Non-equilibrium plasma in contact with water as advanced oxidation process for decomposition of micropollutants

Niels Wardenier

Promotor: Prof. dr. ir. Stijn Van Hulle
Promotor: Prof. dr. Ann Dumoulin
Tutor: Dr. Anton Nikiforov

Master's dissertation submitted in partial fulfilment of the requirements for the degree of Master of Science in Industrial Sciences: Chemistry
Copyright

The author, promotors and tutor give permission to make this master dissertation available for consultation and to copy parts of this master dissertation for personal use. In the case of any other use, the limitations of the copyright have to be respected, in particular with regard to the obligation to state expressly the source when quoting results from this master dissertation.

Kortrijk, June 2016

The author,
Niels Wardenier

The promotors,
Prof. dr. ir. Stijn Van Hulle

The tutor,
Dr. Anton Nikiforov

Prof. dr. Ann Dumoulin
Acknowledgements

Finally finished! After nine months of hard work at the Laboratory of Industrial Water and Ecotechnology (LIWET) and the Research Unit of Plasma Technology (RUPT), it is almost time to finalize my master in chemical engineering technology. However, finishing this work would not be possible, without the help of some important people. Therefore, I would like to thank all of them which has contributed to this work.

First, I would like to thank my both promotors, prof. dr. ir. Stijn Van Hulle and prof. dr. Ann Dumoulin. Stijn and Ann, thank you for providing this very interesting master thesis! Your critical views, and suggestions certainly enhanced the overall quality of this work.

Next, my thank goes go to Dr. Anton Nikiforov, doctor assistant at the RUPT. Anton, thank you for giving me the opportunity of working in your lab, and sharing your enormous knowledge about plasma technology.

Maybe the most important person who has contributed to this work, was RUPT teaching assistant drs. ir. Patrick Vanraes. Patrick, my sincerest gratitude for your tireless efforts, practical support during the experiments, and our numerous discussions about plasma technology for water treatment, AOP systems and science in general. I wish you all the best for your upcoming PhD thesis defence, and your further academic career!

Back in Kortrijk, I also appreciated the help of ir. Yannick Verheust by the analytical part of my thesis. Yannick, thank you for the support with the analytical procedures, especially with GC-MS procedure development and GC-MS troubleshooting in the early months of my research work.

Aside of my supervisors and other teaching staff, also many thanks to all other thesis students working in the analytical lab A206 in Kortrijk, and the lab of plasma technology in Ghent. Together they created a stimulating research environment which was definitely enlightening.

Special thank goes to my girlfriend Lindsey, for the support and continuous motivation during my thesis. Especially, I have appreciated your support in the graphical design of my master thesis. I know this was not evident since you also had a lot of work to do in your own master year.

Last, but not least I would like to thank my parents for all support, received during my whole studying period.
Table of contents

List of abbreviations ......................................................................................................................... VI
Summary ............................................................................................................................................... VII
Samenvatting ....................................................................................................................................... VIII
Introduction ......................................................................................................................................... 1

Chapter 1  Micropollutants .......................................................................................................... 3
  1.1 Historical background .................................................................................................................. 3
  1.2 Classification of micropollutants ................................................................................................. 3
  1.3 Sources of micropollutants ......................................................................................................... 4
    1.3.1 PPCPs ..................................................................................................................................... 5
    1.3.2 Pesticides & industrial compounds ....................................................................................... 5
  1.4 Environmental fate of micropollutants ....................................................................................... 6
    1.4.1 Municipal waste water treatment ......................................................................................... 6
    1.4.2 Environmental fate in MWWTPs .......................................................................................... 8
  1.5 Micropollutant removal mechanisms in MWWTPs .................................................................... 10
    1.5.1 Biodegradation ................................................................................................................... 10
    1.5.2 Sorption ............................................................................................................................. 11
    1.5.3 Volatilization ....................................................................................................................... 12

Chapter 2  Advanced treatment methods for wastewater remediation ..................................... 13
  2.1 Coagulation and flocculation .................................................................................................... 13
  2.2 Activated carbon filtration ........................................................................................................ 14
  2.3 Membrane filtration .................................................................................................................. 14
  2.4 Advanced oxidation processes ................................................................................................. 16
    2.4.1 AOP kinetics ....................................................................................................................... 17
    2.4.2 Energy efficiency ............................................................................................................... 18
  2.5 Conclusion ................................................................................................................................. 20

Chapter 3  Plasma technology ..................................................................................................... 22
  3.1 What is plasma? ....................................................................................................................... 22
  3.2 non-thermal plasmas ................................................................................................................. 22
  3.3 Dielectric barrier discharges .................................................................................................... 24
    3.3.1 Energy efficiency ................................................................................................................. 26

Chapter 4  Experimental setup .................................................................................................... 32
Chapter 5 Analytical procedures ................................................. 41
5.1 Electrical diagnostics .............................................................. 41
  5.1.1 Power measurements ......................................................... 41
5.2 Emission spectrometry ............................................................ 42
5.3 Chemical diagnostics ............................................................. 43
  5.3.1 Determination of \(H_2O_2\) ...................................................... 43
  5.3.2 Gas chromatography – mass spectrometry ......................... 44
5.4 Toxicity analysis ................................................................. 52
  5.4.1 Preparation of test samples ............................................... 53
  5.4.2 Toxicity testing ............................................................... 53

Chapter 6 Characterization of a DBD plasma reactor .................... 54
6.1 Spectral analysis ................................................................. 54
  6.1.1 Air plasma .................................................................. 54
  6.1.2 Oxygen plasma .............................................................. 57
  6.1.3 Argon plasma .............................................................. 57
6.2 Active species production in the water phase ............................ 58
  6.2.1 pH ........................................................................ 58
  6.2.2 Conductivity ............................................................... 61
6.2.3  

H\textsubscript{2}O\textsubscript{2} production ................................................................. 63

6.3  

Conclusion ............................................................................................................ 65

Chapter 7  

Optimization of a DBD plasma reactor ................................................................. 66

7.1  

Adsorption ........................................................................................................... 66

7.2  

Micropollutant removal in batch reactor configuration ........................................ 67

7.3  

Micropollutant removal in single pass reactor configuration ......................... 70

7.4  

Optimization of operational parameters .......................................................... 73

7.4.1  

Effect of the working gas .................................................................................. 73

7.4.2  

Effect of the gas flowrate .................................................................................. 74

7.4.3  

Effect of the water flowrate ................................................................................ 75

7.4.4  

Effect of duty cycle ............................................................................................ 76

7.4.5  

Effect of power ..................................................................................................... 76

7.4.6  

Effect of the initial concentration ...................................................................... 77

7.5  

Concluding remarks ........................................................................................... 78

7.6  

Toxicity ................................................................................................................. 79

Chapter 8  

Optimization of reactor configuration ................................................................. 83

8.1  

Optimization of reactor configuration ........................................................... 84

Chapter 9  

Conclusions and future perspectives ................................................................. 91

9.1  

Conclusions ........................................................................................................ 91

9.2  

Future perspectives ........................................................................................... 92

References ........................................................................................................... 94

Addendum 1 ......................................................................................................... 115

A.  

DICHLORVOS .................................................................................................... 115

B.  

DIURON .............................................................................................................. 116

C.  

ALACHLOR .......................................................................................................... 117

D.  

BISPHENOL A .................................................................................................... 118

E.  

1,7-A-ETHINYLESTRADIOL ............................................................................... 119

F.  

PENTACHLOROPHENOL .................................................................................. 120

G.  

CARBAMAZEPINE ............................................................................................. 120
# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOP</td>
<td>Advanced Oxidation Process</td>
</tr>
<tr>
<td>CAS</td>
<td>Conventional Activated Sludge</td>
</tr>
<tr>
<td>DBD</td>
<td>Dielectric Barrier Discharge</td>
</tr>
<tr>
<td>DC</td>
<td>Duty Cycle</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved Organic Matter</td>
</tr>
<tr>
<td>EEO</td>
<td>Energy efficiency per Order</td>
</tr>
<tr>
<td>GC–MS</td>
<td>Gas Chromatography – Mass Spectrometry</td>
</tr>
<tr>
<td>HRT</td>
<td>Hydraulic retention time</td>
</tr>
<tr>
<td>LC–MS</td>
<td>Liquid Chromatography – Mass Spectrometry</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit Of Detection</td>
</tr>
<tr>
<td>LOQ</td>
<td>Limit Of Quantification</td>
</tr>
<tr>
<td>MWWTP</td>
<td>Municipal Wastewater Treatment Plant</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural Organic Matter</td>
</tr>
<tr>
<td>OES</td>
<td>Optical Emission Spectrometry</td>
</tr>
<tr>
<td>PAC</td>
<td>Powdered Activated Carbon</td>
</tr>
<tr>
<td>RMSE</td>
<td>Root Mean Square Error</td>
</tr>
<tr>
<td>SIM</td>
<td>Single Ion Monitoring</td>
</tr>
<tr>
<td>SRT</td>
<td>Sludge Retention Time</td>
</tr>
</tbody>
</table>
Summary

Since the early 1970s, the detection of micropollutants is systematically reported in different water bodies. Although environmental effects of micropollutants are yet not fully understood, the presence of micropollutants in the environment has been linked to biological effects such as the feminization of fish populations through exposure to endocrine disruptors such as synthetic hormones. Because of the environmental and human effects of micropollutants are still largely unknown, public awareness against micropollutants has risen. Since municipal wastewater treatment plants are often considered as the main access point of micropollutants into the aquatic environment, it illustrates the incapability of biological wastewater treatment to effectively remove micropollutants. Consequently, new advanced treatment methods for micropollutant removal need to be investigated. Among them, advanced oxidation processes (AOPs) have emerged as a promising water remediation technique.

This master thesis focused upon the application of non-thermal plasma as a new and unconventional AOP for water treatment. Specifically, a DBD plasma discharge reactor with falling water film over Zorflex® active textile is investigated towards the removal of micropollutants, occurring in a synthetic wastewater. Therefore, eight representative micropollutants, including the pesticides dichlorvos, diuron, atrazine, the pharmaceuticals carbamazepine and 1,7α-ethinylestradiol and the plasticizer bisphenol A were selected in this research. Since one of the weakest points of AOPs is their high energy consumption, micropollutant removal in the plasma reactor is optimized in terms of energy efficiency of the plasma reactor. Calculation of the energy efficiency is performed by the Electrical Energy per Order (EEO) figure-of-merit. Six operational parameters, including the working gas type, gas flowrate, water flowrate, duty cycle, applied power and initial micropollutant concentration are investigated. Under initial parameter settings (working gas: air, gas flow rate: 1 SLM, water flow rate: 66.30 ml min⁻¹, duty cycle: 0.15 power: 40 W and initial concentration: 100 µg l⁻¹), an initial EEO value of 27.4 kWh/m³ for atrazine is calculated. Optimization of the plasma reactor increased the energy efficiency to a final EEO value of 4.16 kWh/m³. This includes an overall improvement in energy efficiency of 84.8 %. Moreover, it is shown in this work that the EEO value can be further decreased by slightly adapting the reactor design. This way, our investigated DBD reactor system performs equally, or even better than other AOP systems, used for water treatment.

Nevertheless, research into plasma technology for water treatment is not finished yet. Therefore, some important research question still needs to be answered. Based on the experimental results presented in this work, it is clear that additional reactor optimization in terms of effluent toxicity can be very interesting. This should be conducted in two ways. First, overall effluent toxicity test should be performed. Secondly, research needs to elucidate the possible reaction pathways for the formation of harmful by-products in the liquid.

**Keywords**: Micropollutants, AOP, plasma technology, reactor optimization
Samenvatting

Omtrent 1970 werden micropollucenten voor het eerst op een systematische wijze gedetecteerd in het aquatisch milieu. Hoewel de milieueffecten van deze micropollucenten nog steeds niet volledig bekend zijn, is het wel duidelijk dat hun aanwezigheid in het aquatisch milieu gerelateerd is aan bepaalde biologische effecten, zoals de vervrouwelijking van het vissenbestand door blootstelling aan hormoonontregelaars. Doordat de toxische effecten van micropollucenten op mens en milieu grotendeels onbekend zijn, is de algemene bezorgdheid omtrent het voorkomen van micropollucenten in (afval)water sterk gestegen. Bovendien is gebleken dat afvalwaterzuiveringsinstallaties vaak als de belangrijkste bron beschouwd worden voor micropollucenten in het aquatisch milieu. Dit illustreert dat biologische afvalwaterzuivering niet geschikt is voor een effectieve, complete verwijdering van micropollucenten. Verder onderzoek naar nieuwe, geavanceerde methodes voor de behandeling van micropollucenten is dus noodzakelijk. Geavanceerde oxidatieprocessen blijken hiervoor een geschikt alternatief te zijn.

In deze thesis wordt niet-thermisch plasma bestudeerd als een nieuw en niet-conventioneel geavanceerd oxidatieproces voor de behandeling van water. Meer specifiek werd onderzoek verricht naar het gebruik van een DBD-plasmareactor met vallende waterfilm over Zorflex® textiel voor de verwijdering van microverontreinigingen uit een synthetisch afvalwater. Acht veelvuldig voorkomende micropollucenten werden geselecteerd, waaronder de pesticiden dichlorvos, diuron en atrazine, de farmaceutica carbamazepine en 1,7-α-ethinylestradiol en de weekmaker bisfenol A. Aangezien het hoge energieverbruik van geavanceerde oxidatieprocessen één van hun zwakste punten is, werd speciale aandacht besteed aan reactoroptimalisatie in functie van de energie-efficiëntie. Hiervoor werden zes reactorparameters onderzocht, waaronder het gastype, gasdebiet, waterdebiet, duty cycle, elektrisch vermogen en de initiële micropolluentconcentratie. Indien standaardinstellingen gebruikt werden (gas: lucht, gasdebiet: 1 SLM, waterdebiet: 66.30 ml min⁻¹, duty cycle: 0.15 vermogen: 40 W en initiële concentratie: 100 µg l⁻¹), werd een EEO-waarde van 27.4 kWh / m³ berekend voor de verwijdering van atrazine. Door optimalisatie van de plasmareactor kon de energie-efficiëntie verder verbeterd worden tot een minimale EEO-waarde van 4.16 kWh/m³. Dit komt overeen met een toename in energie-efficiëntie van 84.8 %. Bovendien werd in dit werk aangetoond dat nog hogere energie-efficiënties mogelijk zijn door aanpassingen in het reactorontwerp. Hierdoor is de energie-efficiëntie voor de verwijdering van atrazine in de onderzochte DBD-plasmareactor vergelijkbaar, of zelfs lager dan de energie-efficiëntie bekomen bij andere AOP-systemen voor waterbehandeling.

Het onderzoek naar de toepassing van plasmabehandeling voor waterzuivering is evenwel nog niet afgerond. Een aantal belangrijke onderzoeksvragen dienen nog beantwoord te worden. Op basis van de in dit werk beschreven resultaten is het duidelijk dat verdere reactor optimalisatie in functie van effluent toxiciteit nuttig kan zijn. Dit kan op twee manieren gebeuren. Enerzijds kan de algemene toxiciteit getest worden. Daarnaast is het ook nuttig om de vorming van schadelijke bijproducten in de vloeistoffase te bestuderen.

Kernwoorden: Micropollucenten, AOP, plasma technologie, reactor optimalisatie
Introduction

Water is a part of daily life, yet it is not unlimited. Although Earth’s surface is covered for more than 70 %, freshwater is very rare on Earth. It is estimated that only 1 % of Earth’s water, occurring in lakes, rivers and underground sources is directly available for human consumption as drinking water (Kolpin et al., 2002). Consequently, nearly 2.2 billion people in more than 62 countries (i.e. a third of world’s human population), are lacking sufficient water supply. In future, water shortages are expected to be worse, due to predicted exponential growth of human population. Moreover, a raise in human welfare during the second part of last century, has resulted in an increased demand for fuels, processed food, industrial chemicals, pharmaceuticals, pesticides, and other essential products. The high consumption rates of these products go hand in hand with the production of different waste streams. In the specific case of water contamination, the enormous consumption of a wide variety of chemicals has resulted into the emergence of a new type organic contaminants, also called micropollutants, in different water bodies. Municipal wastewater treatment plants (MWWTPs) were considered as the main access point of these micropollutants into the aquatic environment. Indeed, such treatment plants were originally designed for the effective removal of dissolved organic matter (DOM), pathogens and easy biodegradable nutrients such as nitrogen (N) and phosphorus (P). Unfortunately, biological treatment technologies only permit partial micropollutant removal. Because effects on human and environment of these organic contaminants were largely unknown, public concern has raised towards the occurrence of micropollutants in our natural water bodies. Therefore, research interest in advanced removal technologies for micropollutants was stimulated. Among them, both biological (membrane technology, trickling filters) and physicochemical processes (coagulation-flocculation, adsorption, membrane technology, AOPs) have been studied. Physicochemical methods are usually more effective for micropollutant removal from (waste)water, but often only micropollutant transfer from one phase to another is achieved, instead of micropollutant destruction. Advanced oxidation processes (AOPs), on the other hand, have shown a high micropollutant decomposition potential. These oxidation processes aim the production of several chemical active species (predominantly OH radicals). However AOPs are, at least currently, associated with high chemical and energy costs. Therefore, current research focusses on the development of novel, energy efficient AOPs. One example of such an unconventional AOP is based on non-thermal plasma technology. Non-thermal plasma is able to generate different reactive species such as hydroxyl radicals (OH\(^\cdot\)), ozone (O\(_3\)), hydrogen peroxide (H\(_2\)O\(_2\)) and many others.

Outline and objective

Although much progress has been made towards the engineering of non-thermal plasmas, there is still a huge knowledge gap about the main oxidation mechanisms that take place in the plasma and at the plasma-liquid interface. Hence, further research is required to elucidate and optimize the main mechanisms contributing to micropollutant degradation by means of plasma technology. Therefore, this master thesis project envisages the investigation of DBD plasma technology for water treatment purposes.
From a practical point of view, future application of plasma technology for water treatment purposes requires an energy efficient removal of micropollutants. In this regard, the main purpose of this work is to optimize a DBD plasma reactor system for the removal of micropollutants from a synthetic wastewater, containing eight model compounds.

This work consists of nine chapters. Following this introduction, the three next chapters form the literature review of this master thesis. The first chapter deals with the occurrence of micropollutants in the aquatic environment. After a short introduction about micropollutant classification, their environmental fate will be revisited. Special attention will be paid to the mechanisms contributing to an incomplete removal of micropollutants in existing wastewater treatment plants. Building further on these findings, the second chapter deals with some alternative wastewater treatment technologies, and their predicted efficiency for micropollutant removal. The final chapter of this literature review explores the fundamentals of (non-thermal) plasma technology as a possible AOP system for water treatment. The main focus is put on the different reactor designs, and their energy efficiency towards micropollutant removal. The second part of this thesis comprises the experimental section, and is divided in two chapters. Chapter 4 provides a description of all applied reagents, used plasma reactor configurations and other instrumental devices, whereas chapter 5 focusses on the applied analytical methods for micropollutant qualification and quantification.

The third part of this work deals with the experimental results and their discussion. The experimental results are provided in three chapters. Chapter 6 deals with the characterization of the DBD plasma by means of optical emission spectroscopy, and an investigation of solutions parameters such and pH and conductivity. In chapter 7, micropollutant decomposition in the plasma reactor is investigated, and the individual effect of each operational parameter on the energy efficiency of micropollutant degradation is discussed. Finally, additional micropollutant removal is examined by reactor configuration optimization. These results are presented in chapter 8.

The last chapter of this work provides a general conclusion, and a short discussion about some future perspectives about plasma technology for water remediation purposes.
Chapter 1  Micropollutants

1.1 HISTORICAL BACKGROUND

A good water quality is essential for human life. Unfortunately, a lot of our natural water bodies have already been contaminated with chemical, physical or pathogenic substances since ancient times. For example, old Greek and Sanskrit writings reported about the application of early water treatment techniques such as sand filtration for the clarification of water. Around 1500 B.C. the Egyptians applied the chemical ‘alum’ to enhance particle settlement of suspended solids. This way, they invented the early principles of the coagulation-flocculation method. Later, the Romans constructed the first sophisticated systems for wastewater management (Musalaiah et al., 2016). In contrast, the Middle-Ages were characterized by a general lack to any scientific innovation. In the early Middle-Ages, there was no system for wastewater management, and waste was usually discharged into the streets. In the 19th century, raw sewage produced by households and the fast-growing industry was discharged into rivers and channels. It was the catalyst of the rapid development of many severe water-borne illnesses such as cholera and typhoid, which were reported throughout the century. Because water pollution became a public health concern, it was the driving force for the development of the first sewage networks, which transported industrial and raw sewage to the first municipal wastewater treatment plants (MWWTPs). Most of these MWWTPs were based on the activated sludge treatment system (Wiessman et al., 2007).

Around 1950 a global population growth, combined with raising living standards forced industries to the large scale production of pharmaceuticals, inorganic pesticides, plasticizers, and other synthetic materials (Eggen et al., 2014). Since 1970 these anthropogenic substances has been systematically detected in very low concentrations in the effluent of wastewater treatment plants (Deblonde et al., 2011; Verlicchi et al., 2012), surface water (Moons & Van Der Bruggen, 2006), drinking water (Jones et al., 2005; Touraud et al., 2011), and even groundwater (Lapworth et al., 2012). Because of the general lack on information about the toxicity of these trace contaminants to human and environmental health, public concern has risen against these so-called emerging contaminants or micropollutants. Nevertheless, most of these compounds are officially unregulated, or are still undergoing a regulation process.

1.2 CLASSIFICATION OF MICROPOLLUTANTS

To date, many attempts have been made in order to classify trace contaminants. Several researchers have divided identified pollutants in three broad groups: (i) pharmaceuticals and personal care products (PPCPs), (ii) pesticides and (iii) industrial compounds (Murray et al., 2010). According to their chemical structure, micropollutants are further divided in different subclasses. Table 1-1 highlights most important subgroups, and some commonly detected micropollutants belonging to each subgroup.
Table 1-1: Important micropollutants, subgroups and examples of some commonly found micropollutants (Scharf et al., 2002; Murray et al., 2010; Clara et al., 2012; Margot et al., 2015)

<table>
<thead>
<tr>
<th>Group</th>
<th>Subgroup</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceuticals</td>
<td>Analgesics</td>
<td>Paracetamol, Tramadol</td>
</tr>
<tr>
<td></td>
<td>Anti-epileptics and anticonvulsants</td>
<td>Carbamazepine, diazepam</td>
</tr>
<tr>
<td></td>
<td>Antipyretics and NSAIDs</td>
<td>Ibuprofen, naproxen</td>
</tr>
<tr>
<td></td>
<td>Antibiotics</td>
<td>Ciprofloxacin, amoxicillin</td>
</tr>
<tr>
<td></td>
<td>β-blockers</td>
<td>Atenolol, propanol</td>
</tr>
<tr>
<td></td>
<td>Lipid regulators</td>
<td>Gemfibrozil, benafibrate</td>
</tr>
<tr>
<td></td>
<td>Iodinated contrast media</td>
<td>Ioprimide, iomeprol</td>
</tr>
<tr>
<td></td>
<td>Hormones</td>
<td>Estrone, 1,7-α-ethinylestradiol</td>
</tr>
<tr>
<td>Personal care products</td>
<td>UV filters</td>
<td>Octocrylene, butyl methoxydbenzoylmethane</td>
</tr>
<tr>
<td></td>
<td>Preservatives</td>
<td>Methylparabens, ethylparabens</td>
</tr>
<tr>
<td></td>
<td>Fragrances</td>
<td>Galaxolide, tonalide</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Herbicides</td>
<td>Atrazine, alachlor, diuron</td>
</tr>
<tr>
<td></td>
<td>Fungicides</td>
<td>Propramocarb, vinclozolin</td>
</tr>
<tr>
<td></td>
<td>Insecticides</td>
<td>Dichlorvos, aldrin</td>
</tr>
<tr>
<td>Industrial compounds</td>
<td>Food additives</td>
<td>Acesulfame, Saccharin</td>
</tr>
<tr>
<td></td>
<td>Plasticizers</td>
<td>Bisphenol A, diethyl phthalate (DEP)</td>
</tr>
<tr>
<td></td>
<td>Anticorrosives</td>
<td>Benzotriazole</td>
</tr>
<tr>
<td></td>
<td>Chelating agents</td>
<td>Ethylenediaminetetraacetic acid (EDTA)</td>
</tr>
<tr>
<td></td>
<td>Flame retardants</td>
<td>Tetrabromobisphenol A, trimethyl phosphatate</td>
</tr>
<tr>
<td></td>
<td>Heavy metals</td>
<td>Mercury, Cadmium</td>
</tr>
<tr>
<td></td>
<td>Polycyclic aromatic hydrocarbons</td>
<td>Benzo(a)pyrene, napthalene</td>
</tr>
<tr>
<td></td>
<td>Surfactants</td>
<td>Alkyl sulfate, alcohol ethoxylate</td>
</tr>
</tbody>
</table>

1.3 SOURCES OF MICROPOLLUTANTS

The occurrence of micropollutants in the environment has been traced back to three major applicants: (i) household, (ii) industry, and (iii) agriculture (Halling-Sorensen et al., 1998; Heberer, 2002; Kümmener, 2009; Verlicchi et al., 2010). Micropollutants originating from these applicants usually enter the aquatic environment through different pathways. The main entrance routes for micropollutants into the environment are depicted figure 1-1 (Jiménez, 2013).
1.3.1 PPCPs

Pharmaceuticals constitute a diverse group of compounds administered to treat human and animal diseases. They include analgesics, anti-epileptics and anticonvulsants, antipyretics and non-steroidal anti-inflammatory drugs (NSAIDs), antibiotics, β-blockers, lipid regulators, iodinated contrast media and hormones (Ternes et al., 2002; Margot et al., 2015).

When pharmaceuticals are applied to treat human diseases, pharmaceuticals are, at least partly, absorbed by the human body, and subsequently subjected to various metabolic reactions (Cunningham, 2004; Vieno et al., 2007). Hence, pharmaceuticals can be excreted either as parent compound or as a transformation product. These transformation products can be as toxic as the parent compound, or even more toxic (Zwiener & Frimmel, 2000). Excretion of pharmaceuticals and their transformation products usually occurs through urine or faeces. By means of the sewage network, these substances are transported to a MWWTP where they are, in best case, partially removed from wastewater (Ternes & Joss, 2006).

Pharmaceuticals originating from agricultural applications such as animal farming and aquaculture can enter into the aquatic environment in different ways. Animal excretions are commonly used as a fertilizer (Boxall, 2004). Therefore, they end up in the soil. Subsequently, the parent compound and their metabolites can end up in surface water by run-off. Alternatively, persistent compounds with high soil mobility can emerge in the ground water. Pharmaceuticals applied in aquaculture applications are directly released into the surface water.

Personal care products can be found either as an active ingredient or preservative in cosmetics, washing lotions, sunscreen agents, perfumes toiletries, hair styling products or fragrances (Daughton & Ternes, 1999; Margot et al., 2015). Due to their usage on the external body, they enter into the sewage network mainly through wash-off during showering of bathing (Margot et al., 2015; Ternes et al., 2002). Generally, personal care products do not undergo metabolic transformation processes.

1.3.2 Pesticides & industrial compounds

Pesticides include all substances that are used to protect crops against several diseases. They have been largely produced on an industrial scale since 1930. Nowadays, more than 1600 pesticides are commercially available (Gray, 2008). As they are mainly applied by spraying techniques, pesticides are mainly transported in air, and subsequently washed out during periods of rainfall (Autin et al., 2012). If pesticides are directly administered to soil, they may adsorb to soil particles, being further degraded by soil biota. More persistent pesticides are able to percolate through soil, and can eventually reach the ground water.

In addition to PPCPS and pesticides, several other micropollutants are commonly detected into the environment. They are often referred to as “industrial compounds” (Murray et al., 2010). They comprise a wide variety of chemical substances, including food additives, plasticizers,
anticorrosives, chelating agents, flame retardants, heavy metals, polycyclic aromatic hydrocarbons and surfactants (Margot et al., 2015). Many of these compounds are directly discharged in the surface water.

1.4 ENVIRONMENTAL FATE OF MICROPOLLUTANTS

1.4.1 Municipal waste water treatment

After application, most micropollutants are released into the sewage network, being transported to a municipal waste water treatment plant (MWWTP). These MWWTPs has been identified as a major point source of micropollutants into the environment (Heberer, 2002). Municipal wastewater treatment combines several physical, chemical and biological treatment processes in order to remove pathogens, dissolved organic matter (DOM) and nutrients such as nitrogen and phosphorus from wastewater (Michael et al., 2013). A typical MWWTP is represented in figure 1-2 (Monteiro & Boxall, 2010).

As can be seen in figure 1-2, wastewater treatment in a municipal WWTP generally comprises two treatment stages: a primary treatment step, followed by and secondary treatment stage (Michael et al., 2013). In some MWWTPs, the treatment train has been adopted by an additional tertiary treatment step to enhance effluent quality (Shon et al., 2006; Monteiro & Boxall, 2010).
1.4.1.1 Pretreatment and primary treatment

Prior to primary treatment, the incoming water typically undergoes a pretreatment step. Wastewater pretreatment typically consists of a series of mechanical and physico-chemical treatment steps. First, large debris and coarse materials are removed by bar screens. This is a necessary step, since large objects may damage pumps and other mechanical equipment in further treatment steps. Next, floating materials such as fat and oil are removed from the incoming water (Margot et al., 2015). In a last step, primary treatment is initiated. During primary treatment the incoming water is held in a sedimentation tank (primary clarifier) for several hours, allowing particle settlement through a physical sedimentation process. Overall, about 50 – 60 % of total suspended solids (TSS), 15 – 30 % of total nitrogen (TN), and 30 % of total phosphorus (TP) content is removed through primary settlement (Poon & Chu, 1999; Kumar et al., 2007). The solid phase (primary sludge) is discharged, and further treated in an (an)aerobic digester. Subsequently, the liquid phase, also referred to as the primary clarified water, is send to a second treatment stage.

1.4.1.2 Secondary treatment

Secondary treatment usually combines a biological process in an aeration reactor with a sedimentation process in a secondary settler. Although several biological processes have been evaluated, the conventional activated sludge process (CAS) is regarded as the most utilized approach for municipal and industrial wastewater treatment (Verstraete & Vlaeminck, 2011).

In the CAS process, primary effluent is introduced into the aeration tank, and vigorously mixed with activated sludge to form a mixed liquor. Next, soluble and colloidal organic matter is converted by a diversified group of microorganisms to carbon dioxide and water, in the presence of oxygen. Additionally, nitrogen and phosphorus are removed in the CAS process (Stare et al., 2007; Van Veldhuizen et al., 1999). Moreover, a fraction of the converted organic matter is used for the production of new biomass cells. After a certain contact time, the treated wastewater is introduced into the secondary clarifier. The secondary classifier allows the separation of the activated sludge into a solid phase (sludge) and a liquid phase (clarified water) through a sedimentation process. Clarified liquid from the secondary clarifier is discharged to the environment as secondary effluent. Accumulated sludge is partly recycled to the aeration tank, and the excess sludge is managed to an aerobic or anaerobic digester (Verstraete & Vlaeminck, 2011).

In addition to the CAS process, also other secondary treatment processes have found their application in municipal wastewater treatment. Biofilters (trickling filters), membrane bioreactors and rotating biological contactors all have found their application in wastewater technology. In some cases, a more complete micropollutant removal has been observed (De Wever et al., 2007; de Cazes et al., 2014). Better removal efficiencies are mainly attributed through a higher hydraulic retention time (HRT) (Gros et al., 2010), and a longer sludge retention time (SRT) (Clara et al., 2005; Petrie et al., 2014). A complete discussion of these alternative biological water treatment processes, however, is beyond the scope of this work.
1.4.1.3 Tertiary treatment

Before secondary effluent is discharged into the aquatic environment, it can undergo an additional, tertiary treatment step to enhance effluent quality. For example, chlorination is typically used for wastewater disinfection due to its low costs. Nevertheless, the chlorination of secondary effluent induces the formation of harmful, often carcinogenic disinfection products such as trihalomethanes (Nieuwenhuijsen et al., 2000). Therefore, some alternatives, such as disinfection of secondary effluent by ozonation or ultraviolet radiation are increasingly finding their application in wastewater treatment (Lindenauer & Darby, 1994; Hassen et al., 2000; Heberer, 2002).

![Figure 1-2: Schematic overview of a conventional wastewater treatment plant (Monteiro & Boxall, 2010)](image)

1.4.2 Environmental fate in MWWTPs

The presence of micropollutants in the environment has shown that MWWTP are incapable to fully eliminate micropollutants. Indeed, conventional MWWTPs were originally designed for the effective removal of dissolved organic matter (DOM), pathogens and easy removable nutrients such as nitrogen and phosphorus in the gram per liter range (Ternes et al., 2002; Forrez et al., 2011; Luo et al., 2014).

Daughton and Ternes (1999) and Heberer (2002) were some of the first authors to publish some data about the removal efficiency of micropollutants in MWWTPs. Additionally, Verlicchi et al. (2012) reviewed the environmental fate of several hundreds of pharmaceuticals in MWWTPs, mainly in Europe and North America. Very recently, Margot et al. (2015) did the same for a wide variety of commonly detected micropollutants. Table 1-2 summarizes the average removal efficiency in MWWTPs for some selected micropollutants.
As can be seen in table 1-2, strong variations in removal efficiencies between micropollutants are observed. These differences can be mainly ascribed to the differences in physico-chemical properties between micropollutants (Suarez et al., 2008; Omil et al., 2010). Further, it is
noteworthy that some significant differences in removal efficiencies between individual WWTPs are observed. This phenomenon is mainly attributed to different operational conditions, such as biomass concentration, sludge retention time (SRT), hydraulic retention time (HRT), configuration and type of WWTP, between individual treatment plants (Verlicchi et al., 2012).

1.5 MICROPOLLUTANT REMOVAL MECHANISMS IN MWWTPs

Studies concerning the environmental fate of micropollutants have pointed out that some micropollutants are partially degraded in MWWTPs, even though MWWTPs were originally not designed for this purpose (Carballa et al., 2004; Salgado et al., 2012). The removal of micropollutants in MWWTPs is ascribed to MWWTP operational parameters (sludge age, hydraulic retention time, as well as physicochemical properties (Henry’s law coefficient ($k_H$), octanol-water partitioning coefficient (log $K_{OW}$), acidity (pKa) and solid-liquid partitioning coefficient ($K_d$)) of the micropollutants.

Generally, the environmental fate of micropollutants in current MWWTPs can be attributed to three main mechanisms, including: (i) biodegradation, (ii) sorption to solids, and (iii) volatilization (Suarez et al., 2008; Omil et al., 2010; Margot et al., 2015). Additional micropollutant removal can be achieved by the adaptation of tertiary treatment methods on secondary effluent (Luo et al., 2014). Some of these tertiary treatment methods will be discussed in the second chapter.

1.5.1 Biodegradation

Biodegradation refers to the transformation process in which a parent compound is converted to one or more intermediate products by interaction with microorganisms. It is generally recognized as the most important degradation process during wastewater treatment (Margot et al., 2015). The biodegradation of micropollutants has been studied in a few works. For example, the degradation kinetics through biodegradation in a batch reactor was studied by Joss et al. (2006). In their work, the biodegradation rates of 40 pharmaceuticals in a CAS batch reactor was evaluated. From their kinetic modelling results, the authors have calculated the reaction rate constant through biodegradation for every individual compound. It was found that micropollutant removal in the batch reactor followed a pseudo first order degradation kinetics (eq. 1-1):

$$\frac{dC_T}{dt} = -k_{biod}SSC_w$$  \hspace{1cm} \text{eq. 1-1}

With $C_T$ the total micropollutant concentration ($\mu$g l$^{-1}$), $C_w$ the micropollutant concentration in the liquid ($\mu$g l$^{-1}$), SS the amount of suspended solids (g l$^{-1}$), t the reaction time (d) and $k_{biod}$ the reaction rate constant for biodegradation (l g$^{-1}$ SS d$^{-1}$).

According to the reaction rates, micropollutants were classified as (i) hardly degradable if $k_{biod} > 0.1$ g$^{-1}$ SS d$^{-1}$ (ii) moderately biodegradable if $0.1$ g$^{-1}$ SS d$^{-1} < k_{biod} < 10$ g$^{-1}$ SS d$^{-1}$, and (iii) highly biodegradable if $k_{biod} > 10$ g$^{-1}$ SS d$^{-1}$. In addition to the work of Joss et al. (2006), Tadkaew et al.
(2011) evaluated the relationship between the parent compound and their tendency to biodegradation. It was found that short linear molecules were more easily degraded than large aromatic compounds, and that the occurrence of electron withdrawing groups (halogens, sulphate groups) significantly reduces the biodegradation potential of micropollutants.

1.5.2 Sorption

Another important contributor to the elimination of micropollutants in MWWTPs is sorption onto solids such as sludge or particulate matter (Rogers, 1996; Suarez et al., 2008). This is certainly the case when the organic contaminant is hydrophobic or positively charged (Joss et al., 2006). The sorption of micropollutants onto activated sludge comprises two main processes: (i) absorption and (ii) adsorption.

Absorption refers to the hydrophobic interactions of aliphatic and aromatic groups of a compound with the lipophilic cell membrane of the sludge and the lipid fractions of the sludge. Rogers (1996) proposed the octanol-water partitioning coefficient (log $K_{\text{OW}}$) as a general rule of thumb to predict the absorption potential of micropollutants onto sludge: log $K_{\text{OW}} < 2.5$ indicates a low sorption potential, 2.5 < log $K_{\text{OW}}$ < 4.0 indicates a medium sorption potential and log $K_{\text{OW}} > 4.0$ indicates a high sorption potential.

Adsorption is mainly caused by electrostatic and ionic interactions between micropollutants and negatively charged surfaces of biomass cells (Ternes et al., 2004). The solid-liquid partitioning coefficient ($K_d$) has been proposed as a relative accurate indicator for the sorption potential of micropollutants, since it combines the effects of both acidity ($pK_a$) and lipophilicity (log $K_{\text{OW}}$) on the sorption potential (Luo et al., 2014).

The solid-liquid distribution coefficient ($K_d$) is defined as the ratio between the micropollutant concentration in the solid and the liquid phase at equilibrium conditions (eq. 1-2) (Omil et al., 2010).

$$K_d = \frac{C_{\text{sorbed}}}{C_{\text{soluble}} \cdot SS}$$

Where $K_d$ represents the solid-liquid distribution coefficient, in l kg$^{-1}$, $C_{\text{soluble}}$ the pollutant concentration in the liquid phase in µg l$^{-1}$, $C_{\text{sorbed}}$ the sorbed pollutant concentration, in µg l$^{-1}$ and SS the suspended solids concentration, in kg l$^{-1}$ (Suarez et al., 2008). Substances having $K_d$ values higher than 500 l kg$^{-1}$ (log $K_d < 2.70$) are easily sorbed onto sludge, whereas micropollutants with $K_d$ values below 300 l kg$^{-1}$ (log $K_d < 2.48$) are showing low sorption potential (Omil et al., 2010). Below a $K_d$ value of 1 l kg$^{-1}$, sorption onto sludge can be neglected (Carballa et al., 2007).
1.5.3 Volatilization

Volatilization involves the process whereby a pollutant is transferred from the liquid phase to the gas phase. In CAS processes, the volatilization potential is affected by the volatility of the compound (Henry’s law coefficient, \( k_H \)) and the operational conditions of the MWWTP (agitation, aeration, pH and T of the wastewater) (Pomiès et al., 2013). The volatilization potential pollutant can be roughly estimated from the Henry’s law coefficient (\( k_H \)), indicating how easily micropollutants will be removed through aeration. Most micropollutants are characterized by a Henry’s law constant ranging from \( 10^{-2} \) to \( 10^{-3} \) mol/(m\(^3\) Pa) (Stenstrom et al., 1989).

The volatilized fraction \( y_{volatilized} \) of a compound during aeration is given in eq. 1-3 (Joss et al., 2006):

\[
y_{volatilized} = 1 - e^{-\frac{k_H}{1000R.T} q_{air}}
\]

\[\text{eq. 1-3}\]

Where \( k_H \) is the Henry’s law coefficient, in mol/(m\(^3\) Pa), \( R \) the universal gas constant (8,314 J/mol K), \( T \) the temperature in Kelvin, and \( q_{air} \) the applied aeration rate, expressed in m\(^3\) air m\(^3\) wastewater.

In most MWWTPs involving CAS secondary treatment, wastewater is typically aerated with an air flowrate ranging from 5 to 15 m\(^3\) air m\(^3\) wastewater (Pomiès et al., 2013). Under these circumstances, micropollutant removal through volatilization has found to be completely negligible for most pharmaceuticals and hormones, nearly negligible for fragrance compounds such as tonalide and galoxide and very significant for celestolide, which is also a musk fragrance (Suarez et al., 2008).
Chapter 2  Advanced treatment methods for wastewater remediation

In the previous chapter, it was shown that a relative new class of emerging micropollutants was systematically detected in different water bodies. A general lack on scientific knowledge about the potential adverse effects of organic contaminants on both human and environment health has raised public concern towards the occurrence of micropollutants in the environment. Moreover, it was found that current conventional MWWTPs were quite ineffective to remove micropollutants. This has forced the water industry to explore new advanced treatment methods such as the coagulation–floculation method, activated carbon filtration, membrane filtration and advanced oxidation processes to tackle the detrimental effects of micropollutant releasement in the aquatic environment. However, none of these specific treatment technologies assures a complete micropollutant removal for all micropollutants. The first four sections provide a rather theoretical investigation of above mentioned water remediation techniques, whereas the last section of this chapter summarizes the major advantages and drawbacks of each investigated technique for micropollutant elimination.

2.1 COAGULATION AND FLOCULATION

The coagulation-floculation process has been practiced as a water treatment process since ancient times (Musalaiah et al., 2016). The technique was originally applied for the removal of turbidity from wastewater, caused by suspended solids and colloidal particles (Thébault et al., 1981). Because some micropollutants, especially the non-polar ones, tend to adsorb onto suspended solids (see chapter 1), the coagulation-floculation process is studied as a possible water polishing method for the abatement of micropollutants from wastewater and drinking water (Ternes et al., 2002; Thuy et al., 2008).

Wastewater often contains colloidal and suspended particles, which are characterized by a negative surface charge (Thuy et al., 2008). Consequently, aggregation of these charged particles is hindered by electrostatic repulsion forces. Therefore, a neutralization of the net charge will enhance suspended solids to settle down. This particle settlement is achieved by the coagulation-floculation method. The application of the coagulation and flocculation technique usually involves a coagulation step, followed by a flocculation step. During coagulation, a coagulant is added to the wastewater, to destabilize charged particles. Hence, it causes part of the suspended solids to stick together in small aggregates, called microflocs. Commonly used coagulants include positive charged iron- and aluminium salts, such as ferric chloride ($\text{FeCl}_3$), iron sulphate ($\text{Fe}_2(\text{SO}_4)_3$) or aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$) (Westerhoff et al., 2005). In the flocculation the aggregation of small microflocs into large flocs is further enhanced by thoroughly the treated solution. In most cases, this aggregation process is encouraged through the addition of floculants. Among them, polymeric substances are commonly employed as floculants. Finally, large flocs are separated from the treated water by adapting a physical separation technique, such as rapid sand filtration.
2.2 ACTIVATED CARBON FILTRATION

Adsorption is defined as the process in which a chemical substance (adsorbate) adheres on the surface of a solid substance (adsorbent) (Grassi et al., 2012). Adsorption processes are widely used to remove micropollutants from different water bodies. Typical adsorbents used for water treatment purposes are: (i) activated carbon, (ii) zeolites, (iii) molecular sieves and (iv) polymeric adsorbents (Qiu et al., 2009). Among the different materials that have been used as an adsorbent, the vast majority of the studies concerning the removal of micropollutants from (waste)water have used activated carbon as adsorbent. Activated carbon is characterized by a very porous structure with a large surface area, ranging from 600 to 2000 m² g⁻¹ (Grassi et al., 2012). Two types of activated carbon are available for water remediation purposes: powdered activated carbon (PAC) and granular activated carbon (GAC) (Ternes et al., 2002).

Adsorption on solid surface is mainly a physical process, and is called “physisorption”. Therefore, the adsorption process is driven by physical phenomena, such as electrostatic interactions and Van der Waals forces between adsorbent and adsorbate (Grasi et al., 2012). However, the exact amount of adsorbed adsorbate on a specific adsorbent under equilibrium conditions is function of the physical nature of the adsorbate parameters, such as micropollutant concentration and temperature. The adsorption kinetics can be expressed by a number mathematical models, “called isotherms” which are experimentally determined. Among them, the Freundlich model (eq. 2-1) and the Langmuir model (eq. 2-2) are mostly used (Foo & Hameed, 2010).

\[ q_e = K_f c_e^{1/n} \]  
\[ q_e = \frac{Q_0 b c_e}{1 + b c_e} \]

With \( q_e \) the amount of adsorbate adsorbed on the adsorbent at equilibrium conditions (mg g⁻¹). \( K \) and \( n \) are experimentally determined constants, and \( c_e \) is the initial micropollutant concentration (mg l⁻¹)

In this equation \( Q_0 \) represents the maximum monolayer coverage capacity (mg g⁻¹), \( b \) is the Langmuir isotherm constant (dm³ mg⁻¹), and \( c_e \) the micropollutant concentration (mg l⁻¹) under equilibrium concentration.

2.3 MEMBRANE FILTRATION

Another new advanced water polishing technique is based on membrane technology. Membrane filtration processes cover a multitude of physical separation processes in which a gaseous or liquid stream is split into two different side streams. In (waste)water treatment applications, the incoming water is separated over a semi-permeable membrane in two different side streams: a clean water stream, called the retentate, and a concentrate stream which contains the compounds stopped by the membrane (figure 2-1) (Verliefde, 2008).
According to their driving forces, different membrane processes could be distinguished: (i) concentration driven membrane processes, (ii) pressure driven processes, and (iii) electrical potential driven processes (Strathmann, 2001). In most water treatment applications, the driving force is predominantly ascribed to a pressure difference applied over the membrane (Van Der Bruggen et al., 2003).

Membrane processes are divided in four important processes: (i) microfiltration, (ii) ultrafiltration, (iii) nanofiltration and (iv) reverse osmosis (RO). Nanofiltration and RO processes are particularly important for the elimination of organic contaminants (Xu et al., 2010). Microfiltration and ultrafiltration are incapable for micropollutant removal due to a too high pore size (Ozaki, 2004).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Membrane filtration</th>
<th>Ultrafiltration</th>
<th>Nanofiltration</th>
<th>Reverse osmosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size</td>
<td>&gt; 100 nm</td>
<td>2 – 5 nm</td>
<td>3 – 10 nm</td>
<td>10 nm – 1 µm</td>
</tr>
<tr>
<td>MWCO</td>
<td>&lt; 350</td>
<td>&lt; 150</td>
<td>300</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Applied pressure</td>
<td>1 – 10 MPa</td>
<td>0,3 – 1,5 MPa</td>
<td>0,01 – 0,3 MPa</td>
<td>0,005 – 0,2 MPa</td>
</tr>
</tbody>
</table>

The total removal of organic contaminants is often expressed as the percentage of rejection, and can be calculated with eq. 2-3 (Kimura et al., 2003):

\[ R(\%) = \left(1 - \frac{c_{p,i}}{c_{i,f}}\right) \times 100 \]  

\[ \text{eq. 2-3} \]

With R the total removal percentage of compound i across the membrane, \(c_{p,i}\) the micropollutant concentration in the permeate stream (µg l\(^{-1}\)), and \(c_{i,f}\) the micropollutant concentration in the feed stream (µg l\(^{-1}\)).

The rejection of micropollutants on nanofiltration and reverse osmosis membranes is dominated by three key pollutant-membrane interactions, being electrostatic interactions, adsorptive interactions and steric hindrance (sieving effect). All these parameters are affected by the operational conditions (feed composition, pH, temperature) and the physicochemical properties.
of both the micropollutant and the membrane (molecular weight, pore size, hydrophobicity) (Bellona et al., 2004).

2.4 ADVANCED OXIDATION PROCESSES

Most advanced water treatment methods mentioned earlier in this chapter are associated with some inherent disadvantages, such as the production of a toxic waste stream, which should be further treated in an additional treatment step. Moreover, most of these advanced treatment methods are incapable to reduce persistent substances to sufficiently low concentration levels (Mantzavinos & Psillakis, 2004). Therefore, alternative water remediation techniques based on advanced oxidation processes (AOPs) have been proposed to meet our new, stringent environmental quality standards. Advanced oxidation processes (AOPs) have been suggested as an effective and sustainable treatment method, since these techniques can avoid the production of harmful by-products and waste streams.

Advanced Oxidation Processes (AOPs) aim the in situ generation of hydroxyl radicals (OH•) (Glaze & Kang, 1989; Andreozzi et al., 1999; Hernandez et al., 2002) In addition to the generation of hydroxyl radicals (OH•), also other oxidative chemical species can be produced, including ozone (O3), atomic oxygen (O), hydrogen peroxide (H2O2) (Loures et al., 2013). However, hydroxyl radicals have been considered as the main important chemical species in AOPs since they are characterized by a significant higher redox potential 2.80 V in comparison with other oxidative species (table 2-2).

Table 2-2: Standard redox potentials of some commonly used oxidants (Loures et al., 2013)

<table>
<thead>
<tr>
<th>Oxidizing species</th>
<th>Oxidation potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine (F)</td>
<td>3.03</td>
</tr>
<tr>
<td>Hydroxyl radical (OH•)</td>
<td>2.80</td>
</tr>
<tr>
<td>Atomic oxygen (O)</td>
<td>2.42</td>
</tr>
<tr>
<td>Ozone (O3)</td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrogen peroxide (H2O2)</td>
<td>1.78</td>
</tr>
<tr>
<td>Hydroperoxyl radical (HO2•)</td>
<td>1.70</td>
</tr>
<tr>
<td>Permanganate (MnO4)</td>
<td>1.68</td>
</tr>
<tr>
<td>Hypobromous acid (HOBr)</td>
<td>1.59</td>
</tr>
<tr>
<td>Chlorine dioxide (ClO2)</td>
<td>1.57</td>
</tr>
<tr>
<td>Hypochlorous acid (HOCl)</td>
<td>1.49</td>
</tr>
<tr>
<td>Chlorine (Cl2)</td>
<td>1.36</td>
</tr>
</tbody>
</table>

The exact mechanism of the OH radical production depends on the kind of advanced oxidation process that is applied. Currently, these OH• generation mechanisms have been well studied in literature. For the most practical applied methods, more information can be found in several reviews (Munter, 2001; Esplugas et al., 2002; Klavarioti et al., 2009; Poyatos et al., 2010; Ghatak, 2014). In all cases, the generation of highly reactive OH• radicals requires the input of energy. Energy can be delivered by a chemical, photochemical, sonochemical or electrochemical process (Klavarioti et al., 2009). Accordingly, all different AOPs described in literature can be divided into
chemical, photochemical, sonochemical and electrochemical AOPs. Some examples are highlighted in table 2-3.

Table 2-3: Classification of AOPs according to the energy source (Oturan & Aaron, 2014)

<table>
<thead>
<tr>
<th>Chemical AOPs</th>
<th>Fotochemical AOPs</th>
<th>Sonochemical AOPs</th>
<th>Electrochemical AOPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃/OH</td>
<td>O₃/UV</td>
<td>O₃/Ultrasound</td>
<td>Electro-fenton</td>
</tr>
<tr>
<td>O₃/H₂O₂ (peroxone)</td>
<td>H₂O₂/UV</td>
<td>H₂O₂/Ultrasound</td>
<td>Anodic oxidation</td>
</tr>
<tr>
<td>Fe²⁺ + H₂O₂ (Fenton)</td>
<td>Fe²⁺ + H₂O₂ + UV</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiO₂/UV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Among the several types of AOP investigated over the last 30 years, most practical applied AOPs are using combinations of hydrogen peroxide (H₂O₂), ozone (O₃) and/or UV radiation (Tezcanli-Güyer & Ince, 2004). A few pilot-scale or full scale applications of such chemical or photochemical AOPs are mentioned in literature (Heberer, 2002; Kruithof et al., 2007). Other sonochemical and electrochemical AOPs has only been evaluated on laboratory scale (Goel et al., 2004; Sirés & Brillas, 2012).

2.4.1 AOP kinetics

In all AOP processes, it was found that hydroxyl radicals (OH•) were the most important reactive species. These highly reactive oxidants react in a very fast, unselective way with a lot of different pollutants, including phenols (Chen & Ray, 1998; Di Paola et al., 2003; Chiou et al., 2008), textile dyes (Dutta et al., 2001; Houas et al., 2001; Islam et al., 2013), pesticides (Acero et al., 2000; Benitez et al., 2002; Tizaoui et al., 2011), pharmaceuticals (Deng et al., 2013; Rodríguez et al., 2011) and various other micropollutants (Cater et al., 2000; Wang et al., 2009; Tan et al., 2013). AOPs have the potential to fully mineralize micropollutants to carbon dioxide (CO₂) and water (H₂O), although this is rarely applied, since it would require large energy or chemical inputs.

Although the overall AOP degradation chemistry is different for each micropollutant, three major reaction mechanisms have been established, being (i) the abstraction of a hydrogen atom (eq. 2-4), (ii) the electrophilic addition of a OH• radical to a multiple bond (eq. 2-5), and (iii) electron transfer reactions (eq. 2-6) (Legrini et al., 1993):

\[ \text{RH} + \text{OH}^\cdot \rightarrow \text{R}^\cdot + \text{H}_2\text{O} \quad \text{eq. 2-4} \]

\[ \text{R}_2\text{C} = \text{CR}_2 + \text{OH}^\cdot \rightarrow \text{R}_2(\text{OH})\text{C} - \text{CR}_2 \quad \text{eq. 2-5} \]

\[ \text{RX} + \text{OH}^\cdot = \text{RX}^{**} + \text{OH}^- \quad \text{eq. 2-6} \]
Hence, the reaction between micropollutants and hydroxyl radicals produces secondary radicals, which can affect further micropollutant decomposition (Neyens & Baeyens, 2003). The overall degradation progress usually follows a first order kinetics in both micropollutant and hydroxyl radical concentration, and can be described with eq. 2-7:

\[ \frac{dc_M}{dt} = k_{OH,M} \cdot c_{OH} \cdot c_M \]  \hspace{1cm} \text{eq. 2-7}

With \( c_M \) the micropollutant concentration (µg l\(^{-1}\)), \( k_{OH} \) the second order reaction rate constant (M\(^{-1}\) s\(^{-1}\)) for the reaction of OH radicals (OH\(^•\)) with micropollutant molecules M, and \( c_{OH} \) the hydroxyl radical concentration (µg l\(^{-1}\)).

When the concentration of hydroxyl radicals is much lower than the micropollutant concentration (\( c_M >> c_{OH} \)), the reaction kinetics can be simplified from a second-order reaction kinetics to a pseudo first order reaction kinetics (eq. 2-8):

\[ \frac{dc_M}{dt} = k_0 \cdot c_M \]  \hspace{1cm} \text{eq. 2-8}

In this equation, the first-order reaction rate constant (\( k_0 \)) for the pseudo-first order reaction is calculated with eq. 2-9:

\[ k_0 = k_{OH,M} \cdot c_{OH} \]  \hspace{1cm} \text{eq. 2-9}

The second order reaction rate constants have been extensively studied with various methods over the last years. Very fast reactions were generally observed, with second order kinetic constants towards different kinds of micropollutants (\( k_{OH^*,M} \)) varying between 2.2. \( 10^7 \) and 1.8. \( 10^{10} \) M\(^{-1}\) s\(^{-1}\) (Yao & Haag, 1991; Von Gunten, 2003; Jin et al., 2012; Sudhakaran & Amy, 2013).

### 2.4.2 Energy efficiency

A number of AOPs have been developed during the last 30 years (Klavarioti et al., 2009). Most of them have shown to be efficient in the removal of micropollutants from (waste)water. The overall effectiveness of an AOP is affected by a number of parameters, such as the type of organic compound, the initial concentration, the specific process conditions and, in the case of wastewater treatment, the occurrence of radical scavengers such as sulphate (SO\(_4^{2-}\)) and bicarbonate (HCO\(_3^−\)) (Stasinakis, 2008). Although some full-scale applications were already commercially available, a comprehensive comparison of different AOP performances is generally lacking. To this end, Bolton et al. (1996) introduced the electrical energy per order (EEO) figure-of-merit to compare the electrical energy performance of different AOPs. In the case of low micropollutant concentrations, the EEO represents the electrical energy input, expressed in kWh, required to reduce the initial micropollutant concentration with 1 order of magnitude (90%), in 1
m³ contaminated water (Bolton & Tumas, 1996; Cater et al., 2000). In batch reactor systems, the EEO can be calculated according to eq. 2-10 (Bolton & Tumas, 1996):

\[
EEO = \frac{P \cdot t \cdot 1000}{V \cdot 60 \cdot \log \left( \frac{c_i}{c_f} \right)}
\]

With EEO the electrical energy in kWh, P the applied power in W, t the operation time (min) \(c_i\) the initial micropollutant concentration (µg l\(^{-1}\)) and \(c_f\) the final micropollutant concentration after a certain treatment time t.

Note that eq. 2-10 can only be used for batch reactor systems. For continuous flow reactor, eq. 2-10 is adapted to eq. 2-11:

\[
EEO = \frac{P}{F \cdot \log \left( \frac{C_i}{C_f} \right)}
\]

With F the total water flow rate of the solution under treatment, in m³ h\(^{-1}\). The other symbols are defined as in eq. 2-10.

To the authors knowledge, only a limited number of comparative studies are conducted to compare the EEO values for different AOPs. Recently, Lester et al. (2011) evaluated the application of different UV and O\(_3\) based advanced oxidation processes for the decomposition of an antibiotic (ciprofloxacin), and an antineoplastic drug (cyclophosphamide). The energy efficiency (EEO) for removal of both compounds with different AOPs is presented in table 2-4.

<table>
<thead>
<tr>
<th>AOP</th>
<th>EEO Ciprofloxacin</th>
<th>EEO cyclophosphamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>16.3</td>
<td>70.7</td>
</tr>
<tr>
<td>UV/O(_3)</td>
<td>5.2</td>
<td>59.1</td>
</tr>
<tr>
<td>UV/H(_2)O(_2)/O(_3)</td>
<td>5.1</td>
<td>37.8</td>
</tr>
<tr>
<td>O(_3)</td>
<td>3.2</td>
<td>1.7</td>
</tr>
<tr>
<td>H(_2)O(_2)/O(_3)</td>
<td>2.2</td>
<td>7.2</td>
</tr>
</tbody>
</table>

According to the results of Lester et al. it is concluded that O\(_3\) based processes were more efficient than UV based processes. Furthermore, the combination of different treatment methods resulted in a higher energy efficiency. The perozone process (O\(_3\) + H\(_2\)O\(_2\)) was considered as the most energy-efficient process.
Nevertheless, chemical and photochemical AOPs have not been compared with other sonochemical and electrochemical AOPs. However, Oturan and Aaron pointed out in their review that chemical AOPs, such as the Fenton process (Fe$^{2+} + \text{H}_2\text{O}_2$) or the peroxone process (O$_3 + \text{H}_2\text{O}_2$) usually perform worse in comparison with sonochemical and electrochemical methods (Oturan & Aaron, 2014). However, the authors did not validate this claim with research data. Hence, it remains still very interesting to elaborate the exact influence of different chemical, photochemical, sonochemical and electrochemical AOPs on the overall process efficiency.

### 2.5 CONCLUSION

In this chapter, several advanced treatment methods for the elimination of micropollutants from wastewater have been described. However, future application of a certain water remediation method will be based on the capacity of micropollutant decomposition, and its associated energy efficiency.

To this end, Westernhoff et al. (2005) have compared the feasibility of several water treatment methods (coagulation-flocculation, adsorption on activated carbon, O$_3$/H$_2$O$_2$ and nanofiltration) towards micropollutant removal from surface water. These results are presented in table 7-5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coagulation-Flocculation</th>
<th>Adsorption (PAC)</th>
<th>O$_3$/H$_2$O$_2$</th>
<th>Nanofiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FeCl$_3$</td>
<td>Al$_2$(SO$_4$)$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPCPs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,7-α-ethinylestradiol</td>
<td>0</td>
<td>16</td>
<td>67</td>
<td>98</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>0</td>
<td>7</td>
<td>55</td>
<td>98</td>
</tr>
<tr>
<td>Diazepam</td>
<td>0</td>
<td>5</td>
<td>53</td>
<td>85</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>0</td>
<td>0</td>
<td>64</td>
<td>96</td>
</tr>
<tr>
<td>Estriol</td>
<td>0</td>
<td>4</td>
<td>54</td>
<td>98</td>
</tr>
<tr>
<td>Galaxolide</td>
<td>15</td>
<td>33</td>
<td>63</td>
<td>89</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>2</td>
<td>20</td>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>Iopromide</td>
<td>0</td>
<td>12</td>
<td>33</td>
<td>60</td>
</tr>
<tr>
<td>Naproxen</td>
<td>0</td>
<td>0</td>
<td>87</td>
<td>93</td>
</tr>
<tr>
<td>Pentoxyfylline</td>
<td>0</td>
<td>2</td>
<td>65</td>
<td>98</td>
</tr>
<tr>
<td>Triclosan</td>
<td>0</td>
<td>13</td>
<td>93</td>
<td>82</td>
</tr>
<tr>
<td>Pesticides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>0</td>
<td>0</td>
<td>77</td>
<td>91</td>
</tr>
<tr>
<td>Atrazine</td>
<td>0</td>
<td>0</td>
<td>54</td>
<td>52</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>15</td>
<td>18</td>
<td>63</td>
<td>89</td>
</tr>
</tbody>
</table>

According to the results obtained by Westernhoff et al. (2005), micropollutant removal by means of the coagulation-flocculation method is considered to be almost negligible for most micropollutants, especially when FeCl$_3$ is used as a coagulant. In some cases, higher removal percentages, up to 20 %, are reached by applying Al$_2$(SO$_4$)$_3$ as a coagulant. More recent research reports seem to confirm these observations. Vieno et al. (2007) studied the removal of 11
frequently detected pharmaceuticals from surface water. The contribution of coagulation-flocculation with ferric chloride was found to be very low (5-35 %) for all investigated compounds.

Next to coagulation-flocculation, adsorption on activated carbon is commonly employed for micropollutant removal from drinking water. According to table 2-5 an average removal efficiency of 65 % is observed for the majority of micropollutants. However, other compounds, i.e. the more polar ones (atrazine, iopromide) show less tendency to adsorb on activated carbon. Indeed, the degree of adsorption on activated carbon is affected by several physicochemical properties of both adsorbate (log \(K_{OW}\), \(pK_a\), molecular size target molecule) and adsorbent (texture, pore size and surface area). Because activated carbon surface is rather hydrophobic, non-polar micropollutants (log \(K_{OW}\)) are more easily adsorbed (Kovalova et al., 2013).

Aside of drinking water treatment, activated carbon have also been applied for wastewater treatment. Since organic matter is ubiquitously present in wastewater, usually high PAC dosages are required (Margot et al., 2013). Furthermore, competition between micropollutant for adsorption, and pore-blocking by natural organic matter (NOM) significantly reduce the overall adsorption capacity (Koh et al., 2008; Luo et al., 2014).

Just as activated carbon filtration, processes based on membrane technology (nanofiltration, reverse osmosis) also exhibit good micropollutant removal efficiencies. In comparison with activated adsorption slightly higher removal efficiencies are reached for most pollutants. However, some operational and maintenance costs, such as membrane fouling and the high energy consumption especially for reversed osmosis processes, are limiting future applications (Petala et al., 2006).

Although high micropollutant removal efficiencies are reached by adsorption on activated carbon and membrane technology, it should be emphasized that nor activated carbon filtration, nor membrane based technologies succeed in effective degradation of micropollutants. Instead, both treatment realize micropollutant transfer from one phase to another, resulting in a toxic waste stream production, which should be disposed. Moreover, polar micropollutants are still not adequately removed to sufficiently low concentration levels. To overcome these problems, the application of ozonation and other AOPs need to be considered. AOPs have the potential to effectively mineralize micropollutants. Indeed for the peroxone process (\(O_3 + H_2O_2\)), high removal efficiencies (> 90 %) are reported for the majority of the compounds mentioned in table 2-5. However, AOPs are also associated with high energy costs, and further research needs to concentrate on the development of new, energy efficient AOPs.
Chapter 3  Plasma technology

The existence of plasma was discovered by William Crookes, which identified ‘plasma’ as the fourth state of matter in 1879. The term ‘plasma’ was first introduced by Irving Langmuir in 1928, who described the phenomenon ‘plasma’ as an electrically quasi neutral gas, consisting of positive ions, free electrons and neutral gas atoms (Langmuir, 1928).

3.1 WHAT IS PLASMA?

From a fundamental point of view, matter consists of four fundamental states of matter: the solid, liquid, gas and plasma state. Phase transformations between those states of matter are possible through the addition of thermal or electrical energy. For example, when energy is added to a substance in the solid state, it will be converted to a liquid. If sufficient heat is added, the liquid particles will vaporize to the gas phase. Another addition of energy will finally convert the gas to the plasma state. The phase transition from the gas phase to the plasma based is based on the partial ionization of the gas molecules (Yamamoto & Okubo, 2007) (figure 3-1).

![Figure 3-1: the transition states of matter on application of heat (Reddy, 2014)](image)

3.2 NON-THERMAL PLASMAS

In the early research stage, artificial plasmas were easily produced in gas discharge tubes. It consists of two parallel metal electrodes, surrounded by a volume of gas. Originally, few neutral gas molecules in the gas tube are ionized by external influences (cosmic radiation, photoionization, natural radioactivity), resulting in the occurrence of electron-ion pairs (Conrads & Schmidt, 2000; Fridman et al., 2005). If a DC powered voltage is supplied to the electrodes a homogeneous electric field (E) is formed between both electrodes (Mededovic, 2007). Under the influence of the electric field free electrons are accelerated towards the anode, producing a small background current, up to $10^{-6}$ A (Raizer, 1987). As the voltage is increased, primary electrons are further accelerated in the direction of the anode, gaining kinetic energy by the applied electric field. On their way to the anode, primary electrons can collide and react with neutral gas atoms, producing secondary electron-ion pair (Fridman et al., 2005). This process is often referred to as an “electron avalanche” or “Townsend discharge” (figure 3-2). At this point, a strong increase in current is observed (figure 3-3).
Among different low temperature (non-thermal) plasmas dielectric barrier discharges (DBD), corona discharges, microwave discharges, inductively coupled plasmas, gliding discharges and arc discharges (Bogaerts et al., 2002). Some plasma discharges, together with some specific characteristics are highlighted in table 3-1 (Nehra et al., 2008). Since this thesis deals with DBD plasma, only DBD discharges will be briefly discussed.
Table 3-1: Overview of different plasma discharges and their characteristics (adapted from Nehra et al., 2008)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Corona discharge</th>
<th>dielectric barrier discharge</th>
<th>Atmospheric plasma pressure jet</th>
<th>Atmospheric glow micro hollow cathode discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied Power</td>
<td>DC</td>
<td>AC or DF</td>
<td>RF (13.5 MHz)</td>
<td>DC</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 bar</td>
<td>1 bar</td>
<td>1 bar</td>
<td>1 bar</td>
</tr>
<tr>
<td>Electron</td>
<td>+/- 5 eV</td>
<td>1 – 10 eV</td>
<td>1-2 eV</td>
<td>-</td>
</tr>
<tr>
<td>Electron density</td>
<td>$10^{12} - 10^{13}$</td>
<td>$10^{12} - 10^{15}$</td>
<td>$10^{11} - 10^{12}$</td>
<td>-</td>
</tr>
<tr>
<td>Breakdown voltage</td>
<td>10 – 50 kV</td>
<td>5-25 kV</td>
<td>0.05-0.2 kV</td>
<td>-</td>
</tr>
<tr>
<td>$T_{\max}$</td>
<td>273 K</td>
<td>300 K</td>
<td>400 K</td>
<td>2000 K</td>
</tr>
</tbody>
</table>

3.3 DIELECTRIC BARRIER DISCHARGES

In 1857, Ernst Wermer von Siemens reported for the first time about dielectric barrier discharges, also called “silent discharges”, for the generation of ozone from air (Kogelschatz, 2003). Up till the mid 1990s dielectric barrier discharges have found their main application in the construction of industrial ozonators (Eliasson et al., 1987; Kogelschatz, 2003). Over the last two decades, dielectric barrier discharges attracted more and more attention in mostly applications, such as water treatment, air pollution control and green chemistry in general environmental (Aerts et al., 2013; Pringle et al., 2004; Thevenet et al., 2014). Next to the application of dielectric barrier discharges for environmental purposes, DBD plasmas are extensively studied in medicinal and industrial applications.

The scheme of a typical planar DBD device is given in figure 3-4 (Wagner et al., 2003). Such a reactor consists of two parallel (planar) electrodes separated by a dielectric barrier. Specifically, the dieelectrical barrier can be constructed by covering at least one of the electrodes with a dielectric material (silica, quartz, mica, ceramic materials, etc). In most cases, quartz glass is used as a dielectric.
The physics of an atmospheric pressure DBD discharges shows many similarities with those of classical gas discharges, mentioned before (Kogelschatz, 2003). Due to the coverage of on one of the electrodes, DBDs are initiated by the application of an AC powered voltage on the high voltage electrode (anode). This results in the formation of a negative charge on the anode. When the applied electrical field reaches the breakdown voltage, a Townsend discharge is initiated followed by the propagation of a streamer discharge. In a typical DBD, the electron avalanche to streamer transition is finalized on a timescale of ± 10 ns (Chirokov et al., 2005). During the electron avalanche, electrons are accelerated through high energy levels. Subsequently, collisions, of highly energetic electrons with gas molecules leads to the formation of different, reactive species, such as hydroxyl radicals (OH•), ozone (O3), atomic oxygen (O) and hydrogen peroxide (H2O2) in the gas phase, together with physical phenomena such as intense UV radiation (Ghezzar et al., 2013).

The exact generation mechanisms of all these active species will not be discussed in detail here. In the experimental section (chapter 6) the most important reactions, contributing to micropollutant decomposition, are discussed. In order to have a complete overview of the production of highly reactive species in both the gas and the liquid phase, the reader is referred to some excellent review papers. For example, Eliasson et al. (1987) and Kogelschatz (2003) have discussed the gas phase kinetics and ionization reactions taking place in the plasma, together with the gas phase production of ozone. Bruggeman & Schram (2010) have reviewed the production of OH• radicals. According to their review at least 30 possible reactions pathways are identified. In contrast, Locke & Shih (2011) provided an overall reaction mechanism for hydrogen peroxide production in the liquid phase. Finally, Brisset et al. (2008) Lukes et al. (2012) and Lukes et al. (2014) have established the formation of different nitrogen containing species in the bulk liquid for plasma discharges in air.

To date, plasma technology have been performed for the decomposition of different organic compounds in water. In the early research stage, plasma-assisted decomposition of micropollutants was limited to some very simple compounds, including phenols (Bubnov et al., 2007; Marotta et al., 2011), synthetic dyes (Magureanu et al., 2008; Xue et al., 2008) and other easy degradable organic compounds such acetic acid (Ognier et al., 2009). Later, research interest more and more focused upon the application of plasma for the decomposition of pharmaceuticals (Magureanu et al., 2010; Krause et al., 2011; Rong et al., 2014), antibiotics (Rong & Sun, 2014) and pesticides (Vanraes et al., 2015a; Vanraes et al., 2015b, Feng et al., 2016).

Different liquid-liquid and liquid-gas phase reactors have been designed, and evaluated for micropollutant decomposition. For instance, Krause et al., Dobrin et al., Rong & Sun and Banashik et al. have been working with corona discharge reactors (Banaschik et al., 2015; Dobrin et al., 2013; Krause et al., 2009; Rong & Sun, 2014), whereas Jovic et al., Aonyas et al., Rong & Sun, Dojcinovic et al., Vanraes et al., and Feng et al. investigated DBD reactors with falling water films (Aonyas et al., 2016; Dojcinović et al., 2011; Feng et al., 2016; Jovic et al., 2014; Rong & Sun, 2015; Vanraes et al., 2015b). Plasma discharges directly in the liquid phase were also studied (Lukes et al., 2005). In an attempt to classify all existing reactors, Locke et al. (2006) and Bruggeman & Leys
(2009) identified two to three different groups of plasma reactors, depending on the plasma-water phase distribution. Recently, this approach was extended to six reactor groups by Vanraes et al. (2016) (table 3-2).

Table 3-2: Classification of different plasma reactors used for water treatment

<table>
<thead>
<tr>
<th>Discharge</th>
<th>Reactor type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Directly in the water bulk</td>
<td>Electrohydraulic discharge reactor</td>
</tr>
<tr>
<td>Directly in the water bulk with externally applied bubbles</td>
<td>Bubble discharge reactor</td>
</tr>
<tr>
<td>In the gas phase, over a water film</td>
<td>Gas phase discharge reactor</td>
</tr>
<tr>
<td>In the gas phase with water drops</td>
<td>Spray discharge reactor</td>
</tr>
<tr>
<td>Combination of previous type</td>
<td>Hybrid reactor</td>
</tr>
<tr>
<td>Not in contact with the solution under treatment</td>
<td>Remote discharge reactor</td>
</tr>
</tbody>
</table>

This work will predominantly deal with the optimization of micropollutant decomposition in a gas phase reactor design (chapter 6). Due to small adaptations to this reactor type, a remote discharge reactor, and hybrid reactor will also be investigated for the elimination of micropollutants (chapter 8).

3.3.1 Energy efficiency

The optimal reactor design should aim for a high energy efficiency in removing the majority of organic compounds. Unfortunately, only limited comparative studies concerning the energy efficiency of different reactor designs has been conducted (Malik, 2010; Jiang et al., 2014). This can be explained by the limited accessibility to several plasma reactors amongst different plasma groups working on plasma treatment for water remediation. Malik was the first to compare the energy efficiencies of 27 commonly used plasma reactors (Malik, 2010). In his review article, Malik theoretically compared the energy efficiencies of 27 frequently used plasma reactors for the removal of synthetic dyes (Malik, 2010). Accordingly, the energy yield $G_{50}$ (eq. 3-1) was chosen for the comparison of different reactor designs. The energy yield $G_{50}$ gives an indication about the energy required, in order to degrade 50 % of the initial micropollutant concentration:

$$G_{50} = \frac{1}{2} \cdot \frac{k_A \cdot C_0 \cdot V}{P \cdot \ln(2)} \cdot 3.6 \cdot 10^6$$  

eq. 3-1

With $G_{50}$ the energy yield (g/kWh), $V$ the treated volume (l), $C_0$ the initial concentration (µg/l) and $P$ the applied power (W).

According to the comparative research of Malik, it was found that pulsed corona discharges are preferred above dielectric barrier discharges. Further, plasma discharges in the gas phase yielded higher energy efficiencies than plasma discharges directly in the water bulk. Moreover, the usage of oxygen gas as discharge medium resulted in the highest energy efficiency, whereas discharges in air yielded a significant lower energy efficiency. It was also concluded that the most energy
efficient reactors are the ones which spray the treated solution as fine droplets in the plasma zone. The contribution of some reactor parameters (applied power, discharge type, discharge medium and the method of solution treatment) to the energy efficient elimination of micropollutants is illustrated in table 3-3 (Malik, 2010).

<table>
<thead>
<tr>
<th>Energy efficiency</th>
<th>High</th>
<th>Moderate</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied power</td>
<td>Pulsed DC</td>
<td>Pulsed AC</td>
<td>Continuous AC or DC</td>
</tr>
<tr>
<td>Discharge type</td>
<td>Pulsed corona discharge</td>
<td>Pulsed dielectric barrier discharge</td>
<td>DC discharges</td>
</tr>
<tr>
<td>Discharge medium</td>
<td>Oxygen</td>
<td>Air</td>
<td>Liquid</td>
</tr>
<tr>
<td>Treated solution as</td>
<td>Fine droplets</td>
<td>Thin water film</td>
<td>Bulk liquid</td>
</tr>
</tbody>
</table>

However, it should be emphasized that Malik’s review only included a limited number of plasma reactors (27). In literature, many more reactor designs are described for micropollutant decomposition. Moreover a comparison of energy efficiency in different plasma reactors by means of the $G_{50}$ energy yield parameter should be avoided, since it is strongly influenced by the initial micropollutant concentration. Hence, only plasma reactors using a comparable initial concentration should be taken in consideration when evaluating reactor performance. A more suitable calculation method for comparison of energy efficiencies among different plasma reactors was introduced earlier by Bolton et al. (1996), and is based on the energy efficiency per order of magnitude (EEO). A relationship between the EEO and $G_{50}$ is given in eq. 3-2 (Vanraes et al., 2015b):

$$EEO = -0.5 \cdot \ln(10) \cdot 10^{3} \cdot \frac{C_0}{G_{50}}$$

With $C_0$ the initial micropollutant concentration in g l$^{-1}$ and $G_{50}$ the energy yield in g kWh$^{-1}$.

The EEO concept was already described in previous chapter (section 2.4.2, equations 2-10 – 2-11), and is commonly used for a comparison of energy efficiency among AOPs (Cater et al., 2000; Safarzadeh-Amiri, 2001; Lester et al., 2011).

Note that in this research, a pulsed DBD reactor over moving water was used, instead of a pulsed DC corona discharge reactor which is, according to Malik, expected to be more energy efficient. However the choice of a AC pulsed DBD reactor with falling water film above a pulsed DC corona discharge was based on several reasons. First, DBD plasma discharges are usually more stable, and usually operate at relative low powers in comparison of corona discharge reactors. Due to lower applied power, heat losses through Joule heating effects are negligible, just as the thermal decomposition of long living oxidants (O$_3$, H$_2$O$_2$) due to high temperatures.
Further, Malik entirely focused upon the electrical energy applied to the plasma reactor. However, the energy consumption by water pumping needs also to be considered. Usually, the energy cost for water spraying is higher than just pumping water, in order to create a thin water film. Due to these large energy demands for water spraying systems, especially in large scale applications, a reactor design with falling water film is preferred.

Nevertheless, the main problem of micropollutant elimination by plasma technology as a stand-alone process, is its high energy cost. Malik (2010) calculated that the average energy efficiency for removal of textile dyes in different plasma reactors was in the range 0.029 – 12.7 g kWh\(^{-1}\) (EEO = 2.61 - 687 kWh/m\(^3\)), which is still quite high for implementation in existing MWWTPs. To overcome these problems, the combination of plasma technology with the addition of catalysts has been suggested as an interesting way to improve the energy efficiency of micropollutant elimination by plasma. This way, several plasma-catalytic systems has been proposed. Two commonly used catalysts are titanium dioxide (TiO\(_2\)) and activated carbon. The application of these catalysts in plasma systems is discussed below. For a complete overview of other applied catalysts in plasma-catalytic systems, the reader is referred to Jiang et al. (2014).

Heterogeneous photocatalysis, using TiO\(_2\) is considered as a promising stand-alone AOP processes for mineralization of micropollutants in wastewater treatment (Islam et al., 2013). This AOP relies on the production of OH\(^-\) radicals by irradiation of a semiconductor catalyst surface (Fujishima et al., 2000; Herrmann, 1999). To this end, many semiconductors, including ZnO, CdS and TiO\(_2\) have been investigated as possible photocatalysts (Augugliaro et al., 2012). Among them, titanium dioxide (TiO\(_2\)) is a popular choice, since it is a low cost material, characterized by a low toxicity and high chemical inertness (Jiang et al., 2014). To date, however, no commercial applications of TiO\(_2\) based heterogeneous photocatalytical AOPs in pilot scale reactors are known. Major drawback which impedes the practical application of heterogeneous photocatalysis in pilot-scale reactors, is the poor absorption capacity of TiO\(_2\) for solar light (Pichat, 2015). Therefore, the catalyst surface is usually irradiated with UV lamps, which increases the overall cost of this AOP system.

In this context, the application of TiO\(_2\) in plasma-catalytic systems is particularly attractive. Indeed, several plasma reactors (glow discharge reactors, DBD reactors) are known to emit a considerable amount of UV radiation (Ghezzar et al., 2013). Interaction of UV light with a wavelength (\(\lambda\)) smaller than 380 nm may result in the formation of conduction band electrons (\(e_{cb}\)) and valence band holes (\(h_{vb}\)). If the holes subtract electrons from water molecules, adsorbed on the catalyst surface, OH radicals are formed. In the same time, free electrons can react with O\(_2\) molecules, that will be reduced to a superoxide radical anion (O\(_2^•\)). The overall reaction mechanism is presented by the reactions r.3-1 – r.3-3 (Augugliaro et al., 2012; Ghodbane et al., 2014).

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2\left(e_{cb}^- + h_{vb}^+\right) \quad \text{r. 3-1}
\]

\[
\text{O}_2 + e_{cb}^- \rightarrow \text{O}_2^•^- \quad \text{r. 3-2}
\]
According to the reactions r.3-1 – r.3-3, a certain amount of hydroxyl radicals is produced through the interaction between UV radiation produced by the plasma, and the TiO₂ surface. Note that also a significant hydroxyl radical production originates from the plasma discharge. Accordingly, the combination of plasma technology with heterogeneous photocatalysis on TiO₂ may lead to an enhanced hydroxyl radical production in comparison with plasma treatment alone (Jiang et al., 2014).

The synergetic effect of plasma treatment and heterogeneous photocatalysis on TiO₂ have been confirmed in a number of studies. Ghezzar et al. (2013) investigated the degradation of a 54 mg l⁻¹ synthetic dye solution (yellow tartrazine) in a coaxial DBD plasma reactor with and without the dosage of TiO₂. If TiO₂ was added to the liquid phase (concentration: 4 g l⁻¹), 96 % degradation of yellow tartrazine was reported, versus only 11 % degradation in the absence of TiO₂. This corresponds to an EEO value of 106 kWh/m³ with and 897 kWh/m³ without TiO₂. In addition, similar results have also been reported for the degradation of phenol in a pulsed corona discharge system, where the plasma discharge was applied directly in the liquid (Lukes et al., 2005). The energy efficiency of phenol removal (EEO) with and without TiO₂ addition was calculated as EEO = 1312 kWh/m³ and EEO = 1546 kWh/m³, respectively (Lukes et al., 2005).

Next to the application of TiO₂ as a catalyst, activated carbon is also commonly investigated. The usage of powdered activated carbon (PAC) was initially introduced by Grymonpré et al. (Grymonpré et al., 1999; Grymonpré et al., 2003). The authors studied the degradation of phenol in a pulsed corona plasma system, operating in oxygen. Higher removal percentages were observed in the presence of activated carbon (89 % phenol degradation vs. 40 % phenol degradation in the absence PAC. Next to the higher removal percentages, a higher energy efficiency was reached (EEO = 132 kWh/m² with PAC dosage, versus EEO = 291 kWh/m³ without PAC dosage).

Higher micropollutant removal efficiencies in combined plasma-PAC catalytic systems can be explained by the adsorption of micropollutants on PAC. Aside of micropollutant adsorption, ozone (O₃) and hydrogen peroxide (H₂O₂), occurring in the liquid phase due to plasma treatment, tend to adsorb on the activated carbon surface. On the catalytic surface O₂ and H₂O₂ will decompose through reactions with surface functional groups (especially hydroxyl groups) present at the activated carbon catalytic surface. Reactions r.3-4 – r.3-6 illustrate the decomposition of ozone, whereas reactions r.3-7 – r.3-8 show the decomposition of H₂O₂ on PAC. According to these reactions, it can be seen that PAC is continuously regenerated in the reactor system (Sanchez-Polo et al., 2005; Hao et al., 2009; Kurniawan & Lo, 2009).

\[
\begin{align*}
\text{H}_2\text{O} + \text{h}^+_{vb} & \rightarrow \text{OH}^+ + \text{H}^- & \text{r. 3-3} \\
\text{O}_3 + \text{H}^- & \rightarrow \text{AC} - \text{H} & \rightarrow \text{AC} - \text{O} + \text{H}_2\text{O}_2 & \text{r. 3-4} \\
\text{O}_3 + \text{AC} - \text{OH} & \rightarrow \text{O}_2^- + \text{AC} + \text{OH}^+ & \text{r. 3-5} \\
\text{O}_3 + \text{O} - \text{AC} & \rightarrow \text{O}_2^- + \text{O} + \text{AC} & \text{r. 3-6}
\end{align*}
\]
Further, reactions r.3-5 and r.3-7 show that ozone and hydrogen peroxide decomposition on activated carbon is accompanied with the production of OH radicals close to the catalytic surface, resulting in a more efficient reaction between adsorbed micropollutants and hydroxyl radicals (r.3-9 – r.3-10) (Jiang et al., 2014):

\[ AC + M \rightarrow AC - M \]  
\[ AC - M + OH^* \rightarrow AC + \text{intermediates} \]

Different research groups intensively studied the relationship between activated carbon dosage and enhanced micropollutant elimination of phenol (Qu et al., 2013) and other compounds such as methyl orange (Zhang et al., 2007) and pentachlorophenol (Qu et al., 2009; Lu et al., 2012). In all studies, the application of PAC resulted in significant higher degradation percentages and higher energy efficiencies.

Recently, activated carbon fibres (ACF) have also found their application in plasma catalytic reactor designs. For example, Xin et al. (2016) investigated the effect of DBD plasma treatment and activated carbon fibres on the degradation of triclosan. A synergetic effect between DBD plasma treatment and adsorption on ACF fibres system was found. By an input power of 80 W, a 10 mg l\(^{-1}\) triclosan solution was degraded for 93 %, within 18 minutes of operation in the DBD plasma-ACF fibre system. Under the same conditions, 85 % degradation of triclosan was reported by application of only DBD treatment.

Based on the findings of Malik (2010) concerning the energy efficient for different reactor designs, and the benefits of micropollutant elimination by combining plasma technology with the addition of catalysts, the construction of a pulsed DBD reactor with moving water film over an activated carbon textile (“Zorflex®“) has been accomplished at the RUPT in the years 2013-2014. The applicability of this innovative reactor design has already been successfully tested, in single compound tests i.e. for the decomposition of the pesticides alachlor, atrazine, diuron, isoproturon, pentachlorobenzene and α-hexachlorocyclohexane (Vanraes et al., 2015b, Vanraes 2016). Although the results were very promising for single compound elimination of micropollutants, still a lot of research questions needs to be answered, in order to more deeply understand the oxidation mechanisms taking place on the Zorflex® textile, and in the liquid phase. Moreover, the energy efficiency of micropollutant elimination in a certain plasma-catalytic system depends on several other process parameters. These parameters can be loosely divided in (i) operational parameters and (ii) solution parameters (Jiang et al., 2014). Operational parameters, as for example working gas type, gas flowrate, voltage, water flowrate and applied power are easy to control. However, optimization of these experimental conditions is necessary since their exact contribution to the degradation of micropollutants is still partially unknown, and expected to be dependent on the reactor configuration.
It has to be emphasized that it is the aim of this study, to achieve a high energy efficient removal for a wide variety of micropollutants into the developed pulsed DBD plasma reactor. In this regard, a synthetic wastewater containing 5 pesticides (atrazine, alachlor, dichlorvos, diuron, pentachlorophenol), 2 pharmaceuticals (carbamazepine, 1,7-α-ethinylestradiol) and 1 plasticizer (bisphenol A) will be prepared. A selection of these micropollutants was based on the following criteria. First, all micropollutants investigated in this research were already systematically detected in secondary effluent, originating from existing MWWTPs. Secondly, most of these micropollutants are suspected to cause potential adverse effect on human and environment. Thirdly, all of these compounds are easily measurable by adapting chromatographical analysis on GC-MS.
Chapter 4  Experimental setup

Current chapter gives a detailed description about the chemicals used throughout this work. First, all applied chemicals and their preparation procedures are discussed. Then, instrumental devices, and a complete overview of the reactor setup is described. The final section provides a brief explanation of applied experimental procedures.

4.1 APPLIED CHEMICALS

Table 4-1 gives an overview of all applied reagents throughout this work. All chemicals were used without any further purification.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Purity</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>C₈H₁₄ClN₅</td>
<td>&gt; 98 %</td>
<td>Sigma Aldrich®</td>
</tr>
<tr>
<td>Alachlor</td>
<td>C₁₄H₂₀ClNO₂</td>
<td>99.8 %</td>
<td>Sigma Aldrich®</td>
</tr>
<tr>
<td>Diuron</td>
<td>C₆H₁₂Cl₂N₂O</td>
<td>96.6 %</td>
<td>Sigma Aldrich®</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>C₁₅H₁₆O₂</td>
<td>&gt; 99 %</td>
<td>Sigma Aldrich®</td>
</tr>
<tr>
<td>Dichlorvos</td>
<td>C₉H₇ClO₂P</td>
<td>98.8 %</td>
<td>Sigma Aldrich®</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>C₆HCl₃O</td>
<td>99 %</td>
<td>Sigma Aldrich®</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>C₁₅H₁₃N₂O</td>
<td>99 %</td>
<td>Sigma Aldrich®</td>
</tr>
<tr>
<td>1,7-α ethinylestradiol</td>
<td>C₁₂H₂₄O₂</td>
<td>99.8%</td>
<td>Sigma Aldrich®</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>CH₂Cl₂</td>
<td>&gt; 99.8 %</td>
<td>Carl roth®</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>H₂O₂</td>
<td>30 %</td>
<td>Carl roth®</td>
</tr>
</tbody>
</table>

4.1.1 Preparation of micropollutant stock solutions

Due to the low water solubility of most micropollutants, saturated stock solutions (see table 4-2) were prepared in deionized water with a maximal conductivity varying between 0.50 and 2.00 µS/cm. For saturated solutions of DIU, ATR, PCF, ALA, BISA, CARB and ETH, an appropriate amount of powdered micropollutant was weighed on an analytical balance (Sartorius, model Quintix 224-1S), quantitatively transferred into a volumetric flask, and eventually filled up with deionized water to a final volume of 500 ml. A DVOS stock solution was prepared by dissolving 7.6 µl DVOS in 500 ml deionized water. All solutions were continuously mixed at 300 rpm on a magnetic stirrer for at least 3 hours. Next, saturated solution were filtered with Rotilabo cellulose filtration paper (type 601).
Table 4-2: Saturated concentrations of prepared stock solutions

<table>
<thead>
<tr>
<th>Micropollutant</th>
<th>Saturated concentration (mg l(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichlorvos (DVOS)</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>Diuron (DIU)</td>
<td>42</td>
<td>(Giacomazzi &amp; Cochet, 2004)</td>
</tr>
<tr>
<td>Atrazine (ATR)</td>
<td>30</td>
<td>(Edwards et al., 1992)</td>
</tr>
<tr>
<td>Pentachlorophenol (PCF)</td>
<td>14</td>
<td>(Arcand et al., 1995)</td>
</tr>
<tr>
<td>Alachlor (ALA)</td>
<td>242</td>
<td>(Edwards et al., 1992)</td>
</tr>
<tr>
<td>Bisphenol A (BISA)</td>
<td>300</td>
<td>(Shareef et al., 2006)</td>
</tr>
<tr>
<td>Carbamazepine (CARB)</td>
<td>17.7</td>
<td>(Zhang et al., 2008)</td>
</tr>
<tr>
<td>1,7-α-Ethinylestradiol (ETH)</td>
<td>11.3</td>
<td>(Shareef et al., 2006)</td>
</tr>
</tbody>
</table>

4.1.2 Preparation of diluted micropollutant solutions

Solutions containing 1 mg l\(^{-1}\) of each micropollutant were prepared by diluting an appropriate volume of the saturated solutions. Before the start of a plasma experiment, the stock solution was further diluted to the desired concentration (100 µg l\(^{-1}\) or 200 µg l\(^{-1}\)).

4.1.3 Preparation of micropollutant solutions in dichloromethane

Next to micropollutant stock solutions in water, micropollutant stock solutions in dichloromethane (CH\(_2\)Cl\(_2\)) were prepared. A 1 g l\(^{-1}\) stock solution containing the micropollutants dichlorvos (DVOS), diuron (DIU), atrazine (ATR), alachlor (ALA), pentachlorophenol (PCF), bisphenol A (BISA), carbamazepine (CARB), and 1,7-α-ethinylestradiol (ETH) was prepared by accurate weighing 10 mg of each micropollutant in a 20 ml vial. 10 ml dichloromethane (CH\(_2\)Cl\(_2\)) was added, and the solution was gently mixed by hand shaking. Next, a 100 mg l\(^{-1}\) solution was obtained by ten times diluting the stock solution with dichloromethane. Finally, 1 ml solution was transferred into a GC-MS vial for GC-MS method optimization.

4.2 INSTRUMENTAL DEVICES

4.2.1 Voltage and current probes

A dual channel Tektronic TDS 1002 with a maximum frequency of 60 MHz was used for simultaneous, real time monitoring of voltage and current waveforms. Voltage was measured with a Tektronic P6015 HV probe, connected to channel 1 of the oscilloscope. Current was measured with a Pearson 2877 current probe, connected to channel 2 of the oscilloscope. Data-acquisition was performed by transferring the oscilloscope data over a R232 port to a Dell latitude D829 laptop.
4.2.2 UV-VIS spectrophotometer

UV-VIS absorption spectra are recorded using a UV mini 1240 spectrometer from Shimadzu. With this UV-VIS spectrophotometer, spectral data acquisition is possible over a wavelength range between 190 nm and 1100 nm. Therefore, two different types of lamps are used: a 20 W halogen lamp is used in the visible light spectral region, whereas a deuterium lamp is to collect absorption data in the UV-region.

4.2.3 Optical emission spectrometer

The main oxidizing species emitted by the DBD plasma discharge were determined using an OceanOptics® S1000 spectrometer. The spectrometer was able to acquire spectral data over the range of 250 nm to 900 nm.

4.2.4 GC-MS

Gas chromatography-mass spectrometry (GC-MS) was used for both qualification and quantification of micropollutants in water samples. All chromatographical analyses were conducted using an Agilent 6890 GC Series gas chromatograph coupled to a Hewlett Packard 5973 mass selective detector. Chromatographical separations were performed on a capillary (5%-phenyl)-methyl polysiloxane HP-5MS column (0.25 mm x 30 m x 0.25 μm). More information about the method development, instrumental settings and separation conditions is provided in chapter 5.

4.3 REACTOR DESIGN

In chapter three, different reactor designs have been theoretically evaluated with respect to their energy efficiency. It was concluded that reactor systems based on dielectric barrier discharges over a moving water film were both sustainable and energy efficient. Based on this conclusion, the construction of a DBD reactor with moving water film has been accomplished at the RUPT in the years 2013-2014. Subsequently, this innovative reactor design was tested for the removal of atrazine. In this early research stage, micropollutant decomposition was solely studied in batch reactor configuration, where the solution under treatment was continuously recirculated in the reactor.

In contrast, most experiments performed in this work are performed in a continuous flow (single pass) reactor configuration. This configuration is chosen, since it is more representative for real-world application than batch treatment. In the operational parameter optimization experiments only the plasma chamber was applied. This reactor configuration is referred to as the “only plasma configuration” (1 P).
4.3.1 Only plasma (1 P) single pass reactor configuration

In the only-plasma-configuration, experiments were conducted in a coaxial DBD plasma reactor with moving water film over Zorflex® active carbon textile. A complete overview of the experimental setup is given in figure 4-1. Briefly, the plasma chamber consists of a quartz glass vessel (thickness 1.55 mm) with cylindrical geometry. Around the quartz tube, an outer mesh grid was wrapped, which served as the high voltage electrode. Inside, a grounded, stainless steel tube with an outer diameter of 28 mm was placed.

Micropollutant solution was pumped upwards in the inside of the steel tube, using a peristaltic, two channel Carl Roth® pump. Reaching the top of the tube, micropollutant solution flew through a small hole into the overflow channel, and gradually moved down along the Zorflex® active carbon cloth. During operation, working gas (dry air, argon or oxygen) was continuously pumped from the gas reservoir to the reactor, using a PR 4000 mass flow controller (MKS instruments). Plasma was generated between inner and outer electrode by a custom made AC high voltage power supply, triggered by a pulse generator (model TGP110, Thurbly, Thandar instruments).

![Diagram of DBD reactor](image)

Figure 4-1: Schematics of DBD reactor, operating in single pass mode (1P)

The use of Zorflex® active carbon as a reactor membrane, covering the grounded electrode, allowed an increase of energy efficiency, in comparison with other DBD reactors with moving water film, described in literature. Zorflex® activated carbon cloth was supplied by Chemviron Carbon (Chemviron Carbon, 2016). A microscopic and macroscopic image of this textile is given in figure 4-2. Originally, Zorflex® textile was designed for military purposes, such as the production of chemical warfare suits. Nowadays Zorflex® is applied in a variety of applications such as wound
dressing, air cleaning, and water treatment. In this research, a FM50 K type Zorflex® was used. This model had a thickness of 0.5 mm, and was further characterized by a surface density of 130 g/m², a carbon tetrachloride activity varying between 55 and 70 m/m %, and a total adsorption surface area of more than 2000 m²/g. It is therefore considered as highly efficient for air and water pollutant adsorption purposes (Chemviron Carbon, 2016).

4.3.2 Alternative single pass reactor configurations

Plasma discharges are known to produce plasma gas. Hence, additional micropollutant removal can be achieved by additionally plasma gas bubbling through the micropollutant solution. In practice, plasma gas bubbling is performed in another reactor vessel which can be placed before, or after the plasma reactor. Detailed schemes are provided in figures 4-3 – 4-4. In the 1P2O reactor (figure 4-3), the micropollutant solution was first treated with plasma in the plasma chamber, and subsequently transferred to the ozonation chamber. There, plasma gas produced in the plasma chamber was bubbled through the micropollutant solution. In the 1O2P configuration (figure 4-4), the micropollutant solution was first ozonated with plasma gas produced in the plasma reactor and subsequently treated with plasma in the plasma chamber.
Figure 4-3: Schematics of 1P2O reactor configuration, operating in single pass mode

Figure 4-4: Schematics of 1O2P reactor configuration, operating in single pass mode
To compare micropollutant removal through plasma treatment with micropollutant removal by ozonation with exhausted plasma gas, the 1 O reactor configuration is applied (figure 4-5). In the 1 O reactor configuration, micropollutant solution was introduced in the ozonation chamber. Simultaneously, working gas (air or argon) was introduced in the plasma reactor, and plasma gas (mainly containing ozone), produced through the plasma discharge was bubbled through the micropollutant solution. Note that in the 1 O configuration deionized water was introduced into the plasma reactor, instead of micropollutant solution. Furthermore, this reactor configuration operated also in single pass configuration.

4.3.3 Batch reactor configuration

In a limited number of experiments of this work, batch processes were used. In the batch configuration (figure 4-6), 500 ml of micropollutant solution was pumped into the ozonation chamber. Next, the solution under treatment was transferred from the ozonation chamber to the plasma chamber. As in the single pass process, water rose in the steel tube, and subsequently fell down along the Zorflex® textile. After plasma treatment in the plasma chamber, the micropollutant solution was transferred to ozonation chamber, and subsequently bubbled through with plasma gas, produced in the plasma chamber during plasma discharge.
4.4 EXPERIMENTAL PROCEDURES

4.4.1 Optimization of micropollutant degradation in the DBD reactor

In a typical optimization experiment, 2.5 l micropollutant mixture (100 µg l⁻¹) was prepared by dilution from a 1 mg l⁻¹ stock solution. Influent was continuously fed in the plasma chamber with a 2-channel Carl Roth® peristaltic pump, operating at a constant flow rate of 66.30 ml min⁻¹. Effluent was continuously withdrawn from the reactor. At different time intervals (0, 2.5, 5, 10, 15, 20, 25 and 30 min), approximately 60 ml reactor effluent samples were taken. Immediately after sample collection, 19.00 ml sample was accurately weighed in 20 ml vials, using an analytical balance. Micropollutant extractions were performed by means of an optimized liquid-liquid extraction method (see chapter 5, section 5.3.2.2). After extraction, micropollutant concentrations in the initial sample, the sample after adsorption (0 min) and the plasma treated samples, were analyzed using an optimized GC-MS technique.

From the experimental results, the removal efficiency of each micropollutant was calculated as (eq. 4-1):

\[
R(\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100
\]

eq. 4-1

With R the removal efficiency (%), \(C_0\) the initial micropollutant concentration (µg l⁻¹), and \(C_t\) the final micropollutant concentration (µg l⁻¹) after a certain treatment time t.
To optimize our reactor system, a classic one-parameter-at-a-time approach was adapted. The operational parameters, investigated in this work, included: (i) gas type, (ii) gas flowrate, (iii) water flowrate, (iv) duty cycle, (v) applied power, and (vi) initial micropollutant concentration. Reactor efficiency towards the removal of each micropollutant was calculated by the EEO figure-of-merit, which was already introduced in section 2.4.2 (eq. 2-11)
Chapter 5  Analytical procedures

This chapter deals with the analytical procedures applied in this work. The first section provides more information about the electrical diagnostic methods. The electrical diagnostic methods mainly include a monitoring of the current and voltage waveforms, together with the calculation of the applied power to the DBD reactor. The second section gives a detailed description of the chemical diagnostics. The last section provides more information about the used toxicological tests.

5.1 ELECTRICAL DIAGNOSTICS

5.1.1 Power measurements

As previously described, voltage was measured with a Tektronix P601 5HV probe and current was measured with a Pearson model 2877 current probe. Both voltage and current waveforms were simultaneously monitored using a Tektronix S1200 oscilloscope. Figure 5-1 shows a typical voltage and current waveform, as produced by the AC driven DBD plasma discharge. As could be seen of this figure, both signals appear as sine waves. The distorted current sine with sparks on top of it indicated the plasma discharge.

![Figure 5-1: Typical voltage and current waveforms produced by pulsed DBD discharges (Davister, 2015)](image)

The power of the plasma discharge was determined by multiplying the power per period \( P_0 \) by the duty cycle \( DC \). The power per period was calculated by integrating the product of voltage and current and dividing it by the total pulse duration (eq. 5-1).

\[
P_0 = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} I \cdot V \, dt
\]  

eq. 5-1
With $P_0$ the power dissipated in one period (W), $I$ is the momentary current (A), $V$ is the momentary applied voltage (V) during plasma generation, and $T_2 - T_1$ is the length of time interval over which is integrated (s).

It is noteworthy to mention that the voltage applied to the reactor was periodically interrupted to avoid excessive gas and liquid temperatures, since this would induce heat losses in the reactor, combined with ozone decomposition in the liquid and gas phase. Interruption of pulsed voltage was realized by the application of a duty cycle, which expresses the percentage of time that voltage was turned on ($T_{on}$) or off ($T_{off}$) (eq. 5-2):

$$DC = \frac{T_{on}}{T_{on} + T_{off}} \quad \text{eq. 5-2}$$

With $T_{on}$ the time that voltage was applied to the reactor (ms), and $T_{off}$ the interruption time between two voltage pulses (ms). In all experiments, $T_{on} + T_{off}$ was 30 ms. Hence, the total power delivered by the plasma discharge was obtained by multiplying the power per period $P_0$ with the applied duty cycle (eq. 5-3):

$$P = P_0 \cdot DC \quad \text{eq. 5-3}$$

Where $P$ represents the total power (in Watt), $P_0$ the power per period (in Watt) and DC the applied duty cycle.

**5.2 EMISSION SPECTROMETRY**

In last decades, lot of research efforts have been made towards the detection of both long and short living species, produced by plasma discharges. In this work, optical emission spectrometry (OES) has been employed as a diagnostical method to derive more information about the presence of active species in air, oxygen and argon plasmas.

In DBD plasmas, ions, radicals and diatomic molecules are excited through the addition of electrical energy. This excitation process is characterized by the promotion of electrons to higher energy levels. Since the excited state is a highly unstable condition, excited species will rapidly return to the ground state. This phenomenon is associated with the emission of light with a wavelength specific to the target species. The obtained spectrum is characterized by the presence of fine spectral lines, attributed to the presence of atomic radicals and ions, and spectral bands indicating the presence of diatomic molecules ($N_2$, $O_2$) and radicals ($OH^*$).

In the OES experiments, plasma light emitted by air, argon and oxygen DBD plasmas was collected for different power settings by a quartz optic fibre placed at a 90 degree angle relative to the plasma discharge. Plasma radiation was introduced and dispersed in a monochromator. All emission spectra were acquired over the spectral range 200-900 nm with SpectraSuite® software
from Ocean Optics. Analyses focused upon the identification of plasma species by their wavelength in the emission spectrum.

5.3 CHEMICAL DIAGNOSTICS

5.3.1 Determination of H$_2$O$_2$

Hydrogen peroxide (H$_2$O$_2$) concentration in liquid samples was determined by using the UV-VIS spectrophotometrical method proposed by Nogueira et al. (2005). The spectrophotometric method was based on the specific reaction between ammoniummetavanadate (NH$_4$VO$_3$) and H$_2$O$_2$ in acidic media (r. 5-1):

\[
\text{VO}^{3+} + 4\text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{VO}_2^{3+} + 3\text{H}_2\text{O}
\]

In the presence of H$_2$O$_2$, a red-orange coloured peroxovanadium complex was formed. The peroxovanadium complex was characterized by a broad absorption band in the range 300-630 nm with an absorption maximum of 450 nm.

To correlate the absorbance value of the peroxovanadium complex at 450 nm with a H$_2$O$_2$ concentration in the liquid sample, a calibration curve was needed. Six calibration standards were made by dilution of a hydrogen peroxide standard solution with known concentration (30 m/m%). The absorbance of each calibration standard was measured, and plotted against known concentrations for diluted solutions (figure 5-2).

![Calibration curve](image)

Figure 5-2: Calibration curve used for determination of hydrogen peroxide in liquid samples

To measure the concentration of H$_2$O$_2$ in liquid samples, 0.8 ml of vanadate solution was added to 2.0 ml sample. The absorption of the sample was measured over the range 350 nm - 550 nm with the UV-VIS spectrophotometer. Concentration of H$_2$O$_2$ in the liquid samples was calculated by applying Lambert’s-Beer law (eq. 5-4):

\[
y = 0.0002x - 2E-05 \\
R^2 = 0.9986
\]
\[ c_{\text{H}_2\text{O}_2} = \frac{A}{\varepsilon l} \]  

eq. 5-4

With \( c_{\text{H}_2\text{O}_2} \) the experimentally determined \( \text{H}_2\text{O}_2 \) concentration in the calibration standard (µg l\(^{-1}\)), \( A \) the experimentally determined absorbance of the peroxovanadium complex at 450 nm, \( \varepsilon \) the molar extinction coefficient of \( \text{H}_2\text{O}_2 \) (0,000229 l mol\(^{-1}\) cm\(^{-1}\)) and \( l \) the optical path length of the cuvet (1 cm).

### 5.3.2 Gas chromatography – mass spectrometry

Chromatographical techniques combined with mass spectrometry, such as gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) are most commonly employed methods for both qualitative and quantitative determinations of micropollutants in water.

Gas chromatography allows the separation of chemical substances due to their different physicochemical interactions with a stationary phase on the inner wall of a GC column. Consequently, different molecules elute from the GC column on different times (also referred to as the retention time). After separation in the GC column, the chemical substances are transferred into the mass spectrometer (MS) by means of a GC-MS interface. In a typical MS separation procedure, the entering molecules undergo an ionization and fragmentation process. Subsequently, these charged fragmentation products are separated according to their mass-to-charge ratio and eventually detected by a mass selective detector.

It should be noted that mass spectrometers can operate in two different modes: SIM and SCAN mode. In SCAN mode a full mass scan is acquired by continuously scanning a wide mass-to-charge (m/z) range. On the other hand, SIM mode only scans for a few selected ions associated with the analyte.

Most preferable mode depends on the aim of the analysis. Performing a GC-MS analysis in full SCAN mode is particularly useful for determination of unknown substances in a sample. It provides more information than SIM mode since a full mass spectrum is monitored. However, SCAN mode is associated with a significant lower instrumental sensitivity, up to two orders of magnitude. On the other hand, selected ion monitoring (SIM) maximizes the instrumental detection limit of trace contaminants, since only a few mass fragments of interest are monitored.

#### 5.3.2.1 Method optimization

First, a preliminary test run was carried out in SCAN mode to determine all micropollutants, by using a 100 mg l\(^{-1}\) standard solution in dichloromethane. In accordance with procedures described in literature, a wide temperature range was combined with a slow heating rate.
Briefly, our initial column temperature was set on 100 °C. This temperature was held for 1 minute, and then raised to 270 °C with a temperature rate of 10 °C/min. The injection temperature was set on 250 °C. All other constant GC-MS parameters are presented in Table 5-1.

<table>
<thead>
<tr>
<th>Column</th>
<th>MS parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>HP-5MS</td>
</tr>
<tr>
<td>Model number</td>
<td>Agilent 19091s-433</td>
</tr>
<tr>
<td>Nominal length (m)</td>
<td>30</td>
</tr>
<tr>
<td>Nom. diameter (µm)</td>
<td>250</td>
</tr>
<tr>
<td>Nom. film thickness (µm)</td>
<td>0.25</td>
</tr>
<tr>
<td>Solvent delay</td>
<td>2.00</td>
</tr>
<tr>
<td>MS quad (°C)</td>
<td>150 (max 200)</td>
</tr>
<tr>
<td>MS source (°C)</td>
<td>230 (max 250)</td>
</tr>
<tr>
<td>Back inlet</td>
<td></td>
</tr>
</tbody>
</table>

**Injection parameters**

<table>
<thead>
<tr>
<th></th>
<th>Pressure (kPa)</th>
<th>73.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection</td>
<td>Splitless</td>
<td></td>
</tr>
<tr>
<td>Purge flow (ml/min)</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>Injection volume (µl)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Total flow (ml/min)</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>Syringe size (µl)</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>Gas type</td>
<td>Helium</td>
<td></td>
</tr>
</tbody>
</table>

Identification of target compounds is performed by comparison of the obtained mass spectra from the built-in software, with the mass spectra found in the NIST database. Figure 5-3 provides an overview of the mass spectra of all target compounds.
To shorten the GC-MS procedure, an optimization of the chromatographical conditions was carried out, by adapting a classic one-parameter-at-a-time approach. First, an optimization of the injection temperature was carried out, then the effect of the applied oven program on the
In addition to the optimized GC-MS method in SCAN mode, a GC-MS method operating in single ion monitoring (SIM) mode was developed, in order to reach lower detection limits. For each component, 1 target ion and 2 qualifiers were selected (see table 5-3). The selection of a target ion was necessary since it is the major parameter for identification and quantification of the
target compound. The target ion is represented by the most intense mass-to-charge (m/z) ratio found in the mass spectrum. Additionally, two qualifying ions were selected to confirm a correct peak identification. These qualifying ions are respectively represented by the ions with the second and third largest intensity in the mass spectrum.

Table 5-3: Developed GC-MS method in SIM mode (NIST,2016)

<table>
<thead>
<tr>
<th>Target compound</th>
<th>Retention time (t&lt;sub&gt;R&lt;/sub&gt;)</th>
<th>Target ion (m/z)</th>
<th>Quantification ions (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVOS</td>
<td>3.71</td>
<td>109</td>
<td>185, 79</td>
</tr>
<tr>
<td>DIU</td>
<td>4.10</td>
<td>72</td>
<td>232, 234</td>
</tr>
<tr>
<td>ATR</td>
<td>6.31</td>
<td>200</td>
<td>215, 173</td>
</tr>
<tr>
<td>PCF</td>
<td>6.44</td>
<td>266</td>
<td>165, 202</td>
</tr>
<tr>
<td>ALA</td>
<td>7.03</td>
<td>45</td>
<td>160, 188</td>
</tr>
<tr>
<td>BISA</td>
<td>8.05</td>
<td>213</td>
<td>228, 119</td>
</tr>
<tr>
<td>CARB</td>
<td>8.79</td>
<td>193</td>
<td>165, 95</td>
</tr>
<tr>
<td>ETH</td>
<td>10.09</td>
<td>213</td>
<td>296, 160</td>
</tr>
</tbody>
</table>

5.3.2.2 Extraction procedure

Determination of micropollutants in wastewater and other environmental samples is often a challenging task, mainly due to their low concentrations (ng l<sup>-1</sup> – µg l<sup>-1</sup> range) in these samples, and the complexity of the water matrix. Solid-phase extraction (SPE) is generally recognized as an optimal extraction procedure for micropollutants from environmental samples. Nevertheless, other extraction techniques, for example based on liquid-liquid extraction, are also frequently carried out for the extraction of micropollutants from environmental samples. In the specific case of pesticides, liquid-liquid extraction with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) is often recommended (Kotowska et al., 2014).

Based on the recommendations of the EPA and the current knowledge at the RUPT about liquid-liquid extractions for micropollutants, an extraction method with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was tested and further optimized for the isolation of micropollutants from water. The developed extraction procedure is illustrated in figure 5-5. In this method, 1 ml extraction solvent (dichloromethane) was added to 19.00 ml water sample, and adequately shaken by hand. After extraction, the organic phase was removed and transferred into a GC-MS vial. GC-MS analysis was then performed with the optimized GC-MS method, described in section 5.3.2.1.
To gain more insight about the required extraction time, an experiment was designed to determine the influence of different extraction times (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 min) on the extraction efficiency. All extractions were carried out with a mixture containing 100 µg l⁻¹ of each micropollutant.

The results are shown in figure 5-6. DVOS, DIU, ATR, PCF and ALA are rapidly extracted within 5 minutes of operation, whereas BISA, CARB, and ETH needed an extraction time of at least 8 minutes. Nevertheless, all micropollutants were fully extracted after an extraction time of 10 minutes. Consequently, a 10 minutes extraction time was chosen as the optimal extraction time in further experimentations.
5.3.2.3 Method validation

Prior to the application of an analytical method for the analysis of water samples, the analytical procedure should be investigated, in order to confirm its suitability. In this work, the validation of the GC-MS procedure was restricted to an investigation of the parameters: (i) linearity, (ii)
accuracy, (iii) precision (iv) limit of detection (LOD), and (v) limit of quantification (LOQ). A summary of the validation results can be found in table 5-4.

**Linearity – range**

External calibration curves were prepared in water by extracting 8 calibration standards with the optimized extraction method. All calibration curves were found to be linear in the whole concentration range (0 - 1000 µg l\(^{-1}\)), with correlation coefficients (\(r^2\)) ranging from 0.9934 to 0.9999.

**Accuracy – extraction efficiency**

In order to test the accuracy of the analytical method, 1 ml of a test solution, containing a micropollutant mixture in dichloromethane (2 mg l\(^{-1}\)) was added to 19 ml deionized water. Next, liquid-liquid extraction was performed with the optimized extraction procedure, described in section 5.3.2.2. After GC-MS analysis, the accuracy of the optimized chromatographical procedure was determined by calculating the recovery percentage as the ratio between the individual micropollutant concentrations in dichloromethane before and after extraction (eq. 5-5):

\[
\text{Recovery(\%) } = \frac{c_\text{A}}{c_\text{B}} \times 100
\]

With \(c_\text{A}\), the micropollutant concentration in dichloromethane before extraction (µg l\(^{-1}\)), and \(c_\text{B}\) the micropollutant concentration after extraction (µg l\(^{-1}\)), as measured with optimized GC-MS procedure.

**Precision**

Precision measured as intraday precision, was evaluated by assessing three replicate water samples at three different concentration levels (100, 50 and 5 µg l\(^{-1}\)). Next, precision was reported as relative standard deviation (RSD), eq. 5-6:

\[
\text{RSD(\%)} = \frac{s}{x} \times 100
\]

Where \(s\) is the standard deviation, and \(x\) the average concentration. Both statistic parameters were calculated for each concentration level. The reported RSD value (see table 5-4) was determined as the average RSD value calculated from three concentration levels.

**Detection limit**

A popular approach for determining the LOD and LOQ for water samples was proposed by the US EPA (Corley, 2002). Following their recommendations, a 5 point calibration curve was constructed within the concentration range (0 – 20 µg l\(^{-1}\)). According to the proposed root mean square error
(RMSE) method, the limit of detection (LOD) and limit of quantification (LOQ) were estimated as (eq. 5-7 – eq. 5-8):

$$\text{LOD} = 3 \frac{\text{RMSE}}{a}$$  \hspace{1cm} \text{eq. 5-7}

$$\text{LOD} = 10 \frac{\text{RMSE}}{a}$$  \hspace{1cm} \text{eq. 5-8}

With $a$ the slope of the calibration curve, and RMSE the root mean square standard error on the calibration curve. The RMSE was calculated according to eq. 5-9:

$$\text{RMSE} = \sqrt{\frac{\sum (c_i - \hat{c})^2}{n-2}}$$  \hspace{1cm} \text{eq. 5-9}

Where RMSE represents the root mean square standard error on the calibration curve, $c_i$ the concentration of the calibration standards (µg l$^{-1}$), $\hat{c}$ the concentration predicted from the calibration curve, and $n$ the number of calibration standards (5).

<table>
<thead>
<tr>
<th>Component</th>
<th>Recovery (%)</th>
<th>aPrecision (% RSD)</th>
<th>bLOD (µg l$^{-1}$)</th>
<th>cLOQ (µg l$^{-1}$)</th>
<th>Linearity</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVOS</td>
<td>92,9</td>
<td>1,70</td>
<td>0,356</td>
<td>1,19</td>
<td>0 – 1000</td>
</tr>
<tr>
<td>DIU</td>
<td>96,4</td>
<td>1,45</td>
<td>0,499</td>
<td>1,66</td>
<td>0 – 1000</td>
</tr>
<tr>
<td>ATR</td>
<td>92,0</td>
<td>1,21</td>
<td>0,595</td>
<td>1,98</td>
<td>0 – 1000</td>
</tr>
<tr>
<td>PCF</td>
<td>98,2</td>
<td>1,94</td>
<td>4,50</td>
<td>15,0</td>
<td>5 – 1000</td>
</tr>
<tr>
<td>ALA</td>
<td>95,0</td>
<td>1,11</td>
<td>0,287</td>
<td>0,955</td>
<td>0 – 1000</td>
</tr>
<tr>
<td>BISA</td>
<td>90,8</td>
<td>1,22</td>
<td>0,527</td>
<td>1,76</td>
<td>5 – 1000</td>
</tr>
<tr>
<td>CARB</td>
<td>90,6</td>
<td>3,11</td>
<td>3,45</td>
<td>11,5</td>
<td>0 – 1000</td>
</tr>
<tr>
<td>ETH</td>
<td>94,2</td>
<td>2,52</td>
<td>0,58</td>
<td>1,94</td>
<td>0 – 1000</td>
</tr>
</tbody>
</table>

a Relative standard deviation  b Limit of detection  c Limit of quantification

5.4 TOXICITY ANALYSIS

The future implementation of advanced oxidation processes is partly based on the potential toxicity of the effluent into the receiving environment. Hence, toxicity testing is interesting to gain more insight about the effluent toxicity after plasma treatment. These toxicity tests were conducted in close collaboration with the Environmental Toxicology Unit (GhenToxLab) of Ghent University.
5.4.1 Preparation of test samples

An initial toxicity experiment was set up with a micropollutant mixture containing 100 µg l⁻¹ of the micropollutants DIU, ATR, ALA, BISA, CARB and ETH. DVOS and PCF were excluded from the toxicity test since these compounds were respectively too unstable in water, and too volatile. The experiment was performed in the DBD plasma reactor operating in single pass configuration for three different working gases (air, argon and oxygen). Other operational settings (table 5.5) were hold constant for all toxicity experiments. When steady state conditions were reached, 1 l effluent was continuously withdrawn from the plasma reactor. Part of the sample (500 ml) was heated for 1 hour on a heating device at 80 degrees, in order to remove long living oxidants such as ozone (O₃) and hydrogen peroxide (H₂O₂). The other 500 ml did not undergo an additional heating step. Similarly, 1 l of the influent solution and 1 l of effluent without plasma operation were analysed for comparison.

Table 5-5: Operational settings for the toxicity test

<table>
<thead>
<tr>
<th>Operational parameters</th>
<th>Settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow</td>
<td>1 SLM</td>
</tr>
<tr>
<td>Water flow</td>
<td>66.30 ml/min</td>
</tr>
<tr>
<td>Concentration</td>
<td>100 µg l⁻¹</td>
</tr>
<tr>
<td>Duty cycle</td>
<td>0.15</td>
</tr>
<tr>
<td>Power</td>
<td>40 W</td>
</tr>
</tbody>
</table>

* 1 SLM = 1 standard liter per minute. This unit is defined as the gas flow rate in liter per minute, under standard conditions of temperature (273,15 K) and pressure (101325 Pa)

5.4.2 Toxicity testing

A chronic toxicity test, based on an algae test with *Pseudokirchneriella subcapitata* (*Selenastrum Capricornutum*) was initiated immediately after finalizing the plasma experiment. The toxicity of the samples was evaluated for the dilutions 0x, 10x and 100x. As the samples were already prepared in deionized water, dilutions were made in prepared medium. In order to create optimal growth conditions for the algae, nutrients were added to the undiluted samples. Further, the pH of all undiluted samples was adapted to 8.0 ± 0.2. Therefore, these parameters were also measured at the start and at the end of the test.

Algae tests were performed in erlenmeyer flasks containing 50 ml of test medium. Each test consisted of a control and three dilutions of each sample, and for each three replicates. Each replicate was inoculated with 1 X 10⁴ cells/ml (= cell density N₀ at the start (t₀) of testing). Afterwards, all erlenmeyer flasks were incubated at 24 °C on a light table (24 h light, 120 µmol photons/m²/s) and were manually shaken two times per day. Cell densities (N₁, N₂ and N₃) were measured using a particle counter (Coulter Counter Z1, Beckman) after 24 (t₁), 48 (t₂) and 72 (t₃) hours. The pH of the test medium was measured again at the end of the test.
Chapter 6  Characterization of a DBD plasma reactor

Before the DBD plasma discharge reactor was tested for its performance towards the degradation of organic compounds, a preceding characterization of the DBD plasma was performed. Plasma characterization is important, as it provides information about the quantitative and qualitative production of active species in the plasma zone and the liquid. This information can be used for reactor comparison and to gain deeper insight in micropollutant decomposition processes. In the first section, spectral analysis by means of optical emission spectroscopy (OES) is discussed to unravel the gas phase reactions, occurring during plasma discharges in air, argon and oxygen. The three following sections provide more information about the chemical reactions occurring in the liquid phase.

6.1 SPECTRAL ANALYSIS

6.1.1 Air plasma

Knowledge about the production of active species produced by plasma is essential to understand the formation of oxidative species in the plasma. In an air plasma, accelerated electrons are continuously colliding with molecular nitrogen (N₂) and oxygen (O₂) molecules. As a result, nitrogen and oxygen molecules are ionized (r. 6-1 – r. 6-2) (Eliasson et al., 1987; Ahn et al., 2003).

\[ \text{N}_2 + e^- \rightarrow \text{N}_2^+ + 2e^- \quad \text{r. 6-1} \]
\[ \text{O}_2 + e^- \rightarrow \text{O}_2^+ + 2e^- \quad \text{r. 6-2} \]

In this work, optical emission spectroscopy (OES) was employed to get more insight into the production of active species in the plasma zone, under different working gas conditions. Figure 6-1 represents a normalized and time averaged emission spectrum of an air plasma.
As seen in figure 6-1, the emission spectrum of a plasma discharge in air shows only bands. Spectral lines were not observed in the spectrum. Further, the optical emission spectrum is dominated by molecular nitrogen (N\textsubscript{2}) bands. Specifically, different vibrational belonging to the N\textsubscript{2} second positive system C\textsuperscript{3}Σ\textsubscript{u}(v') → B\textsuperscript{3}Π\textsubscript{g}(v'') were successfully identified by comparing the plasma spectrum with spectral data given in literature (Sharma & Saikia, 2008). Δv represents the change in quantum number.

Although the emission spectrum of plasma discharges in air is dominated by different vibrational excitation transitions of molecular nitrogen, also other important nitrogen containing species, such as nitric oxide (NO) can be formed. The formation of NO is described by the Zeldovich mechanism (r. 6-3 and r. 6-4) (Anetor et al., 2014):

\[
\begin{align*}
N_2 + O & \leftrightarrow NO + N \quad \text{r. 6-3} \\
N + O_2 & \leftrightarrow NO + O \quad \text{r. 6-4}
\end{align*}
\]

According to literature, the presence of NO molecules in the plasma is indicated by the appearance of several NO specific bands in the UV region (280-300 nm) of the emission spectrum (Drakes et al., 1997). Together, these spectral bands are referred to as the NO γ-system. NO bands were not visible in our air spectrum. The absence of NO bands could be explained by the very low NO concentrations which are usually detected in DBD plasma reactor systems with falling water film. In such reactors, low NO concentrations are attributed to the rapid oxidation of NO by atomic oxygen and OH radicals, according to the following gas phase reactions (Orlandini & Riedel, 2000):

\[
\begin{align*}
N + O_2 & \leftrightarrow NO + O \quad \text{r. 6-4}
\end{align*}
\]
Although, the emission spectrum of plasma discharges in air is dominated by the presence of nitrogen containing species, plasma discharges in air also involve the formation of oxygen containing species such as hydroxyl radicals (OH\(^*\)), ozone (O\(_3\)) and atomic oxygen (O). The presence of excited OH radicals has been confirmed by the presence of the OH (A-X) spectral band around 308 nm. Due to spectral overlapping with the N\(_2\) vibrational band, the OH (A-X) spectral band was hardly visible. Nevertheless, the presence of OH radical species in air plasmas has been confirmed by other researchers with alternative spectroscopic techniques such as laser induced fluorescence spectroscopy (LIF) (Kanazawa et al., 2011; Ono et al., 2011).

According to a review of Bruggeman & Schram (2010) many different plasma-chemical reactions are responsible for the production of OH\(^*\) radicals. Most of these reactions require the presence of H\(_2\)O molecules. The dissociation of water by electron impact is considered to be the most important source of hydroxyl radicals (r. 6-8):

\[
H_2O + e^- \rightarrow OH^* + H^* + e^-
\]

Next to the electron impact dissociation, vibrational and rotational excitation of water molecules also contribute to the production of OH\(^*\) radicals (Joshi et al., 1995; Vanraes et al., 2015a)

\[
\begin{align*}
H_2O + e^- & \rightarrow H_2O^* + e^- \\
H_2O^* + H_2O & \rightarrow H_2O + H^* + OH^* \\
H_2O^* + H^* & \rightarrow H_2 + OH^*
\end{align*}
\]

Another important molecule formed in the gas phase is ozone (O\(_3\)). By gas discharges in oxygen or air, ozone formation is mainly initiated by the three body reaction (r.6-12) (Kogelschatz, 2003; Brisset et al., 2011):

\[
O + O_2 + M \rightarrow O_3 + M
\]

M represents a third collision partner, which can be O\(_2\) or N\(_2\). Ozone cannot be determined by OES since it is a molecule which occurs in the ground state. Therefore, it will not emit light and is consequently not detectable in the OES spectrum. Contrarily, ozone typically shows absorption of UV light. Therefore, measuring the very characteristic absorption band of ozone, appearing in the UV region near 253 nm is a possible way for studying ozone production in the reactor. Alternatively, absorption lines in the IR region can also be measured. Due to instrumental limitations, ozone production in the gas phase was not measured in this work, but the reader is referred to Davister (2015) for ozone measurements in the same reactor under similar conditions.
6.1.2 Oxygen plasma

A typical normalized emission spectrum of a DBD plasma discharge in oxygen is presented in figure 6-2. Although pure oxygen was used as working gas, the optical emission spectrum of a plasma discharge in oxygen plasma is dominated by the presence of the N\textsubscript{2} second positive system, originating from air impurities in the plasma chamber. In contrast to the air plasma, excited atomic oxygen species, also noted as O I, are visible in the emission spectrum at a wavelength of 777.5 nm (Milosavljevic et al., 2014). It corresponds to the atomic oxygen transition O (3p\textsuperscript{5}P \rightarrow 3s\textsuperscript{5}S) (Krstulović et al., 2006).

Note that the atomic oxygen bands are less intense than the N\textsubscript{2} spectral bands, belonging to the N\textsubscript{2} second positive system. The excitation of N\textsubscript{2} molecules to N\textsubscript{2}\textsuperscript{*} (r.6-13) requires relative low energetic electrons. In contrast, the excitation of atomic oxygen proceeds in two different steps. First, oxygen molecules are dissociated through an electron impact reaction (r.6-14). Next, atomic electrons are excited (r.6-15) (Eliasson et al., 1987; Ahn et al., 2003; Kogelschatz, 2003).

\[ \text{N}_2 + e^- \rightarrow \text{N}_2^* \]
\[ \text{O}_2 + e^- \rightarrow \text{O} + \text{O} \]
\[ \text{O} + e^- \rightarrow \text{O}^* \]

Figure 6-2: Normalized emission spectra of a DBD plasma discharge in oxygen

6.1.3 Argon plasma

Figure 6-3 shows a normalized emission spectrum of a DBD plasma discharge in argon. As mentioned in literature, the plasma gas contains a large number of argon emission lines in the infrared region of the emission spectrum (700 – 850 nm). These bands constitute neutral argon (Ar I) transitions (Wagatsuma & Hirokawa, 1995) Single ionized argon bands (Ar II) were not
observed in the OES spectrum. Together with the argon specific bands, the N\textsubscript{2} second positive system, discussed in section 6.1.1, is visible. The presence of nitrogen specific bands in the argon plasma shows that the argon gas in the plasma chamber was contaminated with a small amount of air, and some dissolved N\textsubscript{2}, present in the liquid phase.

![Normalized emission spectra of a DBD plasma discharge in argon](image)

**Figure 6-3: Normalized emission spectra of a DBD plasma discharge in argon**

### 6.2 ACTIVE SPECIES PRODUCTION IN THE WATER PHASE

In the previous section, the formation of different reactive species in the gas phase was discussed, based on the optical emission spectra of plasma discharges in air, argon and oxygen. However, micropollutant decomposition is expected to occur mostly at the plasma-liquid interface, and in the bulk liquid. In the bulk liquid, micropollutant decomposition in the result of the production of a wide variety of aqueous radicals and ions. Formation of these oxidative species is caused by a series of complex interactions. A complete discussion of all interaction mechanisms between all chemical species with micropollutants is beyond the scope of this work. However, the reactor is characterized for the production efficiency of hydrogen peroxide in the plasma chamber. Moreover an investigation of the solution parameters conductivity and pH is performed, since they are a good representative to give a general view about the chemical processes taking place in the plasma chamber and ozonation chamber.

#### 6.2.1 pH

Figure 6-4 shows the variations in pH for the plasma and ozonation chamber, during the treatment of deionized water. Experiments were performed in single pass reactor configuration, where the treated solution was respectively exposed to only plasma treatment in the plasma chamber (1P process) and only ozonation (1O process).
The experimental results presented in figure 6-4 show that DBD plasma treatment of deionized water in the plasma chamber leads to a strong increase in acidity. Initial pH value of deionized water was measured as 7.78. The initial pH remained unchanged after adsorption on Zorflex®. Then, the initial pH rapidly decreased to a final pH value within 5 minutes of plasma treatment. The strongest decrease in pH was observed for plasma discharges in air (final pH = 3.17). In the case of oxygen, the final pH was more than 1 unit higher (4.48). The lowest pH drop was observed for plasma discharges in argon (final pH = 5.78).

Although a rapid decrease of the initial pH (7.83) was also observed in the ozonation chamber, the pH drop was, both for air and oxygen (final pH 4.41 and 4.69 respectively,) lower than in the plasma chamber. The pH value did not decrease significantly for ozonation with argon (final pH 6.54).

![Figure 6-4: pH variation in the plasma chamber (left) and ozone chamber (right)](image)

The acidification of solutions treated with plasma has been extensively studied in literature. Brisset et al. reported as one of the first authors about the acidic effects, induced by air plasmas (Brisset et al., 1990a ; Brisset et al., 1990b). Additionally, strong pH drops in micropollutant solutions and deionized water have been confirmed by many other researchers. For example, Shainsky et al. (2012) reported about a fast pH drop to a final pH of 2.01 in deionized water after DBD plasma treatment in an air environment. Similar results were obtained through experimentations in other reactor types (Brisset et al., 2008; Ikawa et al., 2010; Oehmigen et al., 2010). In literature, it was suggested that acidification of plasma treated water by air plasmas is the result of nitrous acid (HNO₂) and nitric acid (HNO₃) formation in the bulk liquid. Formation of these species can be understood by the diffusion of nitrogen containing gases produced during the plasma discharge, into the liquid. Especially the production of gaseous nitrogen oxides (NO and NO₂) correlates very well with the appearance nitrite and nitrate in the liquid. In section 6.1, it was shown that the formation of nitrogen oxide (NO) in the gas phase is described by the Zeldovich mechanism (r.6-3 and r.6-4). NO formed in an air plasma is rapidly converted to nitrogen dioxide (NO₂) by reactions r. 6-16 and r.6-17 (Kogelschatz, 2003):
2NO + O₂ → 2NO₂  
NO + O₂ → NO₂ + O₂  

In a next step, nitrogen oxides dissolve into the liquid, leading to the formation of nitrite and nitrate in the plasma chamber (r.6-18 - r.6-19). According to these reactions the formation of nitrite and nitrate goes hand in hand with the formation of hydrogen cations (H⁺) in the water phase, which describes the experimental observed pH drop by plasma discharges in air (Brisset et al., 2008 ; Lukes et al., 2014).

\[ 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{NO}_3^- + 2\text{H}^+ \]  
\[ \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NO}_2^- + 2\text{H}^+ \]

To ensure that nitrite (NO₂⁻) and nitrate (NO₃⁻) were produced in the bulk liquid, concentrations of both species were measured in the liquid samples at the start, and at the end of each experiment. The results are presented in table 6-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NO₂⁻ (mg l⁻¹)</th>
<th>NO₃⁻ (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>&lt; 0.07</td>
<td>&lt; 2.2</td>
</tr>
<tr>
<td>0 min (adsorption)</td>
<td>0.09</td>
<td>&lt; 2.2</td>
</tr>
<tr>
<td>Plasma air</td>
<td>2.0</td>
<td>33</td>
</tr>
<tr>
<td>Plasma argon</td>
<td>0.51</td>
<td>12</td>
</tr>
<tr>
<td>Plasma oxygen</td>
<td>&lt; 0.07</td>
<td>3.8</td>
</tr>
</tbody>
</table>

The results given in table 6-1 indicate a significant higher NO₂⁻ and NO₃⁻ production, when air was used as a working gas. Therefore, the results are in good agreement with the observed pH drop in the plasma chamber. Highest amounts of nitrite and nitrate were produced in the air plasma. Contrarily, significant lower amounts of nitrite and nitrate were detected when plasma discharge occurs in an argon and oxygen environment. Very interesting is the observation that the determined nitrite concentration in air plasmas (2.0 mg l⁻¹) was much lower than the nitrate concentration (33 mg l⁻¹). One of the reasons of a significant lower nitrite concentration, is the disproportionation of nitrite into nitrate and nitric oxide (r.6-20). This reaction is only feasible in strong acidic medium (pH < 3.5 ) (Lukes et al., 2014):

\[ 3\text{NO}_2^- + 3\text{H}^+ \rightarrow 2\text{NO} + \text{NO}_3^- + \text{H}_2\text{O}^- \]  

Next to the conversion of nitrite in acidic media, nitrite can also be oxidized through other reactions involving reactive oxygen species (ROS). Some of these reactions will be explained later in this work. Surprisingly, significant pH drops have also been reported in solutions treated in nitrogen-free plasmas. For instance, Shainsky et al. (2012) found a final pH value of 2.07 after oxygen DBD plasma treatment of deionized water. This suggests that other reactive species,
formed in the liquid phase, contribute as well to the acidification of deionized water in the plasma chamber. Probably, the self-decomposition of ozone, produced in the plasma discharge, contributes to significant lower pH values. Although ozone decomposition in water is mainly initiated under alkaline conditions, it has also been observed, at a slower rate, under acidic conditions (Ershov & Morozov, 2009). Possibly, the formation of charged species in the gas phase, and the subsequent dissolution in the liquid also contributes to the observed pH drops. Further research is definitely needed to validate this claim.

In contrast to plasma discharges in air and oxygen, usually no acidification of plasma treated water is reported by DBD discharges in argon (Shainsky et al., 2012). However, a decrease in pH was observed when argon was used as discharge medium (pH = 5.78). Moreover, relative high amounts of nitrite and nitrate were measured in the liquid phase (see table 6-1). It is therefore an indicator of working gas contamination with nitrogen molecules. Hence, the contribution of nitrite and nitrate formation by plasma discharges in argon and oxygen should not be underestimated in the interpretation of pH data.

When deionized water is subjected to only ozonation by plasma gas bubbling, but without direct contact with plasma, a pH drop to a final pH value of 4.41 and 4.69 is observed for plasma bubbling with air and oxygen, respectively. These pH values are in the same order of magnitude of the final pH value obtained after plasma contact in oxygen (4.48). An explanation of these phenomena is difficult, but just as in the plasma chamber, ozone decomposition and dissolution of species produced in the gas phase can attribute acidification of ozonated water.

### 6.2.2 Conductivity

In addition to the pH measurements, also changes in solution conductivity were measured. Figure 6-5 shows the temporal evolution of conductivity in the plasma chamber and ozonation chamber. Because deionized water was used, the initial conductivity was very low (0.24 µS/cm). The initial conductivity remained unchanged after adsorption on Zorflex®. Then, initial conductivity rapidly increased to a final, constant value within 5 minutes of plasma treatment. Highest increase in conductivity was observed for air (final conductivity 420 µS/cm). For oxygen, the final conductivity was 99.9 µS/cm. Conductivity only slightly raised for plasma discharges in argon (final conductivity 16.9 µS/cm). In the ozonation chamber, measured conductivity was about a factor ten lower than in the plasma chamber. Highest conductivity was measured for oxygen (24.9 µS/cm). The average conductivity for air was 16.9 µS/cm. In case of argon, the increase in conductivity was negligible (1.15 µS/cm). It suggests that only argon gas, without ozone, was introduced into the ozonation chamber.
Together with the pH drop explained in the pH measurements (section 6.2), the increase in conductivity delivers additional experimental evidence about the production of charged species in the treated solution. For discharges in air, the main contribution of the solution conductivity is delivered by the decrease in pH (Magureanu et al., 2013). Moreover, conductivity and pH are closely correlated with each other, as predicted by (Burlica & Locke, 2008):

\[
\Lambda = \Lambda_0 + 1000 \left( 349.82[H^+] + 198.6[OH^-] \right) \quad \text{eq. 6-1}
\]

With \( H^+ \) and \( OH^- \) respectively the concentration of hydrogen cations and hydroxyl anions, expressed in mol l\(^{-1} \). \( \Lambda_0 \) is the initial solution conductivity (\( \mu S/cm \)), and \( \Lambda \) the steady state conductivity, also in \( \mu S/cm \).

By using this model, a steady state conductivity of \( 274.8 \mu S/cm \) is predicted. The model can be extended by adding an additional term for the contribution of nitrate to the steady state conductivity (Burlica & Locke, 2008). Note that nitrite was only produced to a minor extend (see table 6.1), so the contribution of nitrite to overall conductivity was not included in the model (eq. 6-2):

\[
\Lambda = \Lambda_0 + 1000 \left( 349.82[H^+] + 198.6[OH^-] + 71.4[NO_3^-] \right) \quad \text{eq. 6-2}
\]

According to eq. 6-2, a steady state conductivity of 274.8 \( \mu S/cm \) is predicted. The concentration of \( H^+ \) and \( OH^- \) was calculated from the pH measurements discussed in previous section, whereas the \( NO_3^- \) concentration was calculated from the data presented in table 6-1. This conductivity is significantly lower than the experimentally measured steady state conductivity of deionized water treated with air plasma (420 \( \mu S/cm \)). Hence, it confirms that the measured steady state conductivity cannot be fully explained by the presence of only \( H^+ \), \( OH^- \) and \( NO_3^- \) ions. Several other ions clearly contribute to the solution conductivity. Probably, these ions originate from the self-decomposition of ozone, or other ions, present in the liquid sample. Small, but significant increases in conductivity where also measured during the ozonation process with oxygen or air, in
the ozonation chamber. For ozonation with argon, the almost negligible steady state conductivity confirmed that only a very few ozone was produced in ozonation processes with argon.

6.2.3 \( \text{H}_2\text{O}_2 \) production

The production of \( \text{H}_2\text{O}_2 \) in the liquid phase is illustrated in figure 6-6. Since the initial solution and the sample taken after adsorption were not treated with plasma, no \( \text{H}_2\text{O}_2 \) was detected in these samples. A similar \( \text{H}_2\text{O}_2 \) production was observed for discharges in oxygen and argon (147.0 \( \mu \text{mol l}^{-1} \) and 126.7 \( \mu \text{mol l}^{-1} \) respectively). The usage of air resulted in a lower \( \text{H}_2\text{O}_2 \) production (56.5 \( \mu \text{mol l}^{-1} \)). A small amount of hydrogen peroxide production was also observed in experiments by which only the ozonation chamber was used. Again, the amount of detected hydrogen peroxide was the highest for ozonation in oxygen (24.9 \( \mu \text{mol l}^{-1} \)). Ozonation in air produced 18.3 \( \mu \text{mol l}^{-1} \) \( \text{H}_2\text{O}_2 \). No \( \text{H}_2\text{O}_2 \) production was measured for argon.

![Figure 6-6: \( \text{H}_2\text{O}_2 \) variations in the plasma chamber (left) and the ozone chamber (right)](image)

It is very interesting to note that plasma discharges in argon and oxygen yielded a similar \( \text{H}_2\text{O}_2 \) production. Similar results are also reported by Porter et al. (2007), who have investigated the \( \text{H}_2\text{O}_2 \) production after plasma discharges in argon, oxygen, air, nitrogen carbon dioxide and helium. The authors reported a similar \( \text{H}_2\text{O}_2 \) production for plasma discharges in argon, oxygen and carbon dioxide. No \( \text{H}_2\text{O}_2 \) production in air and nitrogen plasmas was found.

In contrast to the results presented by Porter et al. (2007), a low \( \text{H}_2\text{O}_2 \) production (56.5 \( \mu \text{g l}^{-1} \)) for plasma discharges in air is measured in this research. Nevertheless, this \( \text{H}_2\text{O}_2 \) production is approximately three times lower than the \( \text{H}_2\text{O}_2 \) production in oxygen and argon. Hence it could be concluded, that the presence of nitrogen species in the discharge medium results in a lower \( \text{H}_2\text{O}_2 \) production. In this regard, two potential scavenging reactions in the aqueous phase are responsible for the low \( \text{H}_2\text{O}_2 \) production. First nitrite is easily oxidized to nitrate by \( \text{H}_2\text{O}_2 \) (r.6-21) (Anbar & Taube, 1954).

\[
\text{NO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O}
\]

r. 6-21
Simultaneously, oxidation of nitrite to peroxynitrite (O=NOOH), which is an isomer of nitrate, has also been reported (r.6-22). However, in an acidic environment, peroxynitrite is unstable and is rapidly converted to nitrate (Lukes et al., 2014).

\[
\text{NO}_2^- + H_2O_2 + H^+ \rightarrow O=\text{NOOH} + H_2O \quad \text{r. 6-22}
\]

According to Locke & Shih (2011), hydrogen peroxide formation in plasma reactors can be correlated, to some extent, with the amount of hydroxyl radicals produced in the gas phase. There, hydrogen peroxide is predominately produced through the recombination of hydroxyl radicals (r.6-23) or through excitation of water molecules by hydroxyl radicals (r.6-24)

\[
\begin{align*}
\text{OH}^+ + \text{OH}^+ &\rightarrow H_2O_2 \\
\text{OH}^+ + H_2O^- &\rightarrow H_2O_2
\end{align*}
\text{r. 6-23, 6-24}
\]

Because the amount of hydroxyl radicals (and thus hydrogen peroxide production) varies with the power dissipated to the reactor, the energy yield for hydrogen peroxide production has been proposed as an alternative indicator for reactor efficiency (Locke & Shih, 2011). In single pass experiments, the energy efficiency is calculated according to eq. 6-3:

\[
G_{H_2O_2} = \frac{c_{H_2O_2} \cdot M_{H_2O_2} \cdot V}{P \cdot t} \quad \text{eq. 6-3}
\]

With \( c_{H_2O_2} \) the concentration hydrogen peroxide concentration in mol l\(^{-1}\), \( M_{H_2O_2} \) the molar mass of hydrogen peroxide in g mol\(^{-1}\), \( V \) the treated volume in l, \( P \) the applied power in kW and \( t \) the total treatment time in hours.

The results shown in figure 6-6 indicate that the measured \( H_2O_2 \) concentrations in the DBD reactor was quite low. At a power of 40 W plasma discharges in air, argon and oxygen corresponds to an \( H_2O_2 \) energy yield of 25.3, 44.1 and 49.2 mg/kWh respectively. Locke & Shih (2011) have reviewed the \( H_2O_2 \) production yield in different plasma reactors. Overall, typical \( H_2O_2 \) energy yields between 0.04 g/kWh and 80 g/kWh were observed. The highest energy yields (80 g/kWh) were found for reactor designs in which the plasma was generated directly into the liquid phase. Other reactor types resulted in lower energy yields. For most DBD reactors, the \( H_2O_2 \) energy yield was estimated around 2.70 g/kWh. Other recent scientific reports have confirmed these calculated energy yields. In this study, the \( H_2O_2 \) energy was even lower (25.3 mg/kWh in air, 44.1 mg/kWh in argon and 49.2 mg/kWh in oxygen). Low energy yields for hydrogen peroxide production in the plasma reactor used in this research can be explained by the presence of Zorflex® textile. Indeed, activated carbon is known for its decomposition properties towards hydrogen peroxide (Khalil et al., 2001; Takaoka et al., 2007). It has been suggested that the decomposition of hydrogen peroxide is initiated by the exchange of a hydroxyl group, bounded on the activated carbon surface, with a hydroperoxyl (OH\(_2\)) group originating from the ionization of
hydrogen peroxide in water \((r-6.31)\). Subsequently, the formed AC-OOH group can further decompose, resulting into the regeneration of the activated carbon surface \((r.6-32)\) (Huang et al., 2003):

\[
\text{AC} - \text{OH} + \text{H}^+ + \text{OOH}^- \rightarrow \text{AC} - \text{OOH} + \text{H}_2\text{O} \quad r.6-31
\]

\[
\text{AC} - \text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{AC} - \text{OH} + \text{H}_2\text{O} + \text{O}_2 \quad r.6-32
\]

Low amounts of hydrogen peroxide were also determined in the ozone chamber. The highest hydrogen peroxide production was found when oxygen is used. The production of hydrogen peroxide from ozone is the result from the self-decomposition of ozone in the plasma chamber. Lower hydrogen peroxide production by ozonation with air can be explained by the fact that ozone content in air plasma gas is lower.

### 6.3 CONCLUSION

The plasma chemistry is, both in the gas and liquid phase, highly dependent on the plasma discharge medium. Therefore, production of active species was studied in the gas phase by optical emission spectroscopy as well as in the liquid phase through investigation of solution parameters such as pH and conductivity. For plasma discharges in air it was found that, in contrast to plasma discharges in oxygen and argon, a considerable amount of nitrogen containing species such as nitrite and nitrate were detected. For these species, it is known that they can act as a scavenger for hydroxyl radicals, ozone and hydrogen peroxide. Due to scavenging reactions, air plasmas are considered to be less effective for micropollutant removal. Due to the absence of scavengers in argon and oxygen plasmas, higher amounts of reactive species are available for micropollutant decomposition.

In addition, the plasma-catalytic reactor system was characterized towards the energy yield for hydrogen peroxide production \((G_{\text{H}_2\text{O}_2})\). Although the review of Locke & Shih claimed that this parameter is a good representative for hydroxyl radical production, and thus micropollutant decomposition, this is probably not entirely correct. According to their review, the highest energy yields for hydrogen peroxide production are obtained for reactor systems with plasma discharges directly in the liquid. However, another review reported that this reactor type is one of the worst performing reactors according to the \(G_{50}\) energy yield parameter (Malik, 2010). For these reasons, there are some serious doubts about the suitability of both energy yield parameters \((G_{50} \text{ and } G_{\text{H}_2\text{O}_2})\) to assess reactor performance. Moreover the presence of Zorflex® activated carbon cloth in the reactor enhances hydrogen peroxide decomposition, causing additional hydroxyl radical formation. For these species, it is assumed that they are important contributors for micropollutant elimination. Hence the presence of Zorflex possibly leads to a more efficient removal of micropollutants.
Chapter 7  Optimization of a DBD plasma reactor

This chapter summarizes the optimization results for the removal of eight model compounds in a DBD plasma reactor. In the first section, the influence of micropollutant adsorption on Zorflex® active carbon cloth is investigated. Then, the reaction kinetics for micropollutant removal in batch configuration are elucidated. The third section, discusses the micropollutant removal in the single pass mode. Section four discusses the operational parameter optimization for the removal of atrazine in the plasma reactor, operating in single pass configuration. After discussion of the influence of each individual parameter the energy efficiency was summarized. Finally, the optimization results are summarized and optimal settings for an energy efficient removal of micropollutant is proposed.

7.1 ADSORPTION

Plasma-assisted destruction of micropollutants in the plasma chamber can be considered as the result of micropollutant adsorption on Zorflex® active carbon cloth, and micropollutant decomposition by means of plasma interaction. In order to elucidate the exact role of micropollutant removal by adsorption on the active carbon cloth, a single component adsorption test for both alachlor and diuron was performed in a preliminary experiment. In this adsorption experiment, the initial concentration was set on 100 µg l⁻¹. Figure 7-1 shows the adsorption removal profiles for alachlor and diuron.

![Figure 7-1: Diuron and alachlor removal by adsorption on Zorflex® active carbon cloth](image)

From the experimental results, the total removal rate of alachlor and diuron after 30 minutes of adsorption were calculated by eq. 7-1:

$$R = 1 - \frac{C_t}{C_0}$$
eq 7-1
With $R$ the total removal efficiency after 30 minutes of adsorption, $C_0$ the initial concentration ($\mu g \text{l}^{-1}$), and $C_t$ the final concentration (in $\mu g \text{l}^{-1}$) after adsorption.

As can be seen from figure 7-1, a high adsorption potential for Zorflex® (> 75%) was found for both micropollutants. Diuron exhibited the highest removal rate (96.9 %) after 30 minutes of adsorption treatment. For alachlor a significant lower removal efficiency (76.6 %) was found. The substantial lower removal efficiency for alachlor can be understood by a comparison of the micropollutant physicochemical properties. Because adsorption on carbonaceous materials is largely affected by non-polar interactions between adsorbent and adsorbate, adsorption efficiency can be explained by the hydrophobicity of a micropollutant. Since the octanol-water partition coefficient ($\log K_{OW}$) is a good representative for adsorption tendency, this physicochemical parameter is useful for the comparison of adsorption differences between micropollutants. According to a general view in literature, alachlor is characterized by a lower hydrophobicity ($\log K_{OW} = 2.63$) than the diuron ($\log K_{OW} = 2.85$) (El-Nahhal, 2015; Kumar et al., 2013). Therefore, diuron theoretically tends to adsorb stronger on hydrophobic surfaces such as active carbon, which was in agreement with our experimental observations.

Although Zorflex® has shown a high adsorption potential, due to its strong porosity and high surface area, the extensive usage of Zorflex® in adsorption experiments is expected to lead to complete exhaustion of adsorptive capacity. Moreover, it should be emphasized that only micropollutant adsorption does not lead to micropollutant degradation. However, removal percentage of micropollutants by adsorption did not change during the complete series of experiments conducted in this work (data not shown), suggesting that Zorflex is continuously regenerated by plasma treatment (Vanraes, 2016).

### 7.2 MICROPOLLUTANT REMOVAL IN BATCH REACTOR CONFIGURATION

In order to investigate the combined effect of adsorption and plasma initiated decomposition on the micropollutant degradation in the DBD reactor a batch experiment for the single compound removal of alachlor and diuron was performed. Again, an initial concentration of 100 $\mu g \text{l}^{-1}$ was maintained. Further, the experiment was performed with standard operational settings, as presented in table 7-1. These settings were initially chosen as standard settings in accordance with earlier experiments conducted with this plasma reactor (Vanraes et al., 2015b). Experimentally determined degradation kinetics for alachlor and diuron removal in the plasma reactor are depicted in figure 7-2.
Table 7-1: Standard operational settings in batch experiments

<table>
<thead>
<tr>
<th>Operational parameters</th>
<th>Standard settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas type</td>
<td>Air</td>
</tr>
<tr>
<td>Gas flow</td>
<td>1 SLM*</td>
</tr>
<tr>
<td>Water flow</td>
<td>66.30 ml min⁻¹</td>
</tr>
<tr>
<td>Concentration</td>
<td>100 µg l⁻¹</td>
</tr>
<tr>
<td>Duty cycle</td>
<td>0.15</td>
</tr>
<tr>
<td>Power</td>
<td>40 W</td>
</tr>
</tbody>
</table>

* 1 SLM = 1 standard liter per minute. This unit is defined as the gas flowrate in liter per minute, under standard conditions of temperature (273.15 K) and pressure (101325 Pa)

In both cases the micropollutants exhibited a fast removal, with a total removal rate higher than 99% (99.1 % for alachlor and 99.5 % for diuron) after 30 minutes of plasma treatment in the batch reactor. Hence, the experimental results reveal that the combination of adsorption with plasma treatment is very effective in the removal of alachlor and diuron.

For low initial concentrations, micropollutant decomposition by plasma is mostly described by a first order kinetics (Hijosa-Valsero et al., 2013; Mizrahi & Litaor, 2013). This is also the case for micropollutant decomposition with other AOPs. If micropollutant decomposition obeys a first order kinetics, first order reaction rate constants for plasma destruction can be obtained by fitting a first order kinetic model (eq. 7-2) to the experimental data.

\[
\ln\left(\frac{C_t}{C_0}\right) = -k\cdot t
\]

**eq. 7-2**

In this equation, \(C_0\) represents the initial micropollutant concentration (100 µg l⁻¹), \(C_t\) is the final micropollutant concentration (µg l⁻¹) after a certain treatment time \(t\) (min), and \(k\) is the first order reaction rate constant (min⁻¹).
Following this approach, first order reaction rate constants $k_A = 0.51 \text{ min}^{-1}$ for alachlor removal, and $k_D = 0.78 \text{ min}^{-1}$ for diuron removal were obtained. These reaction constants were about 5 times and 7.5 times higher than the removal rate constants calculated for alachlor and diuron removal by adsorption respectively. Due to the higher reaction rate constant for removal of diuron, a better energy efficiency (EEO = 3.90 kWh/m³) was achieved in comparison with the energy efficiency of alachlor removal (EEO = 6.10 kWh/m³) (table 7-2).

<table>
<thead>
<tr>
<th></th>
<th>Diuron</th>
<th>Alachlor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>% removal</td>
<td>96.9</td>
<td>76.6</td>
</tr>
<tr>
<td>Adsorption + plasma</td>
<td>0.78</td>
<td>0.51</td>
</tr>
<tr>
<td>% removal</td>
<td>99.5</td>
<td>99.1</td>
</tr>
<tr>
<td>EEO (kWh/m³)</td>
<td>3.90</td>
<td>6.10</td>
</tr>
</tbody>
</table>

Thus, a higher micropollutant removal efficiency have been observed in the adsorption + plasma experiment in comparison with the adsorption experiment. The higher observed micropollutant removal, together with the higher first order reaction rate constants in the case of the combined adsorption and plasma process indicated that the process efficiency was significantly increased when plasma treatment has been applied in the setup. Indeed, it is known that plasma combines the production of a wide variety of reactive oxidizers ($\text{OH}^•$, $\text{O}_3$, $\text{H}_2\text{O}_2$), which could stimulate additional micropollutant destruction after to adsorption on Zorflex®. No plasma experiment was performed with only plasma, in the absence of the Zorflex® textile, since the presence of the textile is required for formation of a stable water film.

Based on the experimental findings, following explanation has been proposed. First, micropollutants present in the bulk liquid phase diffuse from the bulk liquid to the surface of the Zorflex®. Next, micropollutants are adsorbed on the Zorflex®. This adsorption process allows an increased local micropollutant concentration in the region near the plasma-liquid interface, resulting in more interactions between adsorbed micropollutants and plasma produced species.

Next to the interaction of plasma active species with molecules adsorbed on the Zorflex®, plasma produced species are also able to initiate micropollutant decomposition in the bulk liquid. According to the kinetic model of Hong et al. (1996), micropollutant abatement in the liquid phase is dominated by i) direct ozonation and ii) the perozone process.

Experimental evidence for the claim that micropollutants are predominately degraded at the site of adsorption was delivered by Vanraes et al. (2015a). Atrazine destruction was investigated in a DBD reactor equipped with an adsorptive nanofiber membrane. The exact details about the used reactor setup are discussed elsewhere (Vanraes et al., 2015a). In the absence of the nanofiber membrane, a degradation efficiency of 61.0 % was observed, whereas a significant higher degradation efficiency of 84.6% is found in the presence of the nanofiber membrane (Vanraes et
al., 2015a). Moreover, simulation of atrazine degradation by direct oxidation, the peroxone process, and a combination of both processes could only explain 3.4 %, 10.4 % and 13.5 % atrazine degradation, respectively (Vanraes et al., 2015a). Hence, it can be reasonably assumed that adsorption on a reactor membrane in combination with plasma-assisted destruction on the site of adsorption, and in the liquid results in higher micropollutant degradation efficiencies.

### 7.3 MICROPOLLUTANT REMOVAL IN SINGLE PASS REACTOR CONFIGURATION

Batch plasma reactor systems are ubiquitously found in literature. In such reactor systems, a certain volume of aqueous solution is introduced, and pumped around in the reactor system for a certain treatment time. Although such reactor designs are particularly important for studying the chemical kinetics of micropollutant decomposition, they are unpractical for the treatment of large volumes of wastewater. Moreover, the future implementation of a plasma reactor in existing MWWTPs, requires a certain degree of continuity, since large volumes needs to be treated. Therefore, micropollutant removal in a continuous flow (single pass) reactor configuration is more attractive. Following this line of thought, the batch reactor system was adapted to a single pass configuration. The prepared reactor influent consists of a synthetic wastewater containing all eight micropollutants (dichlorvos, diuron, atrazine, pentachlorophenol, alachlor, bisphenol A, carbamazepine and 1,7-α-ethinylestradiol) dissolved in deionized water. The initial concentration was set on 100 µg l⁻¹. Standard settings, as denoted in table 7.1 were used. In order to measure the amount of micropollutant removal by adsorption of Zorflex®, a first sample was taken before plasma was switched on. Subsequently, plasma was turned on and effluent samples (approximately 60 ml) were taken at 2.5, 5, 10, 15, 20, 25 and 30 minutes after plasma treatment. Figure 7-3 shows the measured effluent concentrations for bisphenol A and carbamazepine, exposed to the combined adsorption and plasma treatment process in the continuous flow reactor design. Note that in single pass experiments equilibrium concentrations in the effluent are measured, in contrast to reaction kinetics in batch mode.

![Figure 7-3: Micropollutant removal of bisphenol A (BISA) and carbamazepine (CARB) in single pass mode under reference conditions, mentioned in table 7.1](image)
From the experimental results, given in figure 7-3 it could be seen that steady-state conditions are quasi immediately reached, as indicated by the stationary concentrations, achieved within the first 5 minutes of operation. Further, it was seen that the combined adsorption-plasma treatment was efficient for the degradation of bisphenol A and carbamazepine, although differences in total removal percentage could be observed. Table 7-3 summarizes the contribution of adsorption on Zorflex® and plasma destruction to the removal of all micropollutants in the plasma reactor. The removal efficiency through adsorption on Zorflex® and plasma destruction was calculated according to eq. 4-1 mentioned in chapter 4. Total removal efficiency is obtained by summation of the individual micropollutant removal efficiency through adsorption and plasma destruction.

The total removal efficiency was found to be different for each micropollutant, as summarized in table 7-3. For example, bisphenol A was removed for 48.1 % by adsorption on the Zorflex® active carbon textile. Next, bisphenol A was further degraded by plasma interaction. A total removal efficiency of 66.7 % was reached after 30 minutes of treatment. On the other hand, carbamazepine showed a similar adsorption behaviour on Zorflex® (46.5 %), but a higher total removal percentage was observed at the end of the experiment (75.0 %), indicating a lower decomposition resistance towards the degradation by DBD plasma, in comparison with bisphenol A. Further, it is noteworthy that the observed degradation percentages of alachlor and diuron were lower in the continuous flow reactor configuration (66.0 % for alachlor, 63.2 % for diuron) than in the batch reactor configuration (99.1 % for alachlor, 99.5 % for diuron), due to the higher volume of treated water and the absence of additional plasma gas bubbling.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Removal by adsorption (%)</th>
<th>Additional oxidation by plasma (%)</th>
<th>Total removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVOS</td>
<td>33.2</td>
<td>50.4</td>
<td>83.6</td>
</tr>
<tr>
<td>DIU</td>
<td>50.6</td>
<td>12.5</td>
<td>63.2</td>
</tr>
<tr>
<td>ATR</td>
<td>37.0</td>
<td>19.5</td>
<td>56.4</td>
</tr>
<tr>
<td>PCF</td>
<td>68.0</td>
<td>10.3</td>
<td>78.3</td>
</tr>
<tr>
<td>ALA</td>
<td>31.7</td>
<td>34.4</td>
<td>66.0</td>
</tr>
<tr>
<td>BISA</td>
<td>48.1</td>
<td>18.6</td>
<td>66.7</td>
</tr>
<tr>
<td>CARB</td>
<td>46.5</td>
<td>28.4</td>
<td>75.0</td>
</tr>
<tr>
<td>ETH</td>
<td>58.9</td>
<td>17.2</td>
<td>76.1</td>
</tr>
</tbody>
</table>

These lower removal efficiencies, observed in the continuous flow reactor design, can be partly explained by a calculation of the hydraulic retention time (HRT). This parameter describes the mean residence time of the treated solution in the plasma reactor. Since a constant volume (500 ml) was treated for 30 minutes in the batch reactor, the hydraulic retention time is 30 minutes. In the continuous flow reactor design, the hydraulic retention time is calculated according to eq. 7-3:
With $V$ the treated volume in the plasma chamber (400 ml) and $F$ the influent flow rate (66.30 ml min$^{-1}$), a hydraulic retention time of 6.03 min$^{-1}$ was calculated. This was approximately 5 times lower. Therefore, it was expected that the removal efficiency is lower in the continuous flow reactor design than in the batch reactor design. According to eq.7-3, the hydraulic retention time is dependent on the volume in the plasma chamber ($V$), and the water flowrate ($F$). Hence, micropollutant removal in continuous flow design can be easily increased, by decreasing the water flow rate.

Although plasma technology is a promising technique to degrade micropollutants, a possible disadvantage of this AOP is its large energy demand. The costs associated with the plasma treatment are obviously an important factor that should be taken into consideration when selecting the most suitable water polishing method. Since the electrical cost largely contributes to the overall energy cost, an estimation of the electrical energy consumption is important. The energy demand of a certain AOP system can be evaluated using the electrical energy per order figure-of-merit (EEO). This important parameter was already introduced in chapter 2 as the required electrical energy, expressed in kWh, for 90 % conversion of a certain compound, occurring in 1 m$^3$ of water (Bolton et al., 1996). For continuous flow reactors the EEO value is calculated with eq. 2-11. The energy efficiency for plasma destruction was calculated for each compound. These EEO values are highlighted in table 7-4.

**Table 7-4: Energy efficiency expressed as EEO for micropollutant degradation in the plasma reactor**

<table>
<thead>
<tr>
<th>Micropollutant</th>
<th>EEO (kWh/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVOS</td>
<td>12.9</td>
</tr>
<tr>
<td>DIU</td>
<td>23.4</td>
</tr>
<tr>
<td>ATR</td>
<td>27.4</td>
</tr>
<tr>
<td>PCF</td>
<td>17.7</td>
</tr>
<tr>
<td>ALA</td>
<td>26.5</td>
</tr>
<tr>
<td>BISA</td>
<td>19.7</td>
</tr>
<tr>
<td>CARB</td>
<td>7.15</td>
</tr>
<tr>
<td>ETH</td>
<td>15.5</td>
</tr>
</tbody>
</table>

From table 7-4 it can be concluded that the energy efficiency of micropollutant degradation in the plasma reactor can substantially differ among the micropollutants. Plasma destruction was found to be most energy efficient for the removal of the pharmaceutical carbamazepine and the pesticide dichlorvos, as indicated by their low EEO value. Other compounds were less effective removed, as indicated by the higher EEO values. This means that experiment as conducted under the standard conditions, mentioned in table 7-1, requires relative much energy for persistent compounds. For both diuron and alachlor, a higher EEO is found in comparison with the batch experiment (EEO = 23.4 vs 3.9 kWh/m$^3$ for diuron and 26.5 vs 6.1 kWh/m$^3$ for alachlor). The lower
EEO value observed in the batch experiment is attributed to additional plasma gas bubbling in the ozonation chamber. Also, it should be pointed out that the calculated EEO values were obtained from a lab scale test on a synthetic wastewater, contaminated with only the previously mentioned micropollutants. In practice, pilot scale experiments with real wastewater will surely be characterized by the presence of other contaminants and radical scavengers, possibly reducing the energy efficiency of the plasma treatment (Hijosa-Valsero et al., 2013).

7.4 OPTIMIZATION OF OPERATIONAL PARAMETERS

In the standard experiment it was shown that plasma treatment required high energy consumption, especially for the removal of persistent compounds such as pesticides. However, it will be possible to lower the energy consumption by performing an optimization of the operational parameters. In this research the individual effect of different physical and chemical parameters on the energy efficiency of micropollutant removal in continuous flow reactor configuration was investigated by adapting a classical one-parameter-at-a-time approach. The operational parameters studied in this research included the working gas type, gas flow rate, water flow rate, duty cycle, applied power and initial micropollutant concentration. Figure 7-4 illustrates the effect of each individual parameter on the energy efficiency (EEO) for the removal of atrazine. Additional information about the relation between the operational parameters and the energy efficiency for the other compounds is presented in addendum (appendix I).

7.4.1 Effect of the working gas

In order to investigate the effect of the working gas on the energy efficiency, the standard experiment was slightly adapted. Although all parameters mentioned in table 7-1 were held constant, the working gas was changed in order to test the effect on the energy efficiency. Three different working gas types (air, argon and oxygen) were investigated, and results were presented in figure 7-4 (a). As could be seen in figure 7-4 (a), the energy efficiency for atrazine removal decreased in the order oxygen > argon > air. The highest energy efficiency was achieved when oxygen was used as a working gas.

The effect of the working gas has been extensively studied in literature. In most studies, air was used as a feed gas (Kobayashi et al., 2009; Dujčinović et al., 2011; Lesage et al., 2014; Aonyas et al., 2016). Plasma discharges in nitrogen (Feng et al., 2016), oxygen (Bubnov et al., 2007; Mok et al., 2008; Bobkova et al., 2014) and noble gases such as argon and helium (Hijosa-Valsero et al., 2013) were also reported. In most studies, plasma discharges in oxygen were reported as the most energy efficient (Feng et al., 2016). Although argon perform worse than oxygen, it was sometimes recognized as the most energy efficient working gas, especially for the degradation of phenolic compounds (Shiota et al., 2013).

The contribution of the working gas to the observed energy efficiency in the plasma reactor can be interpreted by the relative production of long and short living active species (OH*, O3, H2O2, NO3, NO2, peroxynitrite...) in the bulk liquid. If the plasma discharge was conducted in air, the low
energy efficiency in comparison with argon and oxygen plasmas could be predominately ascribed to scavenging reactions of ozone (O₃) and hydroxyl radicals (OH'). Both species can be scavenged by nitrogen containing species. Especially nitrite (NO₂⁻) is generally considered as the most important scavenger for ozone and hydroxyl radicals. The production of nitrogen containing species was already proven in chapter 6. In the presence of nitrite, ozone is scavenged through the reaction (r.7-1):

\[ \text{O}_3 + \text{NO}_2^- \rightarrow \text{O}_2 + \text{NO}_3^- \]  

For this reaction a relative high reaction rate constant (1.6 - 5.0 x 10⁵ M⁻¹ s⁻¹) has been reported by several authors, indicating its high scavenging potential (Garland et al., 1980; Hoigné et al., 1985). Moreover an acidic environment (pH = 3.17) has been observed in the plasma reactor for plasma discharges in air. This high acidity inhibits further dissolution of ozone in water. Hence, the contribution of ozone to micropollutant degradation in the plasma chamber is expected to be relative small. Furthermore, nitrite is not only a known ozone scavenger, but also a hydroxyl radical scavenger (r. 7-2) (Nikitenko et al., 2004; Son et al., 2011):

\[ \text{OH}^\cdot + \text{NO}_2^- \rightarrow \text{OH}^- + \text{NO}_2^\cdot \]  

The reaction rate of this reaction has been reported in the order \( k = 6.0 - 14 \times 10^5 \). Note that OH' scavenging by nitrite gives rise to the production of NO₂ radicals (NO₂'). A redox potential \( E_0 = 1.04 \) V has been reported for NO₂ radicals, which is significantly lower than the redox potential of hydroxyl radicals (2.80 V). Therefore, its contribution to the degradation of micropollutants in the plasma chamber is considered to be significantly lower.

When the plasma discharge took place in pure oxygen (100 % O₂) vs 21 % O₂ in air, a higher production of OH’ and O₃ in the gas phase is expected. Moreover, ozone and radical scavenging reactions does not occur, since nitrogen containing species are absent. Considering both conditions, it is obvious that oxygen plasmas are related with a relative higher OH’ and O₃ production than in air plasmas. Due to higher concentrations of these active species in oxygen plasmas, a more complete micropollutant removal, and thus higher energy efficiency can be explained.

Plasma discharges in argon does not produce ozone. However, OH’ radical production in argon plasmas is observed, due to electron impact ionization of water molecules. In comparison with air, no nitrogen containing species are produced. Therefore, an energy efficiency in between the energy efficiency for plasma discharges in oxygen and air could be expected.

### 7.4.2 Effect of the gas flowrate

Because optimization of the working gas type has shown that oxygen was the preferred working gas our reactor system was further optimized by changing gas flow rate. Hence, oxygen gas was introduced into the reactor at four different gas flow rates (0.1 SLM, 0.225 SLM, 0.5 SLM and 1 SLM). The influence of the gas flow on the energy efficiency is presented in figure 7-4b. As could be seen in this figure, the energy efficiency for atrazine removal increased from EEO = 25.0 kW/m³
at a flowrate of 1 SLM to a EEO value of 7.55 kW/m³ at a flow rate of 0.1 SLM. The results indicate that a higher gas flow rate exerted a detrimental impact on the energy efficiency of atrazine removal in the reactor. Higher gas flow rates were thus considered as less efficient.

Similar results were found by Feng et al. (2014), who has studied the effect of the oxygen flow rate in a DBD reactor with falling water film on the degradation of Rhodamine B, and concluded that an increase in gas flow rate attributed to a decrease in energy efficiency. However, in another DBD reactor with falling water film, the effect of the oxygen flow on the degradation of methylene blue was found to be not significant on the degradation on methylene blue (Magureanu et al., 2008). In bubble discharges DBD reactors, increases in gas flow usually contribute to higher energy efficiencies, as reported by Reddy et al. (2013) for textile dyes, and Kim et al. (2013) for pharmaceuticals.

### 7.4.3 Effect of the water flowrate

In a next optimization step, the effect of different water flow rates (28.17, 50.42, 66.30, 89.55, 116.0 and 160 ml min⁻¹) was tested. In general, lower water flow rates resulted in higher degradation percentages. Moreover, higher micropollutant removal through adsorption on Zorflex® was observed. Indeed, the application of a higher water flow rate is correlated with a decrease in mean residence time in the active plasma zone (Grinevich et al., 2011; Feng et al., 2016). A higher residence time will result in a more effective degradation of micropollutants, since the probability that micropollutants collide with active species appears to be higher. Consequently, micropollutant degradation will be promoted by lower water flow rates.

Although higher degradation percentages were reached by lower flow rates, it was concluded that a higher water flow rate corresponds with a lower energy efficiency as presented in figure 7-4 (c). Indeed, the water flow rate (F) exerted a large influence on the energy efficiency, as illustrated by the EEO formula (eq. 2-11).

However, only a few studies are conducted to unravel the effect of the water flowrate on the overall degradation efficiency. Only Magureanu et al. (2008) reported about the effect of the water flowrate on the degradation of micropollutants in a DBD reactor. In their research the effect of only two solution flow rates (30 ml min⁻¹ and 90 ml min⁻¹) were studied. In contrast to our experimental findings, the authors reported a slightly higher degradation efficiency at the highest flowrate.

In conclusion, high water flow rates are preferred for obtaining high energy efficiencies in the range of the used settings. Nevertheless, maintaining a high water flow rate would consume high volumes of micropollutant solutions in 30 minutes of optimization experiments. Therefore, the water flow rate was kept at reference setting (66.30 ml min⁻¹) in further optimization experiments.
7.4.4 Effect of duty cycle

At the end of the water flow optimization experiments, residual micropollutant concentrations in the plasma treated samples were very low. Further optimization would obtain final micropollutant concentrations, below GC-MS limit of detections. For this reason, further optimization experiments were performed with an initial micropollutant concentration of 200 ìg l\(^{-1}\) instead of 100 ìg l\(^{-1}\). In a next optimization step, the effect of the different duty cycles, ranging from DC = 0.03 to DC = 0.30 on the energy efficiency is investigated. As pointed out earlier, applied duty cycle represents the percentage of time that power is applied to the reactor. From this point of view, increasing the applied duty cycle will be related with an increase in the total power dissipated in the reactor. The experimental results are presented in figure 7-4 (d). Although the experimental results were variable, the general trend was that the EEO value decreases for lower duty cycles. However, further research in this reactor type is definitely needed to confirm these observations.

Moreover, the effect of applied duty cycle to the energy efficiency of micropollutant decomposition is only poorly described in literature. To the best of our knowledge, Olszewski et al. (2014) was the only group who has reported about the effect of the duty cycle on the degradation of micropollutants. In their research, the effect of a 25 %, 50 % and 75 % duty cycle on the degradation of methyl orange was investigated. A linear decrease in duty cycle from 75 % to 25 % resulted in an increase in energy efficiency with a factor 2.11. Therefore, their conclusions are in line with our experiment results.

7.4.5 Effect of power

As a last factor, the influence of the applied power on the energy efficiency was tested. Building further on the experimental results obtained from the duty cycle optimization, a low duty cycle should be preferred. However, 30 % duty cycle was initially chosen instead of a lower one, in order to test reactor performance during heavy duty cycle conditions. With a constant duty cycle of 0.30, five different power settings (40 W, 52.5 W, 65 W, 77.5 W and 90 W) were used. The results are presented in figure 7-4 (e). For the two highest power settings, residual atrazine concentrations were below GC-MS limit of detection. Therefore, only, results for 40 W, 52.5 W and 65 W are shown in figure 7-4 (e). The total degradation efficiency of atrazine was 98.0 % for a power of 40 W and 99.6 % for a power of 65 W. Although residual atrazine concentrations drastically dropped with increased power, the EEO value raised slightly with increasing power, indicating a less energy efficient atrazine removal. Hence it could be concluded that, within the tested power settings, a low power should be preferred as most energy efficient setting. The limited effect of power on EEO indicates power as the control parameter of preference for applications where removal percentage should be adjusted according to the influent micropollutant concentrations.

As the power increases, electrons produced by the plasma discharges will gain more electrical energy from the electric field. Therefore, more gas molecules will be ionized through electron
impact ionization (Zhang et al., 2007; Rong & Sun, 2014). Eventually, this will induce a higher production of active species production in the gas and liquid phase and stronger micropollutant decomposition.

7.4.6 Effect of the initial concentration

In order to check the limited dependence of EEO on initial concentration, the influent concentration was varied. Figure 7-4 (f) shows the energy efficiency of atrazine degradation by different initial concentrations (50 µg l⁻¹, 100 µg l⁻¹, 200 µg l⁻¹ and 300 µg l⁻¹). In this concentration range, only a small increase in EEO was observed (EEO = 5.38 for 50 µg l⁻¹ EEO = 7.21 for 300 µg l⁻¹). Therefore, EEO is indeed a useful comparative parameter between different reactors.

Figure 7-4: Optimization of operational parameters for the removal of atrazine
7.5 CONCLUDING REMARKS

In the previous section, the influence of several operational parameters on the energy efficiency of micropollutant removal in a DBD plasma reactor was discussed. Starting from reference settings, the individual effect of each parameter on the energy efficiency was investigated. Table 7-6 summarizes the overall optimization process and the increase in energy efficiency for all micropollutants. In the first row of table 7-6 calculated EEO values are presented for micropollutant removal under standard settings (working gas: air, gas flow rate 1 SLM, water flow rate: 66.30 ml min$^{-1}$, initial concentration: 100 µg l$^{-1}$, duty cycle 0.15 and power 40 W). The initial EEO values varied between 12.9 kWh/m³ for dichlorvos, and 27.4 kWh/m³ for atrazine. Subsequently, Table 7-6 presents the most optimal EEO value for each series of experiments described in sections 7.4.1 to 7.4.5. In brackets, the percentage of decrease in EEO is given as compared to the EEO corresponding to the reference value of the varied parameter in the same series of experiments.

Because there was worked with unoptimized settings for water flow and duty cycle during the last experiments, an accurate determination of EEO values after full reactor optimization is not performed. Instead, the lowest observed EEO value for optimal working gas, gas flow rate and water flow rate parameters is considered as the most optimal EEO value. These values are reported in the last line of table 7-6. Note that working with an optimized duty cycle of 0.03 will definitely lead to lower EEO values. Within the range of the investigated parameters, it was concluded that the gas flow rate, and the applied duty cycle exerted the highest impact on the increase in energy efficiency. The influence of the applied working gas, on the other hand, was rather limited, especially for atrazine (16.0 % decrease in EEO) and diuron (25.7 % decrease in EEO). However, other micropollutants, i.e. 1,7-α-ethinylestradiol were more effectively degraded when the plasma discharge was performed in oxygen (47.2 % decrease in EEO).

Generally, a decrease in gas flow from 1 SLM to 0.1 SLM resulted in a strong decrease in EEO for DIU, ATR, ALA, BISA. However, the gas flow had less influence, on a decrease in energy efficiency for dichlorvos and 1,7-α-ethinylestradiol. A comparable behaviour was found for the duty cycle. The average increase in energy efficiency was around 45 % for DVOS, DIU, ATR, ALA & BISA, in comparison with the reference setting (DC = 0.15). For 1,7-α-ethinylestradiol, the influence of the duty cycle was even higher (69.4 % decrease in EEO).
0.1 SLM | (29.3 %) | (60.5 %) | (69.8 %) | (72.4 %) | (55.6 %) | (34.4 %)
---|---|---|---|---|---|---
Water flow: 160 ml min\(^{-1}\) | 2.82 (45.7%) | 3.49 (45.9%) | 4.16 (42.5%) | 3.88 (42.3%) | 3.34 (48.5%) | 3.64 (27.3%)
DC: 0.03 | 2.71 (47.6%) | 3.52 (45.7%) | 4.35 (39.2%) | 3.75 (45.1%) | 2.80 (56.3%) | 1.04 (69.4%)
P: 40 W | 4.72 | 5.46 | 5.78 | 5.62 | 5.24 | 4.44
Optimal EEO | < 2.82 | < 3.49 | < 4.16 | < 3.88 | < 3.34 | < 3.64

Based on the data presented in table 7-6, and the relationships between the operational parameter settings and measured energy efficiency (figure 7-4), it could be concluded that the reactor was working most energy efficient for the following settings: gas type oxygen, gas flowrate 0.1 SLM, water flowrate 160 ml.min\(^{-1}\), duty cycle 0.03 and power 40 W.

### 7.6 TOXICITY

Potential implementation of AOP systems in an existing wastewater treatment plant does not only depend on the energy efficiency, but also on the toxicity of the reactor effluent. In this regard, additional attention was paid on toxicity testing of plasma treated water. Three experiments were performed in single pass reactor configuration with air, argon and oxygen as working gas. Other operational parameters were kept at reference settings (gas flow 1 SLM, water flow 66.30 ml min\(^{-1}\), concentration 100 µg l\(^{-1}\), duty cycle 0.15 and power 40 W). These settings were estimated to result in significant differences in the effluent toxicity for the different gases, while these differences were expected to be smaller at the optimized conditions. In order to measure the toxicity after micropollutant adsorption on Zorflex®, a first sample was taken before plasma was turned on. The total collected volume was 1000 ml. In order to investigate the effect of long living oxidants on the toxicity of plasma treated water, half of the sample volume (500 ml) was boiled. The other part was left untreated. Subsequently, plasma was turned on, and another 1000 ml was collected. Again, half of the sample volume was boiled, and to other part was left untreated.

Effluent toxicity of all samples was tested by a grow rate inhibition test on micro-algae (P. subcapitata), in accordance with the OECD guideline for growth inhibition toxicity tests with algae and cyanobacteria (OECD, 2016). All toxicity tests were performed at three dilution levels (0x, 10x and 100x), over a total period of 3 days. These dilutions were prepared by serial dilution from the initial micropollutant solution (100 µg l\(^{-1}\)), before toxicity testing.

Since the presence of toxic compounds could induce algae death, toxicity was tested by observation of algae growth kinetics. Exponential growth of the algae population can be described by a first order kinetics (Kessick, 1974) (eq. 7-4):

\[
\frac{dX}{dt} = \mu X \\
\text{eq. 7-4}
\]
With \( X \) the algae concentration at time \( t \) (days), and \( \mu \) the algae growth rate (d\(^{-1}\)). By integrating and rearranging eq.7-4, an expression is obtained which enables algae growth rate calculation from the experimental data (eq. 7-5):

\[
x = x_0 e^{\mu t}
\]

\( x_0 \) is the initial cell density, \( \mu \) the specific growth rate (d\(^{-1}\)) and \( t \) the total duration of the toxicity test (3 days). After 3 days of operation (72 h) cell densities were measured and algae growth rates were calculated. If toxic compounds were present in the test mixture, inhibition of algae growth could be experimentally observed by a decay in specific growth rate (\( \mu \)). Hence, the observed growth rate after three days (72 h) of toxicity testing, is an indicator of overall mixture toxicity. For the adsorption and plasma experiments calculated average growth rates, as obtained after three days of exposure, are presented in figure 7-5.

In figure 7-5 (a), algae average growth rates after 3 days of exposure are shown for the liquid sample, collected after adsorption on Zorflex textile®. These samples did not undergo any plasma treatment. In comparison to the initial sample, experimentally determined average algae growth rates are significantly higher in the unboiled samples. Therefore the toxicity of the samples was lower than in the initial micropollutant mixture. This was expected, since Zorflex® has shown excellent adsorptive capacity, as already pointed out in chapter 7, section 7.1. Remarkably, the boiled samples have shown a higher toxicity of the initial mixture. This can be explained as follows. Micropollutants are only partially adsorbed on Zorflex® in single pass experiments. For most micropollutants the average adsorption was determined around 50 % (see table 7-3). Thus, significant amounts - up to half of the initial micropollutant concentration – should be expected to remain still unremoved in the liquid phase. By boiling the samples, micropollutant decomposition could be initiated through thermal degradation. Possibly, toxic compounds are formed in this thermal degradation process, and thus largely increasing the overall sample toxicity.

Figures 7-5 (b) and 7-5 (c) give the toxicity results for plasma treated samples with argon and air used as working gas, respectively. For both working gases, comparable growth rates at the 0x and 10x dilution were observed. However, average algae growth rates were significantly lower at the 100x dilution, relative to the growth rate measured in the initial sample. Furthermore boiling the samples had not much influence on the average growth rate. Accordingly, it is assumed that plasma discharges in air and argon induce a higher toxicity of the plasma treated samples due to the formation of long-living aqueous oxidants or toxic by-products.

In contrast to the plasma discharges in air and argon, application of oxygen as discharge medium resulted in lower sample toxicity of the plasma treated samples, in comparison with the initial mixture. The lowest toxicity, as indicated by the highest algae growth rate, was observed in the boiled sample. (figure 7-5 (d)). These results confirmed that plasma treated samples with oxygen significantly reduces the effluent toxicity.
Based on the experimental findings, presented in figure 7-5 it was concluded that plasma discharges in air and argon resulted in a toxicity level which was higher than the original toxicity of the initial mixture. Probably, toxicity increase for treatment with air and argon can be attributed to the formation of harmful by-products. Indeed, a complete micropollutant mineralization of micropollutants due to interaction plasma treatment is rarely achieved. Consequently, plasma treatment will produce some by-products. These by-products can potentially have a higher toxicity than the original micropollutants. However, little is known about the exact decomposition mechanism of micropollutants by plasma technology. Further research is definitely needed to unravel the contribution of by-product formation on the initial toxicity.

There is still some lack about literature data for toxicity tests after plasma treatment. Moreover, no comparative toxicity tests are reported for non-thermal plasma treatment with air, argon and oxygen plasmas. However, some reports about air plasmas are available in literature. Nevertheless, mostly easily degradable test compounds such as phenolic compounds and textile dyes were used. For example, Dojcinovic et al. (2011) studied the effect of DBD plasma treatment in air on the toxicity of three different textile dyes (Reactive Black 5, Reactive Yellow 125 and Reactive Green 15). Textile dyes were applied in high initial concentration, varying between 50 – 100 mg L⁻¹. Only a low toxicity on *A.Salina* was reported for Reactive Green 15 (10 % mortality), whereas zero mortality was found for Reactive Black 5 and Reactive Yellow 125. Furthermore,
Krugly et al. (2015) showed that DBD plasma in air raised the initial toxicity of 2-naphtol with only 5%.

In comparison with non-thermal plasma, other AOPs are more frequently investigated. Especially the effect of ozonation on the effluent toxicity has been extensively studied. Most studies reported a decrease in toxicity after ozonation (Reungoat et al., 2011; Margot et al., 2013). Contrarily, other studies reported about an increase in toxicity (Petala et al., 2008; Magdebrug et al., 2012). Interestingly, Petala et al. found that the toxic potential of treated effluent significantly increased when high ozone doses were applied. According to these findings, it might be assumed that effluent toxicity is largely affected by the amount of active species, produced by the AOP process. Since the relative production of active species is influenced by the operational parameter settings, reactor optimization in function of effluent toxicity might be interesting.

Based on the current toxicity results, plasma discharges in air and argon in single pass reactor configuration should be avoided as a stand-alone technique for water treatment. However, higher effluent toxicity does not necessary indicate a lower biodegradability of the wastewater. This makes plasma treatment still feasible as a pre-treatment method for wastewater treatment, prior to biodegradation in MWWTPs (Comninellis et al., 2008; Mantzavinos & Psillakis, 2004).
Chapter 8  Optimization of reactor configuration

In the previous chapter, a DBD plasma reactor with moving water film and activated carbon textile was optimized for the removal of 8 micropollutants from a synthetic wastewater. The following operational parameters were found to yield the highest energy efficiency: working gas oxygen, gas flowrate 0.1 SLM, water flowrate 66.30 ml min⁻¹, duty cycle: 0.03 and applied power: 40 W. When these optimal settings are applied an optimal EEO value of 4.16 kWh/m³ for removal of atrazine was found. A comparison with literature data showed that the determined energy efficiency was comparable with other reactor systems used for atrazine degradation. Energy efficiency of atrazine removal in different plasma reactors described in literature is reported in table 8-1. Based on the calculated EEO values, it was found that only one plasma reactor performed a better energy efficiency than our optimized reactor system. The most energy efficient plasma reactor consists of a gas phase plasma reactor based on a corona discharge over a falling water film. Moreover, this reactor was the only plasma reactor which operated in single pass configuration. For this reactor system, an EEO value of 3.7 kWh/m³ was calculated for the removal of atrazine (Gerrity et al., 2010).

Table 8-1: Energy efficiency for the removal of atrazine in different plasma reactor systems, adapted from Vanraes et al., (2015b)

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Initial concentration (mg l⁻¹)</th>
<th>EEO (kWh/m³)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulsed corona over water film</td>
<td>0.0011</td>
<td>3.7</td>
<td>(Gerrity et al., 2010)</td>
</tr>
<tr>
<td>AC DBD in oxygen over falling water film with Zorflex*</td>
<td>0.1</td>
<td>4.16</td>
<td>Our work (optimized settings)</td>
</tr>
<tr>
<td>Pulsed corona in liquid phase</td>
<td>5</td>
<td>4.9</td>
<td>(Mededovic &amp; Locke, 2007)</td>
</tr>
<tr>
<td>AC DBD in air</td>
<td>21.6</td>
<td>19.7</td>
<td>(Feng et al., 2016)</td>
</tr>
<tr>
<td>Pulsed arc in liquid phase</td>
<td>0.11</td>
<td>19.7</td>
<td>(Karpel Vel Leitner et al., 2005)</td>
</tr>
<tr>
<td>AC DBD in air over falling water film with Zorflex*</td>
<td>0.1</td>
<td>27.4</td>
<td>Our work (standard settings)</td>
</tr>
<tr>
<td>AC DBD in He over falling water film</td>
<td>5.0</td>
<td>50.6</td>
<td>(Maria Hijosa-Valsero et al., 2013)</td>
</tr>
<tr>
<td>Pulsed corona over water surface</td>
<td>25.9</td>
<td>72.3</td>
<td>Hoeben et al., (2000)</td>
</tr>
<tr>
<td>Ac corona for ionized air bubbling</td>
<td>5.0</td>
<td>86.9</td>
<td>(Wohlers et al., 2008)</td>
</tr>
<tr>
<td>DBD for UV irradiation and ionized air bubbling</td>
<td>5.8</td>
<td>106</td>
<td>(Zhu et al., 2014)</td>
</tr>
</tbody>
</table>
8.1 OPTIMIZATION OF REACTOR CONFIGURATION

Although already an excellent energy efficiency was reached with the optimized plasma reactor system, further increase in energy efficiency is still possible by slightly adapting the reactor configuration. This was tested in a next series of experiments. To this end, the single pass reactor configuration (1P) used in the optimization experiments, described in previous chapter, was adapted to three alternative reactor configurations, denoted as the 1O, 1P2O and 1O2P reactor configuration. All these alternative reactor designs operated in single pass mode. Information about the exact reactor operation was explained in the materials and methods section (see section 4.3.2). Briefly, for the 1O reactor configuration, micropollutant solution was introduced in the ozonation chamber. Next, working gas (air and argon) was introduced in the plasma reactor, and plasma gas (mainly containing ozone) was produced when plasma was applied. Note that in the 1O configuration deionized water was introduced into the plasma reactor, instead of micropollutant solution. Subsequently, produced plasma gas was bubbled through the micropollutant solution.

The 1P2O and 1O2P reactor configurations were constructed in order to investigate the synergetic effect of plasma treatment with additional plasma gas bubbling. In the 1P2O reactor, the micropollutant solution was first treated with plasma in the plasma chamber, and subsequently transferred to the ozonation chamber. There, plasma gas produced in the ozonation chamber was bubbled through the micropollutant solution. In the 1O2P configuration, the micropollutant solution was first ozonated with plasma gas produced in the plasma reactor and subsequently treated with plasma in the plasma chamber.

All experiments were conducted in single pass configuration, with following settings: working gas oxygen, gas flowrate 1 SLM, water flowrate 66.30 ml min$^{-1}$, duty cycle 0.15 and power 40 W. The initial micropollutant concentration was set on 200 µg L$^{-1}$. Note that non-optimized settings were used in these series of experiments. Figure 8-1 shows the effluent concentration for atrazine in function of treatment time for the reactor configurations 1O, 1P, 1P2O and 1O2P. Note that all experiments were performed in single pass mode, resulting in the measurement of equilibrium concentrations, instead of reaction kinetics.

Steady state concentrations were achieved in all reactor configurations, within the first 10 minutes of operation. In all reactor configurations, the application of oxygen as plasma discharge medium resulted into the highest atrazine removal efficiency (1P: 65.6 %, 1P2O: 94.2 %, 1O2P: 95.4 %). Further, the highest removal efficiency for atrazine decomposition was achieved when the 1O2P configuration was used (95.4 %). Similar results were found for the other micropollutants (data not shown).
Additionally, energy efficiency was calculated for micropollutant decomposition in the different reactor designs 1P, 1O, 1P2O and 1O2P, and for different working gases (oxygen, argon and air) tested in this research. For discharges in air, argon and oxygen the results are shown in figures 8-2 to 8-4, respectively. Due to the synergetic effect of plasma treatment with subsequent ozonation, highest energy efficiencies were achieved in the 1P2O and 1O2P configurations. For all micropollutants and all working gases, it was found that the EEO values decreased in the order:

1O > 1P > 1P2O > 1O2P

Moreover, the application of oxygen gas as discharge medium yielded the lowest EEO values. Highest EEO values were found for discharges in air. Moreover, the results presented in figures 8-2 – 8-4 reveal that plasma treatment combined with additional ozonation significantly enhances the energy efficiency of our reactor system. Both the 1P2O and 1O2P reactor configurations show a better energy efficiency than only plasma treatment (1P). Only ozonation (1O) of micropollutants resulted in very poor removal efficiencies for most micropollutants. This was illustrated by the high EEO values, especially for persistent pesticides such as atrazine, alachlor and diuron. The low energy efficiency is the result of a poor micropollutant decomposition efficiency by direct ozonation.
Figure 8-2: Comparison of micropollutant removal in 1O, 1P, 1P2O and 1O2P reactor configurations for plasma discharges in air.

Figure 8-3: Comparison of micropollutant removal in 1O, 1P, 1P2O and 1O2P reactor configuration for discharges in argon.
Micropollutant degradation efficiency mainly depends on two factors: the value of the second order reaction rate constant for the reaction of micropollutants with ozone ($k_{O3}$), and the amount of ozone dissolved in the liquid phase. No ozone concentrations in the gas and liquid phase were measured in this work. According to a general view in literature, it was found that $k_{O3}$ values for reactions of micropollutants with ozone are quite low for most micropollutants. Typical values between $10^{-5}$ and $1.6 \times 10^9$ M$^{-1}$s$^{-1}$ are reported (Jin et al., 2012; Sudhakaran & Amy, 2013; Von Gunten, 2003). Table 8-2 gives an overview of all $k_{O3}$ values for the micropollutants investigated throughout this work.

### Table 8-2: Overview for first order reaction rate constants of ozone with micropollutants studied in this work

<table>
<thead>
<tr>
<th>Micropollutant</th>
<th>$k_{O3}$ (M$^{-1}$s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>3.8</td>
<td>Von Gunten et al. (2003)</td>
</tr>
<tr>
<td>Atrazine</td>
<td>6.0</td>
<td>Acero et al. (2000)</td>
</tr>
<tr>
<td>Diuron</td>
<td>19.02</td>
<td>Solis et al. (2016)</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>10.05</td>
<td>Kim &amp; Moon (2000)</td>
</tr>
<tr>
<td>Dichlorvos</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bisphenol a</td>
<td>$1.6 \times 10^9$</td>
<td>Umar et al. (2013)</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>$3.10^5$</td>
<td>Huber et al. (2003)</td>
</tr>
<tr>
<td>1,7-α-ethinylestradiol</td>
<td>$3.10^6$</td>
<td>Huber et al. (2003)</td>
</tr>
</tbody>
</table>

For alachlor, atrazine, diuron and pentachlorophenol, very low $k_{O3}$ values, ranging between 3.8 – 19.02 M$^{-1}$ s$^{-1}$ were found. Due to the very low $k_{O3}$ values a slow reaction between ozone and these micropollutants is assumed. Contrarily, significant higher $k_{O3}$ values ($10^6$ - $10^9$ M$^{-1}$ s$^{-1}$) are typically reported for reactions of ozone with pharmaceutical compounds (Huber et al., 2003; Von Gunten et al., 2003). Therefore, micropollutant decomposition occurs in a very selective way. Micropollutants with a high $k_{O3}$ value are rapidly degraded, whereas micropollutants with a low...
$k_{O3}$ value tend to react slowly with ozone. This can also be seen in figure 8-2. For compounds with a low $k_{O3}$ value (atrazine, diuron and alachlor) EEO values higher than 60 kWh/m³ were reported, indicating a low energy efficiency. Lower EEO values ( EEO < 40 kWh/m³) are found for carbamazepine, 1,7-α-ethinylestradiol and bisphenol A, showing a more energy efficient micropollutant elimination. If argon gas was used in the 1O configuration, almost no micropollutant degradation was observed. Indeed, plasma discharges in argon do not yield any ozone production (Shainsky et al., 2012).

Plasma treatment in the plasma reactor (1 P), on the other hand, resulted in a significant higher micropollutant removal and energy efficiency. Micropollutant decomposition in the plasma chamber is the result of a complex interaction between micropollutants and a wide spectrum of oxidative species, combined with other chemical phenomena such as UV radiation (Ghezzar et al., 2013; Jiang et al., 2014). The synergetic effect of all chemical species produced by the DBD plasma discharge creates a very unselective environment. Often, the hydroxyl radical is referred to as the major chemical species. The unselective nature of hydroxyl radicals is illustrated by the high $k_{OH}$ values ($> 10^9$ M⁻¹ s⁻¹) for reactions with micropollutants. For each micropollutant used in this work, the $k_{OH}$ value is highlighted in table 8-3. By comparing, the $k_{O3}$ and $k_{OH}$ values, presented in table 7-2 and 7-3 respectively, it is seen that the $k_{OH}$ values are a lot higher than the $k_{O3}$ values, indicating a faster decomposition with OH radicals. This is certainly the case for alachlor, atrazine, diuron and pentachlorophenol. Bisphenol A, carbamazepine and 1,7-α-ethinylestradiol exert higher $k_{O3}$ values (1.6 . 10⁹, 3.10⁵ and 3.10⁶ M⁻¹.s⁻¹, respectively), but even for these compounds the $k_{OH}$ second order reaction rate constants are still higher (1.0 . 10¹⁰, 8.8 .10¹⁰ and 9.8 10⁹ M⁻¹.s⁻¹, respectively). Hence, micropollutant degradation by plasma alone was expected to be more energy efficient than micropollutant degradation by direct ozonation alone, which is in agreement with our experimental findings.

<table>
<thead>
<tr>
<th>Micropollutant</th>
<th>$k_{OH}$ (M⁻¹s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>3.0 . 10⁹</td>
<td>Acero et al. (2000)</td>
</tr>
<tr>
<td>Diuron</td>
<td>6.6 . 10⁹</td>
<td>Solis et al. (2016)</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>3.7 . 10⁹</td>
<td>Weavers et al. (2000)</td>
</tr>
<tr>
<td>Dichlorvos</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>1.0 . 10¹⁰</td>
<td>Rosenfeldt et al. (2004)</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>8.8 . 10⁹</td>
<td>Huber et al. (2003)</td>
</tr>
</tbody>
</table>

A comparison of the reactor configurations 1P2O and 1O2P with only plasma treatment in the plasma chamber (1P), revealed that both the 1P2O and 1O2P reactor configurations were much more energy efficient. The 1O2P process was found to be the most energy efficient reactor configuration. The superiority of the 1O2P configuration in terms of energy efficiency could be related to the specific chemical reactions, occurring in the plasma and the ozone chamber.
In the 1P2O reactor configuration, the influent is first treated in the plasma chamber. There, various chemical species are formed in the liquid phase. In air plasmas, OH\(^\cdot\) radicals, ozone (O\(_3\)) and hydrogen peroxide (H\(_2\)O\(_2\)) are formed as reactive oxygen species. Due to the presence of nitrogen in air, nitrogen containing species such as nitrate (NO\(_3\)), nitrite (NO\(_2\)) and peroxynitrite (ONOO\(^-\)) are also produced in the bulk liquid through different reactions, as already explained in chapter 6. In oxygen plasmas, only oxygen species (OH\(^\cdot\), O\(_3\) and H\(_2\)O\(_2\)) are formed. Furthermore, oxygen plasmas are characterized by a higher O\(_3\) production. Hence, the more energy efficient micropollutant degradation in oxygen plasmas is ascribed to a higher active species production, combined with less scavenging reactions, due to the absence of nitrite and nitrate. The exact scavenging mechanisms were extensively described in section 7.4.1.

In a next step, the plasma treated solution is transported to the ozonation chamber, and subsequently bubbled through with the exhausted plasma gas (mainly ozone). During ozonation of the solution treated with plasma gas, ozone in the plasma gas reacts with residual hydrogen peroxide, present in the plasma treated water. This chemical process is known as the peroxone process (Merényi et al., 2010). Micropollutant degradation in the peroxone process is initiated by the rapid dissociation of hydrogen peroxide into hydrogen (H\(^+\)) and hydroperoxyl (HO\(_2\)) ions:

\[
H_2O_2 \leftrightarrow HO_2^- + H^+ \quad \text{r. 8-1}
\]

Next, hydroperoxyl ions initiate further ozone decomposition through a series of reactions (r. 8-2 – r. 8-5):

\[
\begin{align*}
\text{r. 8-2:} & \quad HO_2^- + O_3 \rightarrow HO_2^+ + O_3^- \\
\text{r. 8-3:} & \quad HO_2^+ \leftrightarrow O_2^+ + H^+ \\
\text{r. 8-4:} & \quad O_3^- + H^+ \leftrightarrow HO_2^+ \\
\text{r. 8-5:} & \quad HO_2^+ \rightarrow O_2 + OH^+
\end{align*}
\]

Ideally, 1 mole of hydrogen peroxide reacts with 2 mole of ozone to yield 2 mole hydroxyl radicals and 3 mole oxygen gas (r. 8-6):

\[
2O_3 + H_2O_2 \rightarrow 2OH^+ + 3O_2 \quad \text{r. 8-6}
\]

Thus, in addition to the production of OH\(^\cdot\) radicals in the plasma chamber, a significant amount of OH\(^\cdot\) radicals is produced in the peroxone process. This higher OH\(^\cdot\) production is the reason for the higher atrazine degradation and the higher energy efficiency, in comparison with only plasma treatment in the plasma chamber.

On the other hand, in the 1O2P process, the micropollutant solution is first ozonated in the ozone chamber with plasma gas generated in the plasma chamber. If air or oxygen is used as discharge medium, the plasma gas contains mainly ozone. When the plasma gas is introduced in the ozonation chamber, self-decomposition of ozone is initiated due to slight alkaline conditions.
(initial pH micropollutant solution = 8.49). It gives rise to the production of multiple radical species, such as OH• and OH₂• (Beltran, 2003).

The different chemical species formed during the decomposition of ozone enhance micropollutant decomposition. In contrast to the 1P2O reactor configuration, no nitrogen containing species are present in the ozonation chamber. Therefore, radical scavenging by NO₂⁻ is supposed to be negligible. Subsequently, additional micropollutant elimination is achieved by interaction between micropollutants and active species produced in the plasma chamber. Due to the absence of scavenging reactions, this configuration is the most optimal one.
Chapter 9  Conclusions and future perspectives

9.1 CONCLUSIONS

In the present research, the applicability of a DBD plasma reactor with moving water film and Zorflex® textile was investigated for the degradation of eight micropollutants (dichlorvos, diuron, atrazine, pentachlorophenol, alachlor, bisphenol A, carbamazepine and 1,7-α-ethinylestradiol) in a synthetic medium. In order to get a deeper understanding about the generation of active species in the gas phase and the micropollutant decomposition mechanisms occurring in the liquid phase characterization techniques such as optical emission spectroscopy, and pH – conductivity measurements were applied.

Because the future implementation of any certain advanced treatment will be largely dependent on the energy efficiency of the system, micropollutant removal in the plasma chamber was optimized in function of the energy efficiency. The influence of different operational parameters, including the working gas, gas flow rate, water flow rate, duty cycle, applied power and initial concentration) on the energy efficiency of micropollutant removal was studied. In a first experiment with standard settings (gas type: air, gas flowrate: 1 SLM, water flowrate: 66.30 ml min⁻¹, initial concentration: 100 µg l⁻¹, duty cycle 0.15 and power: 40 W), an initial EEO value of 27.4 kWh/m³ was observed for the removal of atrazine. An investigation of the effect of individual settings on the degradation of micropollutants showed that the most energy efficient removal of micropollutants was observed if oxygen was applied as working gas. Further, a decrease in gas flowrate and duty cycle combined with an increase in water flowrate had a huge impact on an energy efficiency, whereas the influence of power was rather limited. Furthermore, following parameter settings will led to the most efficient micropollutant degradation: gas type: oxygen, gas flowrate: 0.1 SLM, water flow rate: 160 ml min⁻¹, duty cycle 0.03 and power: 40 W. The concentration only had a small effect on the EEO value. After method optimization, a final EEO value of 4.16 kWh/m³ was found for atrazine, which correlates with an overall increase in energy efficiency of 84.8 % in comparison with the EEO value calculated under reference settings. Similar effects were observed for the removal of other investigated compounds. Hence, it could be reasonably concluded that operational parameter optimization is a very effective way to enhance the energy efficiency of the DBD plasma reactor. Moreover, comparison of the energy under optimal settings, showed that our reactor system performed well in comparison with other reactor systems described in literature. Only one plasma reactor yielded a better energy efficiency for the removal of atrazine (EEO = 3.7 kWh/m³) than the optimized plasma reactor studied in this research (EEO = 4.16 kWh/m³).

Fortunately, the overall reactor performance could be further enhanced. This was tested in a next series of experiments. To this end, the single pass reactor configuration was slightly adapted. With our reactor system, three alternative configurations could be constructed. In the first construction only ozonation with plasma gas, produced in the plasma chamber was performed. This experiment was referred to as the 1O reactor configuration. Comparison with the initial standard experiment in the plasma chamber revealed the energy efficiency for ozonation of atrazine was
higher (EEO, 1O = 63.2 kWh/m³, EEO, 1P = 28.4), and thus less efficient. The combined effect of plasma treatment with ozonation was also studied. Two reactor configurations were possible. In the first reactor configuration, the micropollutant solution was first ozonated and subsequently treated with plasma (1O2P). In the second reactor configuration, the solution and subsequently ozonated with plasma gas produced in the plasma chamber (1P2O). From both experiments, it could be concluded that plasma treatment, combined with additional plasma gas bubbling through the micropollutant solution resulted in a better micropollutant degradation, and hence a higher energy efficiency. It was found that the EEO value was in both cases lower than when only plasma treatment was applied (EEO, 1P2O = 8.12 kWh/m³; EEO, 1O2P = 6.73 kWh/m³). The best, i.e. most energy efficient results were thus observed when the ozone chamber was placed before the plasma chamber (1O2P configuration), due to the absence of scavenging reactions by nitrites and nitrates.

Next to the energy efficient removal of micropollutants, toxicity testing of plasma treated water is important. In this regard, reactor effluent toxicity, is tested after plasma discharges in air, argon and oxygen. It was found that plasma discharges in air and argon resulted in a higher effluent toxicity, in comparison with the original micropollutant mixture toxicity. On the other hand, plasma discharges in oxygen significantly decreased the effluent toxicity. Moreover, in all cases (air plasmas, argon plasmas and oxygen plasmas) it was observed that boiling the initial sample resulted into a decrease in effluent toxicity. This indicates that the presence of long living oxidants, such as hydrogen peroxide and peroxynitrite influence the effluent toxicity in an important way, although also toxic by-product formation by thermal decomposition can play a role.

9.2 FUTURE PERSPECTIVES

Based on the presented results in this work, it can be concluded that plasma assisted destruction of micropollutants is a promising alternative AOP for water treatment, as indicated by the high degradation percentages and energy efficiencies. Although much research is done, and the research results are promising, future investigation of plasma for water treatment is still needed.

First, it should be emphasized that still very little is known about the gas phase chemistry, occurring in the plasma. A more complete understanding about these phenomena should enhance general knowledge about the mechanisms contributing to micropollutant decomposition in the liquid phase. Future application of plasma technology for water treatment will be dependent on the energy efficiency of micropollutant degradation. Hence, reactor optimization will be important. Although reactor optimization was already initiated in this research it was concluded that further improve in terms of energy efficiency is still possible. Since it was found that the single pass 1O2P configuration was more efficient than the 1P single pass configuration, further research should concentrate on the optimization of this reactor configuration. Furthermore, there is still a general lack on literature data about the toxicity of plasma treated water. In this regard a preliminary experiment was already performed in our research group, and the first results reveal that plasmas generated in oxygen may significantly contribute to a
decrease in effluent toxicity. However, plasma discharges in argon and air yielded a higher effluent toxicity in comparison with the initial mixture. With toxicity testing, the observed increase in toxicity could not be addressed to one single component. Therefore, further investigation of possible harmful by-product formation in the liquid phase could be interesting. This can be achieved by advanced chromatographical techniques such as GC-MS and LC-MS. When all further experimental results are promising, the treatment of real wastewater streams in large scale reactors will be the next step. Further optimization of process efficiency will be needed since real wastewater contains a multitude of chemicals and lower degradation and energy efficiencies could be expected.
References


104


VERLICCHI, P., AL AUKIDY, M., & ZAMBELLO, E. (2012). Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment-A


XU, P., BELLONA, C., & DREWES, J. E. (2010). Fouling of nanofiltration and reverse osmosis membranes during municipal wastewater reclamation : Membrane autopsy results from pilo-


Addendum 1

A. DICHLORVOS

a) Gas type

b) Gas flow

c) Water flow

d) Duty cycle

e) Power

f) Concentration
B. DIURON

![Graphs showing the effect of different factors on EEO (kWh/m³)]

- **a) Gas type**
  - Bars representing different gases (Air, Argon, Oxygen) show varying EEO values.
- **b) Gas flow**
  - Line graph showing increasing EEO with increasing gas flow.
- **c) Water flow**
  - Line graph showing decreasing EEO with increasing water flow.
- **d) Duty cycle**
  - Line graph showing increasing EEO with increasing duty cycle.
- **e) Power**
  - Line graph showing increasing EEO with increasing power.
- **f) Concentration**
  - Line graph showing increasing EEO with increasing concentration.
C. ALACHLOR

![Graph a) Gas type]

Micropollutant:
- Air
- Argon
- Oxygen

![Graph b) Gas flow]

![Graph c) Water flow]

![Graph d) Duty cycle]

![Graph e) Power]

![Graph f) Concentration]
D. BISPHENOL A

a) Gas type

b) Gas flow

c) Water flow

d) Duty cycle

e) Power

Concentration

Micropollutant

- ATR
- ALA
- DIU
- BSA
- PCE
- ETH
- DVS
- CBB

- Air
- Argon
- Oxygen

EEO (kWh/m³)

EEO (kWh/m³)

EEO (kWh/m³)

EEO (kWh/m³)

EEO (kWh/m³)

EEO (kWh/m³)

EEO (kWh/m³)

EEO (kWh/m³)

Water flow (ml/min)

Gas flow (sccm)

Duty cycle

Power (W)

Concentration (µg/l)
E. 1,7-A-ETHINYLESTRADIOL

a) Gas type

b) Gas flow

c) Water flow

d) Duty cycle

e) Power

f) Concentration
F. PENTACHLOROPHENOL

![Graph showing gas flow vs. EEO (kWh/m³) for Pentachlorophenol.]

G. CARBAMAZEPINE

![Graph showing gas flow vs. EEO (kWh/m³) for Carbamazepine.]