above the water surface and a grounded plate is submerged in liquid. All active species are generated in the gas phase and react with target compounds after diffusion into the liquid phase [28]. If the electrodes are rearranged, the grounded electrode is above the water and the high voltage electrodes are under the water surface; in this case, active species are generated in the liquid as before, and additionally to that, active species, especially ozone (under an oxygen-containing atmosphere), are formed above the water in the gas phase. As a result, the process of organic abatement became more effective [30].

Despite the prevalence of studies about point-plate reactors, the implementation of such a configuration on a bigger scale is problematic. From the industry point of view, one-dimensional electrodes (wire electrodes) are preferable as they allow for creating a bigger and more uniform distribution of the plasma zone [31]. One of the pioneers in the development of wire electrode reactors was Sano's research group. Originally they proposed a multiple above-liquid wire-plate reactor with a continuous water flow [32]. Later they designed a wire-cylinder reactor with wetted walls, which allows purifying not only water but also air [28, 29]. Also noteworthy is the reactor design proposed by Njatawidjaja et al. It is an electrostatically atomised ring-mesh reactor, consisting of two parts: an electrostatic atomisation part and a corona discharge part [35]. The polluted water goes from the top of the reactor through these parts. In the beginning, a large number of droplets are formed in the first part, thereby increasing a pollutant's exposure to reaction with oxidative species, which takes place in the corona discharge zone. However, in order to provide enough residence time for total pollutant removal in one pass, a long length of time in the reactor is required. This is one of the main drawbacks of this configuration, which is not attractive from the industrial perspective. The aerosol reactor proposed by Bystritskii et al. [36] and further explored by Grabowski [37] and Pokryvailo et al. [38] solves this problem. Contaminated liquid is supplied to the reactor through an atomizing nozzle and treated by a pulsed corona. The implementation of atomising nozzles increases the surface-to-volume ratio, which in turn leads to an intensification of the purification process. The maximum load of such a reactor depends on the number of nozzles. Grabowski managed to reach 200 L/h by installing four nozzles.

The simpler and more convenient configuration of a pulsed corona reactor was studied by Panorel et al. [9, 14, 34, 35], Preis et al. [36, 37] and Kornev et al. [38, 39]. A similar

reactor configuration was used in the current work. A detailed description of the reactor is given in Section 3.2.

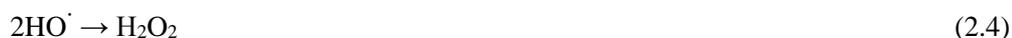
Summing up, it is possible to divide electrical discharge reactors into three groups, depending on the distribution of the plasma phase: reactors with electrical discharge above the liquid surface, reactors with electrical discharge under the liquid surface and reactors with electrical discharges in vapour or bubbles in liquids.

2.2 Reaction mechanisms and physical processes

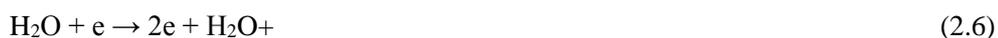
All of the types of reactors described in Section 2.1 combine a number of common physical processes and chemical reactions, which are summarised below.

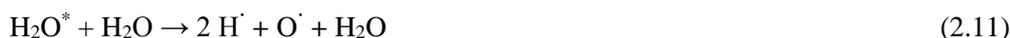
2.2.1 Formation of molecular and radical species

Hydroxyl radicals are the strongest and the main oxidising species in AOPs. The reaction of these radicals with organics has three main mechanisms: the abstraction of the hydrogen atom (Eq. 2.1), electrophilic addition to an unsaturated bond (Eq. 2.2) and electron transfer (Eq. 2.3). Hydrogen abstraction is a primary pathway for organic degradation in the case of saturated aliphatic hydrocarbons or alcohols. In the case of olefins or aromatic hydrocarbons, adding a hydroxyl radical to the unsaturated double carbon-carbon bonds of organics leads to the formation of a C-centred radical with a hydroxyl group at the α -C atom. The reduction of hydroxyl radicals to hydroxide anions by an organic substrate might be of interest in the case where hydrogen abstraction or electrophilic addition reactions are disfavoured by multiple halogen substitution or steric hindrance. It should be noted that the increase in the concentration of hydroxyl ions leads to radical recombination as hydrogen peroxide (Eq. 2.4) [45].



Hydroxyl radicals are formed by discharge in the presence of water via dissociation (Eq. 2.5), ionization (Eq. 2.6, 2.7) and vibration/rotation excitation of water molecules (Eq. 2.8). Rotationally or vibrationally excited molecules then transition into a lower energetic state, and some active radicals may be formed (Eq. 2.9–2.11)[46].





Other important species are O-based species. The presence of oxygen in the electrical discharge process leads to the formation of an O atom via the dissociation of O₂. This atom can accelerate hydroxyl radicals' formation (Eq. 2.12), directly react with target compounds and, most interestingly, react with O₂ in the formation of ozone [47]:



Ozone is a strong oxidant. Ozone can directly react with a target compound and indirectly via the formation of OH radicals when it decomposes in water. Ozone directly reacts with metal ions better if it acts as an electron transfer acceptor. With activated aromatics, ozone has an electrophilic reaction in which it behaves as a dipole addition reagent by its addition to C–C multiple bonds [48]. Ozone is not stable and has a tendency to decompose through a cyclic chain mechanism, yielding hydroxyl radicals in neutral and alkaline media. Additionally, in the case of the presence of H₂O₂, ozone can react with HO₂[−], producing hydroxyl radicals (Eq. 2.13, 2.14) [47,49]:



Hydrogen peroxide is not a primary oxidizing species, and it does not react with organics sufficiently for water treatment. However, hydrogen peroxide has a significant effect on plasma chemistry; its presence increases the formation of OH radicals via various reactions, such as photolysis, dissociation and metal-based catalytic reactions. The most tangible impact H₂O₂ has is found in the case of underwater plasma [46].

The degradation of contaminants can also occur via reductive degradation pathways in the presence of reductive species. For example, an aqueous electron can be generated by the irradiation of water with high energy electrons, and because of its high electron affinity, it plays a valuable role in the removal of contaminants from water [50]. Other important species are H radicals, which typically have two reaction mechanisms with organics: hydrogen abstraction from saturated compounds and hydrogen addition to an unsaturated bond. They are mainly produced by electron collision with molecules of water and also by the interaction of hydrated electrons and acids [51].

2.2.2 UV light and shockwaves

There is always UV light in plasma-water systems due to the relaxation of excited species into lower energetic states (Eq. 2.15). Under the UV irradiation an organic molecule (M) absorbs radiation and becomes excited (M^*). Because of the short lifetime of the excited molecule, it immediately decomposes into a new molecule (M_n) [52]:



Photolytic degradation is not the only pathway for organic decomposition. It can dissociate the hydrogen peroxide and ozone, forming hydroxyl radicals [53].

A shockwave can appear if high electric energy is introduced directly to the water. Usually, there is no shockwave in gas-phase reactors, but plasma in a gas-phase atmosphere has an effect on liquid motion, depending on the plasma generation situation. In turn, the shockwave has an influence on the chemical reactions in a liquid via electrohydraulic cavitation; more active species, such as hydrogen peroxide and OH radicals, can be produced in the liquid via the water dissociation caused by the shockwave [54].

2.3 Factors affecting process efficiency

A short list of the most significant factors which have an effect on the wastewater treatment process by pulsed electrical discharge is set out below:

- reactor design
- energy input
- pH
- conductivity
- temperature
- gas input
- the target compound

2.3.1 Reactor design

The main goal in the reactor design is to ensure the maximum energy utilisation and plasma-water contact surface at a given energy input. The design of electrodes, their materials and a mutual bracing combination are some of the main parameters in regard to this. Section 2.1 mentioned the most commonly used types of electrodes, their location regarding the water surface and the fact that one-dimensional electrodes are preferable to zero dimensional electrodes from an industrial implementation point of view. Also of note is the distance between the electrodes as it has a huge effect on plasma generation. It is possible to decrease the discharge inception voltage by narrowing the gap between

high voltage electrodes. However, too small a gap leads to a reduction in the volume of plasma generation, which in turn decreases the plasma–water contact surface. The optimal gap distance depends on various factors, and it is usually necessary to adjust each reactor individually. For example, in the current work, due to the implementation of non-insulated electrodes and pulsed power, it was possible to increase the gap distance between electrodes compared with pulse double barrier discharge, which increased the volume of the plasma zone.

Another important issue is the electrode material. Electrode materials have a significant effect on chemical processes in a plasma reactor due to erosion, especially in the case of electrical discharge in water. Erosion limits the operating lifetime and even leads to the pollution of treated water with metal particles released from the electrodes. When platinum is used as a high voltage electrode, it is the least-eroded material and also has the ability to promote organics removal from water due to a catalytic effect. On the other hand, platinum electrodes reduce the yield of H_2 , H_2O_2 and O_2 [55].

2.3.2 Energy input

The dependency of organic degradation on the energy input is one of the main factors that determine the efficiency of plasma reactors. Usually, the increased electron density means more HO^\cdot , O^\cdot , H_2O_2 and O_3 are formed. Moreover, the higher energy input leads to an intensification of physical effects, leading to an increase in the organic removal rate. The energy input can be adjusted by changing the pulse-repetition frequency or by the voltage changing. Of course, a higher energy input means higher energy consumption. In general, it is not possible to simultaneously get the best pollutant degradation efficiency and the best energy efficiency. Therefore, when estimating an electrical discharge technology for wastewater treatment, two parameters are usually taken into account: compound removal (%) and energy efficiency (g/kWh).

2.3.3 pH and conductivity

A lot of studies have been made about the effect of solution pH on the electrical discharge process. It is known that OH^\cdot emission increases in neutral and alkaline media [56]. In strongly alkaline media, hydroxyl radicals can be rapidly converted into O^\cdot . It acts as a nucleophile in reaction with organics while OH^\cdot behaves as an electrophile that gives an opportunity for different reaction pathways and the formation of different intermediates. It is also known that during the oxidation process in a plasma reactor, pH decreases due to organic compounds degradation into organic acids [50, 51].

Solution conductivity is an important parameter in electrical discharge processes. The effect of conductivity can differ depending on various discharge processes. For example, it has a significant influence on the formation of active species in the case of liquid discharges and less influence in the case of gas-phase discharges. However, it is possible to make some overall conclusions. High conductivity causes a low rate of formation of active species and leads to decreasing the energy efficiency of the process [7]. According

to Jiang, high conductivity is undesirable in wastewater treatment using plasma technology [28].

Conductivity and pH also have an effect on the formation of nitrate and nitrite ions [43]. Here we touch upon another important factor – gas composition. The simultaneous presence of nitrogen and oxygen in gas composition leads to the formation of such products as NO_2 , HNO_2 and HNO_3 . These products can dissolve in water and cause a reduction in pH, cause an increase in conductivity and they take part in various chemical reactions. It was shown by Kornev et al. [43] that only nitrates are formed during water treatment with corona discharge. The implementation of pure oxygen excludes the possibility of nitrates and nitrites' formation. Besides, a high oxygen level accelerates the production of ozone, which in turn leads to an increase in the degradation of target compounds.

2.3.4 Temperature

Although the temperature is an important operational parameter which has a strong effect on the kinetics of chemical reactions, there are only a few studies about temperature's effect on wastewater treatment process when using electrical discharge technologies. For example, Chen et al. showed that lowering the water temperature leads to increasing of aqueous phenol degradation rate [59]. The same conclusion was made by Jiang [28].

2.3.5 Target compound

The influence of all the listed factors on the process depends to a large extent on the target compounds. For the optimisation of the processes, it is necessary to take into account the composition of the treated water. For instance, Preis et al. [41] compared the oxidation of phenol and oxalic acid in a PCD reactor under equal conditions. They found out that pH has no significant effect on oxalic acid oxidation in air and the energy efficiency of oxalate oxidation does not depend on the pulse-repetition frequency, meaning that ozone plays a minor role in the oxidation. While phenol degradation and energy efficiency are influenced by pH and pulse-repetition frequency, an alkaline media and low frequency are preferable. Ozone contributes significantly to phenol oxidation, in contrast to oxalic acid oxidation.

One more thing should be noted: the greater number of studies about the implementation of electrical discharge technology for wastewater treatment were done using model compounds alone. Further, most of the experiments were carried out with one single compound while the combined effect of a mixture of various compounds has received less attention. Of course, there are a several papers about the treatment of real wastewater by electrical plasma technology, for example, the treatment of hospital wastewaters [60], surface waters [61] and textile wastewaters [62]. However, much more research is required for the investigation of real wastewater treatment.

3 Materials and methods

3.1 Materials

Three antibiotics (sulfamethizole, amoxicillin, doxycycline) and one immunostimulating drug (meglumine acridonacetate [MAA]) were the subjects of study in the current work. All the studied antibiotics are commercially available, supplied by Sigma Aldrich with a purity exceeding 99 % (according to the manufacturer's specification). The MAA was supplied by Polysan Ltd. The purity of the MAA was not provided by the supplier.

Sulfamethizole is a typical representative of the sulfonamides group. This group is one of the most consumed pharmaceutical groups in Europe, with 121.5 tonnes consumed in human medicine and 826.3 tonnes for consumed for veterinary purposes in 2012 [63]. Sulfamethizole itself has the ability to excrete 80 % of the administered dose [64]. Moreover, it is an abundant antibiotic in livestock farming, with the problem that effluents from farms go directly into water bodies. Mostly due to these facts, sulfamethizole is one of the most detectable antibiotics not only in environmental waters but also in tap water [1, 59].

Amoxicillin and doxycycline were chosen based on Verlicchi's proposed risk quotient (RQ) [22]. The RQ is the ratio between the average concentration of the compound in the secondary effluent and the corresponding predicted no-effect concentration (PNEC). According to this quotient, amoxicillin and doxycycline are among the most dangerous antibiotics for flora and fauna.

MAA is a derivative of acridone acetic acid and it is a low-molecular inducer of interferon synthesis. Drugs containing this substance are not in great demand in Europe. However, they are very popular in the countries of the former CIS and Russia.

Two types of lignin were selected for investigation. Commercially available kraft lignin, purchased from Sigma Aldrich, was used in the studies on converting lignin into aldehydes. The same lignin and birch lignin (BLN) were selected for the investigation of the influence of PCD treatment on phenolic and aliphatic OH groups and change in molecular weight. BLN is acquired from a pressurised hot water extraction and the soda-pulped biorefinery process [66]

Commercially available sodium thiosulfate, supplied by Sigma Aldrich, was used for experiments. Sodium thiosulfate is implemented in the leaching process of silver and gold, as well as being used as a medicine with detoxification and antihistamine activity.

3.2 Experimental set-up

Two PCD reactors were used during the experiments. Both are designed on the same principle. The reactors differed from each other in geometric dimensions and technical

characteristics (see Table 3.1). Each reactor includes an individual working chamber, a high voltage pulse generator, a water circulation system and a water tank. The experimental set-up is illustrated in Figure 3.1.

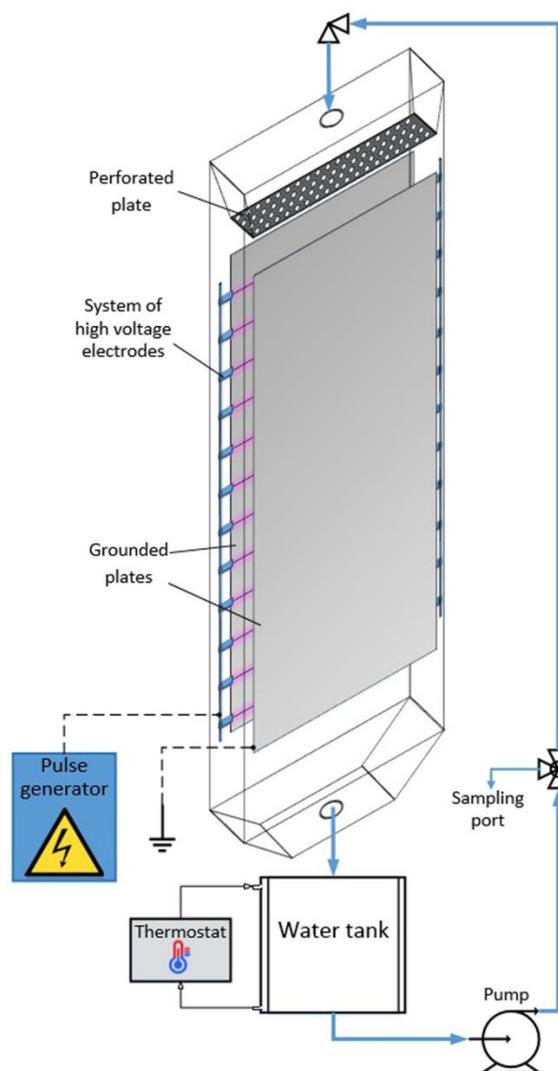


Figure 3.1: The experimental set-up [67].

In a pulse generator, three-phase voltage is rectified, then a pulse with a duration of 5–10 μs is generated by a thyristor. Then the voltage is transformed to 18–22 kV. As the microsecond pulse cannot be applied directly to the electrode system of the corona discharge, magnetic compression rungs, which are shortened to the pulse duration of 100

ns, are wired up to the high voltage transformer's secondary winding. Both reactors are designed to only generate positive corona discharges.

The rectangular working chambers of PCD reactors are made of acrylic glass. The chamber consists of high voltage wire electrodes placed parallel between two vertical grounded plate electrodes and covered by an acrylic glass. The chamber is installed above the water tank.

The operation principle is as follows: an aqueous solution containing target compounds is pumped from the water tank to the top of the working chamber, where it is spread by a perforated plate and falls by gravity between the electrodes through a plasma zone in which reaction with active species takes place.

Table 3.1: The reactors' characteristics

	Reactor 1	Reactor 2
Max. power	100 W	277 W
Grounded plates dimensions	210 x 1000 mm	500 x 2000 mm
Distance between plates	34 mm	34 mm
Total plasma volume, V_{pl}	7.14×10^6 mm	34×10^6 mm
Distance between HV electrodes	29 mm	30 mm
Diameter of HV electrodes	0.5 mm	0.5 mm
Material of HV electrodes	stainless steel	stainless steel
Single pulse energy, W_p	0.12 J	0.33 J
Current in pulse peak	180 A	400 A
Voltage in pulse peak	22 kV	20 kV
Pulse duration, T_p	100 ns	100 ns

3.3 Analytical part

The concentration of pharmaceutical compounds was measured by high-performance liquid chromatography (HPLC) with a kinetex 2.6 μ m C18 100 A 150 x 4.6 mm column. The specific HPLC parameters for the measurements of each compound are shown in the relevant publications: amoxicillin and doxycycline – Publication I, sulfamethizole – Publication II. The parameters for MAA measurements are presented in Table 3.2.

Table 3.2: The HPLC parameters for MAA measurements.

Eluent	0.05 M solution of potassium dihydrophosphate with pH 2.7 to 2.9, acetonitrile, methanol in the volumetric proportion of 65:30:5 respectively
Column temperature	25 °C
Retention time	around 10 min
Wavelength	254
Eluent flow rate	0.35 ml/min
Injection volume	20 µl

The qualitative analysis of the transformation products of amoxicillin, doxycycline and sulfamethizole were carried out by liquid chromatography coupled to an ion trap mass spectrometer equipped with an electrospray ionization interface. A detailed description of the analysis procedure is given in Publications I and II.

The tyrosine (tannin-lignin) method was used for the determination of the lignin concentration. It should be noted that this method allows detecting all hydroxylated aromatic compounds. Due to this, the results of lignin concentration measurements are not absolute but indicative. The PCD effect on phenolic and aliphatic OH groups and changes in the molecular weight of lignin were monitored by nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and high-performance size exclusion liquid chromatography (HPSEC). Aldehydes concentration, formed after lignin oxidation, was measured by the colorimetric method suggested by Evans and Dennis [68].

The used lignin and aldehyde analysis methods are described in detail in Publication III.

The analysis of samples taken during thiosulfate oxidation was carried out by ion chromatography. An anion column is used for the analysis of the thiosulfate concentration. For the mobile phase, 4.5 mM Na₂CO₃ and 9.1 mM NaHCO₃ were used.

3.4 Experimental procedure

Aqueous solutions of all pharmaceuticals and thiosulfates were prepared in deionized water and tap water was used for the preparation of lignin solutions. The experiments were carried out under ambient pressure with different pulse-repetition frequencies under neutral, acidic, and alkaline conditions. Here and throughout the text, the term “neutral” refers to media without any side additives, the term “acidic” refers to media with sulphuric acid as an additive and the term “alkaline” refers to media with sodium hydroxide as an additive. The gas composition was mainly air, except for the experiments with MAA (which had an oxygen-enriched atmosphere) and with lignin (which had an oxygen-thin atmosphere).

To answer the question of how the presence of more than one pharmaceutical compound in water influences the oxidation process, the experiments with the multicomponent system, consisting of a mixture of amoxicillin and doxycycline, were carried out. The binary solution was prepared by dissolving only one compound in the water, the ternary solutions containing water and two antibiotics were prepared by mixing of 50 ppm of both antibiotics.

The main parameters of all experiments are summarized in Table 3.3. To obtain more detailed information, see the relevant publication. All the experiments were repeated several times to ensure accuracy and reliability.

Table 3.3: The main parameters of the experiments.

Compound	Pharmaceuticals			Lignin (Publication III)	Sodium thiosulfate (unpublished)
	AMX/DXC (Publication I)	SMZ (Publication II)	MAA (unpublished)		
Reactor №	№1	№1	№2	№2	№1
Frequency, pps	50/200/500	50/200/500	200/840	840	200/833
Atmosphere	air	air	90% O ₂ , /air	5–7 % O ₂ , rest N ₂ /2– 3 % O ₂ , rest N ₂ /air	air
Temperature, °C	ambient (20)	10/20/50	20	20	20
Flow rate, L/min	4.5/8	4.5/8	15	15	4.5
Initial pH	neutral (additives) / alkaline (with NaOH)	acid (with H ₂ SO ₄) / neutral (no additives) / alkaline (with NaOH)	neutral (no additives) / alkaline (with NaOH)	alkaline (with NaOH)	neutral
Initial concentration, ppm	50	50	100/300/500	370–1600	400/1000
Pressure	ambient	ambient	ambient	ambient	ambient
Volume, L	10	10	40	50	10

3.5 Energy efficiency

Two parameters were chosen for the evaluation of PCD performance: energy efficiency (ε , g/kWh) and target compound removal ($R\%$).

The removal was calculated according to equation (3.1).

$$R = (1 - C_t/C_0) \times 100 \quad (3.1)$$

where C_0 is the initial concentration of the target compound (mg/L), C_t is the concentration at the time t (mg/L) and t is the treatment time (h).

The energy efficiency was calculated according to equation (3.2):

$$\varepsilon = C_0 R/E \quad (3.2)$$

where E is the delivered energy (Wh/m³).

The E value depends on discharge power (P , W), treatment time and the volume of treated solution (V , m³), as shown in equation (3.3):

$$E = P t/V \quad (3.3)$$

The P value is calculated according to equation (3.4):

$$P = fW_p \quad (3.4)$$

where f is the pulse repetition frequency (pps) and W_p is the energy of a single pulse (J).

The pulse parameters were determined with an Agilent 54622D oscilloscope and calculated according to equation (3.5):

$$W_p = \int_0^{T_p} U(t)I(t)dt \quad (3.5)$$

where T_p is the duration of the voltage pulse (ns), and $U(t)$ and $I(t)$ are waveforms of voltage (V) and current (A) respectively.

The amplitude peak at 100 ns duration is similar for both reactors. After the integration of Eq. 3.5, the energy of a single pulse is 0.12 J at 22 kV and 180 A for reactor 1, and 0.33 J at 20 kV and 400 A (see Table 3.1).

Knowing W_p , it is possible to calculate the P value for each reactor. The results are shown in Table 3.4.

Table 3.4 The discharge power for PCD reactors.

Frequency (f , pps)	Discharge power (P , W)	
	Reactor 1	Reactor 2
50	6	16.5
200	24	66
500	60	165
833	100	-
840	-	277

Combining Eq. 3.2 and Eq.3.3 we have the following equation for energy efficiency calculation:

$$\varepsilon = C_0 V R / (P t) \quad (3.6)$$

According to the literature review, the energy efficiency is usually calculated in two ways: (i) as half-life energy efficiency ($\varepsilon_{1/2}$), which is the energy efficiency at treatment time equal to a half target compound removal, and (ii) as a final energy (ε_{final}) efficiency when compound removal approaches 100 %.

Lignin conversion into aldehydes was also studied in the current work. The efficiency parameters were also energy efficiency (Eq. 3.7) and the conversion rate (Eq. 3.8). However, but in this case the energy efficiency shows how much energy is consumed for lignin conversion to aldehydes and the conversion rate is the ratio of aldehydes formed per oxidized lignin.

$$\varepsilon = \Delta C_{Aldehydes} / E \quad (3.7)$$

$$\varphi = \frac{\Delta C_{Aldehydes}}{\Delta C_{Lignin}} \times 100\% \quad (3.8)$$

where $\Delta C_{Aldehydes}$ is the increase in aldehydes concentration and ΔC_{Lignin} is the oxidised lignin.

3.6 Reaction kinetics

A more comprehensive investigation of the behaviour of the target compounds in the field of plasma is impossible without kinetic study. The calculation of the reaction kinetics is challenging due to the unknown quantity of active species and the lack of information about their individual contribution to the reaction. Two ways of kinetic calculation were used in the current work. The first method is based on the assumption that there are always constant amounts of oxidants available at any moment in the plasma volume. In this case, the water flow rate should not have any effect on the process and the contact surface should be constant. Therefore, the combined effect of the oxidants results in a second-

order reaction rate, and the total amount of oxidants involved in the reactions can be characterised by the power delivered to the plasma zone (Eq. 3.9):

$$dC/dt = \frac{k_2 CP}{V_{pl}} \quad (3.9)$$

where k_2 is the second-order reaction rate constant ($\text{m}^3 \text{J}^{-1}$), C is the concentration of the target compound (mg/L), P is the pulse power delivered to the reactor (W) and V_{pl} is the plasma zone volume (m^3).

As P/V_{pl} does not depend on experimental conditions and remains constant, it is possible to write:

$$k_1 = k_2 P/V_{pl} \quad (3.10)$$

Therefore, rewriting Eq. (3.9) we can get the following equation of the first-order reaction:

$$dC/dt = k_1 C \quad (3.11)$$

where k_1 (min^{-1}) is a pseudo-first-order reaction rate constant.

In the case of a first-order reaction, the concentration–treatment time curve should behave according to an exponential law and k_1 is a slope of the $\ln(C/C_0)$ curve.

An integration method is another way of determining the reaction order and reaction rate constant. Using data from experiments, the linear dependence of functions $\ln(C/C_0)$ and $1/C$ versus treatment time indicates whether the reaction is a first- or second-order reaction respectively. The slope of these curves determines the reaction rate constants. In this case, the k_2 value unit is $\text{L mg}^{-1} \text{min}^{-1}$.

4 Results and discussion

To answer the question of how the target compounds behave during the oxidation process in PCD, it was decided that we should study the kinetics of the reactions, as well as the intermediate oxidation products. The effects of such factors as frequency and pH were also taken into account. The experiments with the sulfamethizole, doxycycline and amoxicillin were carried out with a flow rate of 4.5 l/min and 8 l/min. The flow rate had no effect on the results, therefore the following results, figures and tables are for experiments with the flow rate of 4.5 l/min. The results of amoxicillin and doxycycline are shown in Sections 4.1 and 4.2 are the results for a binary solution when a single antibiotic compound was dissolved in the water. Section 4.4. shows the results for the ternary solution of these antibiotics, when both amoxicillin and doxycycline compounds are present in the same aqueous solution. Section 4.5 includes the results for both cases.

4.1 Kinetics

Sulfamethizole (Publication II) and MAA's reaction kinetic were calculated by the first method, described in Section 3.6; k_1 in this case is a pseudo-first-order reaction rate constant. Figure 4.1 and Figure 4.2 show the kinetic curves of MAA oxidation, and Figure 4.3 shows the kinetic curves of sulfamethizole. The kinetic parameters of amoxicillin, doxycycline (Publication I) and sodium thiosulfate were calculated using the second method (see Section 3.6). The kinetic curves of amoxicillin, doxycycline and sodium thiosulfate oxidation are shown in Figure 4.4 and Figure 4.5 respectively. Table 4.1 shows the results of experiments with three antibiotics in air-gas composition with different frequencies, pH values and with a constant (50 ppm) initial concentration of the target compounds. Table 4.2 represents the results of MAA reaction kinetic calculation, with different initial concentrations, gas-phase compositions and pH values. The results of sodium thiosulfate kinetics are shown in Table 4.3 for experiments with two different frequencies and initial concentration in neutral pH and in air atmosphere. All the results presented in Tables 4.1, 4.2 and 4.3 are experimental results obtained at ambient pressure and temperature (20 °C).

Table 4.1: The results of experiments with antibiotics.

	pH	f , pps	k_1 , min ⁻¹	k_2^* , m ³ J ⁻¹	k_2 , L mg ⁻¹ min ⁻¹	$\varepsilon_{1/2}$, g/kWh
SMZ	neutral	50	0.03311	6.57×10^{-7}	-	122.6
		200	0.08760	4.34×10^{-7}	-	81.5
		500	0.15300	3.03×10^{-7}	-	56.2
	alkaline	50	0.03289	6.52×10^{-7}	-	120.9
		200	0.09557	4.74×10^{-7}	-	88.7
		500	0.1616	3.21×10^{-7}	-	60.2
	acid	50	0.03321	6.59×10^{-7}	-	117.8
		200	0.08701	4.31×10^{-7}	-	79.4
		500	0.1380	2.74×10^{-7}	-	49.1

Amo	neutral	50	0.0328 (0.0240)**	-	-	100.6 (72.9)**
		200	0.0850 (0.0633)**	-	-	66.4 (58.8)**
		500	0.1307	-	-	33.5
	alkaline	50	-	-	0.0031	149.8
		200	-	-	0.0096	110.3
		500	-	-	0.0137	63.2
Doxy	neutral	50	0.0974 (0.0894)**	-	-	239.6 (266.6)**
		200	0.2933 (0.1750)**	-	-	163.1 (137.4)**
		500	0.3328	-	-	105.3
	alkaline	50	0.1610 (0.0738)**	-	-	643.1 (212.4)**
		200	0.3110 (0.1832)**	-	-	192.0 (120.0)**
		500	n/a	-	-	91.4

* calculated by the integration method (see Section 3.6)

** the results for a ternary solution

It should be noted that the $\ln(C/C_0)$ curves of all sulfamethizole and doxycycline experiments, regardless of initial pH and frequency, are straight lines with a coefficient of determination not less than 0.99, which indicates a first-order reaction. Amoxicillin in its turn behaves differently, it has a first-order reaction in neutral media and a second-order reaction in alkaline media (as plot $1/C$ gave the best fitting results).

The reaction of MAA oxidation is more complicated. MAA concentration only decreases with treatment time by an exponential law in the case of the experiment with the frequency of 200 pps (see Figure 4.1). The determination coefficient, in this case, approaches 1. The behaviour of oxidation curves at a higher frequency depends on the initial concentration and composition of the gas phase (see Figure 4.2). All reactions with a 500 ppm initial concentration and the reaction with 300 ppm in air can only be described by an exponential function with rough approximation. Therefore, it is not correct to state that the reaction is first order. The remaining three reactions fit well in the exponential model with a high determination coefficient; however, a small number of samples do not let us generalise the model. Therefore, the calculated k_1 values obtained for the MAA experiments at a higher frequency (840 pps) are only regarded as approximate when comparing the kinetics to other studied pharmaceuticals.

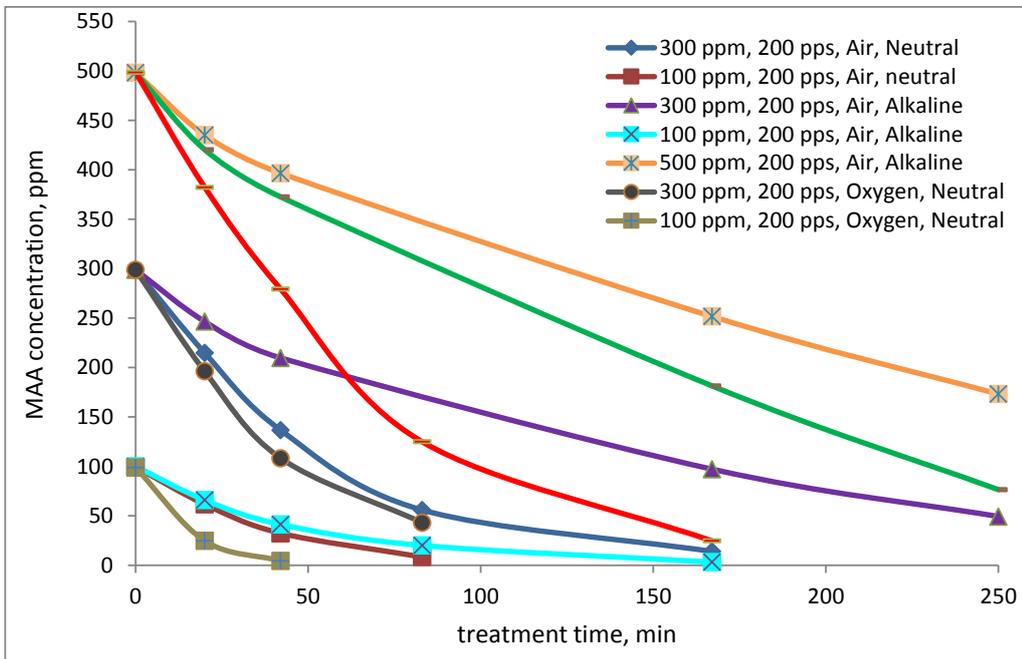


Figure 4.1: MAA concentration over treatment time at 20 °C at 200 pps.

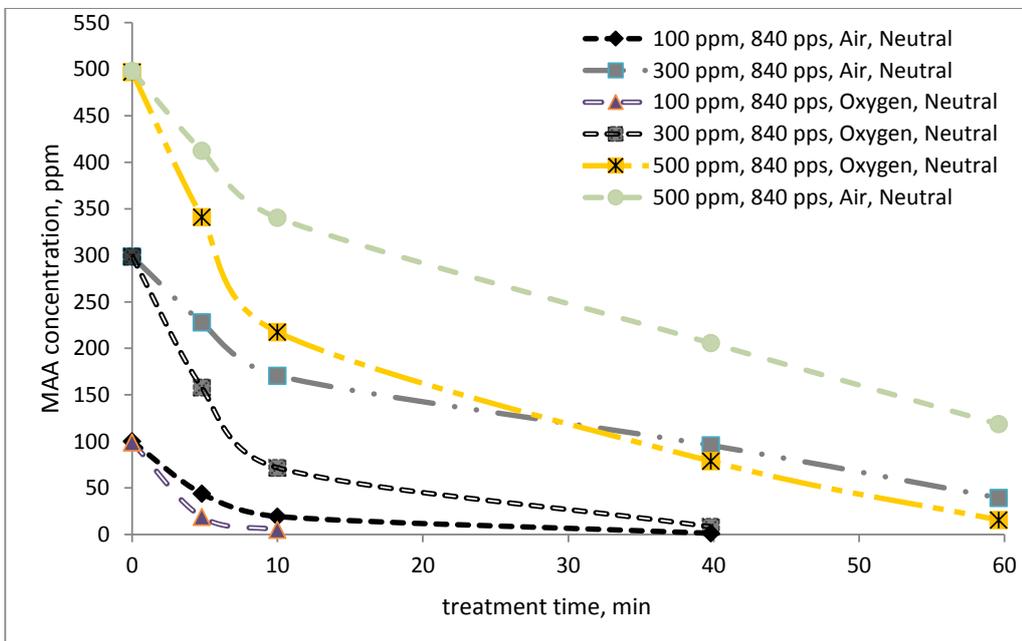


Figure 4.2: MAA concentration over treatment time at 20 °C at 840 pps.

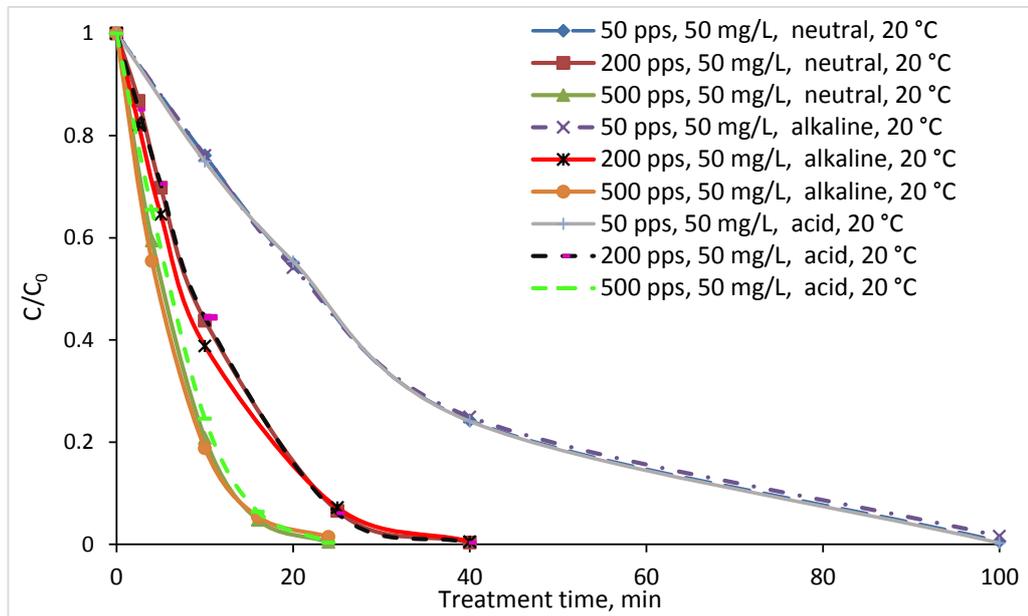


Figure 4.3: The relative concentration of sulfamethizole over treatment time at 20 °C [67].

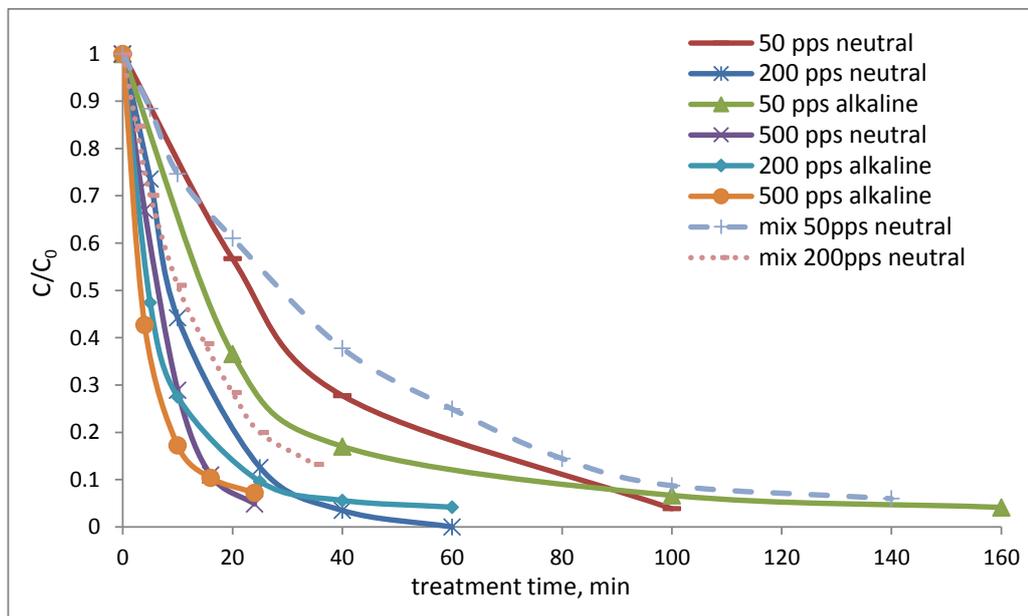


Figure 4.4: The relative concentration of amoxicillin over treatment time at 20 °C.

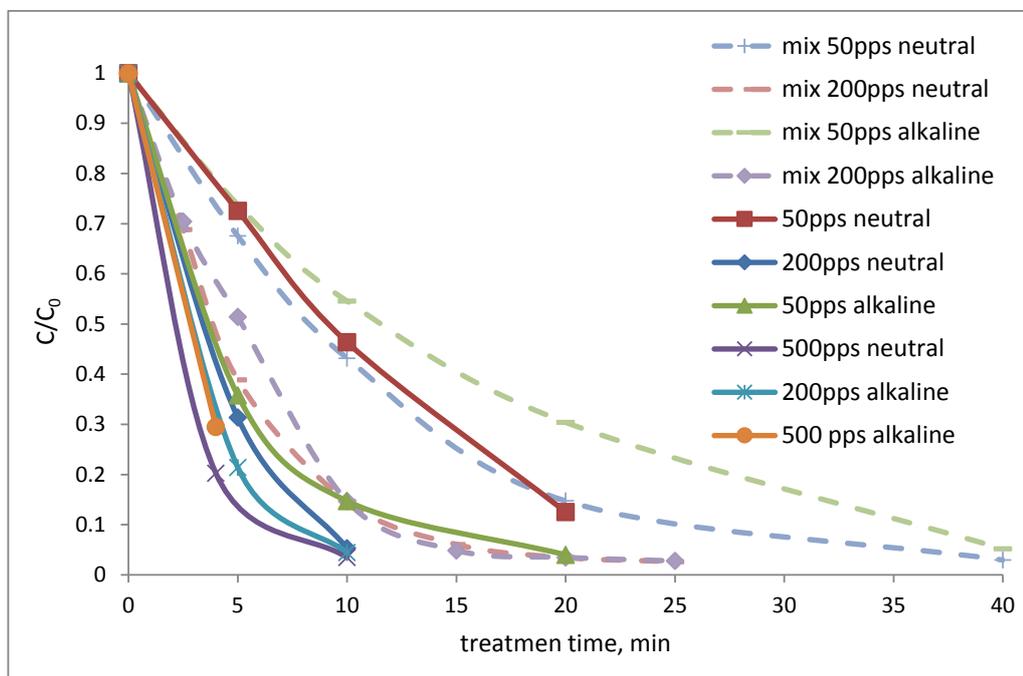


Figure 4.5: The relative concentration of doxycycline over treatment time at 20 °C.

As anticipated, the k_1 value always grows with frequency, increasing for all compounds under any conditions. In contrast, the k_2^* values of sulfamethizole reactions decrease with a frequency increase. Reduced k_2^* values indicates that more energy is required for the degradation reaction at high frequencies; in other words, a low frequency is preferable from the energy efficiency point of view. Regarding the MAA experiment, the energy efficiency of MAA degradation is less dependent on pulsed-repetition frequency since the k_2^* values at 200 pps and 840 pps only differ slightly from each other. For more details on energy efficiency, see Section 3.5.

The doxycycline oxidation reaction is the fastest of all, while the MAA reaction is the slowest. An oxygen-enriched atmosphere accelerates the oxidation process and contributes to less energy consumption. Less energy consumption is evidenced by the increase of the k_2^* value in an oxygen-enriched environment when compared with experiments in the air (see Table 4.2).

The pH of the solution has no significant effect on sulfamethizole reaction kinetic. In all three cases (the alkaline, neutral and acid cases) the reaction rate constants remain almost unchanged. Elevated pH enhances the oxidation of doxycycline. In contrast, in the case of the MAA reaction all the k_1 and k_2^* decrease under alkaline conditions. It is known that under a higher pH the oxidation mechanism by ozone shifts from a direct reaction towards a reaction via the formation of hydroxyl radicals. Thus, increased pH leads to an

increase in the production of OH radicals, which in turn should contribute to speeding up the reaction. However, during the experiments with MAA, the opposite is observed. This can be explained by the fact that, under experimental conditions, MAA reacts better with ozone than with OH radicals. In the case of the amoxicillin experiments, pH has a significant effect on kinetics. As was mentioned earlier in this section, the oxidation reaction of amoxicillin is a first-order reaction in a neutral media and a second-order reaction in an alkaline media.

The influence of the initial concentration of the target compound on reaction kinetics was studied using of an example of MAA reactions. As can be seen from Table 4.2, the k_1 and k_2^* values increase with an increase in the initial concentration, regardless of the frequency, pH and composition of the gas phase.

Table 4.2: The results of experiments with MAA.

C, ppm	pH	Atm	k_1, min^{-1}		$k_2^*, \text{m}^3 \text{J}^{-1}$		$\varepsilon_{1/2}, \text{g/kWh}$	
			200 pps	840 pps	200 pps	840 pps	200 pps	840 pps
500	alkaline	air	0.00409	-	0.35×10^{-7}	-	51.8	-
500	neutral	air	0.00661	0.02322*	0.57×10^{-7}	0.48×10^{-7} *	85.3	68.4
500	neutral	oxy	0.01562	0.07067*	1.34×10^{-7}	1.45×10^{-7} *	208.6	214.5
300	alkaline	air	0.00700	-	0.60×10^{-7}	-	53.3	-
300	neutral	air	0.01895	0.03313*	1.63×10^{-7}	0.68×10^{-7} *	150.5	57.4
300	neutral	oxy	0.02323	0.1379	1.99×10^{-7}	2.82×10^{-7}	183.5	258.1
100	alkaline	air	0.02030	-	1.74×10^{-7}	-	53.0	-
100	neutral	air	0.02656	0.1677	2.28×10^{-7}	3.43×10^{-7}	70.1	104.7
100	neutral	oxy	0.07005	0.3386	6.00×10^{-7}	6.93×10^{-7}	182.0	209.4

Table 4.3: The results of experiments with sodium thiosulfate.

C, ppm	f, pps	$k_0, \text{mg/min}$	$\varepsilon_{1/2}, \text{g/kWh}$
1000	200	13.44	336.0
	833	61.22	367.3
400	200	13.26	331.5
	833	61.02	366.1

Figure 4.6 shows the degradation curves of sodium thiosulfate. The reaction is apparently a zero-order reaction as the concentration–time curve is a straight line. In this case, the speed of the chemical reaction should not depend on the initial concentration of the substance but should be limited by the delivered energy. This was confirmed experimentally. The table shows that k_0 values at 1000 ppm and with 400 ppm are almost equal while the increase in frequency from 200 pps to 833 pps leads to the sharp increase of the reaction rate constant (by 4.5 times).

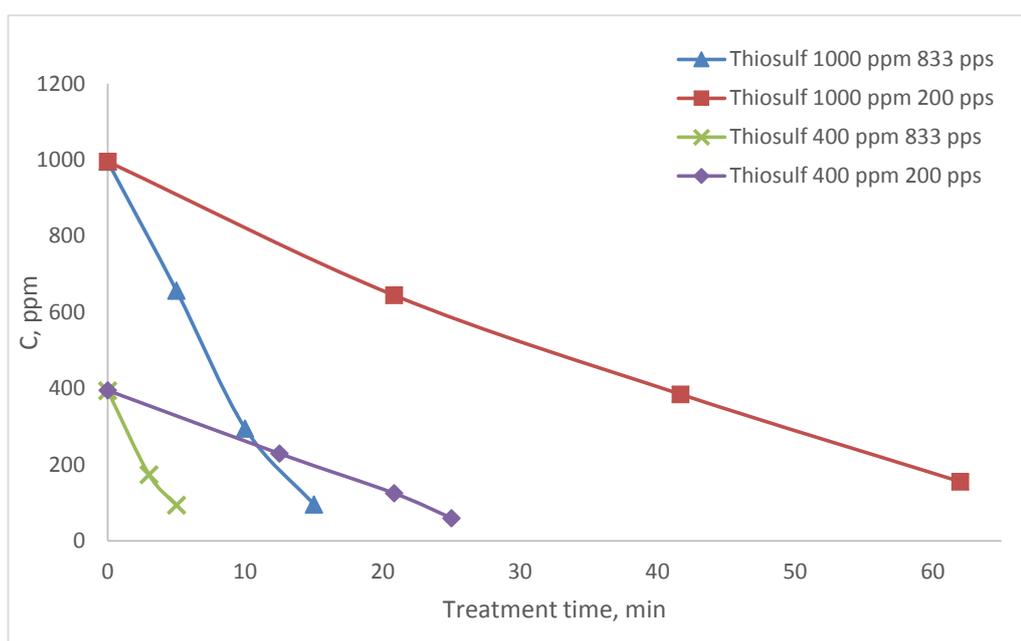


Figure 4.6: Sodium thiosulfate concentration over treatment time.

4.2 Energy efficiency

The figures in Appendix A show how the degradation process of the studied compounds depends on energy delivered to the reactor. It is seen that all the studied compounds are oxidised with relatively low energy consumption. The degradation of doxycycline proceeds with the lowest energy consumption of all the pharmaceuticals; already at delivered energy above 0.4 kWh/m^3 , doxycycline concentrations reached the detection limit of the HPLC analysis method while in the case of amoxicillin it takes more than 1.5 kWh/m^3 to decrease the concentration to the detection limit. It should be noted that, for pharmaceutical compounds starting from a certain concentration value, the amount of energy consumed per mass unit of the oxidised substance increases. This tipping point is

especially clearly seen in the case of the MAA reaction at a higher frequency (Figure A 2). As can be seen from this figure, it is possible to divide all the reactions into two phases, each of which is a straight line. The breaking point in this case is an E value slightly above 1 kWh/m^3 , regardless of the initial concentration and gas phase composition. Unlike pharmaceuticals, in the case of thiosulfate, the curves for “concentration vs delivered energy” are always straight lines no matter what the initial concentration or frequency is (Figure A 7). That indicates that the energy consumed per mass unit of the oxidised compound is constant during the process, which is typical for a zero-order reaction.

The ratio of oxidised mass to the delivered energy is essential for the energy efficiency. The figures in Appendix A show the dynamics of changes in the concentration depending on the delivered energy but do not describe the energy efficiency of the process. As was mentioned in Section 3.5, the most common ways of calculating energy efficiency are the half-life energy efficiency ($\epsilon_{1/2}$), when the target compound removal (R) is 50 %, and the final energy efficiency, when compound removal (R) approaches 100 %. To compare the energy efficiency of processing different compounds under different conditions, a half-life energy efficiency was used since it is more convenient for comparison and it is more accurate in terms of calculation. The calculated values of $\epsilon_{1/2}$ are given in Table 4.1, Table 4.2 and Table 4.3 and shown for visual clarity in figures. The highest energy efficiency, around 643 g/kWh , was achieved for the doxycycline reaction at 50 pps under alkaline conditions (see Figure 4.7). Amoxicillin degradation at 500 pps under neutral conditions has the lowest value, $\epsilon_{1/2} = 33.5 \text{ g/kWh}$ (see Figure 4.8).

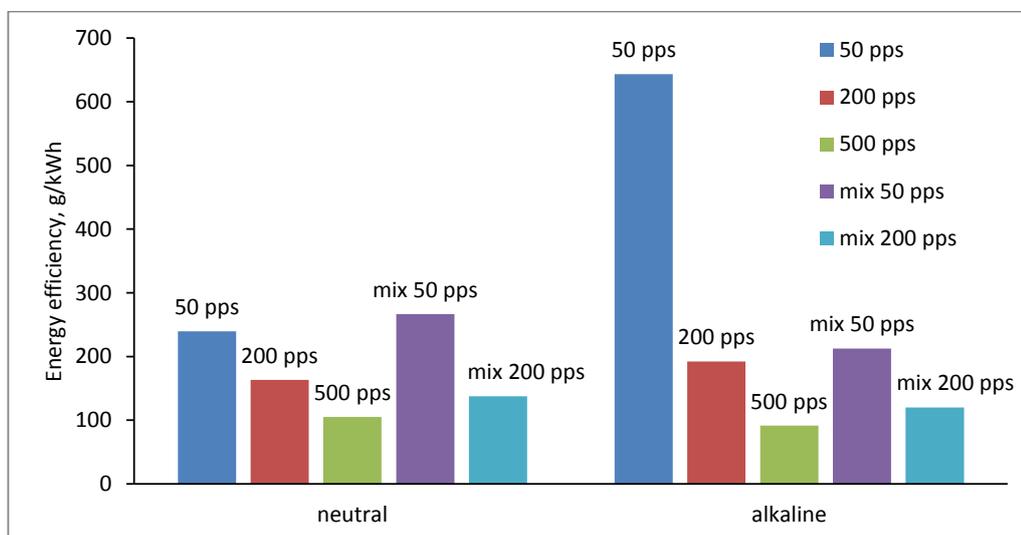


Figure 4.7: The half-life energy efficiency of doxycycline degradation [69].

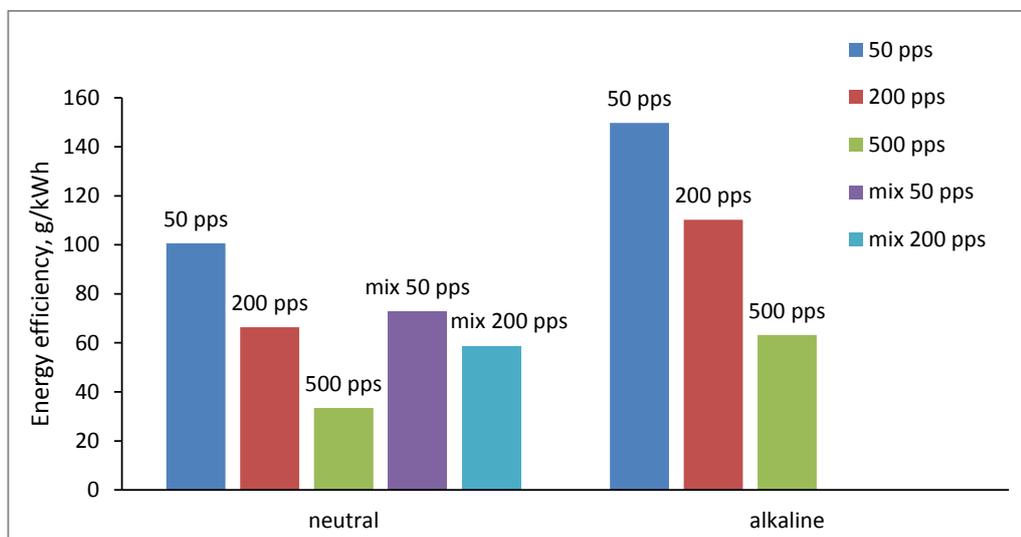


Figure 4.8: The half-life energy efficiency of amoxicillin degradation [69].

Alkaline media at a constant frequency led to the increased energy efficiency of amoxicillin oxidation, increased by approximately 1.5 times. An alkaline media was also preferable in the case of the doxycycline reaction, but its contribution depended on the pulse-repetition frequency. Thus, at 50 pps, the energy efficiency in alkaline media is 2.7 times higher than in a neutral media while at 200 pps this ratio is only 1.2 and at 500 pps the neutral media becomes an even more favourable media with an energy efficiency value of 105.3 g/kWh against 91.4 g/kWh under alkaline conditions. However, it is worth noting the poor accuracy of calculation at 500 pps in alkaline media. The calculations were made based on only two samples, taken at 0.8 kWh/m³ and at 1 kWh/m³ delivered energy, since no doxycycline was detected in subsequent samples. What is clear is that at 500 pps, a neutral media is only preferable at the initial stage of the oxidation, although insignificantly so. Therefore, it is possible to conclude that, in general, the effect of pH on the energy efficiency of doxycycline oxidation at elevated frequencies is not so significant. In the case of the sulfamethizole reaction, pH had no effect on the energy efficiency, both at higher and lower frequencies. As can be seen from Figure 4.9, the energy efficiency values remain at the same level in alkaline, neutral and acid media.

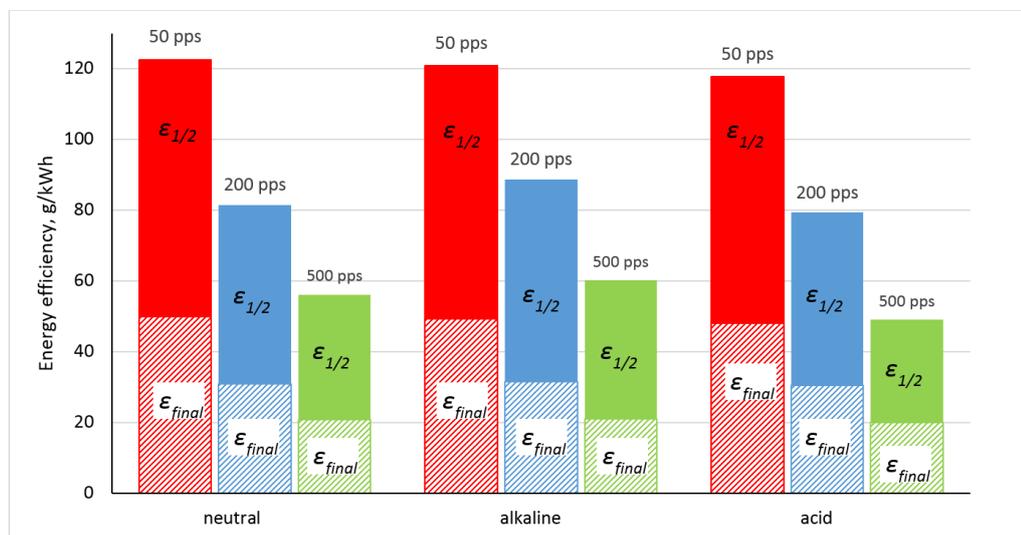


Figure 4.9: The energy efficiency of sulfamethizole degradation. Hatched area: final energy efficiency (ϵ_{final}); solid area: half-life energy efficiency ($\epsilon_{1/2}$) [67].

In general, the review of Figures 4.7–4.9 allows one to conclude that elevated pH was better for the oxidation of antibiotics at the beginning of the process. However, as the treatment progresses, with the decreasing of primary compounds, the effect of pH becomes less significant.

Unlike antibiotics, the efficiency of the MAA reaction is better in neutral media. Compared with neutral media, under alkaline conditions at a constant frequency of 200 pps, energy efficiency reduces 2.8, 1.6 and 1.3 times in experiments with the initial concentrations of 300 ppm, 500 ppm and 100 ppm respectively (see Figure 4.10).

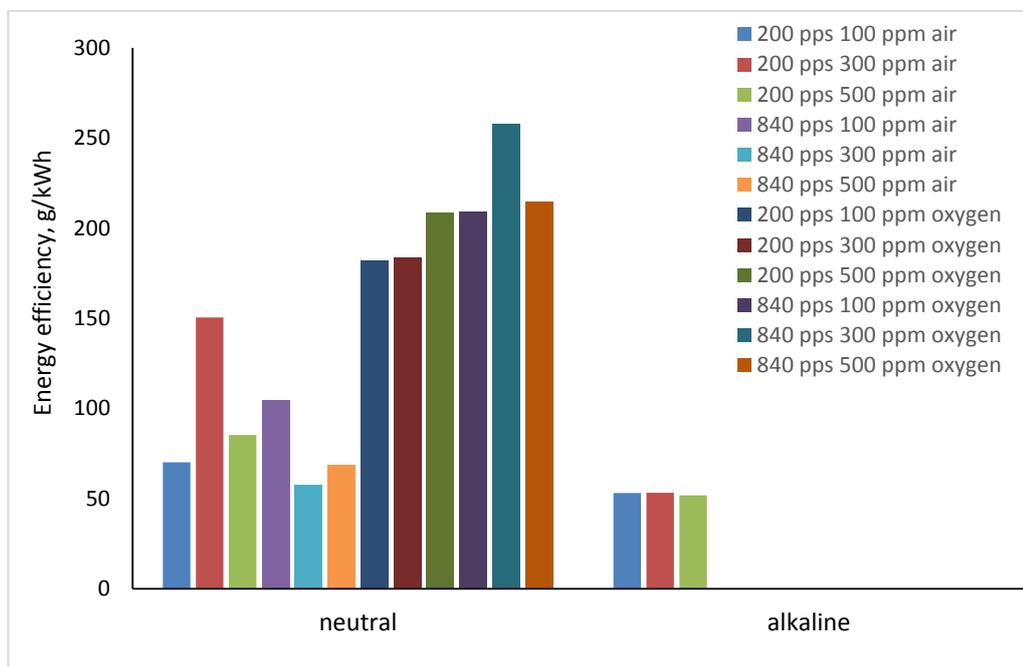


Figure 4.10: The half-life energy efficiency of MAA degradation.

The influence of the pH on thiosulfate oxidation was not studied.

The pulse-repetition frequency has a significant impact on energy efficiency. The effect of frequency is especially noticeable in the case of the reaction of doxycycline in the alkaline media; as the frequency increases from 50 pps to 500 pps, the energy efficiency drops 7 times, from 643.1 g/kWh to 91.4 g/kWh. In the other experiments with antibiotics, increasing the frequency from 50 pps to 500 pps leads to a decrease in efficiency of 2–3 times on average.

The pulse-repetition frequency impacted on the energy efficiency of the MAA reaction in a somewhat different way. In an air atmosphere, as in the case of the antibiotics experiments, the energy efficiency is better at lower frequencies. However, this pattern is only observed at the initial concentrations of MAA 500 ppm and 300 ppm, while at 100 ppm, the energy efficiency is higher at higher frequencies. Although (as pointed out above) at high frequencies and with a low concentration, it was not possible to take a sufficient number of samples for more accurate calculation, thus there is a big error in calculation. The energy efficiency is also better at higher frequencies if the treatment is carried out in an oxygen-enriched atmosphere.

An elevated oxygen content accelerates the oxidation process in general as more ozone is generated, and this is clearly seen in Figure 4.10. It should be noted that the energy

efficiency of oxidation in the oxygen atmosphere at 200 pps increases approximately 2.5 times for the initial concentrations of 100 ppm and 500 ppm, while in the case of 300 ppm, under similar conditions, the increase is only 1.2 times. With the increased frequency in the oxygen atmosphere, on the contrary, the greatest differences are observed in the case of the experiment with an initial concentration of 300 ppm (4.5 times). Of the three tested initial concentrations (100 ppm, 300 ppm and 500 ppm), the highest energy efficiency was achieved for an average concentration of 300 ppm. In the air, it was 150.5 g/kWh, and in the oxygen environment, it was 258.1 g/kWh.

The reaction of thiosulfate oxidation is strongly different from the reaction of the studied pharmaceuticals, primarily because the best energy efficiency was achieved at higher frequencies, though not to a significant extent. The initial concentration also has no effect on energy efficiency (see Figure 4.11).

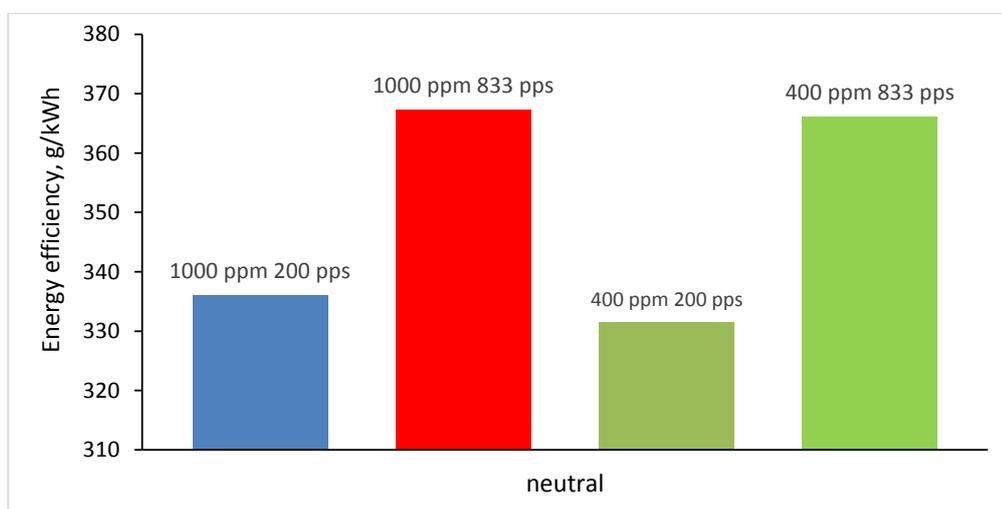


Figure 4.11: The half-life energy efficiency of sodium thiosulfate degradation.

Summarizing Sections 4.1 and 4.2, it is possible to conclude that a lower frequency is preferable from an energy efficiency point of view, but in this case, the treatment takes more time. It can be explained by the greater contribution of ozone in the oxidation process at lower frequencies. Hydroxyl radicals and ozone directly react with target compounds in the gas–liquid interface. Hydroxyl radicals have higher oxidation potential than ozone, therefore, ozone reacts with target compounds more slowly. Furthermore, when dissolved in water, ozone may also decompose via the formation of hydroxyl radicals; such a formation of radicals can be considered as a secondary formation. The dissolving of ozone and the secondary formation of OH radicals both take time. In the case of the experiments with a low pulse frequency, the treatment time required to reach the same value of delivered energy increases compared with the high pulse frequency experiments. Consequently, ozone has more time to accumulate during the pauses

between the pulses, more time to dissolve and more time for the secondary formation of OH radicals.

Higher pH leading to alkaline aqueous solutions accelerates the oxidation process and contributes to better energy efficiency for doxycycline and amoxicillin, whereas it has the opposite effect in the case of the MAA reaction and does not affect the reaction of sulfamethizole.

A too high (as well as a too low) initial concentration of MAA had a negative effect on energy efficiency. In the case of the MAA reaction, it was necessary to determine a certain average option – in studied case it was 300 ppm.

The thiosulfate reaction is unresponsive to changes in the initial concentration, and not very sensitive to changes in frequency.

4.3 Temperature effect

Sulfamethizole was chosen for the investigation of temperature effect on the PCD oxidation process. As the oxidation process of sulfamethizole does not depend on pH and flow rate, experiments with different temperatures of aqueous solution of sulfamethizole (10 °C, 20 °C and 50 °C) were only carried out in neutral media with a 4.5 l/min flow rate at two frequencies (50 pps and 500 pps) and with a 50 ppm initial concentration of sulfamethizole.

All the curves plotted on Figure 4.12 indicate exponential-law behaviour, meaning that all the reactions are first-order reactions and the temperature does not change the order. Therefore, reaction constants and energy efficiency were calculated as described in Section 3.6 and as summarised in Table 4.4. As can be seen from Figure 4.12, the oxidation curves at 10 °C and 20 °C merge no matter what the frequency is. A temperature rise to 50 °C led to a significant deceleration of the process. Energy efficiency at a different temperature is also shown for visual clarity in Figure 4.13. As can be seen, all the values k_1 , k_2^* and $\epsilon_{1/2}$, ϵ_{final} , $t_{1/2}$ are similar at 10 °C and at 20 °C but differ significantly at the elevated temperature of 50 °C. The drop in the oxidation process speed and energy efficiency is clear at 50 °C. This can be explained by decreasing ozone's solubility in water, followed by decreasing the secondary formation of OH radicals, which slows down the hydroxyl radical-induced oxidation. Moreover, a decrease in solubility should mean that more ozone becomes available for a direct reaction with target compounds on the liquid–gas border. However, an elevated temperature speeds up the decomposition of ozone, which decomposes according to the equation $2O_3 = 3O_2$ and shifts the balance towards oxygen formation. The oxidation potential of oxygen is lower compared to ozone. Therefore, the experiments with an elevated temperature give worse results from the energy efficiency and reaction speed points of view. Based on this finding, a reduced temperature should lead to the intensification of the oxidation. However, no difference was observed between experiments at 10 °C and experiments at 20 °C. The potential increase in energy efficiency at a lower temperature as a consequence

of increased ozone reactivity is compensated for by the increase in the reaction speed by a factor 2 or 3 per 10 °C, according to the Van 't Hoff equation.

Table 4.4: The results of the experiments with sulfamethizole at different temperatures.

	Temperature, °C	k_1 , min ⁻¹	k_2 , m ³ J ⁻¹	$t_{1/2}$	$\epsilon_{1/2}$, g/kWh	ϵ_{final} g/kWh	R
50	10	0.03425	6.79×10^{-7}	20.24	127.4	49.38	0.99
	20	0.03311	6.57×10^{-7}	20.93	122.6	49.92	0.99
	50	0.01622	3.22×10^{-7}	42.73	59.8	30.15 (20.5)*	0.97 (0.99)*
500	10	0.1594	3.16×10^{-7}	4.35	58.4	20.84	1
	20	0.1530	3.03×10^{-7}	4.53	56.2	20.75	1
	50	0.0530	1.05×10^{-7}	13.09	19.6	8.11 (6.2)*	0.97 (0.99)*

*after approximation by Matlab

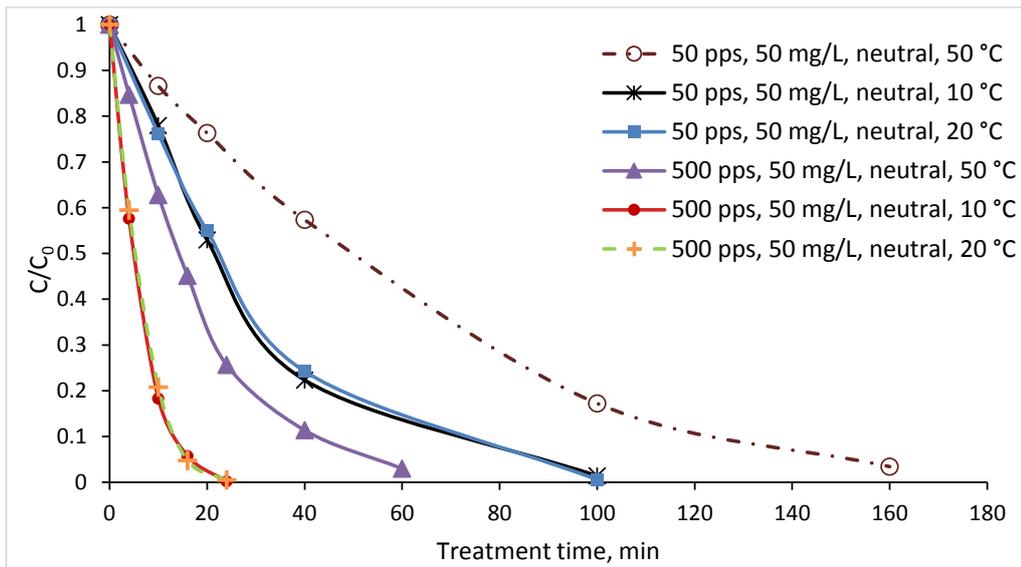


Figure 4.12: Sulfamethizole's relative concentration vs treatment time at different temperatures [67].

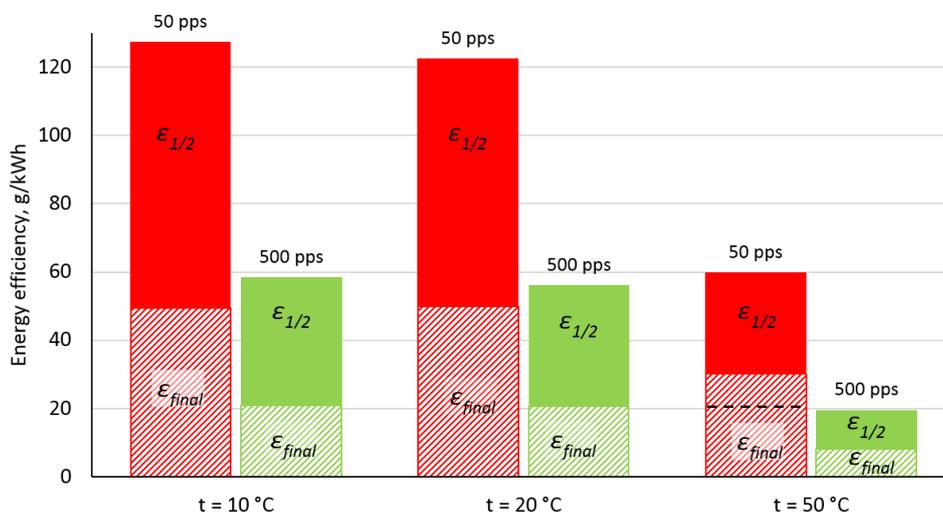


Figure 4.13: The energy efficiency of sulfamethizole degradation at different temperatures. Hatched area: final energy efficiency (ϵ_{final}); solid area: half-life energy efficiency ($\epsilon_{1/2}$); dashed line: the ϵ_{final} value after approximation by Matlab [67].

4.4 Multicomponent system

The multicomponent system, consisting of an aqueous solution of amoxicillin and doxycycline (ternary solution), was studied and the results were compared with binary solutions. The results are given in Table 4.1. To facilitate comparison, the half-life energy efficiency is shown in Figure 4.7 and Figure 4.8, kinetic curves are plotted on Figure A5 and Figure A6.

It may first be noted that the amoxicillin reaction in the neutral media remained first order, despite the presence of doxycycline. However, its presence slowed down the oxidation. Therefore, the reaction rate constant decreased by 26–27 % regardless of the pulse-repetition frequency. The half-life energy efficiency values of amoxicillin oxidation also became lower. Comparing with the binary solution, in the ternary solution more energy is required for oxidation of the same amount of amoxicillin, most likely due to competitive reactions of oxidants with doxycycline. Thus, half-life energy efficiency of amoxicillin decomposition in the presence of doxycycline reduced from 100.6 g/kWh to 72.9 g/kWh at the frequency of 50 pps and from 66.4 g/kWh to 58.8 g/kWh at 200 pps. It should be noted here that the inhibitory effect of doxycycline on amoxicillin oxidation is more significant at a lower pulse-repetition frequency.

The investigation of amoxicillin behaviour during the treatment in alkaline media was not carried out. The implemented analytical method did not enable the detection of amoxicillin in an alkaline medium in a ternary solution.

As mentioned earlier in Section 3.4, the term “neutral” refers to a media without NaOH addition. Practically, the doxycycline-added solution has acidic media, with $\text{pH} \approx 4.5$. Amoxicillin begins to hydrolyse under acidic conditions and amoxicillin penicilloic acid forms, the analysis of transformation products showed the presence of this acid in the untreated samples of the ternary solution. By comparing results of the qualitative analysis of oxidation by-products, the presence of amoxicillin penicilloic acid is the only difference between binary and ternary solutions (see Section 4.5).

Doxycycline oxidation in the ternary solution is decelerated compared to the binary solution. For neutral conditions, the difference between the values of the reaction rate constant in the ternary and the binary solutions is around 8.2 % at 50 pps and 40 % at 200 pps. For alkaline conditions, this difference is 54 % and 41 % at 50 pps and 200 pps respectively. It is important to note here that although high pH enhances the oxidation process of doxycycline (see Section 4.1), the reaction rate constant in the ternary solution under alkaline conditions is smaller compared with neutral media (0.0738 min^{-1} against 0.0894 min^{-1}). This outcome was only observed at a low frequency (50 pps).

As concerns the energy efficiency of doxycycline decomposition in the ternary solution, two main interesting and unexpected findings were made. First, in contrast to the experiments with the binary solution, in the experiments with the ternary solution a neutral media is more preferable from the energy efficiency point of view. Second, the presence of amoxicillin in the system had little impact on the energy efficiency of doxycycline oxidation under neutral conditions.

Also, it should be noted that (as can be seen from Figure 4.7 and Figure 4.8) a low frequency is still better than a high frequency from the energy efficiency point of view.

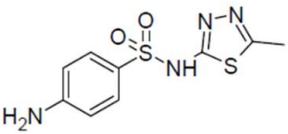
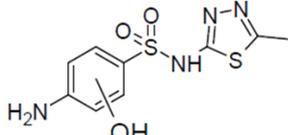
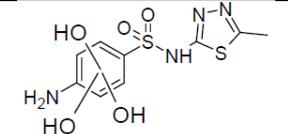
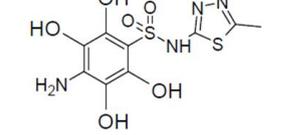
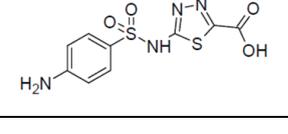
4.5 Oxidation by-products

The oxidation of the target compounds leads to the formation of various transformation products. Qualitative analysis for the identification of organic by-products was carried out for sulfamethizole, doxycycline and amoxicillin. The analysis of the last two antibiotics was done for binary solutions (water-single antibiotic compound) and ternary solutions (water-two antibiotic compounds). Quantitative analysis was performed for monitoring of sulfate formation during sodium thiosulfate treatment.

Table 4.5 shows the oxidation by-products of sulfamethizole with the highest peak at the half-life oxidation time. As can be seen, four organic products (excepting sulfamethizole itself) have the highest peak. Some other products, including organic acids and 2-amino-5-methyl-1,3,4-thiadiazole, were also detected (see Publication II, Supplementary Figure S3). The presence of 2-amino-5-methyl-1,3,4-thiadiazole allows us to make an

assumption that possible reaction pathways start with the preliminary hydroxylation of sulfamethizole, followed by the subsequent breaking of the sulfonamide bond. Klauson et al. [70] suggested similar pathways. None of the intermediates detected at the half-life oxidation time were found at the end of the treatment when sulfamethizole removal reached 99 %.

Table 4.5: The oxidation by-products of sulfamethizole with the highest peak at the half-life oxidation time [67].

Compound	Structure	Identified with	note
Sulfamethizole		Ion trap, positive Ion trap, negative QToF, positive QToF, negative	4 fragments 3 fragments error 3.7 ppm error 3.7 ppm
OH-Sulfamethizole		Ion trap, positive Ion trap, negative	3 fragments 3 fragments
3 OH-Sulfamethizole		Ion trap, negative	2 fragments
4 OH-Sulfamethizole		Ion trap, negative QTOF negative	2 fragments error 6.1 ppm
Carboxy-Sulfamethizole		Ion trap, negative QToF, negative	2 fragments error 9.9 ppm

Two major intermediate products of the doxycycline reaction were detected: OH-doxycycline (DXC-C1) and 2-OH-doxycycline (DXC-C2) (see Figure 4.14).

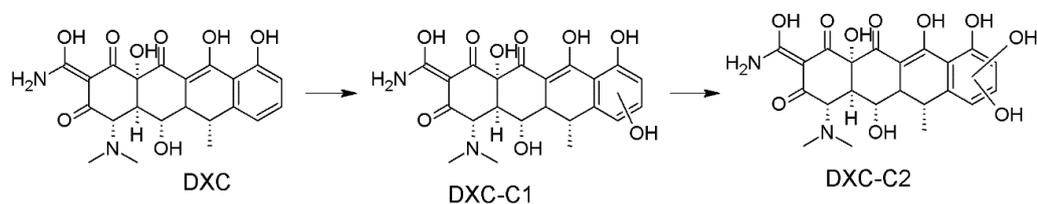


Figure 4.14: The proposed oxidation pathway of doxycycline [69].

For amoxicillin, five transformation products were detected (see Figure 4.15); two of them, OH-amoxicillin (AMX-C1) and amoxicillin penicilloic acid (AMX-C2), have the largest peak area.

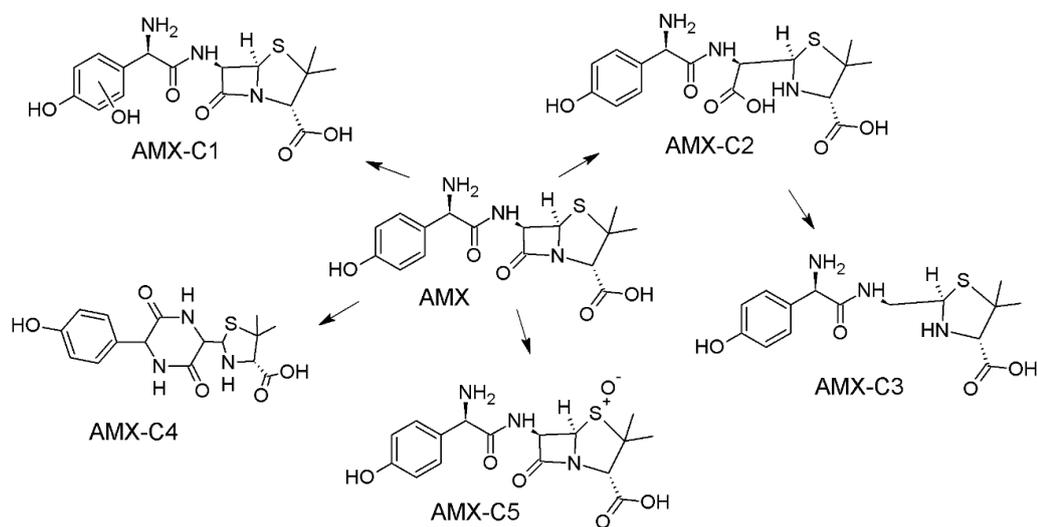


Figure 4.15: The proposed oxidation pathway of amoxicillin [69].

The relative rates of the transformation products were determined by measuring the areas of the peaks in the UV chromatograms for doxycycline and its products and by measuring the areas of the extracted ion chromatograms for amoxicillin and its major products. Dividing the current peak area by the largest peak area allows observation of the change in the content ratio of the studied compound and its intermediate oxidation products.

Figure 4.16 and Figure 4.17 show the changes in the content ratio of amoxicillin and doxycycline, and their transformation products for ternary solution respectively. As can be seen from Figure 4.16, excepting amoxicillin itself, there is some quantity of amoxicillin penicilloic acid in the untreated sample when the delivered energy is 0 kWh/m³. This can be explained by the fact that amoxicillin begins to hydrolyse under

acidic conditions [71], and the presence of doxycycline in a tertiary solution makes the media acidic. Therefore, we can observe the presence of acid in the samples before processing. During the treatment, the content ratio of both compounds is steadily declining. OH amoxicillin only appears when the PCD treatment starts and its quantity grows up to a certain point and then decreases. Figure 4.16 also shows the different content ratio behaviour at different frequencies. First, in contrast to experiments at high frequency, at low frequency all compounds were decomposed at around 1.4 kWh/m³ of delivered energy. Second, the largest mass of components and their diversity is observed in the 0.4–0.5 kWh/m³ interval at a frequency of 50 pps, while at a frequency of 200 pps, this interval expands and shifts to the right: 0.5–1 kWh/m³.

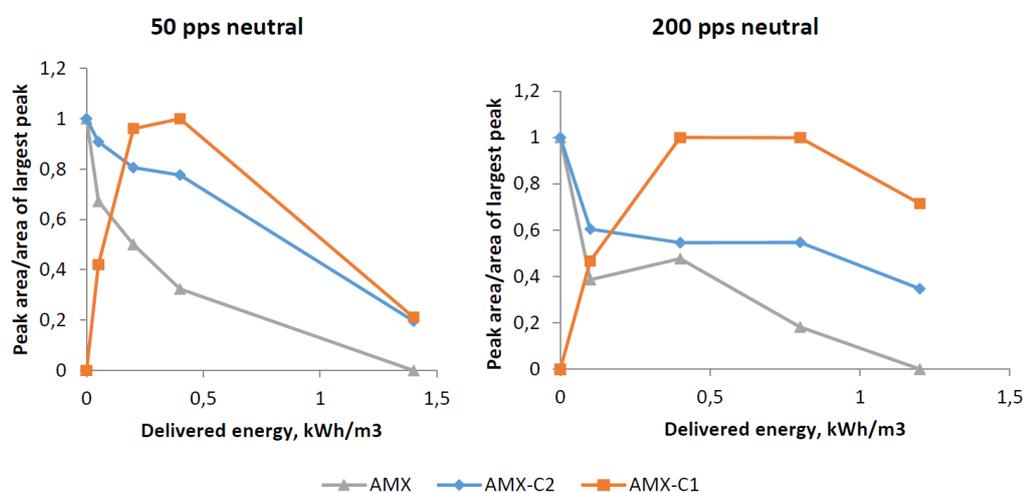


Figure 4.16: The changing content ratio of amoxicillin and its major oxidation products [69].

Figure 4.17 shows the changes in the content ratio of doxycycline oxidation products for a ternary solution in neutral and alkaline media at different frequencies. As can be seen, in neutral media there are no other compounds except doxycycline itself. The oxidation by-products begin to form rapidly with the first doses of energy, especially at low frequencies. It is seen that the content ratio of intermediates increases unless there is an excess of the primary compound. Starting from a certain moment – 0.2 kWh/m³ at 50 pps and 0.4 kWh/m³ at 200 pps – the intermediates start to decompose as well. Some amount of 2-OH-doxycycline OH-doxycycline was detected in the untreated samples under alkaline conditions. Apparently, doxycycline begins to hydrolyse in the presence of NaOH, which was added to the solution to create an alkaline condition. In general, the content ratio behaviour in alkaline media is similar to the behaviour in neutral media.

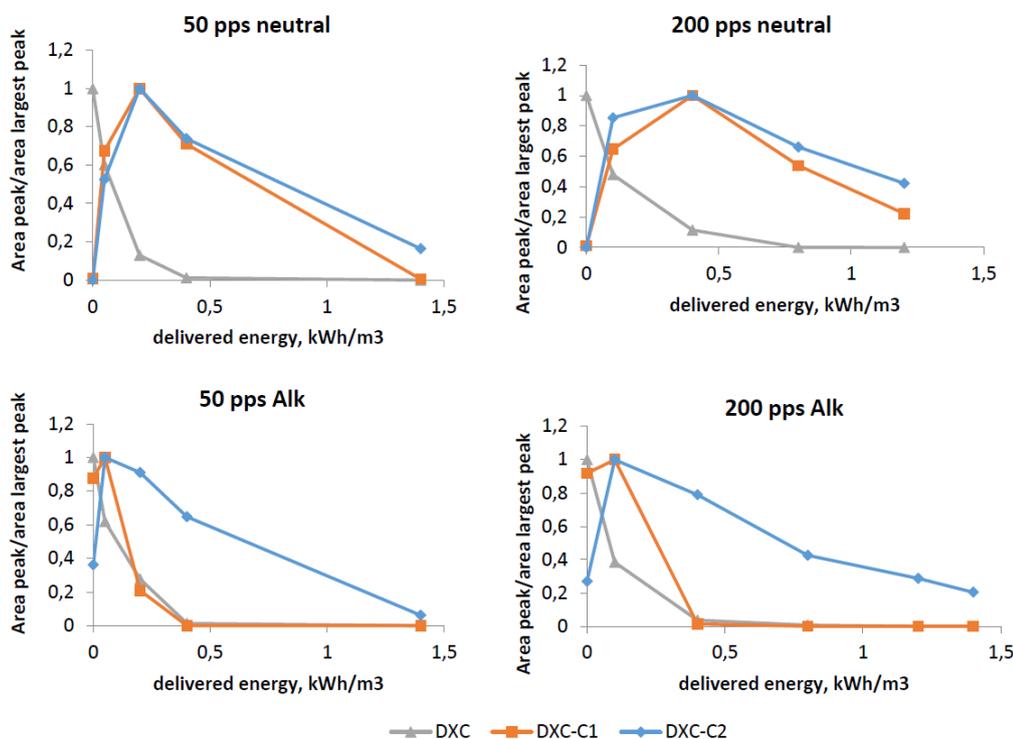


Figure 4.17: The changing content ratio of doxycycline and its major oxidation products [69].

In the case of binary solutions, the same transformation products were detected, and the same changes in content ratio were observed. There is only one difference, in the case amoxicillin binary solution, no amoxicillin penicilloic acid was detected in the untreated sample. Amoxicillin penicilloic acid and OH amoxicillin form during the treatment, and their presence increases the beginning of the treatment and then drops.

To summarise the formation of antibiotics oxidation by-products we can say that, first, the analysis of the figures confirms that low frequencies are more preferable for decomposition from the energy efficiency point of view. Moreover, they are more preferable not only for oxidation primary compounds but also for all intermediates. Second, the presence of one antibiotic has no effect on the oxidation of another in the frame of formation of oxidation by-products and their content ratio behaviour during the treatment.

During the experiment with sodium thiosulfate, it was observed that the solution does not change in colour and no precipitate is formed. Sodium thiosulfate should be oxidised into sulphates or sulphuric acid. Sulphuric acid was not monitored, however, pH dropped from 6 to 2.5 during the treatment, suggesting the formation the sulphuric acid during the process. Sulphates were detected, and their concentration was measured during the

treatment process, Figure 4.18 shows the result of the concentration measurements as a function of delivered energy per unit volume.

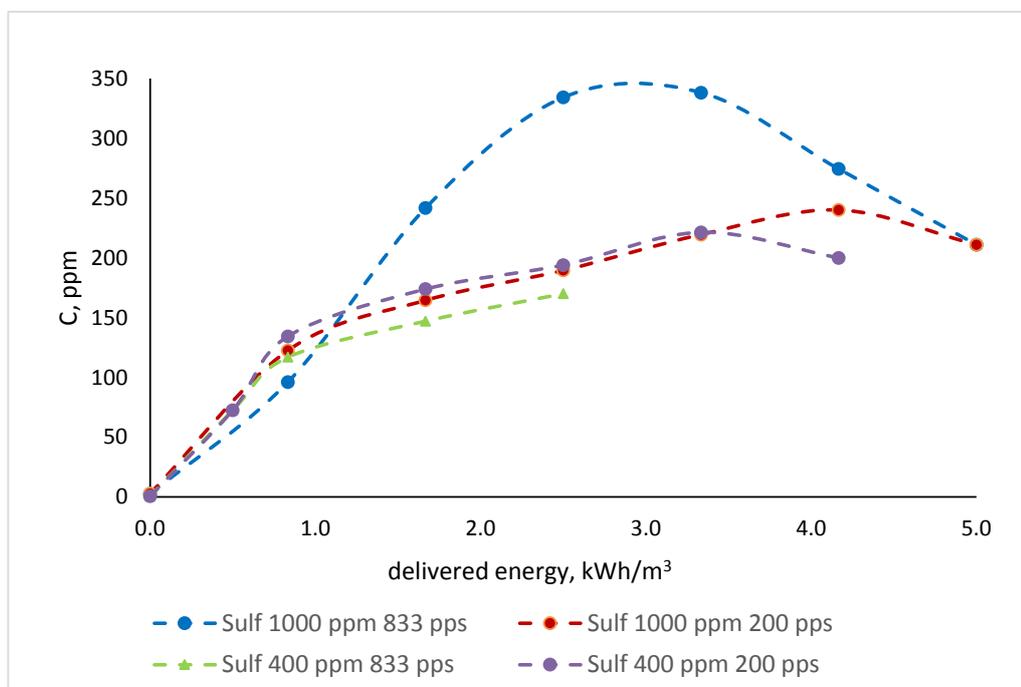


Figure 4.18: Sulphate ions' formation as a function of delivered energy per unit volume.

4.6 Lignin modification

Often, the by-products of oxidation are even more harmful substances than the original compounds. However, it sometimes happens the other way around. Lignin is a potential source of value-added products, including phenolic substances and aromatic aldehydes. The earlier literature reported the possibility of using PCD treatment for the conversion of lignin into aldehydes. It has been found that an increased initial concentration of lignin and soft oxidation conditions contribute to a better yield of aldehydes. In the current work, in order to improve the yield of aldehydes, several experiments were carried out with an increased initial concentration of lignin (up to 1400 ppm) and with a reduced oxygen content in the gas phase (up to 2–3 % oxygen-content), which makes the oxidation conditions softer. Kraft lignin was used in these experiments. Figure 4.19 shows the conversion rate (calculated by Eq. 3.8) and energy efficiency (calculated by Eq. 3.7) of aldehyde formation for different initial lignin concentration in different atmospheres. It is seen that in the air the conversion rate decreases with an increased initial lignin concentration. In the atmosphere with low oxygen content, there is a tendency to increase the conversion rate with an increase in initial concentration. It is especially noticeable in the case of experiments in a 2–3% oxygen-content atmosphere when the rise in

concentration from 370 ppm to 770 ppm gives a growth in the conversion rate of 16 % to 33 %.

It is possible to conclude that the less harsh reaction conditions, provided by the oxygen-thin atmosphere, are favourable for aldehyde formation.

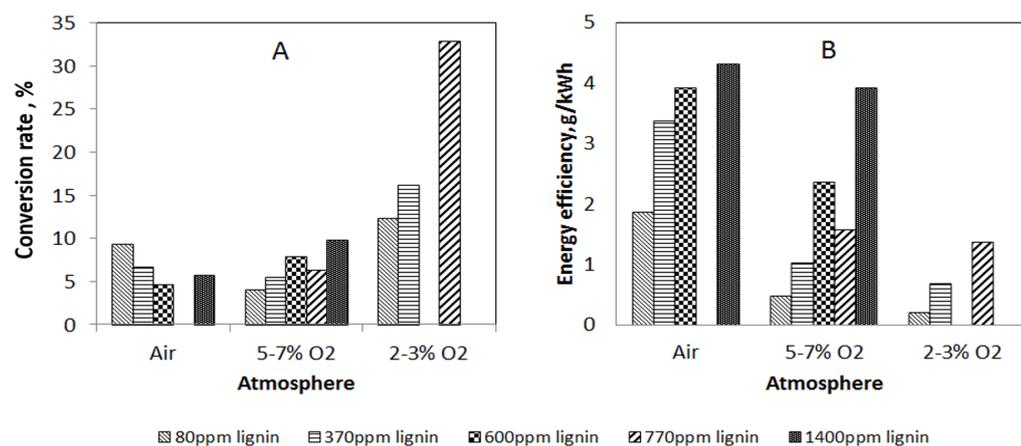


Figure 4.19: The conversion rate (A) and energy efficiency (B) of aldehyde formation in different atmospheres with different initial lignin concentrations [72].

On the other hand, the worst energy efficiency of aldehyde formation is observed in the low oxygen content atmosphere, and the best energy efficiency was observed in the air. It should be pointed out, that a further increase of the concentration in air does not lead to a significant increase in energy efficiency. In the experiments with low oxygen content it is possible to achieve a higher efficiency value, even surpassing those in air, by increasing the initial concentration.

Kraft lignin and BLN were the subjects of an investigation of PCD's influence on lignin structure. Changes in solubility, molecular weight and the proportion of phenolic and aliphatic OH groups, as well as lignin repolymerisation, were observed. The treated lignin became more soluble in water, which can be explained by the formation of carboxylic functional groups. Signals of aromatic compounds could be seen in the ¹³C NMR spectrum for lignin treated in the oxygen-thin atmosphere, but for the lignin treated in air, these signals were not detected. The degradation of the aromatic rings or reaction at the aromatic C-H position can be clearly seen in HSQC spectra (see Figure 8, Publication III). This figure shows a clear degradation of the aromatic C-H correlation peaks approximately at 120–105/6.0–7.5 (δ_C/δ_H) ppm.

In general, it is possible to conclude that PCD treatment changed the lignin structure significantly. The modified lignin had a polymeric or oligomeric structure with a high degree of carboxyl or carbonyl groups. The degradation level is a direct function of the

oxygen content in the gas phase. In the oxygen-thin atmosphere, the initial lignin depolymerisation, with the subsequent polymerisation of lignin fragments, was observed.

5 Conclusions

Two distinct options for PCD implementation were studied: PCD used for the removal of organic and inorganic compounds from water and the potential application of PCD technology for the modification of organics in order to form value-added products.

In the first of these two options, several experiments were carried out with three antibiotics (amoxicillin, doxycycline, sulfamethizole), one immunostimulating drug (MAA) and one inorganic compound (sodium thiosulfate). The kinetics of the reactions and formation of the oxidation by-products were studied by taking into account such factors as pH, the initial concentration of target compounds, gas-phase composition, the recirculation water flow rate, pulse-repetition frequency and the temperature of the liquid phase. Special attention was paid to temperature effect on the oxidation process since, for instance, due to seasonal variation, the temperature of the wastewaters being treated may differ significantly and the influence of solution temperature is not widely studied. In addition, this dissertation pays increased attention to the influence of the presence of one antibiotic on the degradation of another antibiotic in terms of energy efficiency and also in terms of the possible intermediate products of oxidation.

The main evaluation parameter of the PCD process was energy efficiency, which in order to facilitate comparisons, was calculated as half-life energy efficiency when the target compound removal was 50 %. The obtained results helped understand how the studied compounds behave in the cold plasma field and helped find the optimal conditions for their oxidation.

Therefore, the ideal conditions for the reaction of doxycycline and amoxicillin are reduced frequency and alkaline media, for sulfamethizole oxidation, reduced frequency and any pH (since pH has no effect on the energy efficiency of sulfamethizole oxidation). A neutral media, low frequency and the average initial concentration of the target compound provided optimal conditions for MAA oxidation. For all the experiments, an oxygen-enriched atmosphere accelerated the oxidation process and contributed to less energy consumption. Almost all the studied oxidation reactions were first-order reactions, except for the reaction of sodium thiosulfate degradation and the reaction of amoxicillin degradation in alkaline media. The reaction of amoxicillin was a second-order reaction, and the thiosulfate oxidation was a zero-order reaction. The initial concentration of sodium thiosulfate had no effect on its oxidation efficiency, which is typical for a zero-order reaction, and the frequency had little effect. However, it should be noted that the energy efficiency was slightly better at a higher frequency. Therefore, PCD treatment of sodium thiosulfate should be carried out at elevated frequencies, which allows reducing the treatment time.

All oxidation by-products detected during the treatment decomposed by the end of the treatment process. The presence of more than one dissolved compound in water had no effect on the qualitative composition of oxidation by-products. However, there was a

decrease in the energy efficiency and reaction speed of the oxidation of individual compounds in the multicomponent system.

The effect of the temperature of the liquid phase was studied by using the example of sulfamethizole treatment. It was found that the temperature had no effect on reaction order. An ambient temperature (around 20 °C) is the optimal temperature for the treatment of sulfamethizole since an increase of up to 50 °C in temperature led to a significant deterioration in energy efficiency and a decrease in temperature (relative to room temperature) did not affect the process.

In general, it has been demonstrated that PCD can effectively decompose various compounds dissolved in the aqueous solution by utilising the combined physical and chemical effects initiated by gas-phase discharge.

Experiments with two types of lignin were conducted. PCD treatment significantly changed lignin's structure; the modified structure was polymeric or oligomeric and contained a high degree of carboxyl or carbonyl groups. The solubility of treated lignin changed to a more water-soluble lignin.

Lignin degradation is a direct function of the oxygen concentration in the gas phase. Under less harsh conditions with a lower oxygen content, the initial depolymerisation of lignin is observed at the beginning of the PCD treatment with subsequent polymerisation of lignin fragments. Aldehyde formation was detected during the PCD treatment, and it was found that in a thin-oxygen atmosphere, increasing the lignin's initial concentration made it possible to achieve the best result in terms of the energy efficiency of aldehyde formation in the long run. Despite the fact that the formation of aldehydes was observed, the most likely PCD technology cannot be used to obtain them since the PCD oxidation process is non-selective. However, PSD technology can be used for pre-treatment of such materials as lignin in order to improve their chemical reactivity.

References

- [1] D. Quoc Tuc, M.G. Elodie, L. Pierre, A. Fabrice, T. Marie-Jeanne, B. Martine, E. Joelle, C. Marc, Fate of antibiotics from hospital and domestic sources in a sewage network, *Sci. Total Environ.* 575 (2017) 758–766. doi:10.1016/j.scitotenv.2016.09.118.
- [2] B. Tiwari, B. Sellamuthu, Y. Ouarda, P. Drogui, R.D. Tyagi, G. Buelna, Review on fate and mechanism of removal of pharmaceutical pollutants from wastewater using biological approach, *Bioresour. Technol.* 224 (2017) 1–12. doi:10.1016/j.biortech.2016.11.042.
- [3] T.A. Ternes, J. Stüber, N. Herrmann, D. McDowell, A. Ried, M. Kampmann, B. Teiser, Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater?, *Water Res.* 37 (2003) 1976–1982. doi:10.1016/S0043-1354(02)00570-5.
- [4] M. Krichevskaya, D. Klauson, E. Portjanskaja, S. Preis, The Cost Evaluation of Advanced Oxidation Processes in Laboratory and Pilot-Scale Experiments, *Ozone Sci. Eng.* 33 (2011) 211–223. doi:10.1080/01919512.2011.554141.
- [5] W.H. Glaze, J.-W. Kang, D.H. Chapin, The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation, *Ozone Sci. Eng.* 9 (1987) 335–352. doi:10.1080/01919518708552148.
- [6] A.A. Joshi, B.R. Locke, P. Arce, W.C. Finney, Formation of hydroxyl radicals, hydrogen peroxide and aqueous electrons by pulsed streamer corona discharge in aqueous solution, *J. Hazard. Mater.* 41 (1995) 3–30. doi:10.1016/0304-3894(94)00099-3.
- [7] B.R. Locke, M. Sato, P. Sunka, M.R. Hoffmann, J.S. Chang, Electrohydraulic discharge and nonthermal plasma for water treatment, *Ind. Eng. Chem. Res.* 45 (2006) 882–905. doi:10.1021/ie050981u.
- [8] A. Bogaerts, E. Neyts, R. Gijbels, J. Van der Mullen, Gas discharge plasmas and their applications, *Spectrochim. Acta - Part B At. Spectrosc.* 57 (2002) 609–658. doi:10.1016/S0584-8547(01)00406-2.
- [9] M. Malik, K. Schoenbach, A Novel Pulsed Corona Discharge Reactor Based on Surface Streamers for NO Conversion from N₂-O₂ Mixture Gases, *Int. J. Plasma Environ. Sci. Technol.* (2011).
- [10] P. Lukes, M. Clupek, P. Sunka, F. Peterka, T. Sano, N. Negishi, S. Matsuzawa, K. Takeuchi, Degradation of phenol by underwater pulsed corona discharge in combination with TiO₂-photocatalysis, *Res. Chem. Intermed.* 31 (2005). doi:10.1163/1568567053956734.

- [11] S. Tomizawa, M. Tezuka, Kinetics and mechanism of the organic degradation in aqueous solution irradiated with gaseous plasma, *Plasma Chem. Plasma Process.* 27 (2007) 486–495. doi:10.1007/s11090-007-9063-5.
- [12] I. Panorel, I. Kornev, H. Hatakka, S. Preis, Pulsed corona discharge for degradation of aqueous humic substances, *Water Sci. Technol. Water Supply.* 11 (2011) 238–245. doi:10.2166/ws.2011.045.
- [13] T. Oda, Non-thermal plasma processing for environmental protection: Decomposition of dilute VOCs in air, *J. Electrostat.* 57 (2003) 293–311. doi:10.1016/S0304-3886(02)00179-1.
- [14] G.-B. Zhao, S. John, J.-J. Zhang, L. Wang, S. Muknahallipatna, J.C. Hamann, J.F. Ackerman, M.D. Argyle, O.A. Plumb, Methane conversion in pulsed corona discharge reactors, *Chem. Eng. J.* 125 (2006) 67–79. doi:10.1016/j.cej.2006.08.008.
- [15] U. Hübner, U. von Gunten, M. Jekel, Evaluation of the persistence of transformation products from ozonation of trace organic compounds - A critical review, *Water Res.* 68 (2015) 150–170. doi:10.1016/j.watres.2014.09.051.
- [16] R. Rosal, M.S. Gonzalo, K. Boltes, P. Letón, J.J. Vaquero, E. García-Calvo, Identification of intermediates and assessment of ecotoxicity in the oxidation products generated during the ozonation of clofibric acid, *J. Hazard. Mater.* 172 (2009) 1061–1068. doi:10.1016/j.jhazmat.2009.07.110.
- [17] I. Panorel, L. Kaijanen, I. Kornev, S. Preis, M. Louhi-Kultanen, H. Siren, Pulsed corona discharge oxidation of aqueous lignin: decomposition and aldehydes formation, *Environ. Technol.* 35 (2014) 171–176. doi:10.1080/09593330.2013.821144.
- [18] M.G. Aylmore, D.M. Muir, Thiosulfate leaching of gold - a review, *Miner. Eng.* 14 (2001) 135–174. doi:10.1016/S0892-6875(00)00172-2.
- [19] SGS Mineral Services, Thiosulphate Leaching – an Alternative To Cyanidation in Gold Processing Alternatives To Cyanide in Gold, (2008) 2–3.
- [20] A.H. Nielsen, J. Vollertsen, T. Hvitved-Jacobsen, Determination of kinetics and stoichiometry of chemical sulfide oxidation in wastewater of sewer networks, *Environ. Sci. Technol.* 37 (2003) 3853–3858. doi:10.1021/es0340351.
- [21] M. Ksibi, Chemical oxidation with hydrogen peroxide for domestic wastewater treatment, *Chem. Eng. J.* 119 (2006) 161–165. doi:10.1016/j.cej.2006.03.022.
- [22] P. Verlicchi, M. Al Aukidy, E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after

- a secondary treatment-A review, *Sci. Total Environ.* 429 (2012) 123–155. doi:10.1016/j.scitotenv.2012.04.028.
- [23] T.P. Van Boeckel, S. Gandra, A. Ashok, Q. Caudron, B.T. Grenfell, S.A. Levin, R. Laxminarayan, Global antibiotic consumption 2000 to 2010: An analysis of national pharmaceutical sales data, *Lancet Infect. Dis.* 14 (2014) 742–750. doi:10.1016/S1473-3099(14)70780-7.
- [24] M. Fürhacker, The Water Framework Directive - Can we reach the target?, *Water Sci. Technol.* 57 (2008) 9–17. doi:10.2166/wst.2008.797.
- [25] S. Samukawa, M. Hori, S. Rauf, K. Tachibana, P. Bruggeman, G. Kroesen, J.C. Whitehead, A.B. Murphy, A.F. Gutsol, S. Starikovskaia, U. Kortshagen, J.P. Boeuf, T.J. Sommerer, M.J. Kushner, U. Czarnetzki, N. Mason, The 2012 plasma roadmap, *J. Phys. D. Appl. Phys.* 45 (2012). doi:10.1088/0022-3727/45/25/253001.
- [26] J.-S. Chang, A.J. Kelly, J.M. Crowley, *Handbook of electrostatic processes*, CRC Press, 1995.
- [27] W.F.L.M. Hoeben, E.M. Van Veldhuizen, W.R. Rutgers, C.A.M.G. Cramers, G.M.W. Kroesen, The degradation of aqueous phenol solutions by pulsed positive corona discharges, *Plasma Sources Sci. Technol.* 9 (2000) 361–369. doi:10.1088/0963-0252/9/3/315.
- [28] B. Jiang, J. Zheng, Q. Liu, M. Wu, Degradation of azo dye using non-thermal plasma advanced oxidation process in a circulatory airtight reactor system, *Chem. Eng. J.* 204–205 (2012) 32–39. doi:10.1016/j.cej.2012.07.088.
- [29] B.R. Locke, S.M. Thagard, Analysis and Review of Chemical Reactions and Transport Processes in Pulsed Electrical Discharge Plasma Formed Directly in Liquid Water, *Plasma Chem. Plasma Process.* 32 (2012) 875–917. doi:10.1007/s11090-012-9403-y.
- [30] H. Kušić, N. Koprivanac, B.R. Locke, Decomposition of phenol by hybrid gas/liquid electrical discharge reactors with zeolite catalysts, *J. Hazard. Mater.* 125 (2005) 190–200. doi:10.1016/j.jhazmat.2005.05.028.
- [31] L.R. Grabowski, E.M. Van Veldhuizen, A.J.M. Pemen, W.R. Rutgers, Corona above water reactor for systematic study of aqueous phenol degradation, *Plasma Chem. Plasma Process.* 26 (2006) 3–17. doi:10.1007/s11090-005-8721-8.
- [32] N. Sano, T. Kawashima, J. Fujikawa, T. Fujimoto, T. Kitai, T. Kanki, A. Toyoda, Decomposition of organic compounds in water by direct contact of gas corona discharge: Influence of discharge conditions, *Ind. Eng. Chem. Res.* 41 (2002) 5906–5911. doi:10.1021/ie0203328.

- [33] K. Faungnawakij, N. Sano, T. Charinpanitkul, W. Tanthapanichakoon, Modeling of experimental treatment of acetaldehyde-laden air and phenol-containing water using corona discharge technique, *Environ. Sci. Technol.* 40 (2006) 1622–1628. doi:10.1021/es051102y.
- [34] N. Sano, D. Yamamoto, T. Kanki, A. Toyoda, Decomposition of Phenol in Water by a Cylindrical Wetted-Wall Reactor Using Direct Contact of Gas Corona Discharge, *Ind. Eng. Chem. Res.* 42 (2003) 5423–5428. doi:10.1021/ie030075m.
- [35] E. Njatawidjaja, A. Tri Sugiarto, T. Ohshima, M. Sato, Decoloration of electrostatically atomized organic dye by the pulsed streamer corona discharge, *J. Electrostat.* 63 (2005) 353–359. doi:10.1016/j.elstat.2004.12.001.
- [36] V.M. Bystritskii, T.K. Wood, Y. Yankelevich, S. Chauhan, D. Yee, F. Wessel, Pulsed power for advanced waste water remediation, in: *Pulsed Power Conf. 1997*. Dig. Tech. Pap. 1997 11th IEEE Int., IEEE, 1997: pp. 79–84.
- [37] L.R. Grabowski, Pulsed corona in air for water treatment, *Diss. Abstr. Int.* 68 (2006).
- [38] A. Pokryvailo, M. Wolf, Y. Yankelevich, S. Wald, L.R. Grabowski, E.M. van Veldhuizen, W.R. Rutgers, M. Reiser, B. Glocker, T. Eckhardt, P. Kempnaers, A. Welleman, High-power pulsed corona for treatment of pollutants in heterogeneous media, in: *IEEE Trans. Plasma Sci.*, 2006: pp. 1731–1743. doi:10.1109/TPS.2006.881281.
- [39] 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. doi:10.1080/01919512.2013.760415.
- [40] 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. doi:10.1080/09593330.2012.722691.
- [41] S. Preis, I.C. 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. doi:10.2166/wst.2013.399.
- [42] S. Preis, I. Panorel, S. Llauger Coll, I. Kornev, Formation of Nitrates in Aqueous Solutions Treated with Pulsed Corona Discharge: The Impact of Organic Pollutants, *Ozone Sci. Eng.* 36 (2014) 94–99. doi:10.1080/01919512.2013.836955.
- [43] 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. doi:10.1080/01919512.2013.720898.

- [44] I. Kornev, S. Preis, E. Gryaznova, F. Saprykin, P. Khryapov, M. Khaskelberg, N. Yavorovskiy, Aqueous dissolved oil fraction removed with pulsed corona discharge, *Ind. Eng. Chem. Res.* 53 (2014) 7263–7267. doi:10.1021/ie403730q.
- [45] O. Legrini, E. Oliveros, A.M. Braun, Photochemical Processes for Water Treatment, *Chem. Rev.* 93 (1993) 671–698. doi:10.1021/cr00018a003.
- [46] B. Jiang, J. Zheng, S. Qiu, M. Wu, Q. Zhang, Z. Yan, Q. Xue, Review on electrical discharge plasma technology for wastewater remediation, *Chem. Eng. J.* 236 (2014) 348–368. doi:10.1016/j.cej.2013.09.090.
- [47] M.A. Malik, A. Ghaffar, S.A. Malik, Water purification by electrical discharges, *Plasma Sources Sci. Technol.* 10 (2001) 82–91. doi:10.1088/0963-0252/10/1/311.
- [48] W.H. Glaze, Drinking-water treatment with ozone, *Environ. Sci. Technol.* 21 (1987) 224–230. doi:10.1021/es00157a001.
- [49] R.P. Joshi, S.M. Thagard, Streamer-Like Electrical Discharges in Water: Part I. Fundamental Mechanisms, *Plasma Chem. Plasma Process.* 33 (2013) 1–15. doi:10.1007/s11090-012-9425-5.
- [50] P. Lukes, B.R. Locke, J.L. Brisset, Aqueous-Phase Chemistry of Electrical Discharge Plasma in Water and in Gas-Liquid Environments, in: *Plasma Chem. Catal. Gases Liq.*, 2012: pp. 243–308. doi:10.1002/9783527649525.ch7.
- [51] P. Neta, Reactions of hydrogen atoms in aqueous solutions, *Chem. Rev.* 72 (1972) 533–543. doi:10.1021/cr60279a005.
- [52] R.P. Joshi, S.M. Thagard, Streamer-like electrical discharges in water: Part II. environmental applications, *Plasma Chem. Plasma Process.* 33 (2013) 17–49. doi:10.1007/s11090-013-9436-x.
- [53] A.M. Anpilov, E.M. Barkhudarov, Y.B. Bark, Y. V Zadiraka, M. Christofi, Y.N. Kozlov, I. a Kossyi, V. a Kop'ev, V.P. Silakov, M.I. Taktakishvili, S.M. Temchin, Electric discharge in water as a source of UV radiation, ozone and hydrogen peroxide, *J. Phys. D. Appl. Phys.* 34 (2001) 993–999. doi:10.1088/0022-3727/34/6/322.
- [54] P. Lukeš, Water treatment by pulsed streamer corona discharge, *Inst. Plasma Phys. AS CR, Prague, Czech Repub.* (2001).
- [55] P. Lukeš, M. Člupek, V. Babický, P. Šunka, J.D. Skalný, M. Štefečka, J. Novák, Z. Málková, Erosion of needle electrodes in pulsed corona discharge in water, in: *Czechoslov. J. Phys.*, 2006. doi:10.1007/s10582-006-0304-2.
- [56] B. Sun, M. Sato, J.S. Clements, Optical study of active species produced by a

- pulsed streamer corona discharge in water, *J. Electrostat.* 39 (1997) 189–202. doi:10.1016/S0304-3886(97)00002-8.
- [57] D. Dobrin, C. Bradu, M. Magureanu, N.B. Mandache, V.I. Parvulescu, Degradation of diclofenac in water using a pulsed corona discharge, *Chem. Eng. J.* 234 (2013) 389–396. doi:10.1016/j.cej.2013.08.114.
- [58] R.K. Singh, V. Babu, L. Philip, S. Ramanujam, Disinfection of water using pulsed power technique: Effect of system parameters and kinetic study, *Chem. Eng. J.* 284 (2016) 1184–1195. doi:10.1016/j.cej.2015.09.019.
- [59] Y.S. Chen, X.S. Zhang, Y.C. Dai, W.K. Yuan, Pulsed high-voltage discharge plasma for degradation of phenol in aqueous solution, *Sep. Purif. Technol.* 34 (2004) 5–12. doi:10.1016/S1383-5866(03)00169-2.
- [60] P. Ajo, S. Preis, T. Vornamo, M. Mänttari, M. Kallioinen, M. Louhi-Kultanen, Hospital wastewater treatment with pilot-scale pulsed corona discharge for removal of pharmaceutical residues, *J. Environ. Chem. Eng.* 6 (2018) 1569–1577. doi:10.1016/j.jece.2018.02.007.
- [61] E. Njoyim, P. Ghogomu, S. Laminsi, S. Nzali, A. Doubla, J.L. Brisset, Coupling gliding discharge treatment and catalysis by oyster shell powder for pollution abatement of surface waters, *Ind. Eng. Chem. Res.* 48 (2009) 9773–9780. doi:10.1021/ie901118m.
- [62] M.R. Ghezzar, F. Abdelmalek, M. Belhadj, N. Benderdouche, A. Addou, Enhancement of the bleaching and degradation of textile wastewaters by Gliding arc discharge plasma in the presence of TiO₂ catalyst, *J. Hazard. Mater.* 164 (2009) 1266–1274. doi:10.1016/j.jhazmat.2008.09.060.
- [63] European Centre for Disease Prevention and Control, Summary of the latest data on antibiotic consumption in EU: 2016, (2016).
- [64] E.M. Scholar, W.B. Pratt, *The Antimicrobial Drugs*, Oxford University Press, 2000.
- [65] R. Wise, Antimicrobial resistance: priorities for action., *J. Antimicrob. Chemother.* 49 (2002) 585–586. doi:10.1093/jac/49.4.585.
- [66] S.S. VON, Method for extracting lignin, (2015).
- [67] A. Sokolov, M. Louhi-Kultanen, Behaviour of aqueous sulfamethizole solution and temperature effects in cold plasma oxidation treatment, *Sci. Rep.* 8 (2018) 1–10. doi:10.1038/s41598-018-27061-5.
- [68] W.H. Evans, A. Dennis, Spectrophotometric determination of low levels of mono-

-
- {,} di- and triethylene glycols in surface waters, *Analyst*. 98 (1973) 782–791. doi:10.1039/AN9739800782.
- [69] A. Sokolov, M. Kråkström, P. Eklund, L. Kronberg, M. Louhi-Kultanen, Abatement of amoxicillin and doxycycline in binary and ternary aqueous solutions by gas-phase pulsed corona discharge oxidation, *Chem. Eng. J.* 334 (2018) 673–681. doi:10.1016/j.cej.2017.10.071.
- [70] D. Klauson, M. Krichevskaya, M. Borissova, S. Preis, Aqueous photocatalytic oxidation of sulfamethizole, *Environ. Technol.* 31 (2010) 1547–1555. doi:10.1080/09593331003789537.
- [71] E. Nägele, R. Moritz, Structure elucidation of degradation products of the antibiotic amoxicillin with ion trap MS and accurate mass determination by ESI TOF, *J. Am. Soc. Mass Spectrom.* 16 (2005) 1670–1676. doi:10.1016/j.jasms.2005.06.002.
- [72] A. Sokolov, L. Lagerquist, P. Eklund, M. Louhi-Kultanen, Non-thermal gas-phase pulsed corona discharge for lignin modification, *Chem. Eng. Process. - Process Intensif.* 126 (2018) 141–149. doi:10.1016/j.cep.2018.02.028.

Appendix A: Figures. Concentration vs delivered energy

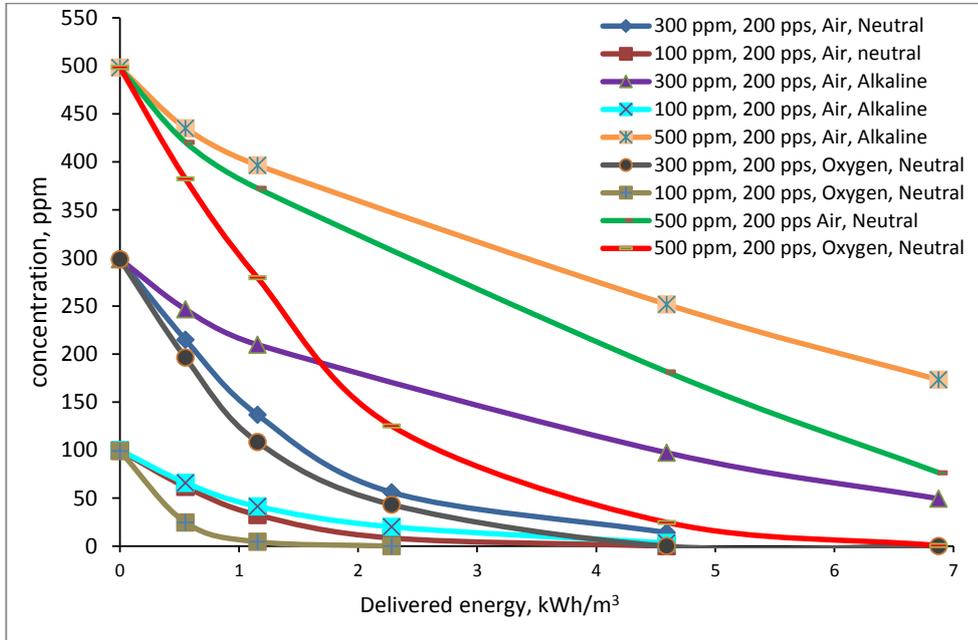


Figure A 1: MAA concentration as a function of delivered energy per unit volume at 200 pps.

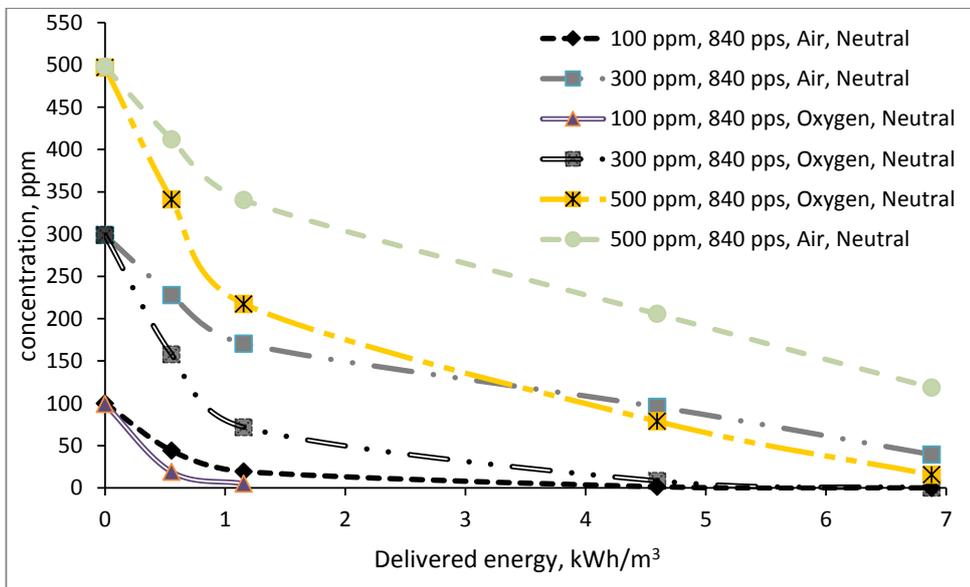


Figure A 2: MAA concentration as a function of delivered energy per unit volume at 840 pps.

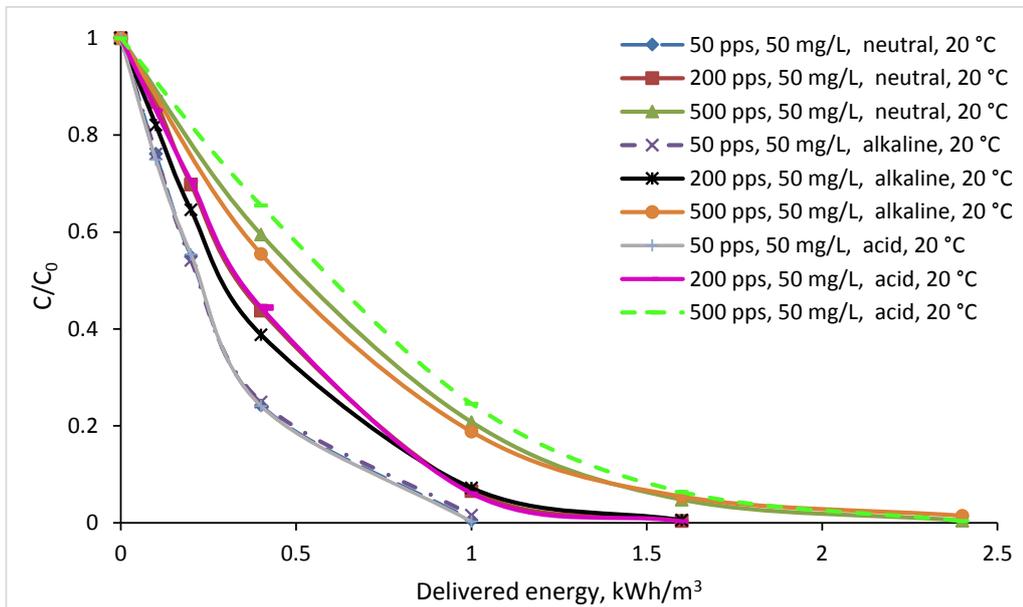


Figure A 3: Relative concentration of sulfamethizole as function of delivered energy per unit volume at $20\text{ }^\circ\text{C}$.

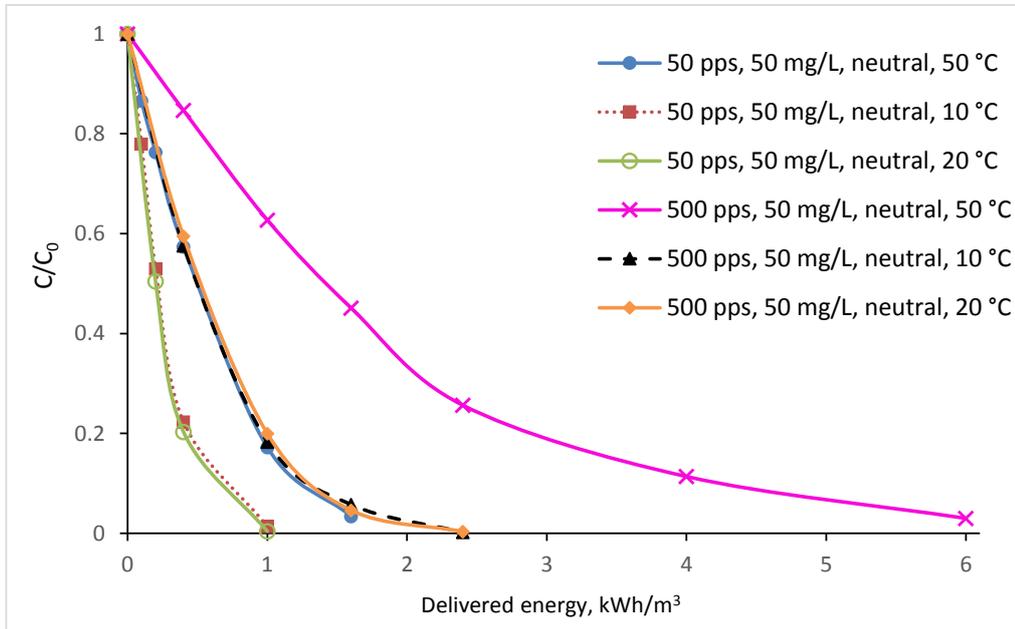


Figure A 4: Relative concentration of sulfamethizole as a function of delivered energy per unit volume at different temperatures.

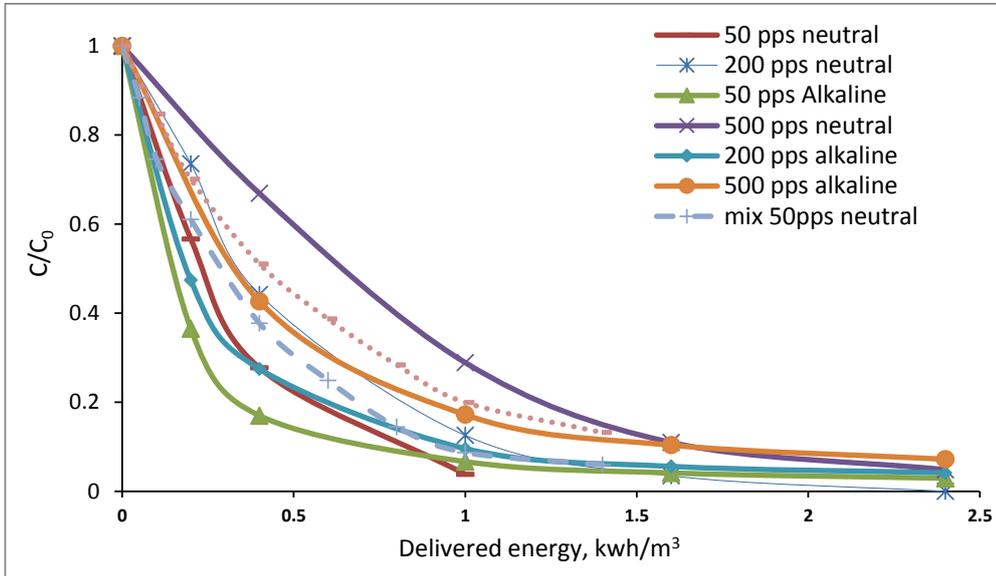


Figure A 5: Relative concentration of amoxicillin as function of delivered energy per unit volume with 50 ppm initial concentration.

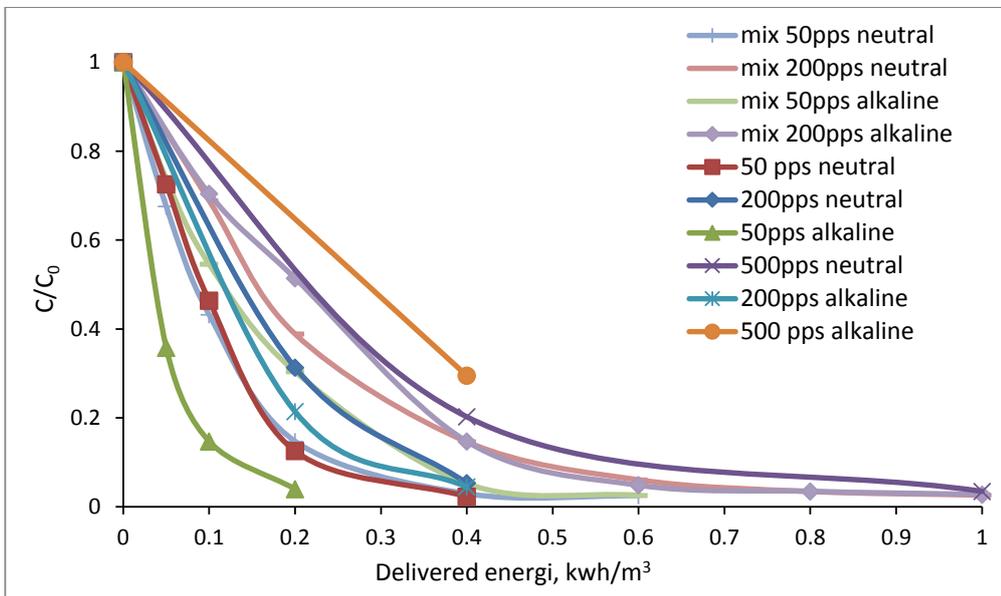


Figure A 6: Relative concentration of doxycycline as function of delivered energy per unit volume with 50 ppm initial concentration at different frequencies and pH.

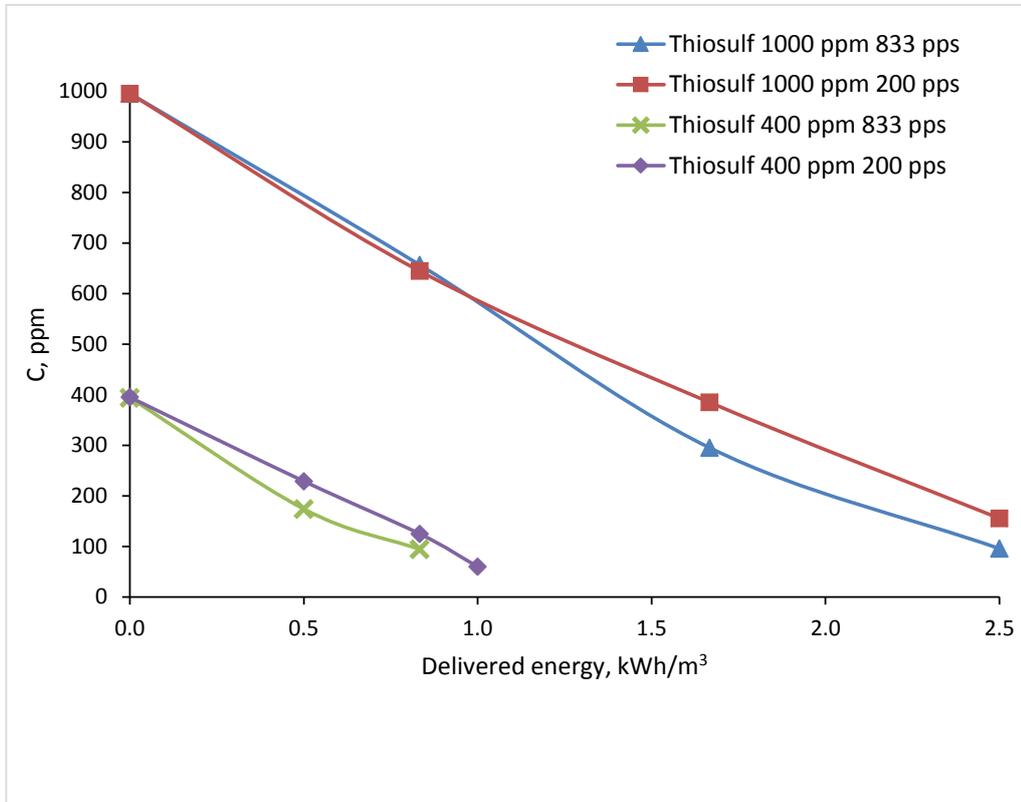


Figure A 7: Sodium thiosulfate concentration as a function of delivered energy per unit volume with various initial concentrations and pulse frequencies.

Publication I

Sokolov, A., Kråkström, M., Eklund, P., Kronberg, L., Louhi-Kultanen, M.
**Abatement of amoxicillin and doxycycline in binary and ternary aqueous
solutions by gas-phase pulsed corona discharge oxidation**

Reprinted with permission from
Chemical Engineering Journal
Vol. 334, pp. 673-681, 2018
© 2018, Elsevier



Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Abatement of amoxicillin and doxycycline in binary and ternary aqueous solutions by gas-phase pulsed corona discharge oxidation

Alexander Sokolov^{a,*}, Matilda Kråkström^b, Patrik Eklund^b, Leif Kronberg^b,
Marjatta Louhi-Kultanen^{a,c}

^a School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53850 Lappeenranta, Finland

^b Johan Gadolin Process Chemistry Centre, Laboratory of Organic Chemistry, Åbo Akademi University, Biskopsgatan 8, 20500 Åbo, Finland

^c School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076 Aalto (Espoo), Finland

ARTICLE INFO

Keywords:

Pharmaceuticals
Wastewater treatment
Cold plasma
AOPs
Ozone

ABSTRACT

The presence of pharmaceutical compound residues in water bodies is becoming an increasingly serious problem. Various pharmaceuticals have been detected in raw municipal wastewaters, after wastewater treatment plant processes, and even in drinking water. Many common pharmaceuticals are bio-accumulating and they can have a harmful impact on aquatic and terrestrial organisms.

In this work, pulsed corona discharge technology (PCD) is studied as a potential method for antibiotic compounds abatement. Two antibiotics, amoxicillin and doxycycline, were chosen as test pharmaceutical compounds. The aim of the study was to investigate the transformation kinetics of binary solutions (water – single antibiotic compound) and ternary solutions (water – two antibiotic compounds) of the compounds and to optimize operational parameters for improved oxidation performance. Ternary solutions were investigated to obtain data on transformation kinetics when two competing pharmaceutical molecules are present in the solution. The experiments showed that reactions of doxycycline oxidation are always first order reactions. Reaction of amoxicillin oxidation has second order in the case of experiments with binary solution in alkaline medium. In other cases, it has first order. The transformation products formed were identified and monitored based on liquid chromatography mass spectrometer analysis. OH-amoxicillin, amoxicillin penicilloic acid, OH-doxycycline and 2-OH-doxycycline had the largest peaks areas. All studied compounds and all transformation products can be easily oxidized by PCD. Approximately 1 kWh/m³ and 0.5 kWh/m³ delivered energy is enough for oxidation of great part of amoxicillin and doxycycline respectively. Low frequency, 50 pps, and high (pH = 12) are preferable for oxidation of both antibiotics from the energy consumption point of view.

1. Introduction

Pharmaceutical compounds were first detected in natural water bodies in the 1970s. At the time, these compounds, i.e. active pharmaceutical ingredients (API), were not considered hazardous as their concentrations were insignificant. However, a continuously growing and ageing of population, improving quality of life and greater use of pharmaceuticals in rearing of livestock have led to increased consumption of pharmaceutical compounds, which in turn has resulted in greater accumulation of pharmaceutical compounds in the environment. Furthermore, an absence of legislation specifically addressing the discharge of pharmaceuticals-containing wastewaters into ground water and surface water bodies has also contributed to continuous growth of these compounds in the natural environment [1,2].

Pharmaceutical compounds are developed to be highly bioactive in

order to react with receptors in humans and animals and produce the desired medicinal effect. They are usually toxic towards health-threatening organisms such as bacteria, fungi and parasites. A significant amount of lower animals have receptor systems similar to humans and higher animals. Furthermore, many of the organism groups affecting human and animal health and targeted by pharmaceuticals play an important role in natural ecosystems. Therefore, pharmaceuticals may impact significantly on aquatic and terrestrial organisms [3].

A number of studies have reported on the impact of pharmaceuticals on environmental health [4–6] and there are special requirements for environmental risk assessment of the effects of human and veterinary medicines on aquatic and terrestrial organisms. Such requirements were first established in 1980 by the US Food and Drug Administration (FDA) [40], and similar requirements were adopted in the EU in 1997. These risk assessments investigate potential negative effects on

* Corresponding author.

E-mail address: alexander.sokolov@lut.fi (A. Sokolov).

<http://dx.doi.org/10.1016/j.cej.2017.10.071>

Received 3 March 2017; Received in revised form 21 August 2017; Accepted 14 October 2017

Available online 16 October 2017

1385-8947/ © 2017 Elsevier B.V. All rights reserved.

daphnids, fish, algae, bacteria, earthworms and plants [3].

One of the main sources of pharmaceuticals contamination in natural waters is wastewater effluent from municipal treatment plants treating hospital effluents and human wastes [7]. Municipal wastewater treatment plants are generally not equipped to deal with complex pharmaceuticals, as most plants consist of primary and secondary treatments (mainly activated sludge systems) without tertiary treatment processes able to efficiently remove medical drugs [8,9]. The concentration of pharmaceuticals in natural water bodies is in the range of ng/L to µg/L [10].

Ozonation can be applied for removal of pharmaceuticals from water [11], but the high cost of ozone makes this method economically unviable [12–14]. The necessity for the novel water treatment methods is thus clear.

The present work investigates, economically and as regards environmental safety, the feasibility of ultra-short gas-phase pulsed corona discharge (PCD) oxidation at ambient conditions for pharmaceuticals removal from water. PCD oxidation is a chemical-free method that generates hydroxyl radicals and ozone as the main oxidation species for oxidation of various organic molecules. PCD has been shown to be an effective method for oxidation of pharmaceuticals by Panorel et al. [15,16], who studied PCD oxidation for removal of compounds such as paracetamol, ibuprofen, β-estradiol, indomethacin and salicylic acid.

Many antibiotics are refractory substances [17] that can pass through biological treatment facilities without degradation, thus ending up in water bodies [18,19]. The compounds investigated in this work were chosen based on risk quotient (RQ), as proposed by Verlicchi [19]; namely, the ratio between the average concentration of pharmaceuticals in a secondary effluent and the corresponding predicted no-effect concentration (PNEC) [20].

Possible oxidation reaction pathways of these compounds have been presented by Klauson et al. [21,22]. Most research into degradation of the studied antibiotics by advanced oxidation processes (AOP) has considered UV photolysis, ozonation, the Fenton reaction and combinations of these methods. Moreira et al. [23] and Elmolla and Chaudhuri [24] report extremely low degradation of amoxicillin under direct single photolysis, and similar results are reported for doxycycline degradation [25]. However, amoxicillin and doxycycline are easily oxidized in processes where ozone is involved [23,26,25]. Although ozonation is an effective approach, its use brings additional costs as the ozone has been generated separately in the ozone generator and transferred to the wastewater treatment unit, and the residual ozone gas has to be recovered. The Fenton process is the most effective method of commonly used AOPs [27–29] but has the drawback of sludge formation when ferrous iron chemical is added to the system.

This work focuses on investigation of process parameters with the aim of increasing the energy efficiency of the oxidation process. Process parameters considered include pulse repetition frequency, treatment time, and pH value.

There is a considerable body of work about the effect of carbonate species (HCO_3^- , CO_3^{2-}), natural organic matter and other organic compounds on oxidation by AOPs. It is well known that such species act like a OH-radicals scavenger and have a negative influence on oxidation [30,31]. Some work has also been presented in which real waste water is used as a solvent for antibiotics [32]. The study found a decrease in AOP efficiency with surface water and water from a wastewater treatment plant compared with ultra-pure water as a solvent. Although the effects of various pharmaceutical compounds in water on AOP efficiency have been investigated in numerous studies, the work has tended to focus on a single parent pharmaceutical compound, and the combined effect of the presence of antibiotics has received little attention. The present work makes an attempt to evaluate the influence of presence of one antibiotic on degradation of another antibiotic in terms of energy efficiency as well as from the point of view of possible intermediate products of oxidation.

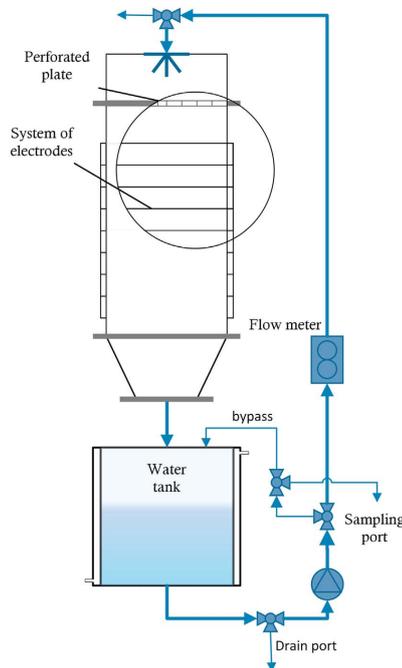


Fig. 1. Experimental setup of 100 W PCD reactor.

Although pharmaceutical oxidation products are usually less pharmacologically active than the parent compound, it has been shown that advanced oxidation processes can lead to the production of oxidation products with enhanced toxicity compared to the parent compound [33–35]. Thus, it is important to study not only the concentration of the parent compound, but also the transformation products formed when pharmaceuticals are oxidized.

2. Materials and methods

Two commercial antibiotics, amoxicillin and doxycycline, were used as test compounds. Both antibiotics were supplied by Sigma Aldrich and the purity of the antibiotics exceeded 99% (analytical grade). Liquid chromatography eluents were prepared with MilliQ water and LC-MS grade acetonitrile (VWR). Formic acid (98%, Merck) was used as an additive.

The experimental system comprised a pulsed corona discharge reactor and a high voltage pulse generator with the setup illustrated in Fig. 1. The chamber of the PCD reactor consists of two grounded vertical plate electrodes and a high voltage wire electrode located parallel between two plate electrodes. The dimensions of the plates are 210 mm in width and 1000 mm in height. The plates are located 34 mm from each other. The total plasma volume is $7.14 \times 10^6 \text{ mm}^3$. The high voltage electrodes are placed at a distance of 29 mm from each other. The diameter of the wire electrode is 0.5 mm. The chamber is covered by a transparent acrylic glass frame. An oscilloscope, Agilent 54622D, was used for determination of the pulse parameters. The energy of a single pulse was calculated using the following equation:

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

where, W_p is the energy of a single pulse, J ; T_p is the duration of the voltage pulse, ns ; $U(t)$ and $I(t)$ are waveforms of voltage and current respectively.

The energy of a single pulse produced by the generator is 0.12 J at 22 kV and 180 A in the amplitude peak at 100 ns duration, which corresponds to average energy density of 16.8 J/m³ in the plasma volume [12].

Aqueous solutions of the test compounds were circulated from the reservoir tank through the reactor by a pump. The solution is fed to the top of the reactor, where it is spread with a perforated plate and falls by gravity between the electrodes. The solution contacts the electrodes and is treated by the oxidants.

The flow rate of the re-circulating water was 4.5 L/min, which ensured sufficient trickling and adequate mixing. The key studied experimental parameters were pH level and pulse repetition frequency. All experiments were carried out at ambient pressure and temperature. Deionized water was used in the solutions.

The experiments were done with constant initial concentration of antibiotics of 50 ppm with two different initial pH levels, neutral and alkaline (in the presence of NaOH). Such relatively high concentration was chosen to make possible to investigate the behavior of tested compounds during PCD treatment. It should be noted that media without the NaOH additive are henceforth referred to as "neutral". The compounds were tested separately with binary and ternary solutions. Ternary solutions were prepared by mixing of 50 ppm of both antibiotic compounds. Initial solution concentration was chosen high enough to obtain accurate data on oxidation rates of the substance. As pulse repetition frequency is one of the primary parameters that determines the efficiency of the process, three different pulse repetition frequencies of 50 pps, 200 pps and 500 pps were used. The samples were taken with treatment time as indicated in Table 1. The total number of experiments is 20, as listed in Table 2. Each experiment was repeated several times. All plots and calculations were based on mean values of compound concentrations. Standard deviation was calculated to estimate the reproducibility of experiments. The maximum values of standard deviation for each experiment are shown in Table 2. As the table shows, the maximum standard deviation is around 0.05 indicating quite high experiment reproducibility. The concentration of pharmaceuticals was measured at least four times after each experiment. The accuracy of these measurements was around ± 0.3 ppm.

The concentration of pharmaceuticals was measured by high performance liquid chromatography (HPLC). A Kinetex 2.6 μ m C18 100A 150 \times 4.60 mm column was used for analysis of the studied solutions. The specific HPLC parameters for each compound are shown in Table 3.

Analysis of the transformation products of doxycycline and amoxicillin was performed using liquid chromatography coupled to an ion trap mass spectrometer (Agilent 1100 series LC/MSD Trap) equipped with an electrospray ionization interface. The analysis was conducted in both positive and negative mode using full scan and auto MS/MS modes. The neutral samples were injected without prior sample treatment and the pH of the alkaline samples was adjusted to 3 with formic acid before injection. For chromatographic separation, an XBridge C₁₈

Table 1
Corresponding energy delivered with treatment time.

Delivered energy dose (kWh/m ³)	Treatment time for 50 pps (min)	Treatment time for 200 pps (min)	Treatment time for 500 pps (min)
0	0	0	0
0.05	5	–	–
0.1	10	2.5	–
0.2	20	5	–
0.4	40	10	4
1	100	25	10
1.6	160	40	16
2.4	240	60	24

Table 2
List of experiments.

		Frequency	pH changing	No of experiments	Max SD
1	DXC	500 pps	4.3 \rightarrow 3.3	2	0.0497
2	DXC	500 pps	11.8 \rightarrow 11.7	2	0.0532
3	DXC	200 pps	4.2 \rightarrow 3.4	4	0.0387
4	DXC	200 pps	11.8 \rightarrow 11.7	4	0.0406
5	DXC	50 pps	4.0 \rightarrow 3.5	4	0.0351
6	DXC	50 pps	11.9 \rightarrow 11.7	4	0.0389
7	AMX	500 pps	6.6 \rightarrow 3.3	3	0.0412
8	AMX	500 pps	11.8 \rightarrow 11.7	3	0.0426
9	AMX	200 pps	6.3 \rightarrow 3.4	4	0.0299
10	AMX	200 pps	11.8 \rightarrow 11.7	4	0.031
11	AMX	50 pps	6.7 \rightarrow 4.0	4	0.0309
12	AMX	50 pps	11.9 \rightarrow 11.7	4	0.0312
13	Mix DXC	200 pps	4.3 \rightarrow 3.9	3	0.0352
14	Mix DXC	200 pps	12.2 \rightarrow 12.1	3	0.036
15	Mix DXC	50 pps	4.7 \rightarrow 4.4	3	0.03
16	Mix DXC	50 pps	12.2 \rightarrow 12.1	3	0.032
17	Mix AMX	200 pps	4.3 \rightarrow 3.9	3	0.049
18	Mix AMX	200 pps	12.2 \rightarrow 12.1	3	–
19	Mix AMX	50 pps	4.7 \rightarrow 4.4	3	0.048
20	Mix AMX	50 pps	12.2 \rightarrow 12.1	3	–

Table 3
Analysis methodology and parameters used in HPLC analysis.

	Amoxicillin	Doxycycline
Eluent	95% phosphate buffer solution (0.01 mol/L) and 5% acetonitrile	Methanol, acetonitrile, 0.01 M oxalic acid solution in volumetric proportion of 2:3:5 respectively
Column temperature	25 °C	25 °C
Retention time	Around 4 min	Around 3 min
Wavelength	229 nm	350 nm
Eluent flow rate	0.6 ml/min	0.8 ml/min
Injection volume	20 μ l	20 μ l

column (2.1 \times 50 mm, 3 μ m, Waters) and an Atlantis T3 C₁₈ column (2.1 \times 100 mm, 3 μ m, Waters) were used for doxycycline and amoxicillin respectively. The flow rate was 0.4 mL/min and MilliQ water with 0.1% formic acid and acetonitrile with 0.1% formic acid were eluents A and B, respectively. The gradient applied in the doxycycline method was: 0–1 min, 5% B; 1–25 min, 5–95% B; 25–26 min, 95% B; 26–27 min, 95–5% B; 27–35 min, 5% B. The gradient applied in the amoxicillin method was: 0–1 min, 0% B; 1–24 min, 0–60% B; 24–25 min, 60–0% B; 25–35 min, 0% B. The injection volume was 30 μ L. The LC instrument was equipped with a variable wavelength UV detector adjusted to 275 nm in the doxycycline method and 229 nm in the amoxicillin method. The source parameters in the doxycycline method were: capillary voltage of ± 3.5 kV, gas temperature 350 °C, gas flow 8 L/min, nebulizer 40 psi. Parameters for the amoxicillin method were the same with the exception that the capillary voltage was ± 4.5 kV.

Further evaluation of the transformation products was carried out with a quadrupole time-of-flight mass spectrometer (Bruker MicroTOF) equipped with an electrospray ionization interface. The analysis was carried out in positive mode in full scan mode. An Agilent series 1200 LC was used for chromatographic separations. The chromatographic method was the same as for the ion trap spectrometry.

3. Results and discussion

The present work studied the effect of pH and pulse repetition frequency on energy consumption during the oxidation process of each model compound. The main parameter to determine the efficiency of the PCD treatment was energy efficiency (ϵ , g/kWh):

$$\varepsilon = 0.5C_0/E \quad (2)$$

where, E is the delivered energy dose, corresponding to the treatment time required for 50% compound degradation, kWh/m³; C_0 is the initial concentration of the compound, mg/L. In other words, the energy efficiency shows how much energy was consumed to oxidize a half of initial concentration of tested compound.

To make sure, that amoxicillin and doxycycline do not degrade them self and do not react with each other in aqueous solution, a several controlling experiments were done. Binary solution of each antibiotic was pumped through the reactor without power supply for 5 h. Samples were taken after each hour. Changes in concentration of both antibiotics were not detected. The same run was carried out for ternary solution. The concentration of doxycycline remained in the same initial level. Decreasing in amoxicillin concentration was observed. It dropped at the beginning by 16% and remained on the same level during 5 h. We assumed that happened due to acidic condition only, and not because of chemical reaction with doxycycline. Explanation of concentration decreasing is given in Chapter 3.3.

3.1. Amoxicillin oxidation

Fig. 2 shows the oxidation results for amoxicillin. The experiments were carried out in neutral and alkaline conditions. The binary test solution was prepared with one compound, in this particular case with amoxicillin only, and the ternary solution contained both amoxicillin and doxycycline. During the treatment in alkaline conditions, the pH remained constant, around 12. In the experiments without sodium hydroxide, the pH dropped from neutral to acidic, Table 2. In treatment of the ternary solution, detection of amoxicillin in the alkaline condition failed. It would thus appear that the implemented analysis method does not give reliable results in the presence of doxycycline and sodium hydroxide.

Description of the reaction kinetics is quite demanding due to the unknown concentration of the oxidants and their share in the reaction. However, using data from the experiments, the reaction order and reaction rate constant can be determined by integration method. Functions $\ln(C/C_0)$ and $1/C$ versus treatment time were plotted to determine whether the reaction is first or second order. The linear dependence of logarithmic amoxicillin degradation in a neutral medium confirmed the first order reaction with respect to the concentration in both binary and ternary solutions, which is agreement with results presented by Dogan and Kidak [36], who also observed a first order reaction. In the alkaline medium, the reaction is a second order reaction (plot $1/C$ gave the best fitting results). The first order reaction rate constant (k_1 , min⁻¹) was determined as the slope of $\ln(C/C_0)$ versus treatment. The second order reaction rate constant (k_2 , L mg⁻¹ min⁻¹) was determined as the slope of $1/C$ versus time. Calculated reaction

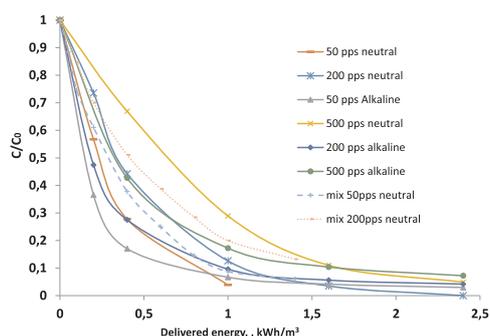


Fig. 2. Amoxicillin relative concentration vs delivered energy.

rate constants are given in Table 4. As amoxicillin could not be detected at alkaline conditions, the reaction order was not calculated for the experiment with ternary solution in an alkaline medium. It is clearly seen that the reaction rate increases with increase in frequency, as expected.

From Fig. 2, it can be concluded that amoxicillin is easily oxidized by PCD. The highest degradation was observed at the beginning of the PCD treatment. After energy delivery of 1 kWh/m³, the great part of amoxicillin was oxidized. It can further be observed that the lowest pulse repetition frequency leads to the fastest degradation rate. In an alkaline medium, the oxidation is more energy-efficient at the very beginning of the treatment than with neutral solutions. It is clearly seen from Fig. 2 that, at constant frequency, the oxidation of amoxicillin is enhanced at higher pH. This result is especially noticeable at higher frequency, when influence of OH-radicals is more significant comparing with ozone, and since the alkaline medium contains more hydroxyl radicals, the oxidation efficiency is higher at high pH. With pulse repetition frequency of 50 pps, alkaline conditions are still preferable but the influence of pH is smaller. At the lowest frequency, 50 pps, amoxicillin seems to almost oxidize fully at delivered energy around 1 kWh/m³. On the other hand, the treatment time at lower pulse repetition frequency becomes longer. In this case, ozone has more time to accumulate during the pauses between pulses and has more time for reaction with target compounds. Consequently, at low frequency, ozone plays a more significant role in the oxidation. Furthermore, the effect of pH decreases at the end of the oxidation, which is clearly seen from Fig. 2.

Energy efficiency of amoxicillin oxidation was calculated according to Eq. (2) after degradation of 50% of the initial amount of the test compound (see Fig. 3). Energy efficiency decreased with high pulse repetition in both alkaline and neutral solutions. The highest energy efficiency was obtained in alkaline solution at pulse repetition frequency of 50 pps with 149.75 g/kWh, indicating that 149.75 g of amoxicillin can be oxidized per 1 kWh. The minimum energy efficiency, 33.46 g/kWh, was detected at 500 pps frequency in neutral media. For comparison, Jin et al. [37] obtained a maximum 6.025 g/kWh for degradation of amoxicillin in aqueous solution with contact glow discharge electrolysis. With PCD treatment, even the worst result gave 5.5 times better efficiency, showing the considerable potential benefits from PCD utilization.

When treatment of the binary solution is compared with ternary solution treatment, it can be concluded that oxidation of amoxicillin in the presence of doxycycline occurs more slowly. The reaction rate constant decreased by 26–27% for the ternary solution irrespective of frequency. Moreover, more energy was required for oxidation of the same amount of amoxicillin than in treatment of the binary solution, most likely due to competitive reactions of oxidants with doxycycline. Energy efficiency of amoxicillin degradation in ternary solution decreased from 100.62 g/kWh to 72.86 g/kWh at frequency 50 pps, and from 66.4 g/kWh to 58.79 g/kWh at 200 pps. It should be noted here, that the inhibitory effect of doxycycline on amoxicillin degradation is more significant at lower pulse repetition frequency. Comparison of amoxicillin behavior during PCD treatment under alkaline and neutral conditions was not carried out. As mentioned earlier, the implemented analytical method did not enable detection of amoxicillin in an alkaline medium in the presence of doxycycline.

3.2. Doxycycline oxidation

Fig. 4 presents the oxidation of doxycycline in binary and ternary solutions in neutral and alkaline conditions. It is important to note, that the term “neutral” means absence of NaOH, practically the pH of doxycycline solutions was around 4.

Doxycycline can be oxidized with lower energy consumption than amoxicillin, and at delivered energy above 0.4 kWh/m³, doxycycline concentrations reached the detection limit of the HPLC analysis method

Table 4
Reaction rate constants; k_1, min^{-1} ; $k_2, \text{L mg}^{-1} \text{min}^{-1}$.

Frequency, pps	Binary solution								Ternary solution							
	Amoxicillin				Doxycycline				Amoxicillin				Doxycycline			
	Neutral		Alkaline		Neutral		Alkaline		Neutral		Alkaline		Neutral		Alkaline	
	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
50	0.0328	-	-	0.0031	0.0974	-	0.161	-	0.024	-	n/a	n/a	0.0894	-	0.0738	-
200	0.0850	-	-	0.0096	0.2933	-	0.311	-	0.0633	-	n/a	n/a	0.175	-	0.1832	-
500	0.1307	-	-	0.0137	0.3328	-	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

used.

In the range of 0–0.4 kWh/m³, the trends of the obtained oxidation curve are very similar as with amoxicillin. However, unlike amoxicillin degradation, the doxycycline degradation is a first order reaction in both alkaline and neutral media. Because of the fast doxycycline oxidation at a frequency of 500 pps under alkaline conditions, it was possible to take only two samples, and therefore, the reaction rate constant could not be determined in this case. As with the amoxicillin experiments, in alkaline conditions the pH remained constant in doxycycline solutions, around pH 12. However, without NaOH, the initial pH was around 4.5 and dropped to 3.5 after PCD oxidation (see Table 2). Calculated reaction rate constants are shown in Table 4. It is clearly seen that the reaction rate constant increases with increasing pulsed repetition frequency in both binary and ternary solutions irrespective of pH. Comparing results for the binary and ternary solutions, it can clearly be seen that the reaction rate constant is higher with binary solutions. For neutral conditions, the difference between the values of reaction rate constant in ternary and binary solutions is around 8.2% at 50 pps ($k_1 = 0.0974 \text{ min}^{-1}$ in binary solution against $k_1 = 0.0894 \text{ min}^{-1}$ in ternary solution) and 40% at 200 pps. ($k_1 = 0.2933 \text{ min}^{-1}$ in binary solution against $k_1 = 0.175 \text{ min}^{-1}$ in ternary solution). For alkaline conditions, this difference is 54% ($k_1 = 0.161 \text{ min}^{-1}$ in binary solution against $k_1 = 0.0738 \text{ min}^{-1}$ in ternary solution) and 41% ($k_1 = 0.311 \text{ min}^{-1}$ in binary solution against $k_1 = 0.1832 \text{ min}^{-1}$ in ternary solution) at 50 pps and 200 pps respectively. The presence of amoxicillin significantly slows down the doxycycline oxidation process. In general, high pH enhances the oxidation, but it is important to note that in the case of ternary solution treatment in alkaline media, the doxycycline oxidation reaction rate constant is a little bit lower than with neutral media. This outcome is observed only at 50 pps.

Energy efficiency of amoxicillin oxidation was calculated according to Eq. (2). The calculation results are presented in the Fig. 5. As in the case of amoxicillin oxidation, lower pulse repetition frequencies are preferable from the energy consumption point of view. As in the case of experiments with amoxicillin, the highest energy efficiency (643.11 g/kWh)

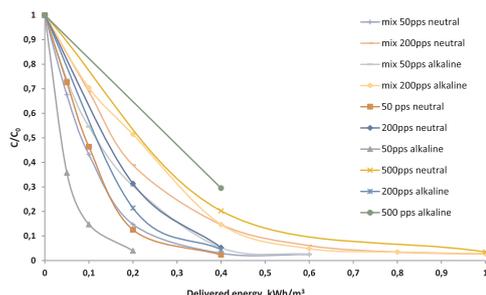


Fig. 4. Doxycycline relative concentration vs delivered energy.

(kWh) was obtained in alkaline condition in binary solution at pulse repetition frequency of 50 pps. This value is four times higher than the similar value for amoxicillin treatment (643.11 g/kWh against 149.75 g/kWh). This proves that oxidation of doxycycline is much more easily comparing with amoxicillin. It can be seen from the Fig. 5, that with increasing of frequency, energy efficiency decreasing. It is interesting observation, that at higher frequency, the influence of pH on energy efficiency become insignificant. The results presented in on the Fig. 5 suggest, that energy efficiency at 200 pps is almost the same in neutral and alkaline conditions, and higher at 500 pps in neutral condition. Better result in energy efficiency in neutral condition at 500 pps is surprising. However, it could be explained by insufficient quantity of samples, only two sample were taken during treatment at 500 ppm. Obviously, two sample are not enough for accurate analysis.

Comparing energy efficiency of treatment in binary and ternary solutions, we can see from the Fig. 5, that low frequency is still preferable in the case of ternary solution. Of course, the absolute value is lower compared to binary solution. The most interesting and unexpected finding is that, in ternary solution energy efficiency

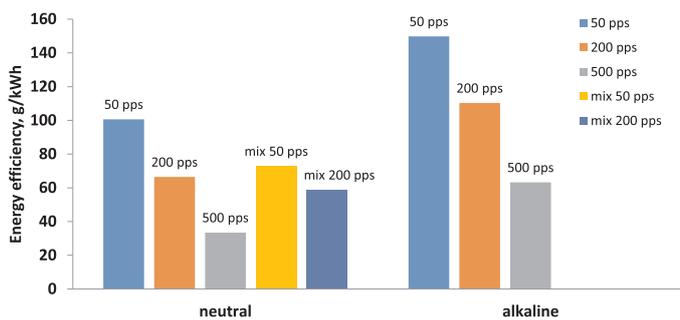


Fig. 3. Energy efficiency of amoxicillin degradation.

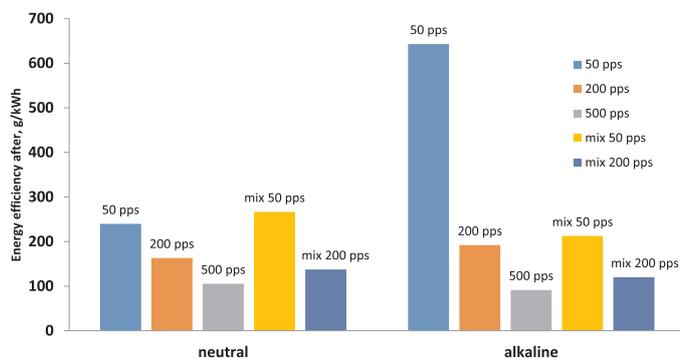


Fig. 5. Energy efficiency of doxycycline degradation.

performance is higher in neutral media.

As stated earlier, the initial concentration of the treated solutions was 50 ppm. However, HPLC analysis suggests that the initial concentration of the untreated samples was lower than prepared. The difference is particularly noticeable with acidic and alkaline conditions. The ternary solution is an acidic medium due to the presence of doxycycline. It is known that amoxicillin starts to oxidize under acidic conditions and amoxicillin penicilloic acid appears [38]. It is reasonable to assume that this is the cause of the lowered concentrations found in the HPLC analysis. Further (see Chapter 3.3) analysis showed the presence of amoxicillin penicilloic acid in untreated solution.

3.3. Identification of transformation products

As stated earlier, the initial concentration of the treated solutions was 50 ppm. However, HPLC analysis suggests that the initial concentration of the untreated samples was lower than prepared. The difference is particularly noticeable with acidic and alkaline conditions. The ternary solution is an acidic medium due to the presence of doxycycline. It is known that amoxicillin starts to oxidize under acidic conditions and amoxicillin penicilloic acid appears [38]. It is reasonable to assume that this is the cause of the lowered concentrations found in the HPLC analysis. Further analysis showed the presence of amoxicillin penicilloic acid in untreated solution.

To investigate the transformation products formed during PCD oxidation, LC-ESI-ion trap analyses were carried out. Oxidation of both doxycycline and amoxicillin leads to the formation of several transformation products. Identification of the major transformation products was based on their fragmentation patterns using ion trap MS and MS² analyses in both positive and negative mode and their exact mass recorded by a time-of-flight mass spectrometer (Table 5).

The relative rates of transformation of the antibiotics and the transformation products were determined by measuring the areas of the peaks in the UV chromatograms for doxycycline and its products and by measuring the areas of the extracted ion chromatograms for amoxicillin and its major products. Dividing the current peak area by the largest peak area enables the behavior of the content ratio of the tested

compound and its degradation products during PCD treatment to be seen. Figs. 6 and 7 show the change in the content ratio of amoxicillin and doxycycline and their transformation products for ternary solution respectively.

Qualitative analysis of ternary solution showed five transformation products of amoxicillin (Fig. 8). The identification was based on observed molecular mass and the fragmentation patterns. The exact masses were recorded for the products OH-amoxicillin (AMX-C1) and amoxicillin penicilloic acid (AMX-C2) and used for structural determination. The structure of the transformation product AMX-C4 has previously been reported by Trovó et al. [39]. Fig. 6 shows the change in the content ratio of amoxicillin and its major (with the largest peak areas) oxidation products. As can be seen from the figure, along with amoxicillin there are some amount of amoxicillin penicilloic acid in the sample without treatment (Delivered energy = 0 kWh/m³). This is largely due to acidic conditions in ternary solution, and, as was mentioned before amoxicillin starts to hydrolyze under acidic conditions and it leads to amoxicillin penicilloic acid formation. The presence of both compounds decreases continuously until the end of the treatment. At the same time, there is now OH-amoxicillin in the 0 sample, it appears when treatment starts and its quantity increases up to certain point, where the value peaks as the hydroxyl radicals start to react with amoxicillin. Finally, all three compounds decompose by the end of the treatment.

The transformation products of both antibiotics were detected in neutral samples. In alkaline samples, only doxycycline oxidation products were detected. Qualitative analysis of amoxicillin oxidation intermediate products in alkaline samples did not give reliable results. The implemented analytical method requires modification to enable detection of amoxicillin and its oxidation products in alkaline media.

Qualitative analysis of the binary solution showed the same transformation products of amoxicillin. The difference is there is no amoxicillin penicilloic acid in the 0 sample. Both amoxicillin penicilloic acid and OH-amoxicillin appear during the experiment, and their quantity increases at the beginning of the treatment and then drops.

For doxycycline, two major transformation products, OH-doxycycline (DXC-C1) and 2-OH-doxycycline (DXC-C2), were detected (Fig. 9). The products were identified based on their exact mass, which suggests the addition of one and two OH groups respectively. The OH groups were most probably added to the aromatic rings. Fig. 7 presents the behavior of the content ratio of doxycycline and its degradation products during PCD treatment of ternary solution with and without the presence of NaOH. Binary solution of doxycycline was also studied and gave approximately the same results in that the relative change in compounds was the same. As can be seen from Fig. 7, in the absence of NaOH, only doxycycline is found at the beginning of the treatment, while other compounds start to appear later due to the reaction of

Table 5
Accurate mass observed by LC-ESI-TOF-MS of amoxicillin and doxycycline transformation products.

Product	Calculated exact mass	Experimentally determined mass	Error, ppm
AMX-C1	382.10673	382.1091	4.4
AMX-C2	384.12238	384.1220	0.9
DXC-C1	461.15546		8.4
DXC-C2	477.15037		6.1

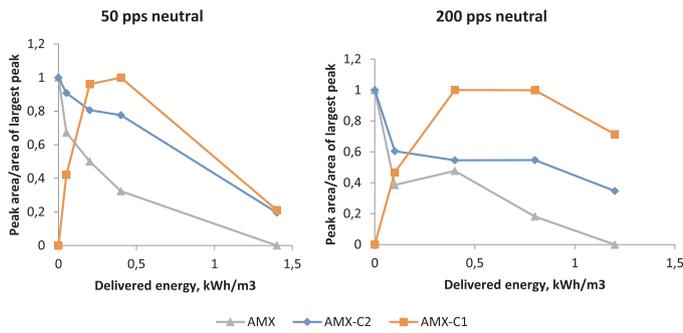


Fig. 6. Changing of the content ratio of amoxicillin and its major oxidation products.

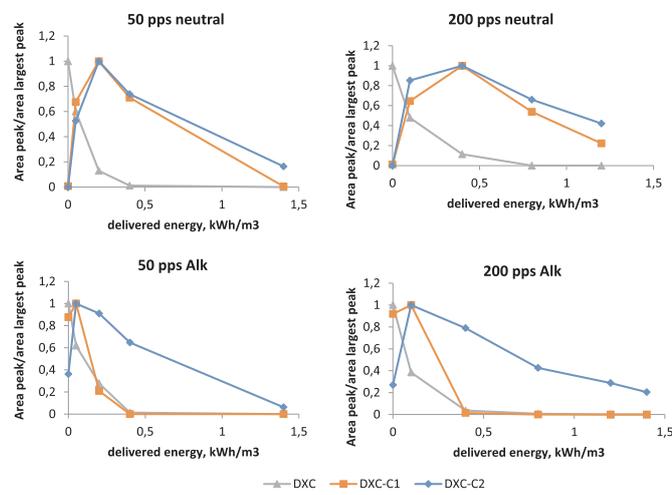


Fig. 7. Changing of content ratio of doxycycline and its major oxidation products.

hydroxyl radicals with doxycycline. It is clearly seen that the concentration of intermediate products increases unless there is enough primary component. In other words, as long as we have excess of

primary compound in the system, we can observe an increasing of concentration of intermediate products. When the required amount of primary component in the system is no longer available, the

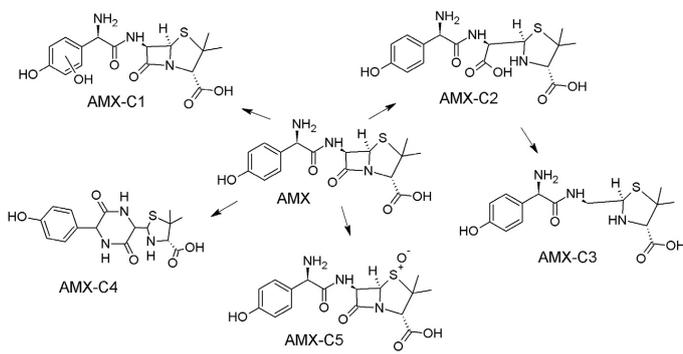


Fig. 8. Proposed oxidation pathway of amoxicillin.

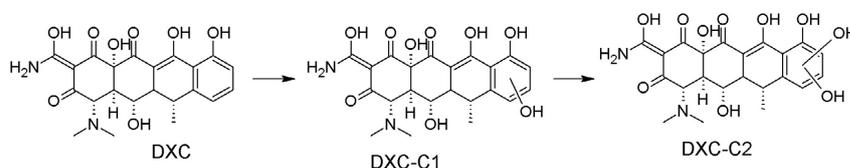


Fig. 9. Proposed oxidation pathway of doxycycline.

intermediate products start to oxidize as well. In experiments with NaOH, some amount of 2-OH-doxycycline and some OH-doxycycline is found at the beginning of the treatment. As against treatment in neutral media, doxycycline and OH-doxycycline oxidize quite fast under alkaline condition, whereas the 2-OH-doxycycline is more resistant to oxidation.

4. Conclusion

The studied antibiotic compounds, amoxicillin and doxycycline, are relatively easy to oxidize with PCD and pulsed corona discharge oxidation is thus an effective degradation approach for these compounds, achieving high rate of degradation in a short period of time with low energy consumption.

The energy efficiency of oxidation of all the compounds increases with reducing pulse repetition frequency. At low frequency, ozone accumulates during pauses between the pulses. Thus, the in situ concentration of ozone increases, it has more time to react with target compounds and the role of ozone in the oxidation becomes more significant.

High pH is preferable for oxidation at the beginning of the process; however, as the treatment progresses, with decreasing of primary compound, the effect of pH becomes less significant.

The reaction of amoxicillin is first order in a neutral medium and second order in an alkaline medium. The doxycycline oxidation reaction is a first order reaction in both neutral and alkaline media. However, the reaction rate constant is higher at alkaline conditions.

Five and two intermediate compounds were detected during oxidation of amoxicillin and doxycycline respectively. OH-amoxicillin, amoxicillin penicilloic acid, OH-doxycycline and 2-OH-doxycycline had the largest peaks areas. All products were oxidized by the end of the treatment. The behavior of all intermediate products was similar to that of the original compounds, i.e. better degradation under alkaline conditions, and low pulse repetition frequency is to be preferred from the energy efficiency point of view.

Acknowledgments

Part of the study was carried out within the framework of the Exploiting Municipal and Industrial Residues (EMIR) project. The authors would like to acknowledge financial support from the South-East Finland-Russia ENPI CBC 2007-2013 programme; Maa- ja vesitekniiikan tuki ry [grant number 32751]; LUT Doctoral School and the Graduate School in Chemical Engineering (Finland).

References

- [1] M. Furracker, The water framework directive—can we reach the target? *Water Sci. Technol.* 57 (9) (2008) 9–17.
- [2] M. Salgot, E. Huertas, S. Webe, W. Dott, J. Hollender, Wastewater reuse and risk: definition of key objectives, *Desalination* 187 (2006) 29–40.
- [3] A. Boxall, The environmental side effects of medication, *EMPO Rep.* 5 (12) (2004) 1110–1116.
- [4] O.A.H. Jonesa, N. Voulvoulisa, J.N. Lestera, Human pharmaceuticals in the aquatic environment: a review, *Environ. Technol.* 22 (2001) 1383–1394.
- [5] O.A.H. Jonesa, N. Voulvoulisa, J.N. Lestera, Potential impact of pharmaceuticals on environmental health, *Bull. World Health Org.* 81 (2003) 768–769.
- [6] S.K. Khetan, T.J. Collins, Human pharmaceuticals in the aquatic environment: a challenge to green chemistry, *Chem. Rev.* 107 (6) (2007) 2319–2364.
- [7] D. Fatta-Kassinos, S. Meric, A. Nikolaou, Pharmaceutical residues in environmental waters and wastewater: current state of knowledge and future research, *Anal. Bioanal. Chem.* 399 (2001) 251–275.
- [8] B. Petrie, E.J. McAdama, M.D. Scrimshaw, J.N. Lester, E. Cartmill, Fate of drugs during wastewater treatment, *Trends Anal. Chem.* 49 (2013) 145–159.
- [9] O. Michael, L. Rizzo, C.S. Mc Ardell, C.M. Mania, C. Merlin, T. Schwartz, C. Dagot, D. Fatta-Kassinos, Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment, *Water Res.* 47 (2013) 957–995.
- [10] P. Bottonia, S. Carolib, A.B. Caracciolo, Pharmaceuticals as priority water contaminants: a review, *Toxicol. Environ. Chem.* 92 (3) (2010) 549–565.
- [11] T.A. Ternes, J. Stüber, N. Herrmann, D. McDowell, A. Ried, M. Kampmann, Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewaters? *Water Res.* 37 (2003) 1976–1982.
- [12] P. Ajo, I. Kornev, S. Preis, Pulsed corona discharge in water treatment: the effect of hydrodynamic conditions on oxidation energy efficiency, *Ind. Eng. Chem. Res.* 54 (30) (2015) 7452–7458.
- [13] Y.O. Lagunova, A.F. Seliverstov, B.G. Ershov, A.G. Basiev, Oxidative decomposition of oxalate ions in water solutions of concentrated ozone, *Atomic Energy* 113 (2) (2012) 112–113.
- [14] M. Krichevskaya, D. Klauson, E. Portjanskaja, S. Preis, The cost evaluation of advanced oxidation processes in laboratory and pilot-scale experiments, *Ozone Sci. Eng.* 33 (3) (2011) 211–223.
- [15] I. Panorel, I. Kornev, H. Hatakka, S. Preis, M. Louhi-Kultanen, Oxidation of aqueous pharmaceuticals by pulsed corona discharge, *Environ. Technol.* 34 (7) (2013) 923–930.
- [16] I. Panorel, I. Kornev, H. Hatakka, S. Preis, M. Louhi-Kultanen, Oxidation of aqueous paracetamol by pulsed corona discharge, *Ozone Sci. Eng.* 35 (2) (2013) 116–124.
- [17] K. Kummerer, A. Al-Ahmad, V. Mersch-Sundermann, Biodegradability of some antibiotics, elimination of their genotoxicity and affection of wastewater bacteria in a simple test, *Chemosphere* 40 (2000) 701–710.
- [18] T. Herberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, *Toxicol. Lett.* 131 (2002) 5–17.
- [19] P. Verlicchi, M. Al Aukidy, E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment, *Sci. Total Environ.* 429 (2012) 123–155.
- [20] EMEA, European Agency for the Evaluation of Medicinal Products (EMA), London, 2001.
- [21] D. Klauson, A. Poljakova, N. Pronina, M. Krichevskaya, A. Moiseev, T. Dedova, S. Preis, Aqueous photocatalytic oxidation of doxycycline, *J. Adv. Oxid. Technol.* 16 (2) (2013) 234–243.
- [22] D. Klauson, J. Babkina, K. Stepanova, M. Krichevskaya, S. Preis, Aqueous photocatalytic oxidation of amoxicillin, *Catal. Today* 151 (1–2) (2010) 39–45.
- [23] N.F.F. Moreira, C.A. Orge, A.R. Ribeiro, J.L. Faria, O.C. Nunes, M.F.R. Pereira, A.M.T. Silva, Fast mineralization and detoxification of amoxicillin and diclofenac by photocatalytic ozonation and application to an urban wastewater, *Water Res.* 87 (2015) 87–96.
- [24] E.S. Elmolla, M. Chaudhuri, Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using UV/TiO₂ and UV/H₂O₂/TiO₂ photocatalysis, *Desalination* 252 (1–3) (2010) 46–52.
- [25] J. Rivas, A. Encinas, F. Beltran, N. Graham, Application of advanced oxidation processes to doxycycline and norfloxacin removal from water, *J. Environ. Sci. Health Part A* 46 (2011) 944–951.
- [26] R. Andreozzi, M. Canterino, R. Marotta, N. Paxeus, Antibiotic removal from wastewater: the ozonation of amoxicillin, *Hazard. Mater.* 122 (3) (2005) 243–250.
- [27] X. Li, T. Shen, D. Wang, X. Yue, X. Liu, Q. Yang, C.J.W. Zheng, G. Zeng, Photodegradation of amoxicillin by catalyzed Fe²⁺/H₂O₂ process, *Environ. Sci.* 24 (2) (2012) 269–275.
- [28] V. Homen, A. Alves, L. Santos, Microwave-assisted Fenton's oxidation of amoxicillin, *Chem. Eng.* 220 (2013) 35–44.
- [29] A.A. Borghi, M.F. Silva, S.A. Arni, A. Converti, M.S.A. Palma, Doxycycline degradation by the oxidative fenton process, *J. Chem.* 2015 (2015).
- [30] R. Hofmann, R.C. Andrews, Impact of H₂O₂ and (bi)carbonate alkalinity on ammonia's inhibition of bromate formation, *Water Res.* 40 (18) (2006) 3343–3348.
- [31] O.H.J. Autin, P. Jarvis, J. MacAdam, S.A. Parson, The impact of background organic matter and alkalinity on the degradation of the pesticide metaldehyde by two advanced oxidation processes: UV/H₂O₂ and UV/TiO₂, *Water Res.* 46 (6) (2013) 2041–2049.
- [32] F. Yuan, C. Hu, X. Hu, D. Wei, Y. Chen, J. Qu, Photodegradation and toxicity changes of antibiotics in UV and UV/H₂O₂ process, *J. Hazard. Mater.* 185 (2) (2011) 1256–1263.
- [33] R.F. Dantas, M. Canterino, R. Marotta, C. Sans, S. Esplugas, R. Andreozzi,

- Bezafibrate removal by means of ozonation: primary intermediates, kinetics, and toxicity assessment, *Water Res.* 41 (2007) 2525–2532.
- [34] R.F. Dantas, S. Contreras, C. Sans, S. Esplugas, Sulfamethoxazole abatement by means of ozonation, *Hazard. Mater.* 150 (2008) 790–794.
- [35] R. Rosal, M.S. Gonzalo, K. Boltes, P. Letón, J.J. Vaquero, E. García-Calvo, Identification of intermediates and assessment of ecotoxicity in the oxidation products generated during ozonation of clofibrate, *Hazard. Mater.* 172 (2009) 1061–1068.
- [36] S. Dogan, R. Kidak, A plug flow reactor model for UV-based oxidation of amoxicillin, *Desalin. Water Treat.* 57 (29) (2016) 13586–13599.
- [37] X. Jin, X. Wang, Y. Wang, H. Ren, Oxidative degradation of amoxicillin in aqueous solution with contact glow discharge electrolysis, *Ind. Eng. Chem. Res.* 52 (29) (2013) 9726–9730.
- [38] E. Nägele, R. Moritz, Structure elucidation of degradation products of the antibiotic amoxicillin with ion trap MSn and accurate mass determination by ESI TOF, *Am. Soc. Mass Spectrom.* 16 (2005) 1670–1676.
- [39] A.G. Trovó, R.F.P. Nogueira, A. Agüera, A.R. Fernández-Alba, Degradation of the antibiotic amoxicillin by photo-Fenton process – chemical and toxicological assessment, *Water Res.* 45 (2011) 1394–1402.
- [40] FDA, US Food and Drug Administration, Online Available: www.fda.com, 2015 Accessed 2015.

Publication II

Sokolov, A., and Louhi-Kultanen, M.

Behaviour of aqueous sulfamethizole solution and temperature effects in cold plasma oxidation treatment

Reprinted with permission from

Scientific Reports,

Vol. 8, pp. article number 8734, 2018

© 2018, Springer Nature

SCIENTIFIC REPORTS

OPEN

Behaviour of aqueous sulfamethizole solution and temperature effects in cold plasma oxidation treatment

Alexander Sokolov¹ & Marjatta Louhi-Kultanen^{1,2}

The increase in volume and variety of pharmaceuticals found in natural water bodies has become an increasingly serious environmental problem. The implementation of cold plasma technology, specifically gas-phase pulsed corona discharge (PCD), for sulfamethizole abatement was studied in the present work. It was observed that sulfamethizole is easily oxidized by PCD. The flow rate and pH of the solution have no significant effect on the oxidation. Treatment at low pulse repetition frequency is preferable from the energy efficiency point of view but is more time-consuming. The maximum energy efficiency was around 120 g/kWh at half-life and around 50 g/kWh at the end of the treatment. Increasing the solution temperature from room temperature to 50 °C led to a significant reaction retardation of the process and decrease in energy efficiency. The pseudo-first order reaction rate constant (k_1) grows with increase in pulse repetition frequency and does not depend on pH. By contrast, decreasing frequency leads to a reduction of the second order reaction rate constant (k_2). At elevated temperature of 50 °C, the k_1 , k_2 values decrease 2 and 2.9 times at 50 pps and 500 pps respectively. Lower temperature of 10 °C had no effect on oxidation efficiency compared with room temperature.

Despite pharmaceuticals having first been detected in natural water bodies more than 40 years ago, these compounds were, until recently, not considered hazardous as their concentrations were very low. To date, there is a trend of increasing pharmaceutical concentrations in lakes, rivers and seas, due to a general increase in usage of pharmaceutical compounds for both medicinal purposes and in livestock production. Through the use of advanced analytical techniques, pharmaceuticals in extremely low concentrations have been detected in tap water^{1,2}. The continuous increase in the prevalence of these compounds in natural water bodies is also due to an absence of legislation specifically addressing the discharge of pharmaceuticals-containing wastewaters into ground water and surface waters³. Existing municipal wastewater treatment plants are not designed for efficient removal of medical drugs from water, especially refractory compounds such as antibiotics⁴⁻⁶.

Over recent years, the global consumption of antibiotics has increased rapidly. According to Van Boeckel⁷, global consumption of antibiotics in the first decade of the 21st century increased by 36%. One of the classes of antibiotics with greatest use is compounds belonging to the sulfonamide functional group. In Europe, total consumption of sulfonamides for human medicine was 121.5 tonnes of active pharmaceutical ingredient in 2012, which places the compound as the fifth most commonly used antimicrobial antibiotic. According to the European Centre for Disease Prevention and Control, Finland is among the largest per capita consumers of sulfonamides in Europe⁸. As regards consumption of veterinary antibiotics (mainly in livestock production), sulfonamides are the third most commonly used antibiotic in Europe with consumption of 826.3 tonnes of active ingredient in 2012.

Sulfamethizole is a typical representative of the sulfonamides group. It is quite popular in livestock farming, which poses problems as effluents from farms often go directly into water bodies bypassing wastewater treatment facilities⁹. Furthermore, according to Scholar and Pratt¹⁰, about 80% of the original intake of sulfamethizole is excreted. Other sources of antibiotic release into the environment are leaching from landfills¹¹, recycled water utilized for groundwater recharge and irrigation¹²⁻¹⁴, and disposal of unused and expired pharmaceuticals¹⁵. Sulfamethizole was chosen as the test compound in this study for the following reasons: it is among the most

¹School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53850, Lappeenranta, Finland. ²School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076, Aalto, Espoo, Finland. Correspondence and requests for materials should be addressed to A.S. (email: alexander.sokolov@lut.fi)

commonly used antibiotics and overall consumption is high; a large amount of the administered dose is excreted; and it is among the most often detected antibiotics in environmental waters and, most importantly, in tap water.

As mentioned earlier, conventional wastewater treatment methods are inadequate for effective abatement of pharmaceuticals in the environment. Implementation of activated carbon treatment, separation by membrane using reverse osmosis, micro- and nanofiltration could be effective methods, but the high maintenance and operational costs of these processes limit the use of such approaches¹⁶. Ozonation has been found to be a quite effective method for antibiotics removal in general^{17,18} and for sulfamethizole in particular¹⁶. However, the ozone dosages commonly implemented in water treatment are insufficient for mineralization. Incomplete mineralization leads to the formation of oxidation byproducts and these products can show greater toxicity than the parent compounds^{19–21}. Furthermore, ozonation remains an expensive method for water purification^{22,23}. In light of the drawbacks of alternative approaches, advanced oxidation processes (AOP) based on hydroxyl radical oxidation have attracted increasing research interest. Ikehata *et al.* review the most popular AOPs and present the advantages and disadvantages of the different approaches²⁴. For sulfamethizole, the most studied AOPs are photocatalytic oxidation, oxidation via the Fenton reaction, and oxidation by Ferrate(VI)^{25–27}. Cold plasma technology can be considered as a novel AOP technology. For the most part, cold plasma treatment, in the form of oxidation of various compounds, has been associated with electric discharge systems. The current work studies implementation of gas-phase pulsed corona discharge for the treatment of recalcitrant pharmaceuticals. This method allows the generation of short-living OH radicals and long-living ozone from water and oxygen. The generation of oxidants takes place *in situ* with low delivered energy, and with minimum production of heat in the working chamber of the PCD reactor.

According to Ikonen *et al.*²⁸, in 2014 there were 154 large (>5000 users or >1000 m³ drinking water/day) EU-regulated waterworks in Finland; 41% of them used groundwater in their drinking water production, 19% used artificially recharged groundwater, and the remaining 40% used surface water sources. Drinking water treatment is strongly dependent on water temperature. Due to the northern location of Finland, the temperature of water in water bodies can vary from 0 °C to 20 °C. Wastewater disposal from industrial plant can reach temperatures of 40–50 °C²⁹. PCD has already proved an efficient method for pharmaceutical oxidation^{30–32} but the effect of the water temperature on the PCD oxidation treatment has not been studied. The current research investigates the oxidation of aqueous solutions of sulfamethizole in a cold plasma field at different water temperatures. The main aim is to estimate the effect of temperature on the oxidation kinetics, oxidation by-products and energy efficiency of the process.

Materials and Methods

Commercially available sulfamethizole, supplied by Sigma Aldrich, was used for the experiments. The purity of the test compound, based on the manufacturer's specification exceeded 99%.

The concentration of sulfamethizole in the studied aqueous solutions was measured by high performance liquid chromatography (HPLC). A Kinetex 2.6 μm C18 100 Å 150 × 4.60 mm column was used for analysis of the studied solutions. The column temperature was 35 °C, retention time was around 13 minutes, and the wavelength was 254 nm. The eluent included 1% acetic acid solution and methanol in a volumetric proportion of 85:15 respectively. Eluent flow rate was 0.6 ml/min. Sample injection volume was 20 μl. The accuracy of these measurements was ± 0.1 mg/L.

The qualitative analysis of the oxidation by-products was carried out with chromatography coupled to an ion trap mass spectrometer (Agilent 1100 series LC/MSD Trap) equipped with an electrospray ionization interface. The analysis was performed with full scan and auto MS/MS modes in both positive and negative polarity. The neutral samples were injected without prior sample treatment and the pH of the alkaline samples was adjusted to 3 with formic acid before injection. An XBridge C₁₈ column (2.1 × 50 mm, 3 μm, Waters Corp.) was used for chromatographic separation. The eluent consisted of acetonitrile with 0.1% formic acid, and the flow rate was 0.4 ml/min. The gradient applied was: 0–1 min, 5% eluent; 1–25 min, 5–95% eluent; 25–26 min, 95% eluent; 26–27 min, 95–5% eluent; 27–35 min, 5% eluent. The injection volume was 30 μL. The LC tool was equipped with an adjustable wavelength UV detector set at 275 nm. The source was: gas temperature 350 °C, gas flow 8 L/min, capillary voltage of ± 3.5 kV, nebulizer 40 psi.

A quadrupole time-of-flight mass spectrometer (Bruker MicroTOF) equipped with an electrospray ionization interface was used for further investigation of the intermediates. The chromatographic method was the same as for the ion trap spectrometry. An Agilent series 1200 LC was used for chromatographic separations.

A schematic drawing of the experimental setup is shown on Fig. 1. The setup includes the PCD reactor, water circulation system, high voltage pulse generator and thermostat. The PCD reactor consists of two vertical grounded plate electrodes and a horizontal high voltage electrode wires between them. More detailed information on the reactor configuration is provided in our previous publication³². The sulfamethizole solution was pumped from the water tank to the top of the reactor, where it was spread by perforated plate and fell by gravity through the system of high voltage electrodes back to the water tank. The reaction between the target compound and oxidants takes place in the plasma zone between the grounded plates. In the plasma field, two main oxidants, ozone and hydroxyl radicals, are generated from water and oxygen via the oxidation reactions:



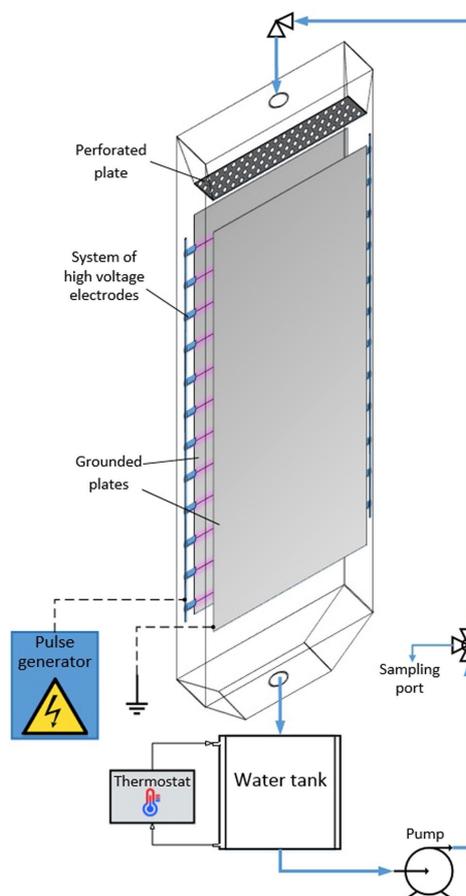


Figure 1. Experimental setup.

To compare our results with other studies on the degradation of pharmaceutical compounds in water by electric discharge, target compound removal (R , %) and energy efficiency (ϵ , g/kWh) were used as the main evaluation parameters. According to the literature review, these parameters are the most frequently used evaluation parameters in the field of degradation of various compounds by cold plasma treatment.

The compound removal and energy efficiency were calculated according to Equation (4) and Equation (5), respectively:

$$R = (1 - C_t/C_0) \times 100 \quad (4)$$

$$\epsilon = C_0 V R / (P t) \quad (5)$$

where C_0 is the initial concentration of the target compound (mg/L) and C_t is the concentration at the time t (mg/L); t is the treatment time (h); V is the volume of treated solution (L); and P is the discharge power (W).

The value P depends on the pulse repetition frequency, which comprised 50, 200 and 500 pulses per second (pps), corresponding to $P = 6$ W, $P = 24$ W and $P = 60$ W, respectively. More detailed description of calculation of the P value is available in previous publications^{22,32}.

All experiments were divided into three parts (see Table 1). The first part included experiments without power supply. The aqueous solution of sulfamethizole was pumped through the reactor for 5 hours at various

Frequency, pps	T, °C	initial pH (after treatment)	Total treatment time, min	k_1, min^{-1}	$k_2, \text{m}^2/\text{J}$	$t_{1/2}, \text{min}$	$\epsilon_{1/2}, \text{g/kWh}$	$\epsilon_{\text{finab}}, \text{g/kWh}$	Removal rate
First set of experiments (without power supply)									
0	20	7.1 (7.1)	300	—	—	—	—	—	—
0	20	12.2 (12.2)	300	—	—	—	—	—	—
0	20	3.5 (3.5)	300	—	—	—	—	—	—
0	50	7.2 (7.2)	300	—	—	—	—	—	—
0	50	12.0 (12.0)	300	—	—	—	—	—	—
0	50	3.5 (3.5)	300	—	—	—	—	—	—
Second set of experiments*									
50	20	7.1 (4.0)	100	0.03311	6.57×10^{-7}	20.93	122.6	49.92	0.99
50	20	12.1 (11.9)	100	0.03289	6.52×10^{-7}	21.07	120.9	49.17	0.99
50	20	3.5 (3.1)	100	0.03321	6.59×10^{-7}	20.87	117.8	48.11	1.00
200	20	7.2 (4.0)	40	0.08760	4.34×10^{-7}	7.91	81.5	30.89	1.00
200	20	12.2 (12.0)	40	0.09557	4.74×10^{-7}	7.25	88.7	31.47	0.99
200	20	3.6 (3.1)	40	0.08701	4.31×10^{-7}	7.97	79.4	30.45	1.00
500	20	7.2 (4.1)	24	0.15300	3.03×10^{-7}	4.53	56.2	20.75	1.00
500	20	12.1 (12.1)	24	0.1616	3.21×10^{-7}	4.29	60.2	21.00	0.99
500	20	3.5 (3.2)	24	0.1380	2.74×10^{-7}	5.02	49.1	19.92	1.00
Third set of experiments									
50	50	7.0 (5.8)	160	0.01622	3.22×10^{-7}	42.73	59.8	30.15 (20.5)**	0.97 (0.99)**
50	10	7.0 (4.7)	100	0.03425	6.79×10^{-7}	20.24	127.4	49.38	0.99
500	50	6.9 (4.4)	60	0.05295	1.05×10^{-7}	13.09	19.6	8.11 (6.2)**	0.97 (0.99)**
500	10	7.0 (4.9)	24	0.1594	3.16×10^{-7}	4.35	58.4	20.84	1.00

Table 1. List of experiments. *The same set was repeated with the flow rate 8 L/min. **After approximation.

Delivered energy dose (kWh/m ³)	Treatment time for 50 pps (min)	Treatment time for 200 pps (min)	Treatment time for 500 pps (min)
0	0	0	0
0.1	10	2.5	—
0.2	20	5	—
0.4	40	10	4
1	100	25	10
1.6	160	40	16
2.4	240	60	24
4.0	—	—	40
6.0	—	—	60

Table 2. Corresponding energy delivered with treatment time.

temperatures of solution (20 °C and 50 °C) under neutral, alkaline and acidic conditions. Here and throughout the work, the term “neutral” refers to media without any additives (initial pH is around 7), the term “acidic” refers to media with sulfuric acid as an additive (initial pH is around 4), and the term “alkaline” refers to media with sodium hydroxide as an additive (initial pH is around 12). Samples were taken after each hour. This set of experiments was necessary to make sure that the sulfamethizole is stable and does not degrade by itself without treatment.

The second set of experiments were carried out at three different pulse repetition frequencies (50 pps, 200 pps and 500 pps) under initial neutral, alkaline and acidic conditions. The process was operated with two flow rates of circulating aqueous solution – 4.5 L/min and 8 L/min. Samples were taken with treatment time as indicated in Table 2. The second set was necessary to obtain information about the general behavior of sulfamethizole in a cold plasma field.

The third set of experiment were carried out at two temperatures (10 °C and 50 °C) with two pulse repetition frequencies (50 pps and 500 pps) under neutral condition. The temperature, which differed from room temperature, was kept constant with a T4600 Lauda process thermostat. All experiments were carried out under ambient pressure with 50 mg/L initial prepared concentration of sulfamethizole. A list of all experiments with operating parameters is shown in Table 1. With the exception of experiments without power supply, all experiments were repeated 4 times in order to improve accuracy and make sure that the experiments are reproducible. The standard deviation did not exceed 0.05 for all experiments.

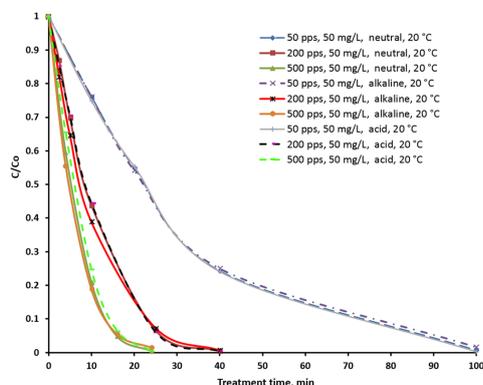


Figure 2. Relationship between sulfamethizole relative concentration (C/C_0) and treatment time at different pulse frequencies (50 pps, 200 pps, 500 pps) and initial pH. Temperature of treated solution is 20 °C.

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

Results and Discussion

As mentioned earlier, three sets of experiments were carried out (see section 2, Table 1). In this section the three sets are considered separately and then a summary of the main findings is given.

First set of experiments. The experiments without power supply showed that the sulfamethizole is stable and does not degrade itself. No changes in sulfamethizole concentration were detected. Neither pH nor temperature had any effect on oxidation without power supply. The experiments were carried under ambient pressure and at room temperature (20 °C).

Second set of experiments. To investigate the effect of temperature, the general behavior of sulfamethizole in a cold plasma field should be studied. This was the main goal of the second set of experiments. Figure 2 shows the oxidation curves of sulfamethizole with the 4.5 L/min flow rate of circulating aqueous solution. It is possible to conclude that sulfamethizole is easily oxidized by PCD. The highest degradation was observed at the beginning of the PCD treatment followed by a deceleration. The concentration of sulfamethizole decreases below the measurement limit after 24 min, 40 and 100 min of treatment time at 500 pps, 200 pps, and 50 pps respectively. As can be seen from the figure, initial pH has no significant effect on the oxidation. At 50 pps, the three oxidation curves merge into one. At higher frequencies, a slight difference in the behavior of the oxidation curves can be observed in the case of alkaline media. It seems that high pH is a little bit more preferable for oxidation, but in general, the effect of pH is insignificant. It should be noted that throughout the treatment process the temperature remained constant (around 20 °C) regardless of treatment time or energy supplied. The experiments with 8 L/min of circulating aqueous solution gave similar results, indicating that the flow rate has no effect on the process.

The unknown quantity of OH-radicals and ozone, as well as lack of knowledge about their individual contribution to the reaction may pose a considerable challenge for calculation of the reaction kinetics. Taking into account that the water flow rate has no effect on the process and assuming that contact surface remains constant, it is possible to conclude that there are constant amounts of oxidants available at any moment in the plasma zone. Therefore, the reaction rate constant can be calculated by assuming that the combined effect of the oxidants results in a second order reaction rate (first order relative to the sulfamethizole and first order relative to oxidants). Power delivered to the volume of the plasma zone can be used for characterization of the total amount of oxidants involved the process:

$$dC/dt = k_2CP/V_{pl} \quad (6)$$

where k_2 is the second order reaction rate constant (in $\text{m}^3 \text{J}^{-1}$), C is the concentration of the sulfamethizole (in mg/L), P is the pulse power delivered to the reactor (in W), and V_{pl} is the plasma zone volume (in m^3).

The V value depends on the reactor design, in our case $V_{pl} = 0.00714 \text{ m}^3$, and the P value depends on the pulse repetition frequency (see section 2). For each experiment, P/V_{pl} is a constant, and therefore it is possible to rewrite Eq. (6) in the following way:

$$dC/dt = k_1C \quad (7)$$

Equation 7 is a first order reaction, where k_1 (in min^{-1}) is a pseudo-first order reaction rate constant:

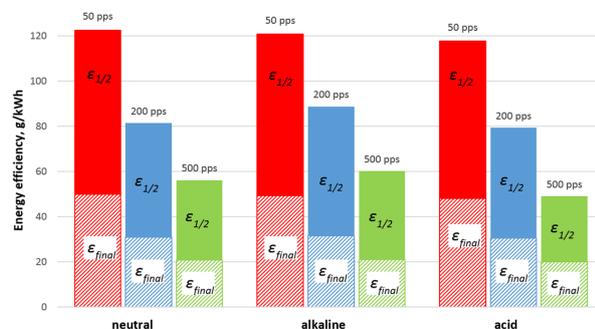


Figure 3. Energy efficiency of sulfamethizole degradation at different pulse frequencies (50 pps, 200 pps, 500 pps) and initial pH. Hatched area – final energy efficiency (ϵ_{final}), solid area – half-life energy efficiency ($\epsilon_{1/2}$).

$$k_1 = k_2 P / V_{pl} \quad (8)$$

In the case of a first order reaction, the function of the change in concentration with the treatment time should behave by exponential law. An approximation of the experimental data was made using the MatLab software package. Oxidation curves for all experiments are functions of exponential type with a coefficient of determination not less than 0.99, which indicates a first order reaction. The k_1 value, calculated by MatLab, and k_2 , calculated from Eq. 8, are given in Table 1. As can be seen, the pseudo-first order reaction rate constant grows with increase in pulse repetition frequency and does not depend on pH. In the case of the calculated k_2 values, by contrast, decreasing frequency leads to a reduction of the second order reaction rate constant. The obtained kinetics results are comparable with other studies. For example, Chamberlain and Adams³³ utilized chlorine and monochloramine for sulfamethizole oxidation. In their study, the reported values of a pseudo-first order reaction rate constant (0.015 min^{-1} , 0.021 min^{-1} and 0.006 min^{-1}) are lower than the results found herein.

The experimental results in this work showed that after 1 kWh/m^3 delivered energy the great part of sulfamethizole was oxidized. The dependence of sulfamethizole concentration on delivered energy is presented in Supplementary Figure S1. It can be observed that the lowest frequency leads to the fastest degradation rate. With the lowest frequency (50 pps), sulfamethizole seems to have been completely oxidized at around 1 kWh/m^3 , whereas operating with 500 pps more than 2 kWh/m^3 is required to reduce the sulfamethizole concentration to the detection limit.

Energy efficiency is calculated by Equation (5). The most common ways of calculating energy efficiency are half-life energy efficiency ($\epsilon_{1/2}$) at treatment time equal to a 50% reduction in the target compound ($t_{1/2}$), and energy efficiency when compound removal approximates 100%, which can be termed the final energy efficiency.

Knowing k_1 values, it is possible to calculate $t_{1/2}$ by the following equation:

$$t_{1/2} = \ln 2 / k_1 \quad (9)$$

Substituting $t_{1/2}$ in Eq. (5) gives the $\epsilon_{1/2}$ value.

As mentioned earlier, in this study the sulfamethizole seems to have been completely oxidized after 24 min, 40 and 100 min of treatment time at 500 pps, 200 pps, and 50 pps, respectively. The final energy efficiency was calculated for these times for maximum compound removal ($R = 9\%$). The calculated values of $\epsilon_{1/2}$ and ϵ_{final} are given in Table 1 and shown for visual clarity also in Fig. 3. As can be seen, the maximum half-life energy efficiency, around 120 g/kWh , was achieved at 50 pps, which is 1.5 and 2.2 times higher than with the experiments at 200 pps, and 500 pps respectively. A similar trend persists in the case of final energy efficiency. It should be noted that pH has insignificant effect on both efficiencies. The better result, from the energy efficiency point of view, with the low pulse frequency can be explained by the greater contribution of ozone in the oxidation process. Hydroxyl radicals and ozone react with target compounds directly in the gas-liquid interface. Ozone has lower oxidation potential than OH-radicals, and it reacts with target compound more slowly; furthermore, when dissolved in water ozone may also decompose via formation of OH-radicals. Such formation of OH-radicals can be considered as secondary formation. Dissolving of ozone and secondary formation of OH-radicals take time. In the case of experiments with low pulse frequency, the treatment time to reach the same value of delivered energy increases compared with the high pulse frequency experiments (see Table 2). Consequently, ozone has more time to accumulate during the pauses between the pulses, and more time to dissolve and for the reaction. The results for the impact of ozone on the oxidation process are consistent with earlier gas-phase PCD studies^{34,35}.

Oxidation of sulfamethizole leads to the formation of several transformation products. Qualitative analysis focused on identification of organic by-products only. Except sulfamethizole itself, the 4 identified organic products have highest peak at the half-life oxidation time (see Table 3). Some other compounds, including

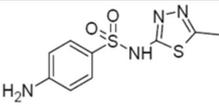
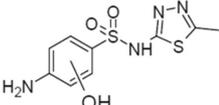
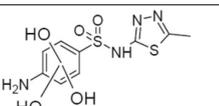
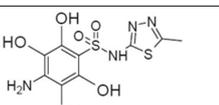
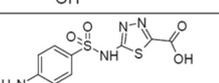
Compound	Structure	Identified with	note
Sulfamethizole		Ion trap, positive Ion trap, negative QToF, positive QToF, negative	4 fragments 3 fragments error 3,7 ppm error 3,7 ppm
OH-Sulfamethizole		Ion trap, positive Ion trap, negative	3 fragments 3 fragments
3 OH-Sulfamethizole		Ion trap, negative	2 fragments
4 OH-Sulfamethizole		Ion trap, negative QToF negative	2 fragments error 6,1 ppm
Carboxy- Sulfamethizole		Ion trap, negative QToF, negative	2 fragments error 9,9 ppm

Table 3. Oxidation by-products with the highest peak at the half-life oxidation time.

organic acids, were also detected and are given in Supplementary Figure S3. The presence of organic acids explain the decreasing of pH during PCD treatment. This is especially noticeable with neutral initial pH³⁶. As 2-amino-5-methyl-1,3,4-thiazolidine was also observed in the samples, it is reasonable to assume that possible reaction pathways start with preliminary hydroxylation of sulfamethizole with subsequent sulfonamide bond breaking. Similar pathways were suggested by Klauson *et al.*²⁵. At the end of the treatment time, when sulfamethizole compound removal reached a maximum (R = 99%) none of the mentioned intermediates were detected at the resolution of the analysis method used.

Based on the second set of experiments, it is possible to present a number of interim findings. pH and circulating aqueous flow rate have no significant effect on the oxidation process either in terms of energy efficiency or reaction kinetics. Treatment at low frequency is preferable from the energy efficiency point of view. The second reaction rate constant decreases with increasing pulse repetition frequency. The ozone as an oxidant starts to play a more significant role in the oxidation process at low pulse frequency. None of the transformation products detected at the time of 50% sulfamethizole compound removal were identified during the final period of the treatment process.

Third set of experiment. As the oxidation process is not dependent on pH and flow rate, experiments with temperature variation were carried out only in neutral media and only with 4.5 L/min flow rate. Pulse frequency of 50 pps and 500 pps were used in these experiments. Three temperatures were tested – room temperature (approx. 20 °C), 10 °C and 50 °C.

Figure 4 shows the oxidation curves of sulfamethizole at different temperatures. As can be seen, there is no difference between treatments at 10 °C and room temperature, whereas a temperature of 50 °C leads to significant deceleration of the oxidation process. 24 and 100 minutes treatment time at 500 pps and 50 pps respectively were sufficient for almost complete removal of sulfamethizole, but at a temperature of 50 °C and with the same frequencies, removal takes 60 and 160 minutes. Nevertheless, the dependency of concentration changes on treatment time remains exponential. Reaction order, reaction constant, half-life oxidation time, and energy efficiency were determined in the same way as described in section 3.2 (see Table 1). All values in Table 1 were calculated based on experimental data. Energy efficiency at different temperatures is shown in Fig. 5.

At elevated temperature of 50 °C, it is possible to observe a decrease in the k_1 , k_2 , $\varepsilon_{1/2}$ values and increase in the $t_{1/2}$ value of 2 and 2.9 times at 50 pps and 500 pps respectively. Half-life energy efficiency at 50 °C and 50 pps becomes almost equal to the half-life energy efficiency at 20 °C (10 °C) and 500 pps. With the temperature of 50 °C, the final energy efficiency decreased 1.7 times at 50 pps and 2.5 times at 500 pps (see Fig. 5). It is worth mentioning that unlike the second set experiments, when $\varepsilon_{1/2}$ was calculated for R = 0.99 with increased temperature, the removal rate was 0.97 in the calculation of final energy efficiency. The curve (relative concentration vs delivered energy) at 50 °C and 50 pps almost merges with the curves at 20 °C and 10 °C and 500 pps (see Supplementary

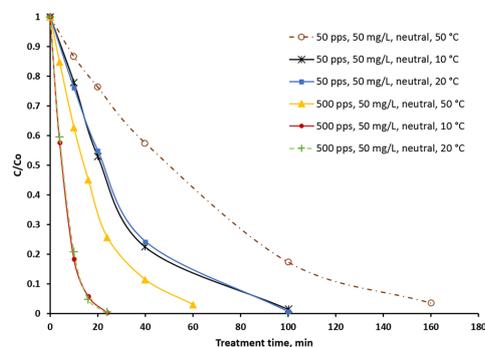


Figure 4. Sulfamethizole relative concentration (C/C_0) vs treatment time at different temperature (10 °C, 20 °C, and 50 °C) and pulse frequencies (50 pps and 500 pps). Initial pH is neutral.

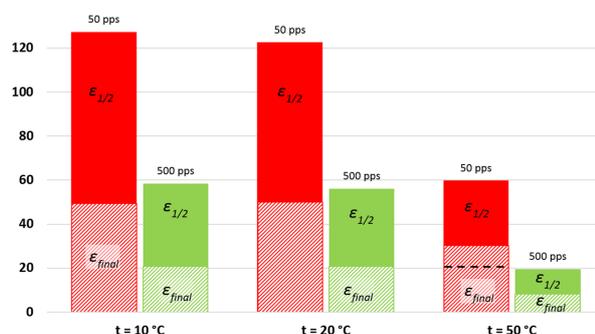


Figure 5. Energy efficiency of sulfamethizole degradation at different pulse frequencies (50 pps, 500 pps) and temperature (10 °C, 20 °C, and 50 °C). Initial pH is neutral. Hatched area – final energy efficiency (ϵ_{final}), solid area – half-life energy efficiency ($\epsilon_{1/2}$), dash line – $\epsilon_{1/2}$ value after approximation by Matlab.

Figure S2). It is reasonable to assume that if the process is prolonged at 50 °C and 50 pps until compound removal reaches 0.99, the final energy efficiency will also become equal to the final energy efficiency at 20 °C (10 °C) and 500 pps. An approximation made by Matlab software lends support to this assumption (See Table 1).

The drop in oxidation process speed and energy efficiency at elevated temperature can be explained by the decrease in ozone solubility with temperature increase. Moreover, decomposition of ozone increases at higher temperature. As mentioned earlier, ozone can react with the target compound directly on the border of liquid-gas interface or in the bulk. Dissolved ozone also reacts with compounds in the solution by formation of OH radicals. The lower ozone solubility in the aqueous solution at higher temperature leads to decrease in the secondary formation of OH radicals, which in turn slows down the OH radical-induced oxidation; and, secondly, more ozone becomes available for direct reaction on the border of liquid-gas interface. However, gaseous ozone decomposes according to the equation $2O_3=3O_2$. Elevation of the temperature accelerates the ozone decomposition and the balance shifts towards oxygen formation. Oxygen, in turn, has lower oxidation potential compared to ozone. Therefore, the role of ozone in such a case is small. It should be noted here that when discussing the temperature, the temperature of the treated solution is meant. The temperature in the plasma zone consisting of a continuous gas phase and dispersed liquid droplets is slightly different.

The results in this set of experiments are slightly inconsistent with those of the second set of experiments. It was concluded based on the second set of experiments that ozone starts to play more significant role in the oxidation process at lower pulse frequencies. Consequently, excluding ozone from the process, it was reasonable to assume that the oxidation reaction will slow to a greater degree at lower frequency than higher frequency, but the results evidence the opposite. It is possible to explain this in the following way: already at 40 °C the ozone solubility is about zero, and thus it can be considered that there is no ozone in the bulk solution. However, there is still gaseous ozone in the plasma zone, and oxygen formed after ozone decomposition and atomic oxygen are also

present in the gas phase. Such oxidants require longer reaction time, as they are less reactive towards the target compound comparing with OH radicals, and treatment at lower frequency extends the time available for the reaction. Therefore, even with high temperature, a low frequency is preferable for sulfamethizole oxidation from the energy efficiency point of view. Based on this hypothesis, a reduction in temperature should be followed by intensification of the oxidation process. However, the same results were observed with 10 °C and room temperature. It appears that the potential increase in energy efficiency at lower temperature as a consequence of increased ozone reactivity is compensated by the increase in the reaction speed with a factor 2 or 3 per 10 °C according to the Van 't Hoff equation. That is why, change in temperature of water between 10 °C and room temperature does not affect the outcome of the sulfamethizole oxidation process. Such temperature range corresponds to the average and maximum water surface temperature in Finland. Thus, PCD technology can be applied for water purification or disinfection just after potable abstraction from water bodies. From the point of view of energy efficiency, the results of this study show that PCD technology is an effective method for sulfamethizole removal. For comparison, Klauson *et al.*²⁵, who implemented aqueous photocatalytic oxidation, managed to obtain a maximum 21 g/kWh after removal of 25% of target compound. With PCD treatment, the best result gives almost 6 times better efficiency, which is an indication of the considerable potential benefits from PCD utilization.

Conclusion

The plasma field in the PCD reactor promotes fast and effective oxidation of sulfamethizole. By replacing oxidants concentration with power delivered to the plasma zone, the oxidation reaction could be expressed by a second order reaction and then well approximated as a pseudo-first order reaction.

The parent compound and its aromatic by-products seemed to be fully degraded after relatively short treatment time and with low energy consumption. Neither pH nor water recirculation flow rate had any significant effect on the process. Treatment temperature of 50 °C dramatically decreased energy efficiency and slowed down the process compared to room temperature. No differences in oxidation efficiencies were observed between the results obtained at room temperature and at 10 °C. Treatment at low pulse frequency is preferable from the energy efficiency point at any temperature within the studied framework. In the case of low frequency treatment, ozone has more time to react with target compound and makes the most significant contribution to the oxidation process at low frequency. However, temperature increasing leads to decreasing of ozone contribution due to reducing its solubility in water.

References

- Verlicchi, P., Al Aukidy, M. & Zambello, E. Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment-A review. *Science of the Total Environment* **429**, 123–155 (2012).
- Petrie, B., McAdam, E. J., Scrimshaw, M. D., Lester, J. N. & Cartmell, E. Fate of drugs during wastewater treatment. *TrAC - Trends in Analytical Chemistry* **49**, 145–159 (2013).
- Fürhacker, M. The Water Framework Directive - Can we reach the target? *Water Sci. Technol.* **57**, 9–17 (2008).
- Quoc Tuc, D. *et al.* Fate of antibiotics from hospital and domestic sources in a sewage network. *Sci. Total Environ.* **575**, 758–766 (2017).
- Kim, S. D., Cho, J., Kim, I. S., Vanderford, B. J. & Snyder, S. A. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Res.* **41**, 1013–1021 (2007).
- Tiwari, B. *et al.* Review on fate and mechanism of removal of pharmaceutical pollutants from wastewater using biological approach. *Bioresour. Technol.* **224**, 1–12 (2017).
- Van Boeckel, T. P. *et al.* Global antibiotic consumption 2000 to 2010: An analysis of national pharmaceutical sales data. *Lancet Infect. Dis.* **14**, 742–750 (2014).
- European Centre for Disease Prevention and Control. Summary of the latest data on antibiotic consumption in EU: 2016. (2016).
- Wise, R. Antimicrobial resistance: priorities for action. *J. Antimicrob. Chemother.* **49**, 585–586 (2002).
- Scholar, E. M. & Pratt, W. B. *The Antimicrobial Drugs*. (Oxford University Press, 2000).
- Holm, J. V., Ruegge, K., Bjerg, P. L. & Christensen, T. H. Occurrence and Distribution of Pharmaceutical Organic Compounds in the Groundwater Downgradient of a Landfill (Grindsted, Denmark). *Environ. Sci. Technol.* **29**, 1415–1420 (1995).
- Drewes, J. E., Heberer, T., Rauch, T. & Reddersen, K. Fate of Pharmaceuticals During Ground Water Recharge. *Ground Water Monit. Remediat.* **23**, 64–72 (2003).
- Hirsch, R., Ternes, T., Haberer, K. & Kratz, K. L. Occurrence of antibiotics in the aquatic environment. *Sci. Total Environ.* **225**, 109–118 (1999).
- Kümmerer, K. Antibiotics in the aquatic environment - A review - Part I. *Chemosphere* **75**, 417–434 (2009).
- Ternes, T. A. *et al.* Removal of Pharmaceuticals during Drinking Water Treatment. *Environ. Sci. Technol.* **36**, 3855–3863 (2002).
- Garoma, T., Umamaheshwar, S. K. & Mumper, A. Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation. *Chemosphere* **79**, 814–820 (2010).
- Moreira, N. F. F. *et al.* Fast mineralization and detoxification of amoxicillin and diclofenac by photocatalytic ozonation and application to an urban wastewater. *Water Res.* **87**, 87–96 (2015).
- Ben, W. *et al.* Distribution of antibiotic resistance in the effluents of ten municipal wastewater treatment plants in China and the effect of treatment processes. *Chemosphere* **172**, 392–398 (2017).
- Pak, G. *et al.* Comparison of Antibiotic Resistance Removal Efficiencies Using Ozone Disinfection under Different pH and Suspended Solids and Humic Substance Concentrations. *Environ. Sci. Technol.* **50**, 7590–7600 (2016).
- Rosal, R. *et al.* Identification of intermediates and assessment of ecotoxicity in the oxidation products generated during the ozonation of clofibrac acid. *J. Hazard. Mater.* **172**, 1061–1068 (2009).
- Dantas, R. F., Contreras, S., Sans, C. & Esplugas, S. Sulfamethoxazole abatement by means of ozonation. *J. Hazard. Mater.* **150**, 790–794 (2008).
- 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).
- Krichevskaya, M., Klauson, D., Portjanskaja, E. & Preis, S. The Cost Evaluation of Advanced Oxidation Processes in Laboratory and Pilot-Scale Experiments. *Ozone Sci. Eng.* **33**, 211–223 (2011).
- Ikehata, K. & Gamal El-Din, M. Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. *Ozone Sci. Eng.* **27**, 83–114 (2006).
- Klauson, D., Krichevskaya, M., Borissova, M. & Preis, S. Aqueous photocatalytic oxidation of sulfamethizole. *Environ. Technol.* **31**, 1547–1555 (2010).

26. Sharma, V. K., Mishra, S. K. & Nesnas, N. Oxidation of Sulfonamide Antimicrobials by Ferrate(VI) [FeVIO₄]²⁻. *Environ. Sci. Technol.* **40**, 7222–7227 (2006).
27. Kim, C. *et al.* Ferrate promoted oxidative cleavage of sulfonamides: Kinetics and product formation under acidic conditions. *Chem. Eng. J.* **279**, 307–316 (2015).
28. Ikonen, J. M. *et al.* Drinking water quality in distribution systems of surface and ground. *J. Water Secur.* **3**, 1–10 (2017).
29. Ahsan, S. *et al.* Effect of temperature on wastewater treatment with natural and waste materials. *Clean Technol. Environ. Policy* **7**, 198–202 (2005).
30. Banaschik, R., Koch, F., Kolb, J. F. & Weltmann, K. D. Decomposition of pharmaceuticals by pulsed corona discharges in water depending on streamer length. *IEEE Trans. Plasma Sci.* **42**, 2736–2737 (2014).
31. Panorel, I., Preis, S., Kornev, I., Hatakka, H. & Louhi-Kultanen, M. Oxidation of aqueous pharmaceuticals by pulsed corona discharge. *Environ. Technol.* **34**, 923–930 (2013).
32. Sokolov, A., Kråkström, M., Eklund, P., Kronberg, L. & Louhi-Kultanen, M. Abatement of Amoxicillin and Doxycycline in Binary and Ternary Aqueous Solutions by Gas-phase Pulsed Corona Discharge Oxidation. *Chem. Eng. J.* <https://doi.org/10.1016/j.cej.2017.10.071> (2017).
33. Chamberlain, E. & Adams, C. Oxidation of sulfonamides, macrolides, and carbadox with free chlorine and monochloramine. *Water Res.* **40**, 2517–2526 (2006).
34. Panorel, I., Preis, S., Kornev, I., Hatakka, H. & Louhi-Kultanen, M. Oxidation of Aqueous Paracetamol by Pulsed Corona Discharge. *Ozone Sci. Eng.* **35**, 116–124 (2013).
35. Preis, S., Panorel, I. C., 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).
36. 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).

Acknowledgements

The authors would like to acknowledge the contribution of Matilda Kråkström for a part of chemical analyses. This study was supported by Maa- ja vesitekniiikan tuki ry [grant number 32751], LUT Doctoral School and the Graduate School in Chemical Engineering (Finland).

Author Contributions

A.S. planned and conducted the great part of experiments, made the calculation and wrote the body of the manuscript. M.L.-K. participated in the result discussion and reviewing of the manuscript

Additional Information

Supplementary information accompanies this paper at <https://doi.org/10.1038/s41598-018-27061-5>.

Competing interests: The authors declare no competing interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2018

Publication III

Sokolov, A., Lagerquist, L., Eklund P., and Louhi-Kultanen, M.
Non-thermal gas-phase pulsed corona discharge for lignin modification

Reprinted with permission from
Engineering and Processing: Process Intensification
Vol. 126, pp. 141-149, 2018
© 2018, Elsevier



Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

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

Non-thermal gas-phase pulsed corona discharge for lignin modification

Alexander Sokolov^{a,*}, Lucas Lagerquist^b, Patrik Eklund^b, Marjatta Louhi-Kultanen^{a,c}^a School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, FI-53850, Lappeenranta, Finland^b Laboratory of Organic Chemistry, Åbo Akademi University, Piispankatu 8, FI-20500, Turku, Finland^c School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076, Aalto (Espoo), Finland

ARTICLE INFO

Keywords:

Lignin
Modification
Aldehydes
Cold plasma
AOPs

ABSTRACT

Lignin has the potential to become a significant resource of renewable aromatics for the chemical industry. The current work studies pulsed corona discharge (PCD) as an alternative method for lignin modification. The effect of initial lignin concentration and gas phase composition on aldehydes formation was studied experimentally. Kraft lignin was used as a test compound. It was concluded in the work, that treatment in low oxygen content atmosphere and high initial lignin concentration leads to higher lignin conversion to aldehydes. Despite the proven aldehydes formation, the precise nature of the changes in the lignin structure during oxidation with PCD remained unclear. To address this question, a number of advanced analytical techniques were implemented: NMR, GPC, HSQC, HPSEC, and GCMS. The effect of PCD treatment on lignin structure was studied for two types of lignin: kraft lignin, purchased from Sigma Aldrich, and birch lignin acquired from a pressurized hot water extraction and soda pulped biorefinery process (BLN lignin). Changes in solubility, molecular weight and proportion of phenolic and aliphatic OH groups, as well as lignin repolymerization were detected. The findings are of value to efforts to make lignin modification tunable to the production of desired products.

1. Introduction

Lignin is a potential raw material for the production of various products including phenolic substances and aromatic aldehydes. The pulp and paper industry is currently the main source of lignin. For annual production of 130 million tons of chemical pulps, approximately 60 million tons of kraft lignin and 4 million tons of lignosulfonates are produced. It has been estimated that only 1–2% of the lignin is isolated from pulping liquors and used for chemical and material applications; the major part of industrial lignin is used as fuel for the production of process steam and energy [1].

Lignin decomposes very slowly and generates very high amounts of solid residue compared to other lignocellulose components. Thus, most biorefinery processes focus on utilization of more easily convertible fractions, and lignin has attracted much less attention [2]. However, lignin is a complex chemical compound and potentially a good source of valuable chemicals. One of the main challenges to its utilization is the irregular structure of lignin arising from the uncertain order of the phenylpropane unit linkages. Moreover, the structure of isolated lignin differs from that of native lignin, and composition, structure, types of monolignols and their combinations depend on the origin of the lignin, the pulping method, and the lignin isolation method [3–5]. The proportions of the structural elements derived from the three

phenylpropanoid units (trans-coniferyl, *trans*-sinapyl, and *trans*-p-coumaryl alcohols) can vary significantly [6,7].

In spite of the difficulties, the subject of lignin chemical modification and its conversion to more value-added products has attracted researchers' attention since the beginning of the twentieth century. Currently, products obtained from lignin are mostly phenolic products. The reported yields for production of vanillin and syring aldehydes range from 8 to 15% depending on the lignin type [8]. However, drawbacks of existing methods include severe toxicological problems with nitrocompounds. Furthermore, current methods are only effectively applicable to lignosulfonates and are not well-suited to kraft and hydrolysis lignins. Since only lignosulfonates are used as a raw material, the production of phenolic products, especially vanillin, exists as a supplementary operation in pulp mills with sulphite cooking. Other lignin types give much smaller yield [9–11].

The pulp and paper industry generates a significant amount of wastewater containing high concentrations of lignin, which cause increased COD and brown-colored effluents. The problem of high lignin concentration in wastewaters is more acute with thermomechanical and mechanical pulping processes than chemical pulping [12]. Lignin is difficult to degrade by microorganisms, and the lifetime of lignin in aqueous media in nature is counted in months. Consequently, conventional biological wastewater treatment is insufficient from the lignin

* Corresponding author.

E-mail address: alexander.sokolov@lut.fi (A. Sokolov).<https://doi.org/10.1016/j.cep.2018.02.028>

Received 21 January 2018; Received in revised form 28 February 2018; Accepted 28 February 2018

Available online 01 March 2018

0255-2701/ © 2018 Elsevier B.V. All rights reserved.

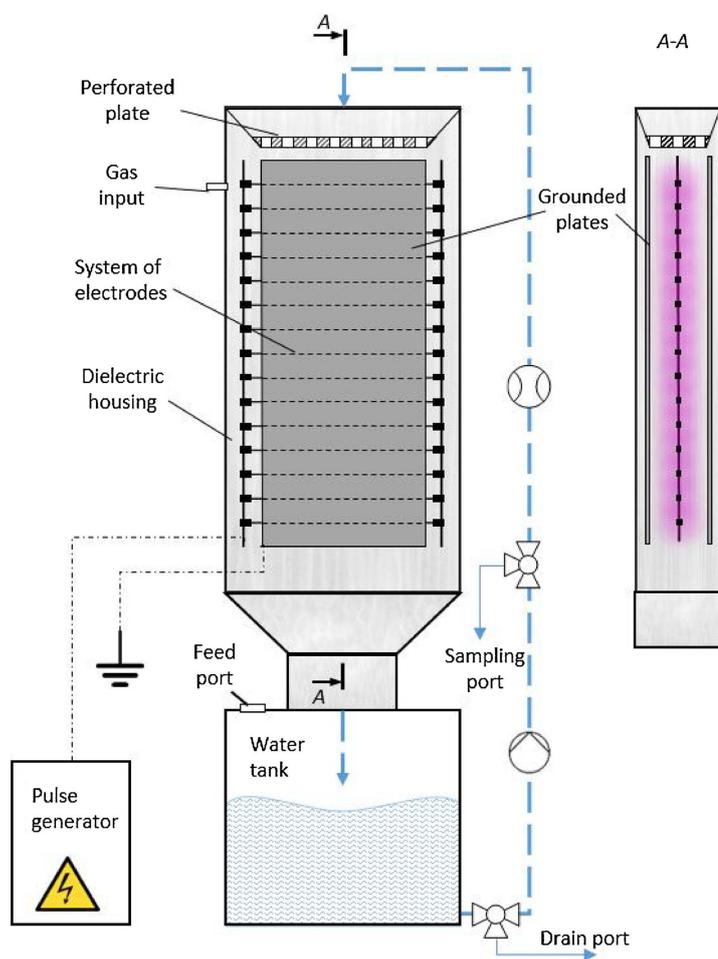


Fig. 1. Experimental setup.

removal point of view [13].

Pulsed corona discharge (PCD) can be applied as a treatment process not only for lignin removal from water but also for lignin modification to transform the lignin into a high value feedstock. The method has hydroxyl-radicals and ozone as the main oxidation species and is effective in oxidation of many organic molecules. The application of this electric discharge technique has previously been investigated by [14–17]. These studies showed a concentration of gas-phase discharges in close vicinity of the gas-liquid border.

The commercial application of electric discharge systems for such treatments is still in its infancy, and they are the subject of much study. The various systems and phenomena studied include: pulsed streamer discharges in liquid and gas-bubbled reactors with pulses at micro-second diapason [18,19], gas-phase dielectric barrier discharge (DBD) of various configurations [16,20,21], spark discharge (SD) in gas bubbles [22], pulsed corona discharge (PCD) over the water surface [23,24], plasmatrons utilizing gliding arc discharge (GAD) for

bombardment of treated surfaces with ionized gas [25–27], and PCD in water aerosol [28].

PCD generates plasma in the gas-phase atmosphere. While some research has been presented investigating how plasma affects lignin, very little work has specifically considered effect of plasma on lignin structure modification. Zhou et al. [29] studied the effect of oxygen plasma treatment on the glass transition temperature of enzymatic hydrolysis lignin. However, the lignin structure after treatment was not reported. Chirila et al. [30] and Nistor et al. [31] investigated modification of organosolv lignin powder with different carboxylic acids such as oleic, lactic and butyric acids and butyrolactone under cold plasma discharge. Although these papers studied the influence of carboxylic acids and butyrolactone, the plasma effect was not considered. In general, most work on lignin and plasma discharge effects presents information about changes in solubility, decrease in particle size, reduction in conductivity of the aqueous solutions and decrease in homogeneity, whereas consideration of changes in phenolic and

aliphatic OH groups of lignin and changes in molecular weight have attracted less attention.

Panorel et al. [32] investigated implementation of PCD for lignin removal from water and for conversion of lignin into aldehydes. The PCD method was found to be an energy-efficient form of wastewater treatment, including for lignin removal from water. It was shown that the lignin oxidation efficiency of PCD is significantly higher than that of ozonation. Aldehydes formation was also detected during PCD treatment, but the yield was insignificant. Panorel used tannin-lignin method for determination of lignin concentration [33], however the test measures all hydroxylated aromatic compounds, including tannin, lignin, phenol and aldehydes. Therefore, it is not possible to accurately measure the concentration of lignin. Due to this reason, the results of calculations reported by Panorel can be unreliable. Nevertheless, the main findings of the Panorel's research are unquestionable – if recovery of aldehydes is the main purpose, reduced oxygen content and high initial lignin concentration would offer potential for higher yields.

In spite of recent research, PCD methods can be considered as being under-investigated, especially as regards their use in modification of various materials into valuable products. This study has two main goals: to improve the lignin conversion to aldehydes during PCD treatment, and to investigate the influence of PCD treatment on phenolic and aliphatic OH groups and changes in molecular weight.

2. Materials and methods

Kraft lignin was selected as a test compound for investigation of the lignin conversion to aldehydes. The kraft lignin was a commercially available lignin purchased from Sigma Aldrich. Two types of lignin were selected for investigate the influence of PCD treatment on phenolic and aliphatic OH groups and changes in molecular weight; Sigma Aldrich kraft lignin and BLN lignin. BLN lignin was a birch lignin acquired from a pressurized hot water extraction and soda pulped biorefinery process [34,35].

The experimental system contains a pulsed corona discharge reactor and a high voltage pulse generator in the setup illustrated in Fig. 1.

The reactor has a wire-plate corona geometry typical for electrostatic precipitators where the electrode wires are located between grounded plate electrodes. The high voltage electrodes are made from stainless steel, have a diameter of 0.5 mm, and are located 17 mm from the vertical grounded plate electrodes. The distance between the HV-electrodes is 30 mm. The discharge pulse parameters are voltage amplitude of 20 kV, current of 400 A, and pulse duration of 100 ns, giving single pulse energy of 0.33 J at a pulse repetition frequency of 840 pulses per second (pps). The treated solution is circulated from the 100-L tank through the reactor by a pump. The solution is dispersed between the electrodes, where it is treated with the oxidants.

The main parameters of estimation of the efficiency of PCD treatment are energy efficiency (ϵ , g/kWh) and lignin conversion rate to aldehydes (hereinafter – conversion rate, φ , %). The energy efficiency shows how much energy PCD consumes for lignin conversion to aldehydes and is calculated with following equation:

$$\epsilon = \Delta C/E \quad (1)$$

where ΔC is the difference between the initial and the final concentration of aldehydes, g/m³; E is the delivered energy dose, kWh/m³, calculated with the equation:

$$E = P \times t/V \quad (2)$$

where P is the pulse integral power delivered to the reactor, 0.25 kW; t is the treatment time, h; and V is the volume of the treated sample, m³.

The conversion rate is the ratio of aldehydes formed per oxidized lignin. It is calculated according to the equation:

$$\varphi = \frac{\Delta C_{\text{Aldehydes}}}{\Delta C_{\text{Lignin}}} \times 100\% \quad (3)$$

where $\Delta C_{\text{Aldehydes}}$ is the increase in aldehydes concentration; and ΔC_{Lignin} is the oxidized lignin concentration.

The oxidized lignin concentration is the difference between initial lignin concentration and lignin concentration after PCD treatment. It should be noted here, that tannin-lignin method (see description below) is used for determination of lignin concentration. This method measures all hydroxylated aromatic compounds. Due to this reason, the results of lignin concentration measurements are not absolute but indicative.

To prepare working solutions, the lignin was dissolved in 1 L of millipore water in the presence of NaOH. This solution was later diluted with tap water at ambient temperature in the reactor tank. The desired volume was 50 L. The flow rate of the re-circulating water was 15 L/min, which ensured sufficient trickling and mixing. The samples were taken after 5, 10, 20, 30 and 40 min of PCD treatment. After each interval, but before sample collection, the treated solution circulated continuously for 7 min without power supply for PCD in order to unify the concentration in the tank. The experiments were carried out with different initial concentrations of 370 to 1400 mg/L of lignin. The pH was in the range 11–12 during all experiments. The temperature was around room temperature (20 °C). The composition of the gas phase was air and nitrogen-enriched air with volumetric oxygen concentration of 5 to 7% and 2 to 3%, respectively. Every experiment was repeated several times to ensure accuracy and increase reliability.

The concentration of lignin was measured photometrically using the tyrosine method (tannin-lignin method). In this colorimetric method, the chromogenic reaction of the sodium carbonate solution and Tanniver[®] solution (tannin-lignin reagent, HACH), also known as a folin tannin-lignin reagent, which contains tungstophosphoric and molybdophosphoric acids, forms a blue colour with phenolic groups [33]. The result is reported as mg/L of tannic acid recalculated to lignin mass concentration units based on a calibration plot for the particular lignin. A HACH DR/2000 spectrophotometer was used as the analytical tool.

Aldehydes concentration was determined by the colorimetric method presented in [36]. A mixture of 5 mL of lignin-containing sample, sulphuric acid, sodium arsenite solution and 3-methylbenzothiazol-2-one hydrazone hydrochloride was immersed in boiling water for 6 min with subsequent cooling to room temperature. Iron (III) chloride-sulphamic acid reagent was then added to the cooled mixture, which was then allowed to stand for 20 min before measurement. An HACH DR/2000 spectrophotometer was used for aldehydes quantitative analysis. The analysis was carried out at a wavelength of 630 nm and absorbance was shown in relative units. The aldehydes concentration was recalculated based on a calibration curve where the absorbance was related to the concentration of glyoxylic acid.

NMR, GPC and HPSEC analyses were carried out to determine the effect of PCD treatment on phenolic and aliphatic OH groups and changes in molecular weight of the lignin.

³¹P NMR sample preparation: 20 to 25 mg of the lignin sample was dissolved in 400 μ L of a 1.6/1 (v/v) mixture of dry pyridine and deuterated chloroform. 100 μ L of a standard solution comprising 1 mmol of cholesterol and 50 mg of a spin relaxing agent Cr(III) acetyl acetonate in 10 mL of the aforementioned solvent mixture was added. For characterization of aromatic OH groups, 100 μ L of 2-chloro-4,4,5,5 tetramethyl-1,3,2 dioxaphospholane was added, and the reaction mixture was stirred at room temperature for two hours. For characterization of aliphatic OH groups, 2-chloro-1,2,3 dioxaphospholane was used instead of 2-chloro-4,4,5,5 tetramethyl-1,3,2 dioxaphospholane. The mixture was directly transferred into an NMR tube, and the sample was measured immediately.

GPC analysis of the Kraft lignin after acetobromination: A 5 mg sample was stirred for 2 h at room temperature in a 9/1 (v/v) mixture of glacial acetic acid and neat acetyl bromide before the reagents were removed in a vacuum. The residue was dissolved in 1 mL of HPLC grade tetrahydrofuran (THF) and the volatiles were removed, again in a vacuum. This procedure was repeated once. Final residues were dissolved in 1 mL of HPLC grade THF and filtered through a 5 μ m syringe filter

before being injected into a 20 μ L sample loop. GPC-analyses were performed using a set-up consisting of a pumping unit (LC 20AT), a degasser unit (DGU-20A3), a column oven (CTO-20AC), a diode array detector (SPD-M20A), a refractive index detector (RID-10A) and, if required, a controller unit (CBM-20A). For the analyses, two analytical GPC columns (each 7.5 \times 30 mm) were connected in series: an Agilent PLgel 5 μ m 500 \AA column followed by an Agilent PLgel 5 μ m 1000 \AA column. The columns were heated to 30 $^{\circ}$ C. HPLC-grade THF was used as a solvent for sample preparation and GPC analyses. An isocratic flow rate of 0.5 mL/min was applied for a run-time of 60 min. Calibration was performed using polystyrene beads with molecular weights in the range between 100000 and 200 Da. Final analyses of each sample were performed using the intensities of the UV signal at $\lambda = 280$ nm.

HPSEC analysis of the crude lignin: 10 mg of lignin sample was dissolved in 5–10 mL of DMSO, ultrasonicated for 20 min and stirred overnight. The solutions were filtered with a Teflon syringe filter, 0.2 μ m, and then subjected to HPSEC analysis. The molar-mass characteristics of underivatized lignins were determined by HPSEC using an Agilent 1100 Series liquid chromatograph (Hewlett-Packard Comp., USA) equipped with either a Jordi Gel GBR Mixed Bed (Glucose) 250 mm \times 10 mm i.d. column + a Jordi Gel (Glucose) DVB 500 $^{\circ}$ A 50 mm \times 7.8 mm i.d. guard column or a Waters Linear column, with DMSO and 0.05 M LiBr as the mobile phase with the flow rate 0.5 mL min $^{-1}$. The temperature of the column oven was 60 $^{\circ}$ C. An Agilent 1100 Series G1315B diode-array detector and a Shimadzu RID-10A refractive index detector were connected in series. The injection volume was 30 μ L.

3. Results and discussion

Previous research [32] has reported that the highest lignin conversion to aldehydes was obtained by increasing initial lignin concentration to 600 mg/L for a reaction in a 5–7% volumetric oxygen gas phase. With the aim of improved conversion rate, lignin concentration was raised to 1400 mg/L and the volumetric oxygen content was reduced to 2–3%. The results of these experiments are given in Fig. 2.

The trend of improved conversion rate with increasing initial lignin concentration in a low oxygen content atmosphere can be clearly seen. The opposite trend is observed in the air atmosphere. The highest recorded conversion rate was around 33% at 2–3% oxygen content with 770 mg/L initial lignin concentration.

However, determination of aldehydes and lignin concentration after PCD treatment in an oxygen-thin atmosphere is rather complex. At 2–3% volumetric oxygen, the oxidation rate is rather low and changes in concentrations insignificant. Analytical tools with higher accuracy are thus required, and it would be rash to assert the high accuracy of the obtained results without additional investigation using more advanced analytical tools. Nevertheless, an oxygen-thin atmosphere provides less

harsh reaction conditions due to limited availability of oxidants [37,38]. Based on results of our experiments, it is possible to say, that such atmosphere is favorable for aldehydes formation.

From the energy efficiency point of view, PCD treatment in oxygen-thin conditions is less efficient than treatment in an air atmosphere (see Fig. 2). At the same time, higher initial lignin concentration contributes to better energy efficiency. However, it is significant that the relationship between energy efficiency and initial lignin concentration is not linear, especially in air conditions. In air conditions, increase in initial lignin concentration by 17.5 times, from 80 mg/L to 1400 mg/L, results in energy efficiency enhancement of 2.3 times only. Furthermore, the rate of increase in energy efficiency slows with increasing initial lignin concentration. As can be observed in Fig. 2, energy efficiency increases rapidly at first, as the lignin concentration rises from 80 mg/L to 370 mg/L, and is then followed by a reduction in the energy efficiency growth rate. It is arguable that further increase in initial lignin concentration will not lead to any significant improvements in energy efficiency. Similar calculations for the oxygen-thin atmospheres show that energy efficiency increases 8.3 times (at 5–7% O $_2$) and 6.7 times (at 2–3% O $_2$) with increased initial lignin concentration of 17.5 times and 9.6 times, respectively. It is possible to conclude that the energy efficiency growth rate will continue to increase with increasing initial lignin concentration and will not decline in the same way as with the experiment in an air atmosphere. Consequently, by increasing the lignin concentration and using oxygen-thin conditions, it may be possible to exceed the energy efficiency rate of the experiment in an air atmosphere.

To study the effect of the PCD treatment on lignin, two types of lignin were tested: kraft lignin and BLN lignin. Initially the kraft lignin was subjected to the PCD treatment for 40 min in air atmosphere and 2.2% O $_2$ in N $_2$ atmosphere. Each of the solutions was then acidified to pH 5.5, freeze-dried and analyzed by HP-SEC (see Fig. 3).

The kraft lignin PCD treated in air atmosphere was not completely soluble in DMSO which indicates a change in solubility during the treatment but both of the lignin analyzed was still polymeric. The kraft lignin was then subjected to further PCD treatment for 20 and 40 min in an air atmosphere, in 5–7% O $_2$ in N $_2$ atmosphere and in 2–3% O $_2$ in N $_2$ atmosphere (see Table 1). All experiments were performed with three different concentrations of lignin (400, 800 and 1600 ppm).

It was then attempted to precipitate the lignin from the alkaline solution by neutralization with aqueous HCl followed by isolation by centrifugation. With most of the samples, no precipitate could be isolated; and where precipitate could be isolated, only small amounts were found. In an attempt to isolate any lignin degradation fragments from the samples, the water phase was extracted with EtOAc. However, no EtOAc soluble compounds could be isolated. Based on these results it was concluded that the solubility of the treated lignin had changed to a more water soluble lignin. The small amount of precipitate that had

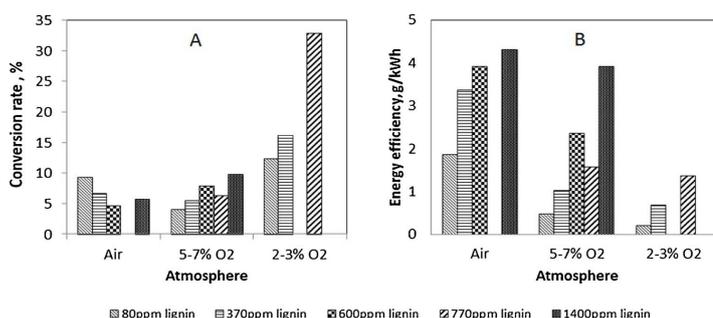


Fig. 2. Conversion rate (A) and energy efficiency (B) of aldehydes formation in different atmospheres with different initial lignin concentration.

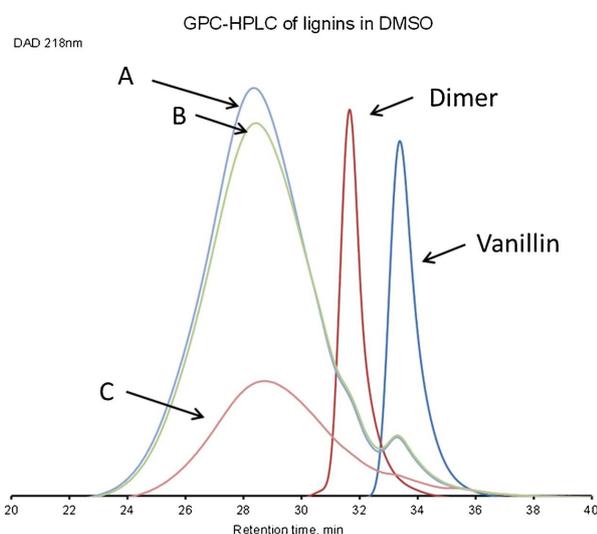


Fig. 3. HPSEC using DMSO as eluent and a UV-detector. A) Sigma Aldrich kraft lignin, B) 40 min in air atmosphere and C) 40 min in 2.2% O₂ in N₂ atmosphere.

been isolated was analyzed by GPC and ³¹P NMR and the differences between the experiments were summarized in Table 1. It should be noted that the samples are not representative of the whole lignin but the precipitated fraction could give us information of the PCD induced changes to the lignin. The experiments in an air atmosphere yielded no precipitates; the experiments done in 5–7% O₂ in N₂ atmosphere yielded small amounts of precipitate from experiments of 40 min duration with concentrations of 400 and 800 ppm; and all of the experiments performed in 2–3% O₂ in N₂ atmosphere yielded small amounts of precipitate except for experiments of 20 min duration with concentrations of 800 and 1600 ppm lignin, which yielded no

precipitate. Based on the change in solubility, the PCD treatment clearly induces changes in the kraft lignin, and as most of the precipitation occurs after the longer 40 min PCD treatment, it would appear that the lignin continues to react, possibly in the form of condensation of the lignin. The PCD treatment with the lowest O₂ concentration yielded the most filtrate, which indicates that it is less oxidized and as such is possible to re-polymerize.

To study the PCD induced structural changes further, a lignin isolated from a pressurized hot water extraction and soda pulp biorefinery process (BLN lignin) was subjected to PCD treatment. All the PCD treatments were done for 40 min at a concentration of 400 ppm lignin

Table 1
PCD treatment of kraft lignin.

	Air	5–7% O ₂ ; rest N ₂	2–3% O ₂ ; rest N ₂
0 min, untreated sample	GPC: M _n = 5951 M _w = 16711. NMR: primary aliphatic OH groups = 4.34 mmol/g, secondary aliphatic OH groups = 1.89 mmol/g, coniferyl alcohol = 1.05 mmol/g, sinapyl-type phenolic end groups = 1.83 mmol/g, p-coumaryl-type phenols = 0.32 mmol/g		
20 min	no precipitate	no precipitate	small precipitate, not enough for full NMR. Only aromatic OH characterization was done. No significant changes comparing with untreated sample. GPC: M _n = 3484 M _w = 10029 – significant decreasing comparing with untreated sample
40 min	no precipitate	small precipitate, not enough for NMR. GPC: M _n = 3287 M _w = 10995, significant decreasing comparing with untreated sample	NMR: Significantly increasing of primary (from 4.34 mmol/g to 7.51 mmol/g) and secondary (from 1.89 mmol/g to 4.46 mmol/g) aliphatic OH groups comparing with untreated sample. Coniferyl alcohol and sinapyl phenolic units stay in the same level; the p-coumaryl-type phenols seem to be slightly decreased. GPC: M _n = 6579 M _w = 19020 increased and exceeded of untreated sample values
		initial lignin concentration 800 ppm	
20 min	no precipitate	no precipitate	no precipitate
40 min	no precipitate	small precipitate. NMR: slight increasing of coniferyl end groups, and slight decreasing amounts of p-coumaryl and sinapyl-type phenolic end-groups. M _n = 5715 M _w = 15109 GPC: insignificant decreasing of M _n and M _w comparing with untreated sample	small precipitate, small precipitates, not enough for full NMR. Only aromatic OH characterization was done. No significant changes. GPC: M _n = 5271 M _w = 15230 insignificant decreasing of M _n and M _w comparing with untreated sample
		initial lignin concentration 1600 ppm	
20 min	no precipitate	no precipitate	no precipitate
40 min	no precipitate	no precipitate	small precipitates, not enough for full NMR. Only aromatic OH characterization was done. No significant changes comparing with untreated sample. GPC: M _n = 5842 M _w = 19877

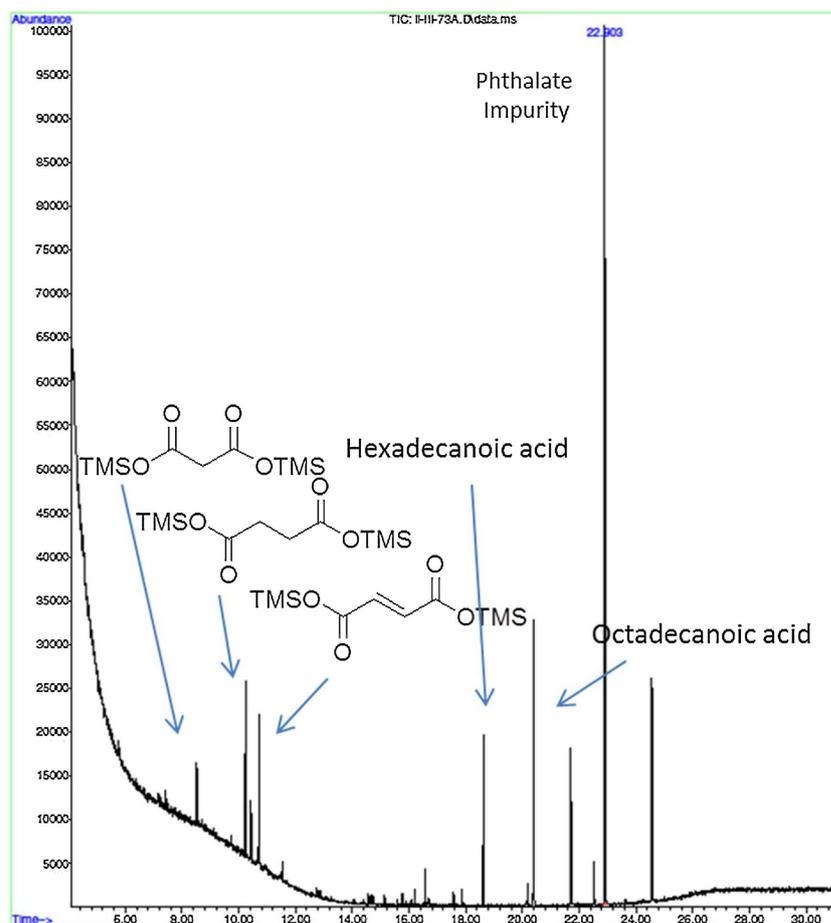


Fig. 4. GC-MS of salivated MTBE soluble compounds after 40 min of PCD treatment of BLN lignin in air atmosphere.

in either air atmosphere, 5–7% O₂ in N₂ atmosphere or 96% O₂ atmosphere. The experimental procedure after the PCD treatment was similar to that of the kraft lignin; the pH of the alkaline solution was reduced to pH 2.5 with 1 M HCl. The aqueous solution was then extracted with MTBE to remove any small organic compounds that could have been cleaved during the process. Both the MTBE and aqueous phases were then concentrated separately by evaporation. Only small amounts of MTBE soluble compounds were isolated, and based on GCMS analysis, the compounds consisted of fatty acids, impurities and small amounts of lignin fragments (see Fig. 4 and 5).

Due to the high amount of inorganics in the remaining solid, attempts were made to selectively dissolve the organics from the dried aqueous phase with organic solvents (THF and acetone). However, all attempts were unsuccessful or only partially dissolved the lignin. All the samples were dried and analyzed as such with HPSEC, ¹³C NMR and HSQC. While the size of the PCD treated lignin was slightly reduced in all samples (see Fig. 6) the lignin was still polymeric or oligomeric and no smaller structures could be observed in the HPSEC-chromatogram.

From the NMR experiments, it was concluded that the aromatic rings were partially cleaved compared to the starting material and it was noted that a large amount of carboxyl/carbonyl groups were formed (see Fig. 7).

The amount of oxygen used in the treatment seems to correlate to the amount of degradation of the starting material. Aromatic signals could still be seen in the ¹³C NMR spectrum of the sample subjected to PCD treatment in 5–6% O₂ atmosphere, but the samples PCD treated at higher O₂ concentrations had considerably less aromatic signals. From the HSQC spectra (see Fig. 8) a clear degradation of the aromatic C–H correlation peaks approximately at δ_C/δ_H (120–105/6.0–7.5) ppm is observed, which indicates degradation of the aromatic rings or reactions at the aromatic C–H positions.

The formation of carboxylic functional groups may explain the drastic change in solubility of the lignin. The sharp peaks from the NMR experiments indicate the presence of small molecules, presumably water soluble, such as carboxylic acids, which would explain why the MTBE extraction was unsuccessful. Low or no UV-absorbance could

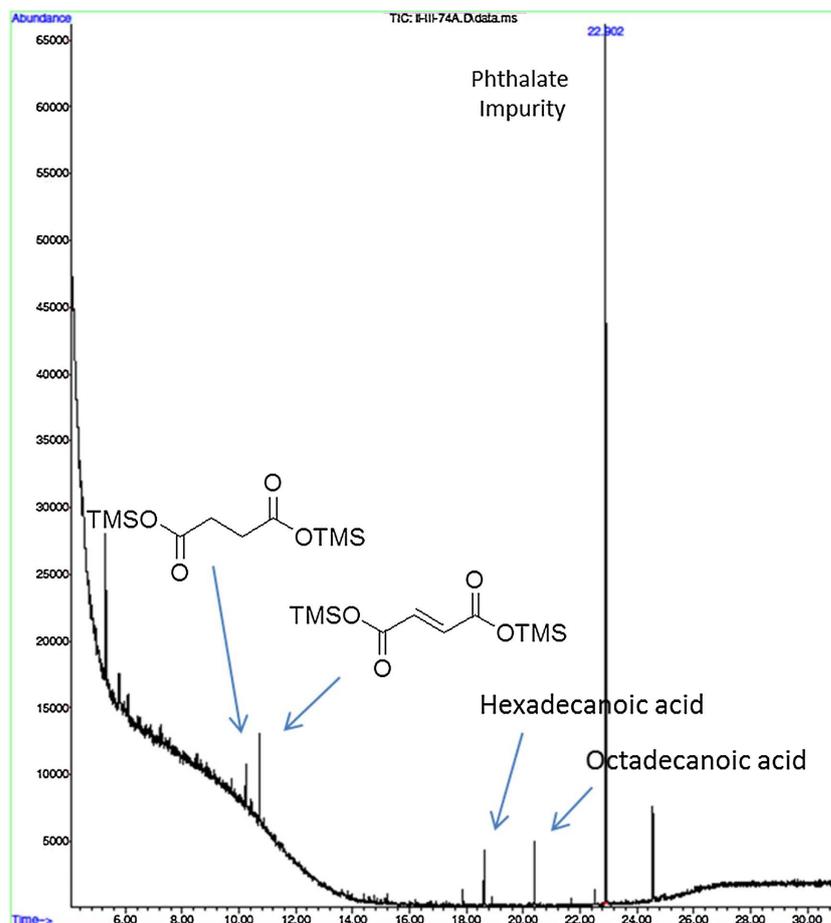


Fig. 5. GC-MS of salivated MTBE soluble compounds after 40 min of PCD treatment of BLN lignin in 5–6% O₂ in N₂ atmosphere.

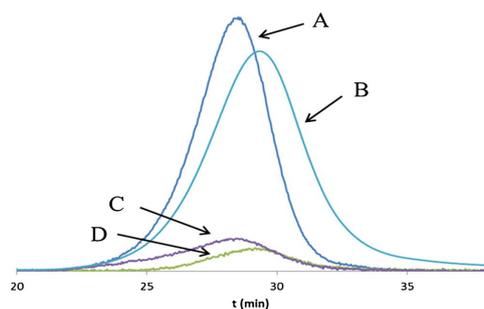


Fig. 6. HPSEC using DMSO as eluent and a UV-detector. A) BLN Lignin; B) 40 min in 96% O₂ atmosphere; C) 40 min in air atmosphere; and D) 40 min in N₂ atmosphere with 5–7% O₂.

explain the absence of these molecules in the HPSEC-chromatogram.

4. Conclusion

PCD treatment is able to oxidize lignin to aldehydes, but also may further oxidize aldehydes to carboxylic acids and induces oxidative cleavage of aromatic rings. To avoid this undesirable effect, softer oxidation conditions are required.

Increasing the lignin concentration in oxygen-deficient conditions consequently increased the aldehydes formation relative to the oxidized lignin.

Diminished oxygen conditions are more favorable for aldehydes formation, as seen by the higher conversion rate, and potentially have better energy efficiency.

Two different lignins, a kraft lignin and BLN lignin, were subjected to PCD treatment. The treatment considerably altered the structure of the lignins. The results indicate that the formed structure is polymeric or oligomeric and contains a high degree of carboxyl or carbonyl

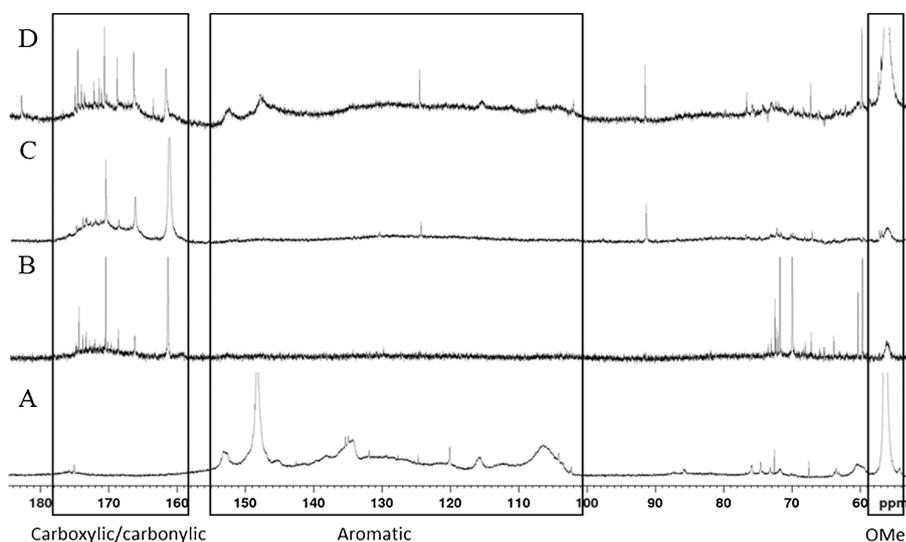


Fig. 7. C-13 NMR spectra. A) BLN lignin; B) 40 min in 96% O₂ atmosphere; C) 40 min in air atmosphere; D) 40 min in 5–6% O₂ in N₂ atmosphere.

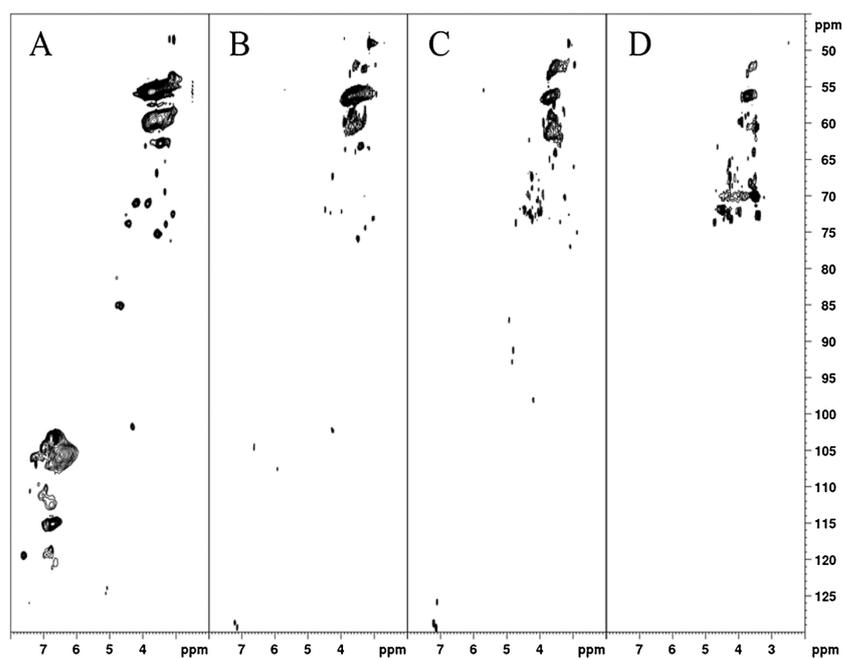


Fig. 8. HSQC spectra. A) BLN lignin; B) 40 min 5–6% O₂ in N₂ atmosphere; C) 40 min in air atmosphere; and D) 40 min in 96% O₂ atmosphere.

groups. The amount of degradation seems to be a direct function of the oxygen concentration in which the PCD treatment is performed.

Under less harsh conditions with lower oxygen content, initial

depolymerization of lignin occurs at the beginning of the PCD treatment with subsequent polymerization of lignin fragments.

Acknowledgments

A part of the experiments was carried out at the University of Tor Vergata, Rome, Italy within the framework of the COST Action FP 1105 programme. The authors would like to acknowledge financial support from LUT Doctoral School and Graduate School in Chemical Engineering.

References

- [1] K. Poppius-Levlin, E.-L. Hult, J. Ropponen, Lignin-based sustainable packaging solutions, 4th Nord. Wood Biorefinery Conf. VTT, Helsinki, Finland, 2012, pp. 174–179 <http://www.vtt.fi/inf/pdf/technology/2012/133.pdf>.
- [2] M. Kleinert, T. Barth, Phenols from lignin, *Chem. Eng. Technol.* 31 (2008) 736–745, <http://dx.doi.org/10.1002/ceat.200800073>.
- [3] R.J. Evans, T.A. Milne, M.N. Sollys, Direct mass-spectrometric studies of the pyrolysis of carbonaceous fuels. III. Primary pyrolysis of lignin, *J. Anal. Appl. Pyrolysis* 9 (1986) 207–236, [http://dx.doi.org/10.1016/0165-2370\(86\)80012-2](http://dx.doi.org/10.1016/0165-2370(86)80012-2).
- [4] O. Derkacheva, D. Sukhov, Investigation of lignins by FTIR spectroscopy, *Macromol. Symp.* 265 (2008) 61–68, <http://dx.doi.org/10.1002/masy.200850507>.
- [5] J. Zakzkeski, A.L. Jongerius, P.C.A. Bruijninx, B.M. Weckhuysen, Catalytic lignin valorization process for the production of aromatic chemicals and hydrogen, *ChemSusChem* 5 (2012) 1602–1609, <http://dx.doi.org/10.1002/cssc.201100699>.
- [6] A. Sakakibara, V. Sano, No title, in: D.N.-S. Hon, N. Shiraishi (Eds.), *Wood Cellul. Chem.* 2nd ed., Marcel Dekker, Inc, New York, 2001, pp. 109–173.
- [7] R. Hatfield, Lignin formation in plants. The dilemma of linkage specificity, *Plant Physiol.* 126 (2001) 1351–1357, <http://dx.doi.org/10.1104/pp.126.4.1351>.
- [8] P.C. Rodrigues Pinto, E.A. Borges Da Silva, A.E. Rodrigues, Insights into oxidative conversion of lignin to high-added-value phenolic aldehydes, *Ind. Eng. Chem. Res.* (2011), pp. 741–748, <http://dx.doi.org/10.1021/ie102132a>.
- [9] E.A.B. da Silva, J.D. Arajio, C.A. Cateto, M.F. Barreiro, M.N. Belgacem, A.E. Rodrigues, An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin, *Chem. Eng. Res. Des.* 87 (2009) 1276–1292, <http://dx.doi.org/10.1016/j.cherd.2009.05.008>.
- [10] F.G. Sales, C.A.M. Abreu, J.A.F.R. Pereira, Catalytic wet-air oxidation of lignin in a three-phase reactor with aromatic aldehyde production, *Brazilian J. Chem. Eng.* (2004) 211–218, <http://dx.doi.org/10.1590/S0104-66322004000200010>.
- [11] J.C. Villar, A. Caperos, F. Garcia-Ochoa, Oxidation of hardwood Kraft-lignin to phenolic derivatives with oxygen as oxidant, *Wood Sci. Technol.* 35 (2001) 245–255, <http://dx.doi.org/10.1007/s002260100089>.
- [12] K.L. Anderson, M. Eriksson, M. Norgren, Removal of lignin from wastewater generated by mechanical pulping using activated charcoal and fly ash: adsorption isotherms and thermodynamics, *Ind. Eng. Chem. Res.* 50 (2011) 7722–7732, <http://dx.doi.org/10.1021/ie200378s>.
- [13] D.W.S. Wong, Structure and Action Mechanism of Ligninolytic Enzymes, (2009), <http://dx.doi.org/10.1007/s12010-008-8279-z>.
- [14] J. Kornev, N. Yavorovskiy, S. Preis, M. Khaskelberg, U. Isaev, B.-N. Chen, Generation of active oxidant species by pulsed dielectric barrier discharge in water-air mixtures, *Ozone Sci. Eng.* 28 (2006) 207–215, <http://dx.doi.org/10.1080/01919510600704957>.
- [15] S. Chauhan, E. Yankelevich, V.M. Bystritskii, T.K. Wood, Degradation of 2,4,5-trichlorophenol and 2,3,5,6-tetrachlorophenol by combining pulse electric discharge with bioremediation, *Appl. Microbiol. Biotechnol.* 52 (1999) 261–266, <http://dx.doi.org/10.1007/s002530051519>.
- [16] N. Yavorovskiy, S. Boev, E. Myratov, N. Polyakov, Reactor and Method of Water Treatment, (1997) (2133600).
- [17] 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) 133–137.
- [18] P. Lukes, N. Aoki, E. Spetlikova, S.H.R. Hosseini, T. Sakugawa, H. Akiyama, Effects of pulse frequency of input power on the physical and chemical properties of pulsed streamer discharge plasmas in water, *J. Phys. D Appl. Phys.* 46 (1252) (2013) 125202–125210, <http://dx.doi.org/10.1088/0022-3727/46/12/125202>.
- [19] K.Y. Shih, B.R. Locke, Chemical and physical characteristics of pulsed electrical discharge within gas bubbles in aqueous solutions, *Plasma Chem. Plasma Process.* 30 (2010) 1–20, <http://dx.doi.org/10.1007/s11090-009-9207-x>.
- [20] E. Marotta, E. Ceriani, M. Schiorlin, C. Ceretta, C. Paradisi, Comparison of the rates of phenol advanced oxidation in deionized and tap water within a dielectric barrier discharge reactor, *Water Res.* 46 (2012) 6239–6246, <http://dx.doi.org/10.1016/j.watres.2012.08.022>.
- [21] M. Malik, K. Schoenbach, A novel pulsed Corona discharge reactor based on surface streamers for NO conversion from N₂-O₂ mixture gases, *Int. J. Plasma Environ. Sci. Technol.* (2011) http://digitalcommons.odu.edu/bioelectrics_pubs/36 (Accessed June 11, 2017).
- [22] A.M. Anpilov, E.M. Barkhudarov, Y.B. Bark, Y.V. Zadiraka, M. Christofi, Y.N. Kozlov, I. a Kossyi, V. a Kop'ev, V.P. Silakov, M.I. Taktakishvili, S.M. Temchin, Electric discharge in water as a source of UV radiation, ozone and hydrogen peroxide, *J. Phys. D Appl. Phys.* 34 (2001) 993–999, <http://dx.doi.org/10.1088/0022-3727/34/6/322>.
- [23] M. Magureanu, C. Bradu, D. Piroi, N.B. Mandache, V. Parvulescu, Pulsed corona discharge for degradation of methylene blue in water, *Plasma Chem. Plasma Process.* 33 (2013), <http://dx.doi.org/10.1007/s11090-012-9422-8>.
- [24] L.R. Grabowski, E.M. Van Veldhuizen, A.J.M. Pemen, W.R. Rutgers, Corona above water reactor for systematic study of aqueous phenol degradation, *Plasma Chem. Plasma Process.* 26 (2006) 3–17, <http://dx.doi.org/10.1007/s11090-005-8721-8>.
- [25] B. Benstaali, N. Al-Bastaki, A. Addou, J.L. Brisset, Plasma-chemical and photocatalytic degradation of methyl orange, *Int. J. Environ. Waste Manage.* 11 (2013) 158–177, <http://dx.doi.org/10.1504/IJEW.2013.051824>.
- [26] D.R. Merouani, F. Abdelmalek, M.R. Ghezzer, A. Semmoud, A. Addou, J.L. Brisset, Influence of peroxyinitride in gliding arc discharge treatment of alizarin red s and postdischarge effects, *Ind. Eng. Chem. Res.* 52 (2013) 1471–1480, <http://dx.doi.org/10.1021/ie302964a>.
- [27] B.R. Locke, S.M. Thagard, Analysis and review of chemical reactions and transport processes in pulsed electrical discharge plasma formed directly in liquid water, *Plasma Chem. Plasma Process.* 32 (2012) 875–917, <http://dx.doi.org/10.1007/s11090-012-9403-y>.
- [28] A. Pokryvaio, M. Wolf, Y. Yankelevich, S. Wald, L.R. Grabowski, E.M. van Veldhuizen, W.R. Rutgers, M. Reiser, B. Glocker, T. Eckhardt, P. Kempenaers, A. Welleman, High-Power Pulsed Corona for Treatment of Pollutants in Heterogeneous Media, *IEEE Trans. Plasma Sci.* 1743, <http://dx.doi.org/10.1109/TPS.2006.881281>.
- [29] X. Zhou, F. Zheng, X. Liu, L. Tang, G. Xue, G. Du, Q. Yong, M. Chen, L. Zhu, Glass transition of oxygen plasma treated enzymatic hydrolysis lignin, *BioResources* 7 (2012) 4776–4785 http://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_07_4_4776_Zhou_Glass_Transition_Oxygen_Plasma_Lignin.
- [30] O. Chirila, M. Totolin, G. Cazacu, M. Dobromir, C. Vasile, Lignin modification with carboxylic acids and butyrolactone under cold plasma conditions, *Ind. Eng. Chem. Res.* 52 (2013) 13264–13271, <http://dx.doi.org/10.1021/ie4015183>.
- [31] M. Nistor, O. Chirila, G. Cazacu, M.I. Totolin, C. Vasile, Solution properties of some modified lignins, *Cellul. Chem. Technol.* 48 (2014) 855–862.
- [32] I. Panorel, L. Kajjanen, I. Kornev, S. Preis, M. Louhi-Kultanen, H. Siren, Pulsed corona discharge oxidation of aqueous lignin: decomposition and aldehydes formation, *Environ. Technol.* 35 (2014) 171–176, <http://dx.doi.org/10.1080/09593330.2013.821144>.
- [33] M.B. Kloster, The Determination of Tannin and Lignin Published By: American Water Works Association The Determination of Tannin and Lignin 66 (1974), pp. 44–46.
- [34] S.S. VON, Method for extracting biomass, (2014) <https://www.google.com/patents/WO2014009604A1?cl=ru>.
- [35] S.S. VON, Method for Extracting Lignin, (2015) (<https://www.google.com/patents/WO2015104460A1?cl=en>).
- [36] W.H. Evans, A. Dennis, Spectrophotometric determination of low levels of mono-, di- and triethylene glycols in surface waters, *Analyst* 98 (1973) 782–791, <http://dx.doi.org/10.1039/AN9739800782>.
- [37] R. Ono, T. Oda, Measurement of hydroxyl radicals in pulsed corona discharge, *J. Electrostat.* 55 (2002) 333–342, [http://dx.doi.org/10.1016/S0304-3886\(01\)00215-7](http://dx.doi.org/10.1016/S0304-3886(01)00215-7).
- [38] R. Ono, T. Oda, Dynamics of ozone and OH radicals generated by pulsed corona discharge in humid-air flow reactor measured by laser spectroscopy, *J. Appl. Phys.* 93 (2003) 5876–5882, <http://dx.doi.org/10.1063/1.1567796>.

ACTA UNIVERSITATIS LAPPEENRANTAENSIS

- 822. IMMONEN, KIRSI. Ligno-cellulose fibre poly(lactic acid) interfaces in biocomposites. 2018. Diss.
- 823. YLÄ-KUJALA, ANTTI. Inter-organizational mediums: current state and underlying potential. 2018. Diss.
- 824. ZAFARI, SAHAR. Segmentation of partially overlapping convex objects in silhouette images. 2018. Diss.
- 825. MÄLKKI, HELENA. Identifying needs and ways to integrate sustainability into energy degree programmes. 2018. Diss.
- 826. JUNTUNEN, RAIMO. LCL filter designs for parallel-connected grid inverters. 2018. Diss.
- 827. RANAELI, SAMIRA. Quantitative approaches for detecting emerging technologies. 2018. Diss.
- 828. METSO, LASSE. Information-based industrial maintenance - an ecosystem perspective. 2018. Diss.
- 829. SAREN, ANDREY. Twin boundary dynamics in magnetic shape memory alloy Ni-Mn-Ga five-layered modulated martensite. 2018. Diss.
- 830. BELONOGOVA, NADEZDA. Active residential customer in a flexible energy system - a methodology to determine the customer behaviour in a multi-objective environment. 2018. Diss.
- 831. KALLIOLA, SIMO. Modified chitosan nanoparticles at liquid-liquid interface for applications in oil-spill treatment. 2018. Diss.
- 832. GEYDT, PAVEL. Atomic Force Microscopy of electrical, mechanical and piezo properties of nanowires. 2018. Diss.
- 833. KARELL, VILLE. Essays on stock market anomalies. 2018. Diss.
- 834. KURONEN, TONI. Moving object analysis and trajectory processing with applications in human-computer interaction and chemical processes. 2018. Diss.
- 835. UNT, ANNA. Fiber laser and hybrid welding of T-joint in structural steels. 2018. Diss.
- 836. KHAKUREL, JAYDEN. Enhancing the adoption of quantified self-tracking wearable devices. 2018. Diss.
- 837. SOININEN, HANNE. Improving the environmental safety of ash from bioenergy production plants. 2018. Diss.
- 838. GOLMAEI, SEYEDMOHAMMAD. Novel treatment methods for green liquor dregs and enhancing circular economy in kraft pulp mills. 2018. Diss.
- 839. GERAMI TEHRANI, MOHAMMAD. Mechanical design guidelines of an electric vehicle powertrain. 2019. Diss.
- 840. MUSIIENKO, DENYS. Ni-Mn-Ga magnetic shape memory alloy for precise high-speed actuation in micro-magneto-mechanical systems. 2019. Diss.

841. BELIAEVA, TATIANA. Complementarity and contextualization of firm-level strategic orientations. 2019. Diss.
842. EFIMOV-SOINI, NIKOLAI. Ideation stage in computer-aided design. 2019. Diss.
843. BUZUKU, SHQIPE. Enhancement of decision-making in complex organizations: A systems engineering approach. 2019. Diss.
844. SHCHERBACHEVA, ANNA. Agent-based modelling for epidemiological applications. 2019. Diss.
845. YLIJOKI, OSSI. Big data - towards data-driven business. 2019. Diss.
846. KOISTINEN, KATARIIINA. Actors in sustainability transitions. 2019. Diss.
847. GRADOV, DMITRY. Experimentally validated numerical modelling of reacting multiphase flows in stirred tank reactors. 2019. Diss.
848. ALMPANOPOULOU, ARGYRO. Knowledge ecosystem formation: an institutional and organisational perspective. 2019. Diss.
849. AMELI, ALIREZA. Supercritical CO2 numerical modelling and turbomachinery design. 2019. Diss.
850. RENEV, IVAN. Automation of the conceptual design process in construction industry using ideas generation techniques. 2019. Diss.
851. AVRAMENKO, ANNA. CFD-based optimization for wind turbine locations in a wind park. 2019. Diss.
852. RISSANEN, TOMMI. Perspectives on business model experimentation in internationalizing high-tech companies. 2019. Diss.
853. HASSANZADEH, AIDIN. Advanced techniques for unsupervised classification of remote sensing hyperspectral images. 2019. Diss.
854. POPOVIC, TAMARA. Quantitative indicators of social sustainability applicable in process systems engineering. 2019. Diss.
855. RAMASAMY, DEEPIKA. Selective recovery of rare earth elements from diluted aqueous streams using N- and O –coordination ligand grafted organic-inorganic hybrid composites. 2019. Diss.
856. IFTEKHAR, SIDRA. Synthesis of hybrid bio-nanocomposites and their application for the removal of rare earth elements from synthetic wastewater. 2019. Diss.
857. HUIKURI, MARKO. Modelling and disturbance compensation of a permanent magnet linear motor with a discontinuous track 2019. Diss.
858. AALTO, MIKA. Agent-based modeling as part of biomass supply system research. 2019. Diss.
859. IVANOVA, TATYANA. Atomic layer deposition of catalytic materials for environmental protection. 2019. Diss.



ISBN 978-952-335-390-9
ISBN 978-952-335-391-6 (PDF)
ISSN-L 1456-4491
ISSN 1456-4491
Lappeenranta 2019