LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
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Master's Degree Program in Environmental Technology

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COMBINATION OF PULSED CORONA DISCHARGE WITH TiO$_2$ PHOTOCATALYSIS: VERIFICATION OF HYPOTHESIS

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ABSTRACT

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The oxidation potential of pulsed corona discharge concerning aqueous impurities is limited in respect to certain refractory compounds. This may be enhanced in combination of the discharge with catalysis/photocatalysis as developed in homogeneous gas-phase reactions. The objective of the work consists of testing the hypothesis of oxidation potential enhancement in combination of the discharge with TiO$_2$ photocatalysis applied to aqueous solutions of refractory oxalate. Meglumine acridone acetate was included for meeting the practical needs. The experimental research was undertaken into oxidation of aqueous solutions under conditions of various target pollutant concentrations, pH and the pulse repetition rate with plain electrodes and the electrodes with TiO$_2$ attached to their surface. The results showed no positive influence of the photocatalyst, the pollutants were oxidized with the rate identical within the accuracy of measurements. The possible explanation for the observed inefficiency may include low UV irradiance, screening effect of water and generally low oxidation rate in photocatalytic reactions. Further studies might include combination of electric discharge with ozone decomposition/radical formation catalysts.

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LIST OF SYMBOLS AND ABBREVIATIONS

AOP	Advanced oxidation process
BOD	Biochemical oxygen demand
CAW	Corona above water
COD	Chemical oxygen demand
DBP	Disinfection byproduct
HPLC	High performance liquid chromatograph
IPC	In-plasma catalysis
MAA	Meglumine acridone acetate
NTP	Non-thermal plasma
PCD	Pulsed corona discharge
PPC	Post plasma catalysis
THM	Trihalomethane
VOC	Volatile organic compound

1 INTRODUCTION

1.1 Background

Introduction of pharmaceutical substances to aquatic environments through various routes is a growing concern. A typical passage for pharmaceuticals to access the environment is via wastewater streams. Conventional wastewater treatment typically consists of primary and secondary, and sometimes tertiary systems. Respectively, they are generally designed to remove suspended solids mechanically, biodegrade organic pollutants and disinfect the treated water. A range of compounds pass through the primary and secondary treatment unchanged. These substances that resist biological treatment are defined recalcitrant. Tertiary treatment aims to control microbial content and further improve the quality of treated water by removal of, for example, phosphorus. Classical disinfection methods used for bacterial control are e.g. ozonation and chlorination. These methods have certain weaknesses such as costly application and production of ozone and the formation of carcinogenic nitroso-compounds trihalomethanes (THMs), a problem particularly related to chlorination.

Pharmaceuticals present an example of group including a variety of recalcitrant substances. While a portion of the substances ends up in wastewater through direct disposal, many waterborne drugs or their metabolites originate from human body wastes. Due to ineffective treatment, these substances are introduced to the environment along with sludge or effluent. The effects of medicinal substances in the environment can be classified in three groups: general toxic effects, antibiotics and endocrine disrupters, i.e. chemicals that may disturb hormonal function (Jørgensen & Halling-Sørensen 2000). Public discussion has brought to general attention the fact that residues of medicinal substances are widely found in water environments and aquatic species, e.g. fish population.

1.2 Research problem and study objectives

As conventional treatment is often insufficient in removing slowly degrading pharmaceuticals and other refractory substances from wastewater, more effective measures

are required (Ternes, 1998). As the mechanism of organic pollutants degradation is generally their oxidation, the utilization of highly reactive oxidants is a logical field for research. The most powerful feasible oxidant is the hydroxyl radical, and the water treatment systems generating this substance are collectively referred to as advanced oxidation processes (AOPs) (Glaze et al. 1987). A modern and in economic view particularly interesting AOP is the application of pulsed corona discharge (PCD). A number of studies during the last decade have suggested that PCD seems to be both effective and efficient in removal of various pollutants in water (Pokryvailo et al. 2006, Grabowski et al. 2007, Gerrity et al. 2010, Joubert et al. 2013, Dobrin et al. 2013, Panorel et al. 2013). Concrete benefits with PCD treatment are its superior energy efficiency over other methods (Panorel 2013), and that the system is operated in ambient conditions and no additional treatment chemicals are included in the process.

The objective of the study was to investigate the efficacy and efficiency of PCD in oxidation of the medical substance MAA and to explore the possible effect of a photocatalyst introduction to the process. Meglumine acridone acetate is a trademark compound named Cycloferon by the EMIR partner company Polysan Ltd, St. Petersburg, Russia. Experiments were also conducted with oxalic acid that was selected as a refractory model compound to provide a clear indication of the possible catalyst contribution.

1.3 Environmental and economic prospects

The global problem of declining fresh water supplies augments the significance for a research on cost efficient water purification. As the necessity of inexpensive water treatment in poor countries is self-explanatory, the need is apparent in developed countries as well; the markets for cost efficient and effective water purification technologies should be worldwide. This assertion follows the logic that the issues listed below technically concern any country regardless of its wealth:

- Common problems of high energy consumption and possible secondary pollution are not commendable neither in economic nor in environmental perspective

- Recalcitrant compounds endure biological treatment, and often conventional tertiary treatment is insufficient as well
- Industries may produce difficult wastewaters that require more powerful treatment than traditional methods can offer, and it still is expected to be cheap
- Trends of tightening regulation set new requirements for water treatment

Overcoming the economic deficiencies and environmental after-effects of traditional water treatment methods yields obvious benefits. The degradation of recalcitrant compounds is relevant for the simple generalization that a substance that withstands microbial treatment is harmful to the microbes that cannot consume it (Önder et al. 2009). Moreover, for the same reason recalcitrant organic compounds are apt for accumulation in the environment. For industries that produce large amounts of wastewater containing organic substances, it would be beneficial in terms of economy and image to acquire energy efficient treatment systems. Shortly concluded, both economy and environment profit from advanced water treatment.

The asset of PCD is that each of the abovementioned issues is met with an improvement. A process that harnesses the power of hydroxyl radicals, involves no chemical addition, exhibits low energy intensity and is operated in ambient conditions, should be notably attractive at any perspective. With these aspects, the core of this thesis is to investigate if the advanced PCD technology might be even further improved along the introduction of a catalyst.

2 PULSED CORONA DISCHARGE IN WATER TREATMENT

A corona discharge is a form of an electric discharge. Electric discharge is a phenomenon where electric current passes through an insulator, i.e. matter that normally does not conduct electricity. This is the result of potential difference between two conductors high enough to ionize a conductive pathway into a dielectric medium.

Pulsed corona discharge application is strongly based on the use of pulsed power. Certain chemical reactions require certain energy to initiate, and by supplying the energy in pulses,

the peak power of the pulses may well exceed the needed activation energy for that process. Pulsed power prevents ohmic dissipation i.e. temperature increase. With short pulsed high voltages, electrons migrate longer distance compared to ions that have heavier mass, so electrons are driven across larger voltage drop, hence most of the input energy is used to energizing electrons. The flux of energy is therefore more concentrated to the target than in continuous flow of energy. The relevance of energizing electrons is discussed in the following chapters along the physics and the oxidation application of pulsed corona discharge. (Ahlfont et al. 1999)

2.1 Corona discharge physics

Corona discharge is applied in atmospheric pressure. It is utilized in various applications, such as photocopiers, ozone manufacturing or electrostatic precipitators and can also occur unwantedly in e.g. transmission lines. Perceptible characteristics for corona discharge are the soft violet glow and the distinct odor of ozone that is formed from oxygen in air. Corona discharge also generates audible noise. (Peek 1920, Veldhuizen & Rutgers 2001, Chen 2002)

Corona discharge is similar to dielectric barrier discharge (DBD), both of which have been studied for applications in environmental science. The two mechanisms compete in applicability as both have advantages over the other: DBD may achieve higher electrical power density, but corona application is simpler and generally easier to scale up to larger flows. Corona discharge differs also from the phenomenon of electric arc, but with high enough voltage and insufficient distance between the electrodes, undesirable arcing or sparking may occur. (Peek 1920, Veldhuizen & Rutgers 2001)

A corona is a positive or a negative electric discharge occurring from the electrode of higher curvature in an asymmetric electrode configuration with high voltage. The curved electrode is connected to a high voltage power source and the electrode of lower curvature is grounded. In practical applications, the curved electrode is often a pin or a wire while the ground electrode is of plate or cylindrical form. As the asymmetric electrode configuration is generally applied in practice, a corona discharge can nevertheless also occur between

e.g. two equal spheres. The required distance between the spheres in such case is twice their radii as shorter distance results in sparkover. The strong electric field created by the voltage ionizes the fluid that surrounds the curved electrode. The fluid becomes therefore conductive and provides a pathway for the discharge. The ionized zone is non-thermal plasma (NTP) and in air, visible to the eye in faint violet glow. As the plasma region is the region where electron impact reactions are significant, the field strength is insufficient to produce more free electrons beyond it. (Peek 1920, Veldhuizen & Rutgers 2001)

The discharge is initiated when a neutral atom or molecule is ionized producing a positive ion and a free electron. The free electron is then accelerated towards the anode and, along collision with another atom or molecule, ionizes it creating a new positive ion and another free electron. This continues as a progressive chain reaction called electron avalanche. Secondary electrons that support sustaining the process are formed in the gas phase through photoionization, which is caused by photons originating from the recombination of electrons and positive ions. Recombination of free electrons and positive ions may occur, but it is considered negligible. Ionization thus competes primarily with electron attachment to electronegative gas molecules. In the vicinity of the curved electrode, ionization predominates over attachment producing new electrons. (Veldhuizen & Rutgers 2001, Chen 2002)

2.1.1 Positive corona

A corona discharge is positive when the sharper electrode is connected to the positive output of a generator. In a positive corona the free electrons are accelerated towards the sharp electrode. Collisions between the electrons and gas molecules create new free electrons and positive ions. In the case of dry air, O_2^+ and N_2^+ are the most abundant positive ions that are formed. The plasma region in a positive corona is uniform and close to the curved electrode. Ionization occurs only within the plasma region, i.e. the ionization boundary is at the edge of the plasma. Thus only the positive ions comprise the current beyond the ionization boundary. The direction of this current is therefore towards the passive ground electrode. A sketch illustrating the principles of a positive corona discharge

is presented in Figure 1. The illustration is not to scale. (Veldhuizen & Rutgers 2001, Chen 2002)
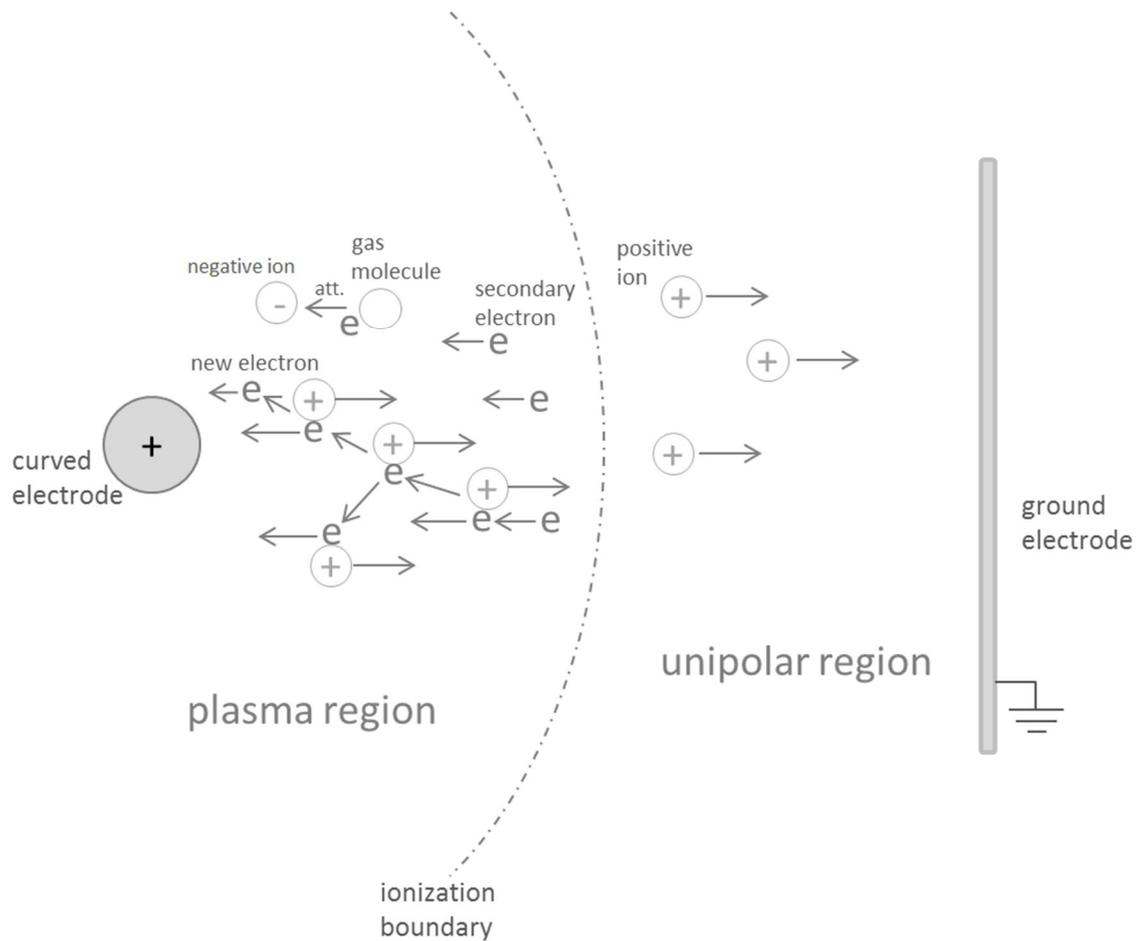
Figure 1. Illustration of positive corona principle (Chen 2002).

2.1.2 Negative corona

A negative corona is created when the curved electrode is connected to the negative terminal of the generator. Correspondingly, the electrons are accelerated towards the grounded electrode, i.e. the sharper electrode is the cathode. The mechanisms with the formation of free electrons and ions differ from those of positive discharge. In contrast to positive corona, free electrons are present outside the ionization region because they are attracted to the ground electrode. Negative corona discharge consists of individual tufts placed irregularly at the curved electrode and secondary electrons are produced at the electrode surface by photoemission. The discharge tufts occur preferentially at places of

irregular geometry along the electrode surface. The number of tufts grows with increasing voltage. (Veldhuizen & Rutgers 2001, Chen 2002)

Negative corona is not possible in pure gases like argon or nitrogen that exhibit no affinity for electrons; it only occurs in electronegative gases such as oxygen and water vapor. In pure gases, corona onset voltage results in sparkover. A sketch of the negative corona principle is presented in Figure 2. The illustration is not to scale. (Veldhuizen & Rutgers 2001, Chen 2002)
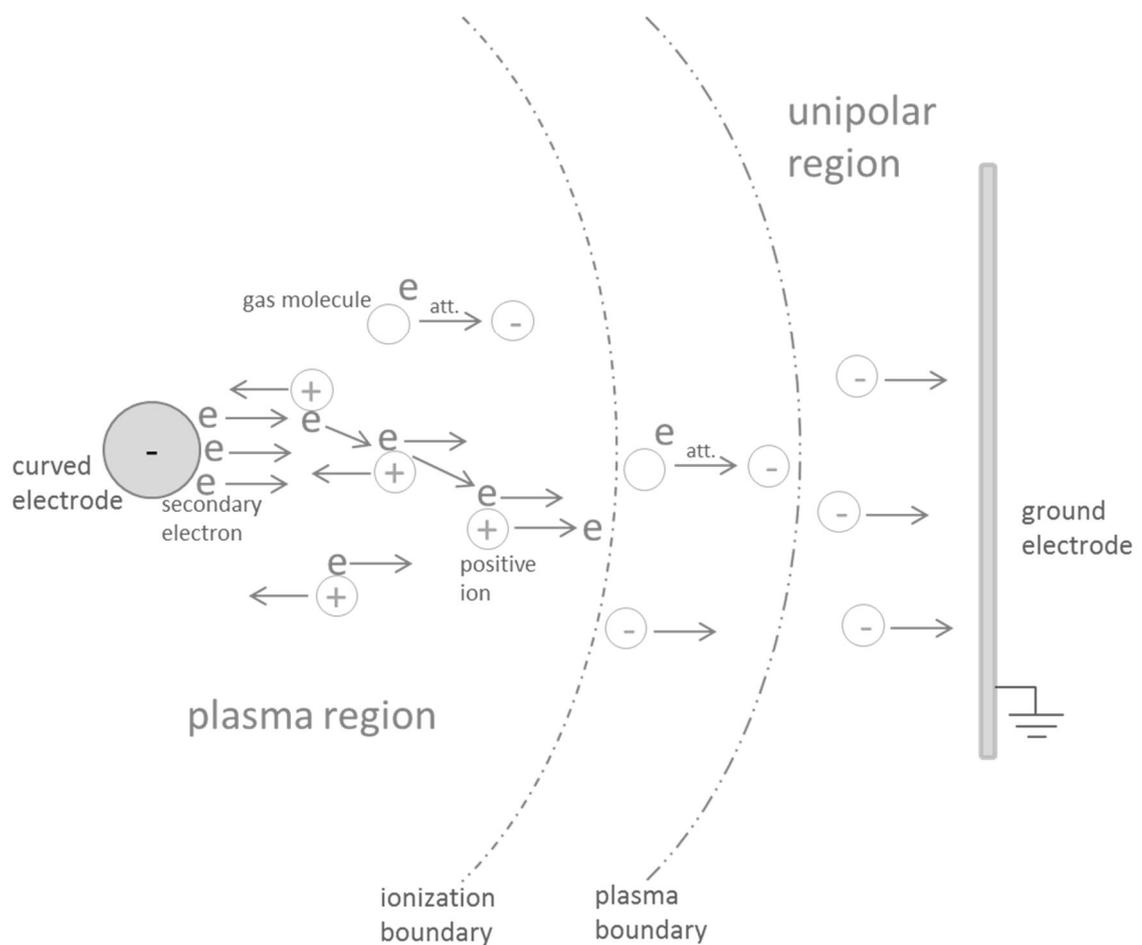
**Figure 2.** Illustration of negative corona principle (Chen 2002).

2.2 Application of corona discharge to oxidation

Water or gas treatment with electric discharge is also known as plasma treatment because the process bases on the non-thermal plasma formation. Non-thermal plasma is sometimes

also referred to as non-equilibrium plasma or cold plasma, due to the substantial temperature differences between electrons (T ≈ 10 000 K) and other particles (room temperature), such as ions, atoms and molecules (Müller & Zahn 2007). The ionization and the forming plasma create highly reactive species, such as ozone, OH-radicals and atomic oxygen (Ono & Oda 2003). The formed reactive species are the desired oxidative agents for the process and the ultimate oxidation objective is the mineralization of organic compounds to carbon dioxide, water and inorganic ions (Hoeben et al. 2000). Because OH-radicals are utilized for pollutant oxidation, plasma treatment of water is considered as an AOP. The oxidation potentials of ozone and hydroxyl radical are significantly greater than that of e.g. the commonly used chlorine, making AOPs attractive choices for advanced water treatment. The oxidation potentials of some common oxidative species are presented in Table 1.

Table 1. Oxidation potentials of some common oxidants (Munter 2001).

Oxidant	Electrochemical oxidation potential [V]	Relative oxidation power (Cl as reference)
Chlorine	1.36	1.00
Hypochlorous acid	1.49	1.10
Permanganate	1.68	1.24
Hydrogen peroxide	1.78	1.31
Ozone	2.08	1.52
Atomic oxygen	2.42	1.78
Hydroxyl radical	2.80	2.05
TiO_2^+	3.20	2.35

From Table 1, it can be seen that the oxidation potential of ozone is over one and a half times, and the potential of OH-radical more than twice that of chlorine. Excluding the contribution of ozone, the oxidative power of corona-induced oxidants is therefore significantly greater than with traditional oxidants. Although some halogen based oxidants may also exhibit greater oxidation potentials than the OH-radical, one of the advantages with AOPs is particularly the absence of halogens. Table 1 reveals also that positively

charged titanium dioxide (TiO_2) as well exhibits higher oxidation potential than the OH-radical. TiO_2 is a commonly used photocatalyst and has been studied for joint application with some AOPs (Zhang et al. 2013, Dixit et al. 2011, Wang et al. 2007). The application of TiO_2 is further scrutinized in chapter 2.3.2.

Ozone formation in a PCD application takes place primarily in the plasma region, and in negative corona, where electron density is greater and the plasma region extends farther than in corresponding positive corona, more ozone is produced. The ozone generation in negative corona is an order of magnitude higher. The electrons in positive corona are, however, concentrated closer to the surface of the sharp electrode where the potential gradient is high. Therefore, they possess higher energy which is desirable when high activation energy is needed. This is favorable in plasma treatment where highly reactive, short-living oxidants are desired. Positive corona has also been observed to be more effective in many cases, and, with refractory pollutants, the role of shorter-living oxidants is emphasized over ozone. (Chen 2002, Veldhuizen & Rutgers 2001, Preis et al. 2013b)

The application of PCD has been studied with different configurations. In water treatment, the discharge may be formed in either liquid phase (homogeneous media) or gaseous phase (heterogeneous media). Previous studies on different configurations are further discussed in chapters 2.2.5, 2.2.6 and 2.2.7.

2.2.1 Oxidation mechanisms

The use of PCD in water treatment bases mainly on the formation of ozone and hydroxyl radicals that are produced within the reactor from oxygen and water (Ono & Oda 2003). Direct interaction between electrons and pollutants is considered to be negligible due to the typical pollutant concentration of several hundred parts per million (Müller & Zahn 2007). The formation of OH-radicals and ozone is described as follows (Ono & Oda 2003):

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

$$e^- + 3O_2 \rightarrow e^- + 2O_3 \tag{2}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{3}$$
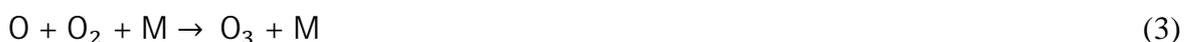
Both ozone and OH-radical can react either directly with the pollutant or indirectly via formation of other oxidants. Ozone may form e.g. OH-radicals or hydrogen peroxide from water. Ozone can also be decomposed into a singlet oxygen atom and singlet oxygen molecule by photons with under 310 nm wavelength, or thermally into atomic and molecular oxygen. In humid air, the singlet oxygen atom can react with water to form OH-radicals. The decomposing reactions of ozone and singlet oxygen atom in water and humid air are described as follows (Hoeben 2000, Ono & Oda 2003):

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{4}$$

$$O_3 + O_2 \rightarrow O + 2O_2 \tag{5}$$

$$O(^1D) + H_2O(l) \rightarrow H_2O_2 \tag{6}$$

$$O(^1D) + H_2O(g) \rightarrow 2\,^{\cdot}OH \tag{7}$$

Hydroxyl radical is likely to abstract hydrogen atoms or react through addition into the unsaturated bonds of organic molecules. In addition to direct oxidation, OH-radical can form atomic oxygen or hydrogen peroxide. Atomic oxygen can further produce either ozone with molecular oxygen or hydrogen peroxide with water (Hoeben 2000). The atomic oxygen and hydrogen peroxide formation from OH-radical via recombination reactions are described as follows (Ono & Oda 2003):

$$^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O + O \tag{8}$$

$$^{\cdot}OH + {}^{\cdot}OH + M \rightarrow H_2O_2 + M \tag{9}$$

Inside a PCD reactor, the gas-liquid interface i.e. the surface of the treated solution is an important environment for OH-radical activity. Preis et al. (2013b) investigated the surface activity of OH-radicals by adding an OH-radical scavenger substance and a surfactant to the treated solution. The authors did not observe any effect of the OH scavenger to the oxidation, while the addition of a surfactant resulted in noticeable slowdown. The surface activity of OH-radicals was therefore suggested to be considerable.

2.2.2 Roles of hydroxyl radicals and ozone

The roles of hydroxyl radical and ozone in the oxidation of target pollutants have been discussed in several reports and depend on various variables, such as the recalcitrance of the target pollutant, composition of the gas phase, pulse repetition frequency and the overall system configuration (Hayashi et al. 2000, Hoeben et al. 2000, Panorel et al. 2011, Preis et al. 2013b). In the context, composition of the gas phase generally refers to oxygen and water content. The composition of the gas phase affects both efficiency and efficacy of a PCD oxidation. Ono & Oda (2003) reported that humidity affects ozone formation reductively in comparison to dry air. The authors suggested that water vapor might reduce atomic oxygen levels which would result in reduction of ozone production according to equation (3).

Phenol is perhaps the most common target compound for research on plasma treatment of water. Therefore, the amount of data accumulated on phenol oxidation is substantial, making it a convenient reference substance. The substance is also convenient for its chemical structure where a good proportion of bonds are unsaturated. Hayashi et al. (2000) studied the corona-induced degradation of phenol in air, oxygen and argon atmospheres. They reported that the highest rate of degradation was achieved under oxygen atmosphere and the lowest rate under air atmosphere. As the rate in argon atmosphere came out in the middle, the authors concluded that with PCD, phenol could be degraded without the oxygen from air; part of the energy from PCD under air atmosphere went to the dissociation of gaseous nitrogen. The authors also suggested that the degradation rate in humid argon atmosphere (no oxygen present) refers to oxidation by OH-radicals, and since the ratio in oxygen atmosphere was 1.5-2 times higher, oxygen reagents such as ozone and atomic oxygen induce degradation rate comparable to that of the OH-reagents. Hoeben et al. (2000) concluded also in their study that the composition of the gas phase has a strong influence on the oxidation mechanism of phenol. Their study suggested that although the conversion rate is higher in argon than in air, the efficiency of phenol degradation with PCD in air atmosphere is slightly higher than in argon and that the oxidation process is more complete. Similarly to the studies of Hayashi et al. (2000), the authors also reported that the oxidation mechanisms are different in atmospheres with and without oxygen:

attack of ozone and oxygen on the ring cleavages of the target compound was observed to prevail in oxygen atmosphere, whereas hydroxylation was suggested to be the main degradation pathway in argon atmosphere. Other studies also support the observation that increased oxygen concentration has a positive effect to the oxidation rate due to the apparent increase in ozone formation. Panorel et al. (2011) observed a near linear correlation with increased oxygen concentration and increased ozone formation. The authors reported that the achieved increase in efficiency, however, was less proportionate: when initial oxygen concentration was increased fourfold, the oxidation efficiency was improved by mere 30 to 40 %. The authors suggested that this indicates the dominant role of OH-radicals. They also examined the roles of OH and ozone by comparing the results from normal operation of PCD to oxidation with only the ozone produced in the reactor. The latter was conducted by generating the ozone in the PCD reactor during applied pauses in the solution flow; the former was operated with high pulse repetition frequency to emphasize the difference. The authors reported that oxidation rate was roughly five times higher with plasma treatment than with ozone alone. Pulse frequency was observed to have a significant effect on the role of ozone in the oxidation process. As shorter-living oxidants like OH-radical exhibit a lifetime of microsecond scale, they contribute to the process only in the discharge zone. Lower frequency is thus considered to give more time for ozone to react between pulses, leading to increased energy efficiency. Higher frequency, however, increases the role of shorter-living oxidants, thus increasing the efficacy of the process. (Panorel et al. 2011)

The reactor configuration has also significant effect on the deviation between the roles of hydroxyl radical and ozone. In a vertical configuration where the water falls between the electrodes, both species are considered essential (Panorel et al. 2011). In case the high voltage electrode is placed in water, the role of ozone is emphasized. This is because ozone is produced from oxygen of air and hydroxyl radicals are produced from water. Grabowski et al. (2006) reported that if the electrode is placed above the water surface, i.e. in the gas phase, oxidation is likely to occur mainly via direct attack of ozone for the reason that since hydroxyl radicals are very short-lived, only ozone may dissolve into the water. In contrast, Dobrin et al. (2013) reported that ozone contribution is minor when corona is induced above water surface. The authors observed that only a fraction of the produced

ozone reacted with the target substance while most of the ozone leaves the reactor with the gas flow. In this case, hydrogen peroxide was suggested to play a significant role in the oxidation. It should, however, be noted that although the authors observed no dissolved ozone after treatment, they did not discuss the possibility that the oxidation of target species would be responsible for the absence of dissolved ozone. In addition, it was not reported how significant share of the target compound the small reacted portion of ozone oxidized. The roles of different oxidants in a corona above water configuration could therefore be considered to require further examination.

2.2.3 Effect of pH

As acidity of the treated solution has been observed to have a significant influence on the oxidation process of target pollutants, pH is one of the most commonly monitored parameters in plasma treatment of water. The decomposition rate of ozone in water increases with elevated pH (Munter 2001). Both efficiency and mechanisms of oxidation can vary with pH. Elevated pH accelerates hydroxyl radical production and shifts the oxidation mechanism of ozone more from direct reaction towards reaction via OH-formation (Baird 1997, Grabowski et al. 2006).

Grabowski et al. (2006) studied the effect of pH on phenol removal by adjusting the acidity of the subject solution with sodium hydroxide (NaOH) and hydrochloric acid (HCl). The authors observed an expectable increase in ozone dissolution in water with increased pH. High enough pH level (10.2 observed by the authors) was suggested to further promote ozone dissolution rate due to increasing self-decomposition rate of dissolved ozone. Phenol removal was also increased with higher pH, increasing slower with pH elevation within acidic conditions and faster above pH 6.

As pH impacts the plasma treatment, it may also be reversely affected by the discharge. Kornev et al. (2013) studied the effect of electric discharges on pH and reported that the discharges cause a decrease in pH of a solution due to nitric acid formation. The authors observed a decrease from about 6.4 to approximately 3.3 with DBD and PCD treatment of near neutral solutions. With acidic and alkaline solutions, however, no significant changes

on pH levels were reported. Different pH behavior along PCD treatment of water was observed by Panorel et al. (2013), who reported that pH decreased even with initially high pH conditions.

2.2.4 Formation of byproducts

Formation of harmful DBPs is often related to conventional disinfection methods like chlorination and, to some extent, ozonation. Chlorination e.g. may produce toxic THMs. Trihalomethanes include harmful compounds such as chloroform, bromo-dichloromethane, dibromo-chloromethane and bromoform, all of them declared carcinogenic. Trihalomethane concentration in treated waters is therefore strictly regulated. The harmful species produced in ozonation depend mainly on the presence of bromine and organic matter, as small amounts of bromate ion (BrO_3^-) or bromoform ($CHBr_3$) may be formed. (Elshorbagy et al. 2000, Wright et al. 2010)

Some research on DBP formation in plasma treatment of water has nevertheless been conducted. Pokryvailo et al. (2006) studied the application of PCD in pollutant treatment in heterogeneous media, i.e. purification of gaseous and aqueous fluids. The authors suggested that the BOD/COD ratio could be increased in some cases of non-biodegradable wastewater, enabling or enhancing the efficiency of subsequent biodegradation. A limiting factor was concluded to be the formation of nitrogen oxide, which could be solved with the use of oxygen atmosphere instead of air. Although the formation of aqueous nitrite and nitrate is undesirable especially in potable water treatment, air atmosphere is more convenient than oxygen in practical application. Kornev et al. (2013) studied the formation of nitrite and nitrate in pulsed electric discharge treatment (PCD and DBD) and reported that treatment in water-air mixture results in accumulation of these ions. The rate of accumulation and the anion content was concluded to depend on the characteristics of the discharge and the treated solutions. The authors reported that PCD produced only nitrates while DBD treatment produced both nitrates and the more toxic nitrites. The nitrate production with PCD was also suggested to be minimal, relatively to the permissible concentrations in potable water treatment. No significant influence of initial pH level on the total sum of nitrogen species was observed in solutions that were treated with either

PCD or DBD treatment. Instead, pH level was reported to affect mostly the nitrite-nitrate ratio. Preis et al. (2013a) also reported that pH has little effect on nitrate formation, but also observed that the concentration of organic pollutants has a significant effect on the formation of nitrate. High concentrations of certain medicinal compounds as well as increased electric conductivity were observed to have suppressive effect on nitrate formation. However, opposite results were obtained with carboxylic acids: the presence of oxalate and formate was observed to drastically increase nitrate formation.

Another issue with byproduct formation is incomplete oxidation, i.e. the appearance of intermediate oxidation products in the treated water. The problem is case-specific and seems to be dependable on at least residence time in the reactor and the recalcitrance of the intermediate products. Residual ozone is a problem mainly related to the plasma treatment of gaseous streams. With e.g. phenol degradation, Hoeben et al. (2000) reported a range of oxidation products after PCD treatment, including hydroquinone, formic acid, glyoxylic acid and oxalic acid. These substances are common intermediate oxidation products reported also in other studies on plasma treatment of organic pollutants (Panorel et al. 2013). As the composition of the intermediate oxidation products depends on the oxidation process, the gas phase composition among other parameters essentially influences the formation of byproducts.

2.2.5 Corona in water configuration

A widely studied electrode configuration is the corona in water system, where both electrodes are placed within the treated solution. The preliminary idea with the latter is to create OH-radicals right where they are needed in order to reduce loss of radicals due to recombination. However, the discharge in water is acquainted with evaporation at the anode tip, which leads to reduced energy efficiency (Hoeben 2000). A corona discharge is also more difficult to produce in water than in air due to higher density of dielectric medium. Regardless of the abovementioned decreased energy efficiency, water treatment with corona in water application is constantly studied. The system has been studied with a variety of target pollutants with various outcomes. Joubert et al. (2013) studied a wire-in-cylinder configuration in inactivation of vegetative and spore forms of bacteria, reporting

different mechanisms for the two: hydrogen peroxide formation was observed to affect the vegetative bacteria whereas shockwaves were considered responsible in inactivation of the spores.

Pulsed corona discharge combined with other simultaneous treatment has been so far studied mainly with corona in water configurations. This is probably explained by the overall popularity in research of the configuration. Qu et al. (2013) studied the combination of PCD and granulated active carbon (GAC) in an underwater pin-to-plate corona system where the interelectrode volume was filled with GAC. The authors observed synergy in removal of phenol and cadmium, the latter of which was solely improved by corona induced surface modification of the GAC. Cadmium reduction was expectedly not observed with sole PCD treatment. Zhang et al. (2013) studied the combination of PCD and TiO_2 photocatalyst in similar pin-to-plate configuration and reported higher efficiency and degree of oxidation than with sole PCD. The TiO_2 was applied as a nanofilm in the plate electrode and the walls of the reactor, and the authors observed that the coating remained undamaged in the reactor walls but was destroyed at the plate electrode. The wall coating also proved to be more efficient.

2.2.6 Corona above water configuration

The corona above water (CAW) configuration has been observed to be more effective than in-water configuration and it is therefore considered more feasible (Hoeben 2000). When the electrode is out of water, the composition of the gas phase becomes an essential parameter. When the high voltage electrode is placed above the water surface and the plate electrode under water, the corona discharge streamer propagates from the upper electrode towards the water surface. Analogous to the DBD, the water is a dielectric in between the electrodes. Ionization and dissociation occur at the surface, although in negligible amounts in comparison to reactions in the gas atmosphere. The relatively modest surface to volume ratio of water in a CAW reactor emphasizes the role of gas phase reactions. As the most powerful oxidants like OH-radical and singlet or atomic oxygen exhibit a lifetime of microseconds, ozone is the only oxidant formed in the gas phase that is capable of diffusing into the aqueous phase. (Hoeben et al. 2000)

Grabowski et al. (2006) investigated the oxidation of phenol in water with a wire-plate CAW system. The CAW configuration included a reactor, on the bottom of which a thin layer of the treated solution flowed through with the anode wiring set horizontally above. The authors studied the influence of various parameters under different electrical, physical and chemical conditions. They observed that higher voltage and higher pulse frequency both resulted in increased ozone concentration in the reactor. A maximum solution depth of 6.6 mm in the reactor was reported for effective ozone penetration of the treated volume. The depth was suspected to be substantially affected by the observed turbulence on the water surface resulting from the high voltage pulses: increased turbulence results in increased ozone penetration depth. The authors also concluded that in a CAW reactor, ozone uptake at the water surface is a limiting factor in the process due to the surface to volume ratio.

Hayes et al. (2013) studied a different kind of CAW reactor, where the high voltage electrodes were vertical pins instead of horizontal wires. The authors compared the PCD configuration to a pulsed UV system in killing of a protozoan species, and reported that the plasma treatment was not very effective in comparison to the UV. They also observed inconvenient residual toxicity with the plasma treated waters and notable pin electrode corrosion. These two drawbacks were suggested to be related due to metal nanoparticles from the electrodes causing toxic effects.

2.2.7 Vertical wire-plate configuration

Vertical wire-plate configuration relies on the same electrical and chemical phenomena as the CAW system. However, the vertical system provides two apparent advantages compared to the CAW reactor. First, in regard of the aforementioned effective maximum depth of water layer in a CAW system, the water in a vertical system is not introduced to the reactor as a uniform layer, but in droplets, films and jets. Another advantage is that the water-air contact surface is substantially increased when water is showered to the reactor through a perforated plate, instead of a horizontal and uniform flow stream. The advantage of increased water surface area relates to the proposed surface oxidation reactions

discussed earlier. In practice however, although the OH-radicals that react with the pollutants in water are considered to form in the gas-liquid interface, the water flow and the contact surface, above certain m^2/m^3 number, has been observed to make little difference to the discharge treatment efficiency, indicating that a constant amount of oxidants determined by the pulse generator power are available in the discharge zone (Panorel et al. 2013). Nevertheless, the role of hydroxyl radicals in vertical system is reported to be more essential than in a CAW system, where the roles of oxidants have been discussed with variable conclusions. Panorel et al. (2011) reported that in oxidation of humic substances, the PCD treatment with a showering configuration showed a few times better energy efficiency than conventional ozonation. Another advantage of the showering configuration over the CAW is that it enables more compact electrodes configuration in a package setup.

2.3 Plasma catalytic treatment

A number of studies have investigated the plasma catalytic treatment of polluted fluids. The studies generally report an increase in treatment efficiency compared to non-catalytic plasma treatment. Generally, a catalytic system can be homogeneous or heterogeneous: in heterogeneous catalysis the catalyst and reactants are in separate physical phases, whereas in homogeneous catalysis the catalyst and the reactant (or their solution) form a common physical phase. Being more feasible in practice, plasma catalytic treatment therefore generally refers to a heterogeneous catalytic system. Inorganic solids like metals and their salts, oxides or sulfides are typical heterogeneous catalysts, although some organic materials such as hydroperoxides and enzymes apply as well. (van Durme et al. 2008, Deutchmann et al. 2012)

The catalyst in NTP systems can be placed e.g. into the discharge zone or downstream from it: two configurations referred to as in-plasma catalysis (IPC) and post plasma catalysis (PPC), respectively. Basically, the catalyst can be in the system either fixed, or in case of liquid stream, as suspension. The studies on plasma catalytic treatment emphasize the previous, partially because the studies focus on gaseous streams. Various different catalysts have been studied for plasma catalytic treatment, such as aluminum, silicon,

titanium and manganese based oxides with varying carrier materials. Of these, dioxides of manganese and titanium were initially considered for the catalyst in the present study, and are therefore further scrutinized in chapters 2.3.1 and 2.3.2, respectively. (van Durme et al. 2008, Deutchmann et al. 2012)

The oxidation mechanisms with PPC are relatively simple in comparison to those with IPC due to the reported interaction between the catalyst and the plasma. This interaction has been widely investigated; some studies report that the catalyst affects the plasma characteristics while others suggest that the plasma influences catalytic activity (van Durme et al. 2008). Both assertions seem to be case specifically true. Guo et al. (2006) studied the effect of a DBD to the surface of a manganese and aluminum based catalyst supported on nickel foam, and suggested that the discharge enhanced the catalyst surface increasing its activity and oxidation capability. The authors reported that images produced with an electron microscope implicated smaller granularity of the catalyst with more uniform distribution on the foam surface. The IPC configuration was therefore suggested to improve the catalytic performance of the manganese and aluminum based catalyst with nickel foam carrier. The application of NTP in direct preparation and regeneration of catalysts has also been studied for a few decades and is already widely in use (Kizling & Järås 1996). The catalyst applied in the discharge zone is also reported to affect the propagation of the discharge and suggested to enable the generation of microdischarges inside catalyst pores, which increases the discharge per volume ratio (van Durme et al. 2008). The phenomenon is inherently dependable on the porosity of the catalyst particles and the applied carrier material.

Along plasma conditioning of catalyst surfaces, acid treatment has also been investigated for enhancing the catalytic performance. Moutusi & Bhattacharyya (2013) studied the oxidation of orange II dye with H_2SO_4 treated ZnO and MnO_2 catalysts and reported a significant improvement on the efficacy in comparison to untreated catalysts. The acid treatment was reported to damage the metal oxide surface and the authors suggested that the treatment might expose new surface on the catalyst particles through erosion.

2.3.1 Manganese based catalyst

Some research has been done on the combination of NTP applications and specifically a manganese based catalyst. Jarrige & Vervisch (2009) investigated the removal of volatile organic compounds (VOCs) with PCD and MnO_2-catalyst in ambient temperature, reporting that the ozone produced in PCD further increases the decomposition of VOCs in the presence of a catalyst. The catalyst was a fixed bed located downstream from the plasma reactor and the studied fluid was gaseous. Delagrange et al. (2006) studied the combination of a DBD and a series of manganese based catalysts on toluene removal from air. Their study also concluded that catalytic post-plasma treatment increased the oxidation of the studied pollutant. Harling et al. (2009) also studied the combination of NTP with two MnO_2-based catalysts in VOC oxidation in ambient temperature, reporting similar results. While investigating the oxidation of toluene, the authors also tested and reported that the catalyst had no effect on the pollutant without combined plasma treatment, underlining that ozone produced by the plasma was destroying toluene with the assistance of the catalyst. Pokryvailo et al. (2006) studied also the effect of two manganese oxide based catalysts combined with PCD. The tests were conducted in 155-165 °C and in comparison to plasma treatment alone, at a reasonable considered power, substantial increase in VOC reduction rates were reported. The testing was done with synthetic waste gas. Guo et al. (2010) reported also a significant increase in toluene removal efficiency with combined DBD and Mn-based catalyst system in treatment of gaseous streams.

Although the previous studies on combination of NTP with Mn-based catalysis report an increase in efficacy in comparison to non-catalytic plasma treatment, the focus in these studies is on treatment of gaseous fluids. The present study investigates water treatment, which sets different premises for the system configuration and the practical application of the catalyst. In aqueous systems, the catalyst can be either a suspension of small particles in the fluid, or solid state as in fixed bed type. Suspension gives generally more catalytic surface area, which is favorable for the catalysis. However, it would require mechanical separation such as filtration for catalyst recycling, and possibly stirring during process. The fixed catalyst can be applied in a few ways generally applicable to both IPC and PPC configurations: the reactor walls or the electrodes can be coated with the catalyst, or the

catalyst can be in packed bed or layer of particles that are substantially larger than in suspension (e.g. pellets, granulates etc.) and therefore not subject for suspending into the flow stream (van Durme et al. 2007).

2.3.2 Photocatalysis with titanium dioxide

In photocatalysis the catalyst or a reactant absorbs light during the reaction. A common example of the utilization of photocatalysis is with self-cleaning surfaces (Deutschmann et al. 2012). The process bases on photo-excitation of a semiconductor solidified through absorption of electromagnetic radiation generally in the near UV spectrum. A suitable semiconductor material may be excited under near UV irradiation by photons of sufficient energy, which produces conduction band electrons and valence band holes. The valence band holes possess extremely positive oxidation potential and are thus able to induce oxidation of even highly refractory chemicals. Photocatalysis may also induce OH-radical through mechanism presented in equation (10). (Munter 2001)

$$h^+ + OH^- \rightarrow \ ^{\cdot}OH \tag{10}$$

TiO_2 can be activated by UV irradiation with wavelengths up to 387.5 nm. For its photocatalytic properties, TiO_2 is widely used in destruction of organic pollutants as well as in synthetic organic photochemistry. It is one of the most widely used metal oxides in industry and also used as pigment substance in material coating. Naturally, titanium dioxide occurs with titanium trioxide compounds in some minerals. The most important TiO_2 containing minerals are ilmenite, rutile, leucoxene, brookite and anatase. Although the first three are economically most important, the photocatalysis with TiO_2 especially in its photoactive anatase modification is widely studied. (Munter 2001, Pfoertner & Oppenländer 2012)

TiO_2 catalyst is often used as particulate suspension, i.e. slurry, since its photocatalytic activity is significantly reduced when it is immobilized in a carrier substance (Pfoertner & Oppenländer 2012). If the catalyst is applied in slurry particulates, an optimal catalyst concentration exists: Way & Wan (1991) studied the heterogeneous photocatalytic

oxidation of phenol with TiO_2 and concluded that the optimal catalyst concentration in their study was 1-3 g/l. The optimal catalyst concentration varies between different studies with different parameters such as target compounds and catalysts. Ku & Hsieh (1992) studied the effect of TiO_2 in UV-irradiation of aqueous dichlorophenol reporting that while the catalyst provided a noticeable effect on the degradation of the target compound, the optimal catalyst load was dependent on the initial pollutant concentration. Photocatalytic oxidation is pH dependent to a large extent because several of the involved parameters, like adsorption of pollutants and generation of OH-radicals in the vicinity of the catalyst, are affected by acidity. The solution matrix therefore strongly affects the optimum pH for photocatalysis. Way & Wan (1991) observed in their study that pH under 2 is not favorable for photocatalysis. Strongly alkaline conditions may in contrast improve the photocatalytic oxidation. Malygina et al. 2005 reported that the oxidation of estrogen β-estradiol with suspended TiO_2 catalyst and applied UV radiation was most efficient in strongly alkaline medium as the target compound was observed to absorb to the catalyst surface better in alkaline conditions. Regarding high pH levels, the authors emphasized the significance of the absorptive character of TiO_2 over photocatalytic performance in the case of β-estradiol. In strongly acidic media the absorption was observed to be very poor. The optimal pH in photocatalysis depends on the target compound. Krichevskaya et al. (2003) studied the photocatalytic oxidation of methyl *tert*-butyl ether (MTBE) and reported that the substance was most efficiently oxidized in slightly acidic media.

Although the active surface area is reduced, the need for stirring and mechanical separation after treatment is removed when the applied catalyst is immobilized on the surface of a carrier material (Preis et al. 1997). Fixed bed photocatalytic reactors also seem applicable in contaminant removal at low, ppb-scale concentrations (Pfoertner & Oppenländer 2012). Preis et al. (1997) studied the use of a buoyant titanium dioxide catalyst in treatment of wastewater containing phenol, cresol, resorcinol and methylresorcinol. The applied anatase catalyst was thermally immobilized on the surface of hollow glass microspheres to keep the catalyst close to the treated water surface. The authors reported that the initial pollutant concentration and pH levels expectedly had an effect to the oxidation. Both acidic and strongly alkaline (pH over 11) solutions were observed to be more favorable for the process efficiency than pH levels closer to neutral. Of the target compounds, phenol was

observed to be less susceptible towards photocatalytic oxidation than its derivatives cresol, resorcinol and methylresorcinol; the difference increased with higher alkalinity. The authors also reported that the presence of known radical scavengers, carbonate ions, had little reductive impact on the process efficiency. It was stated in early 1990's that photocatalytic oxidation is not affected by aeration i.e. the absorption of oxygen by the liquid phase, suggesting that the absorption of oxygen by the solution surface is sufficient for the process (Munter 2001).

2.3.3 Catalyst deactivation

Although catalyst deactivation, or catalyst poisoning, has been reported in an NTP system by Roland et al. (2010), the phenomenon has received little attention with particularly manganese based plasma catalytic configurations. The desired ultimate oxidation product, CO_2, is observed to cause catalyst poisoning with e.g. γ-Al_2O_3 catalyst (Roland et al. 2010). With Mn-based catalyst, the deactivation has been related to the presence of sulfur due to the formation of $MnSO_4$ on the catalyst surface (Kijlstra et al. 1998).

Einaga et al. (2002) studied the deactivation of titanium dioxide photocatalyst in a gas-solid heterogeneous photocatalytic system. The authors observed catalyst deactivation due to carbon deposition on the catalyst surface from the oxidation of VOCs. The catalyst color changed from white to brownish along deactivation. However, the regeneration of the catalyst was discovered possible through decomposition of the deposited carbon to carbon oxides by the introduction of humid air. Gandhi et al. (2012) instead studied the deactivation of a common commercial Degussa P25 titanium dioxide catalyst in an aqueous system. The authors reported that in photocatalytic oxidation of phthalic acid, some carboxylic acid compounds reduced the catalytic activity due to surface adsorption that reduces active catalyst sites. These carboxylic acids were suggested to consist of the initial target compound and its intermediate oxidation products. Pore blockage was, however, observed to be negligible. Complete regeneration of the catalyst was reported after H_2O_2 treatment, by which near original catalyst activity was regained.

3 MATERIALS AND METHODS

## 3.1 Experimental configuration

The PCD system used for experiments was of simple construction of mostly non-commercial elements. Only the Jabsco pump and the used flow meter were commercially available products. The catalytic experiments were conducted with the same system with a catalyst coating applied on the plate electrodes. The overall system is presented in Figure 3 and the grey, vertical plate electrodes are seen in the middle of the reactor.

Figure 3. The experimental setup: pulse generator (left), PCD reactor (middle above), solution tank (middle below) and pumping unit with flow control and sampling valve (bottom right).

3.1.1 Reactor

The plasma reactor was an acrylic chamber containing two grounded vertical plate electrodes. Between the plates oscillated a parallel high voltage wire electrode, suspended stringent between two adjustable metal rods. The interelectrode area and the wire suspension are presented in Figure 4.
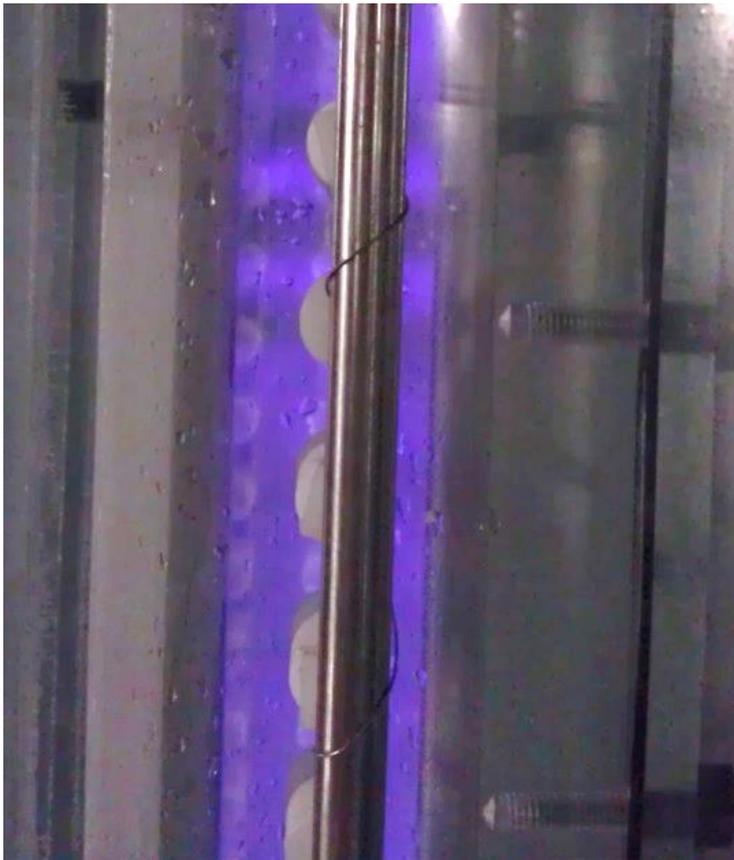
Figure 4. Interelectrode area (violet) with the pulsed discharge generation at 833 pps and 100 W. The view is from the side of the reactor and the wire electrode can be seen going around the suspension rod.

Above the electrode chamber, a smaller chamber is located where the treated solution is pumped from the container tank. The chamber is with perforated bottom plate to provide even distribution of water to the plasma zone in form of droplets, films and jets. The small chamber can be seen above the reactor chamber in Figure 3.

3.1.2 Pulse generator

The applied high voltage pulse generator was a non-commercial construction tuned for 100 W maximum power output. The generator had a six-step pulse frequency converter for which corresponding power and pulse frequency were defined with an oscilloscope and are presented in Table 2.

Table 2. Pulse generator parameters.

Time per pulse [ms]	Frequency [pps]	Generator power [W]
20	50	6
5	200	24
3.3	300	36
2	500	60
1.5	667	80
1.2	833	100

Derived from the oscillograms, the energy of a single pulse was 0.12 J at 22 kV and 180 A in the amplitude peak. The numbers correspond to the 100 W maximum power of the generator.

3.1.2 Water circulation system

A small electrically powered pump with a maximum capacity of 10 L/min was used to circulate the treated solutions in the system. The flow meter for monitoring the flow rate to the reactor, however, enabled a maximum measurable flow rate of 4.5 L/min. The calibration of the flow meter is presented in Figure 5.
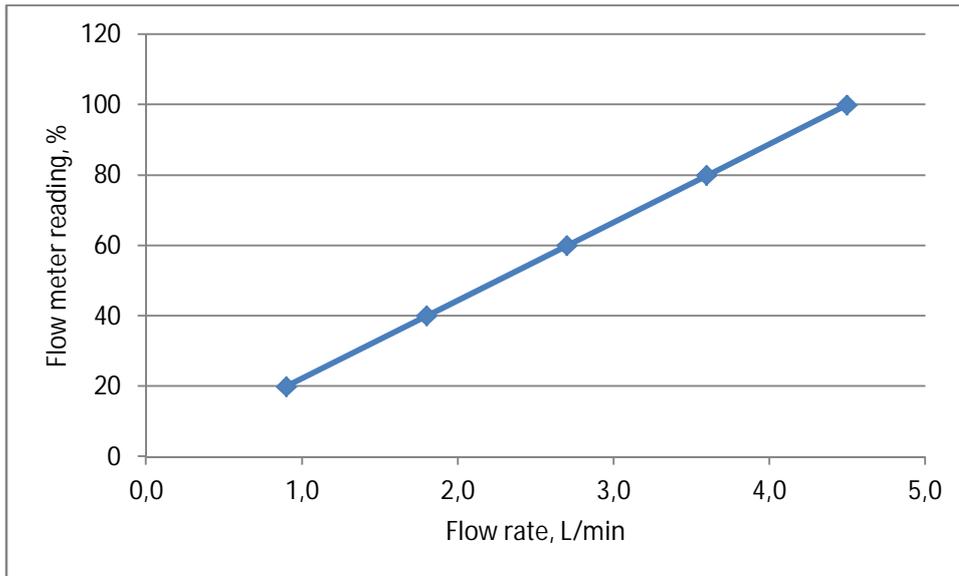
Figure 5. Flow meter calibration.

3.2 Target compounds

3.2.1 Oxalic acid

Recalcitrant organic compounds resist biological treatment due to their chemically and metabolically unreactive nature. These compounds are therefore toxic to microorganisms and oxalic acid, although abundant in nature, belongs to this group of substances. (Önder et al. 2009)

Oxalic acid, or ethanedioic acid, is strong and the simplest saturated dicarboxylic acid and it occurs as dihydrate, or in anhydrous form in some industrial cases. Oxalic acid has the molecular weight of 90.04 g/mol with the chemical formula $C_2H_2O_4$. The chemical structure of oxalic acid is presented in Figure 6. (Riemenschneider & Tanifuji 2011)
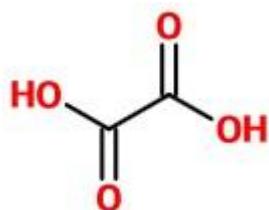
Figure 6. The chemical structure of oxalic acid.

Both anhydrous and dihydrate forms appear in colorless and odorless crystals. Of these two, the anhydrous form is slightly hygroscopic and transforms back to dihydrate form as it absorbs air humidity. The more common commercial form, dihydrate, is stable in room temperature and physically in granules or prisms of HOOC-COOH · $2H_2O$. The molecular weight of oxalic acid dihydrate is 126.0 g/mol.

Oxalic acid decomposes to formic acid, carbon monoxide, carbon dioxide and water. The decomposition may occur e.g. upon rapid heating to 100 °C or oxidation. Oxalic acid is relatively easily oxidized by oxygen in air or other oxidants, particularly in the presence of heavy metals or salts. It is also easily esterified producing acidic mono esters or neutral diesters, both of which react relatively easily with water or ammonium species. Oxalic acid is corrosive to eyes, skin and lungs as well as on ingestion (IPCS 2009). (Riemenschneider & Tanifuji 2011)

Oxalic acid is common in nature, especially in form of weakly soluble salts, oxalates, and widely in use for industrial purposes. In plants, e.g. rhubarb, cocoa and tea, oxalic acid is formed by incomplete carbohydrate oxidation. Animals produce oxalic acid through metabolism of the carbohydrates and mammal urine usually contains some calcium oxalate. As a typical salt of oxalic acid, the chemical structure of sodium oxalate ($Na_2C_2O_4$) is presented in Figure 7. Oxalates are also found in minerals as their calcium and iron salts. (Riemenschneider & Tanifuji 2011)
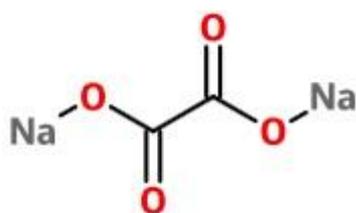
Figure 7. The chemical structure of sodium oxalate.

Oxalic acid and its salts have been generally used as reducing agents due to the ultimate mineralization to water and CO_2 when oxidized. In industry, oxalic acid is used in metal and textile treatment, bleaching and other chemical purposes. As for metal treatment,

oxalic acid salts are used e.g. for rust removal or as a constituent in metal and electronic device cleaners. In textile treatment it is widely used as mordant for printing and dyeing of fabrics and as removal agent for rust stains in laundries. Oxalic acid is also used in tanning and bleaching of leather, and in bleaching of many other materials with the emphasis on pulpwood. In chemical industry, oxalic acid is used in e.g. preparation of esters and salts, as a reagent in chemical synthesis or in concentration of rare earth elements. In addition, oxalic acid is a common intermediate product in the mineralization process of many organic pollutants. (Önder et al. 2009, Riemenschneider & Tanifuji 2011)

Oxalic acid is found in wastewaters especially originating from abovementioned industries where it is used. Its availability, simplicity and recalcitrance make oxalic acid also a practicable model pollutant in wastewater treatment research (Önder et al. 2009). For the present study, the tedious degradation of the substance was anticipated to facilitate the detection of any improvement in oxidation resulting from the application of a catalyst. A modest range of intermediate products in oxalate oxidation was also considered convenient from the analytical point of view.

3.2.2 Meglumine acridone acetate

MAA, or Cycloferon, is a medicinal compound with the chemical formula $C_{22}H_{26}O_8$ and molecular weight of 418.4 g/mol. It is a yellow, water soluble powder presented in Figure 8. The chemical structure of MAA is presented in Figure 9.


Figure 8. MAA powder on aluminum foil.
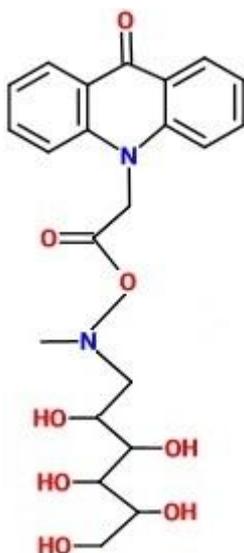
Figure 9. The chemical structure of meglumine acridone acetate.

MAA is a relatively new compound that was applied for patent by Polysan Ltd in 1994 (Patent application EP 0692475 A1). Cycloferon is an interferon inducer, i.e. a substance that activates intrinsic interferon production (Polysan 2010). Interferons are an organism's natural response of immunity. Synthetic interferons are used in treatment of various diseases, e.g. influenza, hepatitis and multiple sclerosis and often in combination with other medication (Polysan 2010, Amaria et al. 2008). Consumption of exogenic interferons in Finland ranged from 1.03 to 1.09 defined daily doses per 1000 inhabitants in 2009-2011 i.e. over two million doses annually (Finnish Medicines Agency 2012). Interferon inducers of low molecular weight that are derived from acridone acetic acid are not metabolized in liver and are not accumulated in the organism (Polysan 2010). Little public information is available on the environmental fate of MAA and no reports on oxidation of the compound, or its degradation, are available. Therefore, the molecular components of the compound (meglumine and acridone acetic acid) are discussed in the following.

MAA is a combination product of meglumine, acridone and acetic acid. Of these three, meglumine is an amino sugar also referred to as n-methyl-d-glucamine. The chemical formula of meglumine is $C_7H_{17}NO_5$ with a molecular weight of 195.22 g/mol. The chemical structure of meglumine is presented in Figure 10.
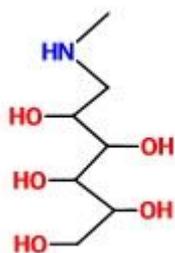
Figure 10. The chemical structure of meglumine.

As in the case of Cycloferon, some medicinal substances contain meglumine as an excipient i.e. they are available as their meglumine salts. Other drug examples are meglumine antimoniate in treatment of leishmaniasis, the veterinary drug flunixin and some nonsteroidal anti-inflammatory drugs (Miranda et al. 2006, Sams 2000, Friedrichs et al. 2011). Although no reports on the oxidation of MAA are available, some studies have been made on the oxidation of amino sugars with different media. For example, in production of nitro sugars that are used in various antibiotics, amino sugars are reported to be susceptible towards oxidation with e.g. ozone/oxone system or with dimethyldioxirane. As such, meglumine is irritating in case of skin and eye contact and through inhalation or ingestion. In normal conditions, meglumine is solid and stable. (Noecker et al. 2002, ScienceLab 2013)

In MAA, meglumine is connected to acridone acetate from the nitrogen atom at the head of the amino sugar structure. Acridone acetate is attached to that nitrogen atom on the functional group, OH, of the acetic acid. The chemical formulas of acridone and acridone acetic acid are $C_{13}H_9NO$ and $C_{15}H_{11}NO_3$ and molecular weights 195.2 g/mol and 253.2 g/mol, respectively. The chemical structures of acridone and acridone acetic acid are presented in Figure 11.
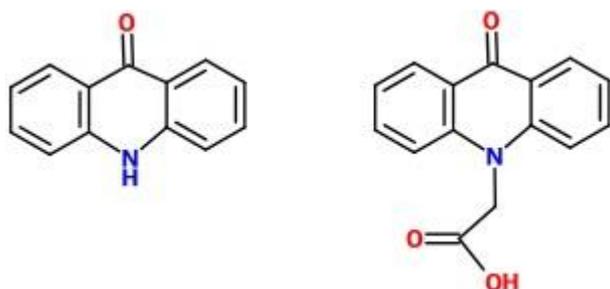
Figure 11. The chemical structures of acridone (left) and acridone acetic acid.

Acridone, sometimes referred to as acridanone, is a tricyclic oxidation product of acridine, which is sometimes used as an antioxidant, corrosion inhibitor or as an additive for other purposes. Acridine can be obtained in its acridone form from coal tar anthracene. (Collin & Höke 2000)

As such, acridone is skin and eye irritating, green to gold colored powder and stable under normal conditions (Fisher Scientific 2008). Acridone acetic acid is white to yellowish powder, also irritating and stable under normal conditions (Hamchem 2013).

3.3 Experimental conditions

The experiments were carried out in ambient conditions i.e. room temperature and pressure. As discussed in chapters 2.2.3 and 2.3.2, pH has an impact both in the plasma treatment of the solution and the photocatalytic activity of titanium dioxide. The experiments for oxalate were therefore conducted with two different initial pH levels, acidic and alkaline. For MAA, only high pH solutions were used for experiments as preliminary testing had indicated that the substance is poorly soluble in acidic conditions. Instead, the effect of initial concentration for MAA was studied with two different starting concentrations of 100 and 300 mg/L. Solution concentrations were chosen high enough for clear observation of the degradation rates of the substances.

For a batch reactor of similar construction, the flow rate of the treated solution has been observed to have little effect to the oxidation, provided that the flow is sufficient to produce even distribution of water along electrode plates (Panorel et al. 2011). For the present study, the flow rate was therefore set for well sufficient 4.5 L/min to equal a convenient 100 % value of the used flow meter. As pulse frequency is also one of the primary parameters that determine the efficiency of the process, two different frequencies of 833 pps and 500 pps were used for both substances.

3.4 Solution preparation

Four kinds of solutions were prepared for the experiments: acidic oxalate solution, alkaline oxalate solution and alkaline MAA solutions with two different concentrations. All solutions were prepared to tap water and each batch was of 10 liter volume.

3.4.1 Acidic oxalate solution

The acidic oxalate solution was prepared by adding solid oxalic acid dihydrate to the tap water. For the 10 liter volume, 10 mmol of oxalic acid was weighed to achieve a 1 mM oxalate solution. With two water molecules in the dihydrate, 1.26 g of the solid powder was weighed for each 10 liter batch. The pH of 3.4 that resulted from the addition of oxalic acid was considered to be suitable for the experiments; the addition of any other acid to further control the pH was considered unnecessary. The used oxalic acid was of technical quality with announced minimum purity of 98 %.

3.4.2 Alkaline oxalate solution

For the alkaline oxalate solution, pH level was increased by adding 100 ml of 0.1 M sodium hydroxide (NaOH) to 9.9 liters of tap water, making the total volume of 10 liter batch. Instead of using oxalic acid, the alkaline oxalate solutions were prepared by adding the oxalate in form of its sodium salt to the high pH tap water. For each 10 liter batch, 1.34 g equaling 10 mmol of sodium oxalate was weighed to achieve 1 mM oxalate solution. pH of the prepared solutions was approximately 10.5. The used sodium oxalate was of analytical quality with the announced minimum purity of 99.8 %.

3.4.3 MAA solutions

As discussed earlier, the experimental MAA solutions were prepared in tap water with elevated pH. The pH was increased with NaOH as described in chapter 3.4.2. The 100 ppm and 300 ppm MAA solutions were prepared by weighing respectively 1.0 g and 3.0 g of

the powdered substance into 10 liter batches of tap water with elevated pH. pH level for the prepared solutions was approximately 10.

3.5 Experimental procedures

Since oxalate was known to degrade slowly, relatively long experiments of 2 to 4 hours were carried out for the two frequencies of 833 and 500 pps, respectively. Samples were taken with respectively 15 and 30 min intervals. For being a commercial substance, MAA was desirable to be treated with decent energy consumption and therefore with shorter treatments of 30 to 60 minutes for the 833 and 500 pps frequencies, respectively. Sampling was conducted with respectively 5 and 10 min intervals. Zero samples for every experiment were taken after the solution was circulated within the system for roughly 10 minutes. The PCD was switched on immediately after zero samples were taken. Every experiment was repeated once to provide an indication of repeatability.

Temperature was not monitored during the experiments as no mentionable temperature change is involved in the process; as discussed earlier in chapter 2, one of the advantages of pulsed power is the avoidance of ohmic dissipation. Also, Panorel et al. (2011) reported only a minor temperature increase using similar configuration.

After each experiment, the system was washed by circulating tap water in it. This was also done before the very first experiment and when the device had been long unused, so that the starting conditions would be equal for every experiment: small amount of residual water was always present in the system between experiments. A good time was also given between experiments for proper ozone ventilation to guarantee every experiment with zero initial ozone level.

The catalytic experiments were conducted after the non-catalytic ones. For the purpose, the reactor was disassembled and the plate electrodes were coated with commercial Degussa P25 titanium dioxide. The powdered substance was added to water to make sludge that was sprayed onto the plates and dried, thus attaching the suspension on the plate surfaces. The procedure was repeated several times until the plates were well covered. A close taken

photo of the surface of a catalyst coated plate electrode is presented in Figure 12. After the electrode coatings were well dried, the reactor was reassembled and washed repeatedly to flush any loose titanium dioxide.

Figure 12. A plate electrode surface with titanium dioxide coating.

3.6 Analytical methods

The analytical methods used for quantifying oxalate and MAA concentrations were ionic chromatograph (IC) and high performance liquid chromatograph (HPLC), respectively. For supplemental data, the increasing nitrate concentrations were also derived from the IC curves. Samples from the treatment of MAA solutions were diluted with 1:10 ratio and filtered for analysis with a 2 µm syringe filter. The oxalate samples required no pretreatment as the concentrations were initially suitable for the analysis and the IC vials are capped with filters.

3.6.1 IC

IC was a method of choice for the oxalate analysis for its convenience and precision. An Ionex AS22 column was used for the analysis of oxalate concentrations. For the mobile phase, an eluent of 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ was used.

3.6.2 HPLC

The procedure for MAA analysis was provided by the manufacturer of the substance, Polysan Ltd. A Kinetex 2.6 µm C18 column was considered most suitable and for the mobile phase, and an eluent was prepared from 0.05 M potassium dihydrophosphate, acetonitrile and methanol in proportion of 65:30:5, respectively. The analysis was run with 0.35 mL/min flow rate and the wavelength of 254 nm.

4 RESULTS AND DISCUSSION

4.1 Observations

Visual change in color was observed in treated MAA solutions and in alkaline oxalate solutions. The initial, somewhat fluorescent yellow color of MAA solution had lost its fluorescence by first sampling at 0.83 kWh/m^3 energy delivered, and reached maximum visual intensity by third sampling at 2.5 kWh/m^3. The color change of MAA solution is presented in Figure 13. Alkaline oxalate solutions were initially slightly opaque but completely clear after treatment. Complete clarification was observed to be achieved by approximately 18 kWh/m^3 of energy delivered. Oxalic acid solutions were initially bright and no change in color appeared.
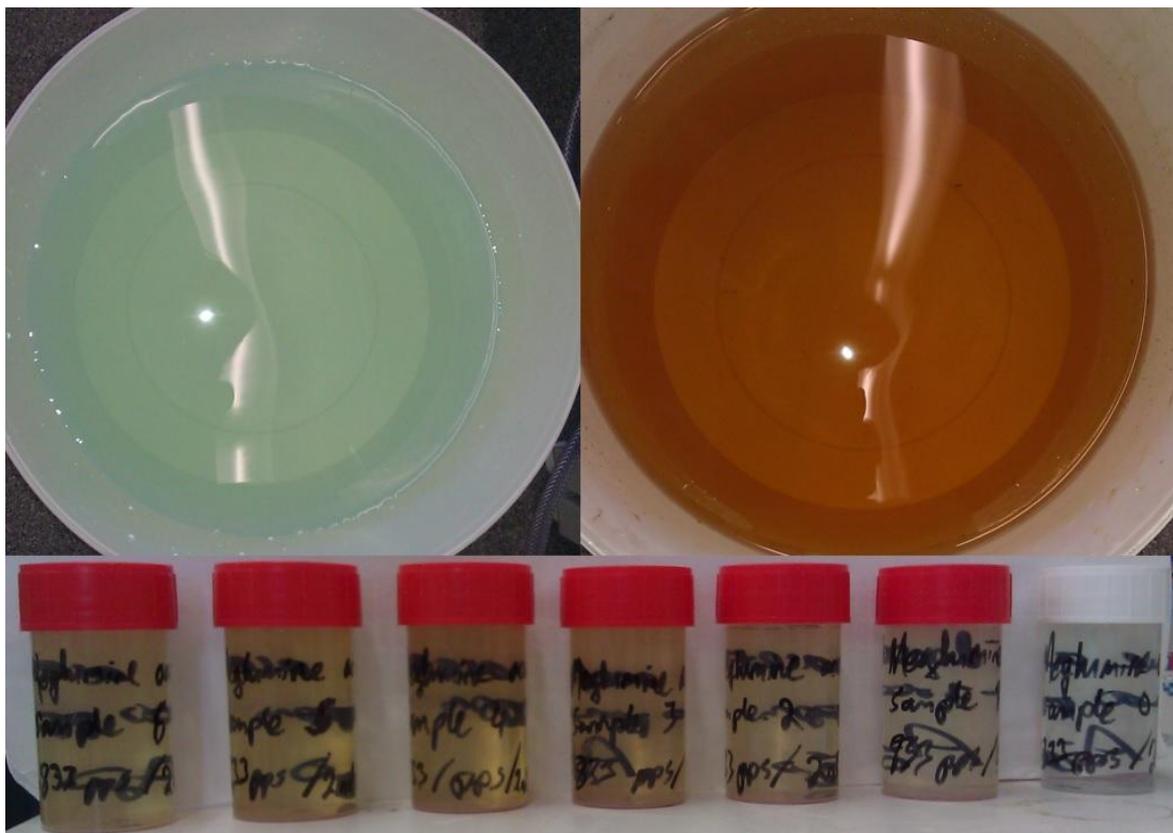
Figure 13. Changes in color of MAA solution before, during and after PCD treatment: Untreated 300 ppm solution (above left), the solution after treatment at 500 pps (above right) and samples from 300 ppm solution treated at 833 pps (below). The samples are chronologically ordered from right to left (rightmost sample 'zero' before PCD treatment).

For the experiments, pH was not maintained but merely adjusted along solutions preparation and measured in the samples collected during experimental runs. pH development during catalytic oxalic acid treatment is presented in Figure 14, from which one can see the expectedly stable development in acidic conditions. pH decreased from alkaline to acidic due to, most probably, formation of nitric oxides and nitric acid (see end of chapter 4.2). This assumption is supported by the fact that formation of nitrate and decrease of pH are both dependent on delivered energy and indifferent towards pulse frequency. No difference in pH development between catalytic and non-catalytic experiments was observed within accuracy of measurement. pH development was slower in MAA solutions, not decreasing under 4.5 in any experiment. pH data for catalytic treatment of oxalate solutions is presented in Figure 14. The data from non-catalytic oxidation of oxalate and oxidation of MAA are showed respectively in Figures A1 and A2 of Appendix I.
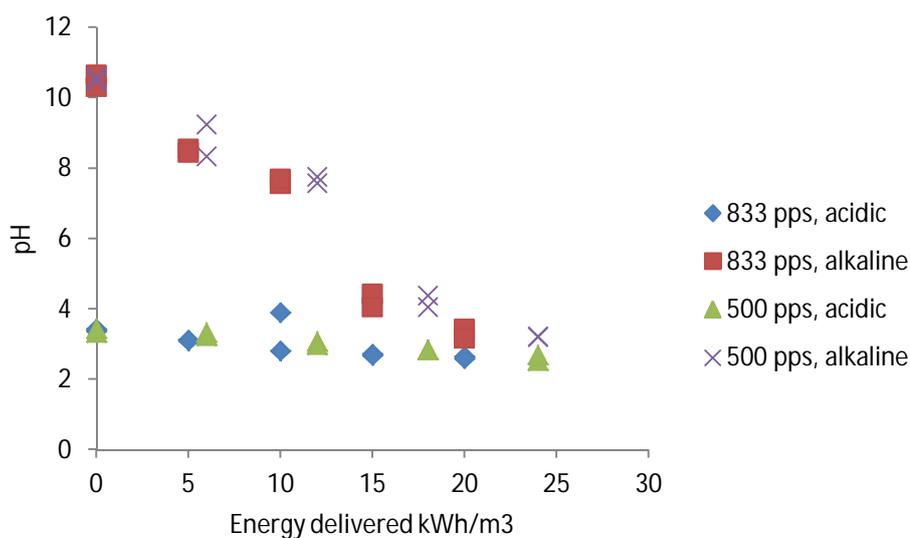
Figure 14. pH development in oxalate solutions during catalytic treatment.

Flow rate deviated around 3.5 to 4.5 L/min throughout the experiments as the pumping unit experienced minor instability. Regardless of this, no visual unevenness was observed in the distribution of water into the reactor chamber. In addition, despite of washing the system from loose catalyst particles after coating the plates, an amount of the substance was found settled onto the tank bottom after the first six catalytic experiments with oxalate. Some loose TiO_2 can be seen in Figure 15 which presents the emptied tank bottom after fifth catalytic experimental run on catalytic treatment of oxalic acid. After the first six experiments, no loose TiO_2 was found in the bottom of the tank, except for very fine amounts that were only detected by wiping the bottom with paper. The plate electrodes experienced visual loss of catalyst coating. As loose catalyst was found on the tank bottom only for six first experiments, it indicates that the catalyst coating was not eroded much during the following experiments, including two of the remaining experiments with oxalate and all MAA solutions. The TiO_2 coated plates before and after the catalytic experiments are presented in Figures 16 and 17. From Figure 16, one can clearly see that with the front plate, the catalyst layer erosion has focused vertically in the middle part of the plate, and particularly as horizontal stripes. This can be explained by the method of attaching the catalyst: for practical reasons, the catalyst sludge easily migrated to the edges of the plate and spraying the sludge between the wires did not enable perfect distribution. The locations where catalyst attachment proved the most difficult are seen washed clean in Figure 16. Figure 17 presents the coated rear electrode before and after the catalytic

treatment, and it can be seen that the catalyst erosion areas are not regularly focused. This is logical as the disconnected rear electrode was easier to coat.

Figure 15. Loose titanium dioxide particles in the tank bottom after fifth catalytic treatment of oxalic acid (833 pps).
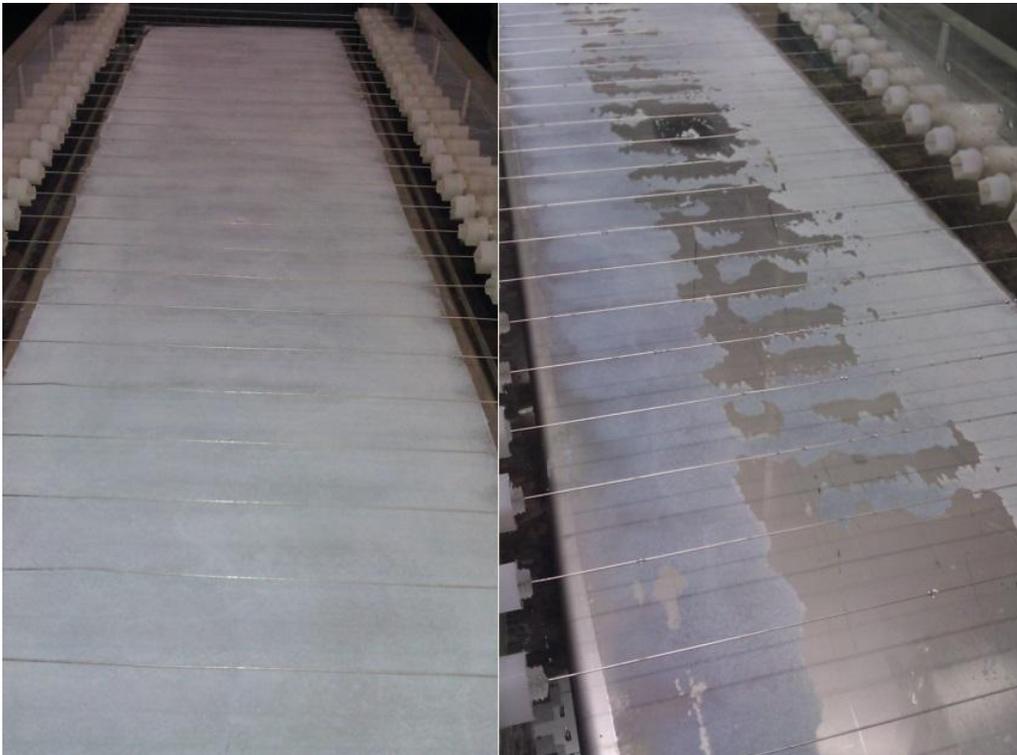
Figure 16. The front plate electrode with catalyst before (left) and after (right) the experiments.

**Figure 17.** The rear plate electrode with catalyst before (left) and after (right) the experiments.

4.2 Oxidation of oxalate

Experiments on oxalate oxidation were operated with a single oxalate starting concentration of around 0.5 mM at two various pH, acidic and alkaline, and two pulse repetition frequencies of 500 pps and 833 pps. Oxalate was oxidized slowly as was anticipated. The degradation was observed more energy efficient with the lower pulse repetition rate. The phenomenon was discussed earlier in chapter 2.2.2 and could be explained by the increased contribution of longer-living species that have more time to react between pulses. Complete or near complete degradation (95 to 100 %) of oxalate was achieved with 4-h treatment at 500 pps, corresponding to the energy consumption of 24 kWh/m^3.

The results of 2-h treatment at 833 pps, corresponding to the energy consumption of 20 kWh/m^3, indicated a beneficial character of acidic media for oxidation performance. Approximately 50-% degradation of oxalate was observed in alkaline solutions and 80-% degradation in acidic. The modest degradation of oxalate in alkaline solutions is connected to an interesting phenomenon that was observed after 12.5 kWh/m^3 of energy delivered at 833 pps: the degradation of the product seizes to 50 % level of the initial concentration, although the initial oxidation rate in alkaline solutions was even higher than in acidic ones. This tendency did not find a proper explanation in this work and needs further clarification.

The 2 h treatment results with 833 pps indicated some dependence on initial pH levels. A 50 % degradation was observed with the alkaline solutions, and 80 % degradation with the acidic. The modest degradation with the alkaline solutions is connected to an interesting phenomenon that was observed after 12.5 kWh/m^3 of energy delivered with the 833 pps treatment: the degradation of the product seizes to 50 % level of the initial concentration.

When the experiments were repeated with catalyst coated plate electrodes, similar trend was observed: the treatment at low frequency was generally more energy efficient and the degradation was inexplicably suppressed at 12.5 kWh/m^3 with 833 pps treatment in alkaline solutions (Fig. A4, Appendix I). With catalytic experiments, the achieved degradation ranged 55 to 70 % and 84 to 100 % at 833 pps and 500 pps, at the energy doses of 20 kWh/m^3 and 24 kWh/m^3, respectively. Efficiency for 30 % removal of oxalate, which all experiments well reached, is presented with different operating parameters in Figure 18.
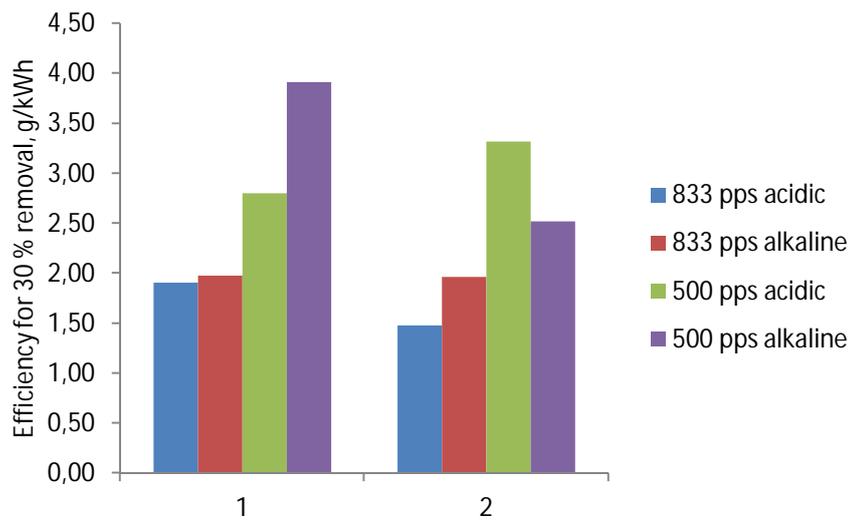
Figure 18. Oxidation of acidic and alkaline oxalate solutions with pulse frequencies of 833 pps and 500 pps. 1: non-catalytic treatment, 2: catalytic treatment.
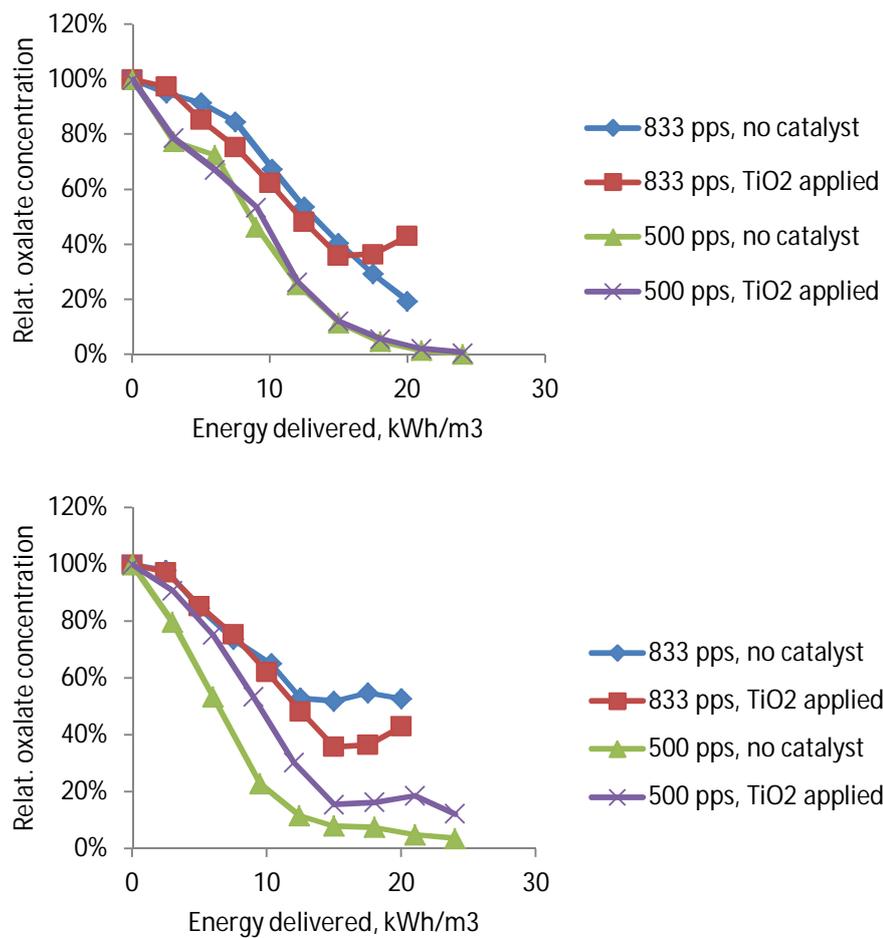

Figure 19. Non-catalytic and catalytic oxidation of oxalate in acidic (above) and alkaline solutions (below). The values represent average results of repeated experiments.

Comparison between the results of non-catalytic and catalytic experiments is presented in Figures 18 and 19. The results do not suggest any enhancement in oxidation attributable to the catalyst presence. Moreover, it seems that the treatment with TiO_2 coated plate electrodes might even have a slightly deteriorating effect on the oxidation rates at 500 pps under alkaline conditions (Fig. 18 and 19). This indicates that the catalyst coating might have had insulating or obstructing effect, thus somewhat altering the discharge conditions. However, considering the whole picture (Fig. 19), deviations within the accuracy of measurements and the relatively difficult degradability of oxalate most probably form the explanation for the observed deviation. Ultra violet radiation in the system might also be insufficient and the water flow is assumed to cause a screening effect for the catalyst surface electron bombardment that distracts photocatalytic activity. All non-catalytic and catalytic oxalate oxidation results are presented in Figures A3 and A4 of Appendix I.

Nitrate concentrations exhibited linear increase directly proportional to delivered energy. The formation of nitrate was nearly identical in both non-catalytic and catalytic experiments. Although very small, a consistent difference was observed as nitrate formation rate was slightly higher with non-catalytic treatment. Derived from the data of all experimental runs with oxalate, nitrate yield was 11.8 and 11.2 g/kWh in non-catalytic and catalytic experiments, respectively. The development of nitrate concentrations is presented in Figure 20.
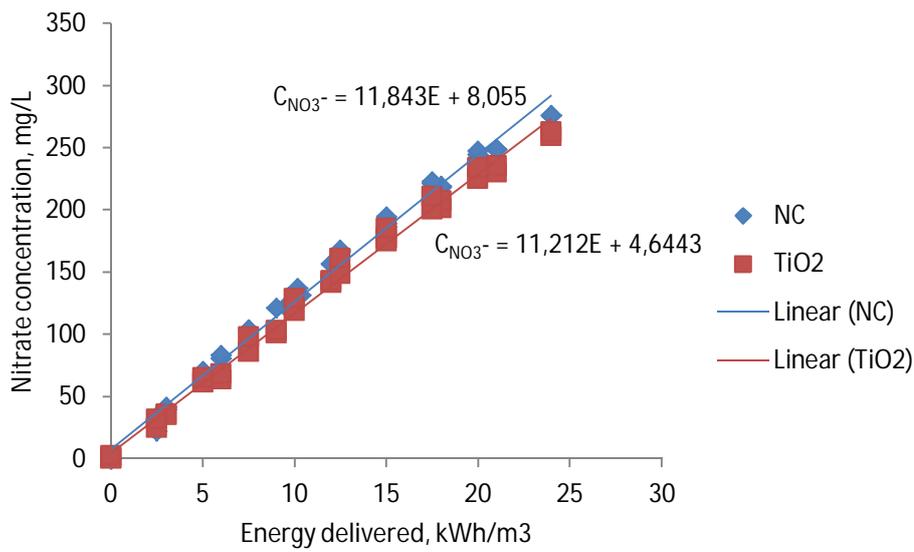
Figure 20. Nitrate formation. NC = non-catalytic experiment, TiO2 = catalytic experiment.

4.3 Oxidation of MAA

The energy efficiency of MAA oxidation was observed to be less dependent on pulse repetition frequency than with oxidation of oxalate. However, since the substance was observed to be readily degradable with PCD treatment, the indifference in pulse frequency may indicate that the majority of the oxidants produced by a single pulse are immediately consumed. This makes the amount of oxidants produced by a single pulse a limiting factor to the oxidation process. Efficiency for 30 % removal of MAA, which all experiments well reached, is presented with different operating parameters in Figure 21.
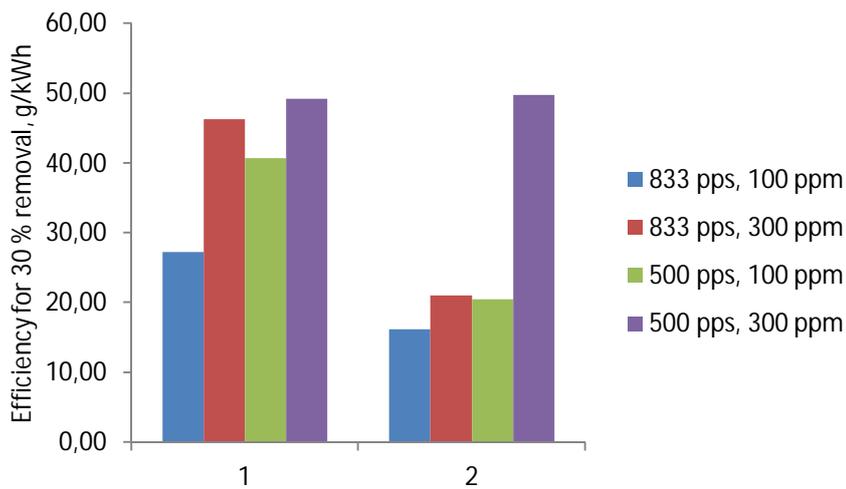
Figure 21. Oxidation of 100 ppm and 300 ppm MAA solutions with pulse frequencies of 833 pps and 500 pps. 1: non-catalytic treatment, 2: catalytic treatment.
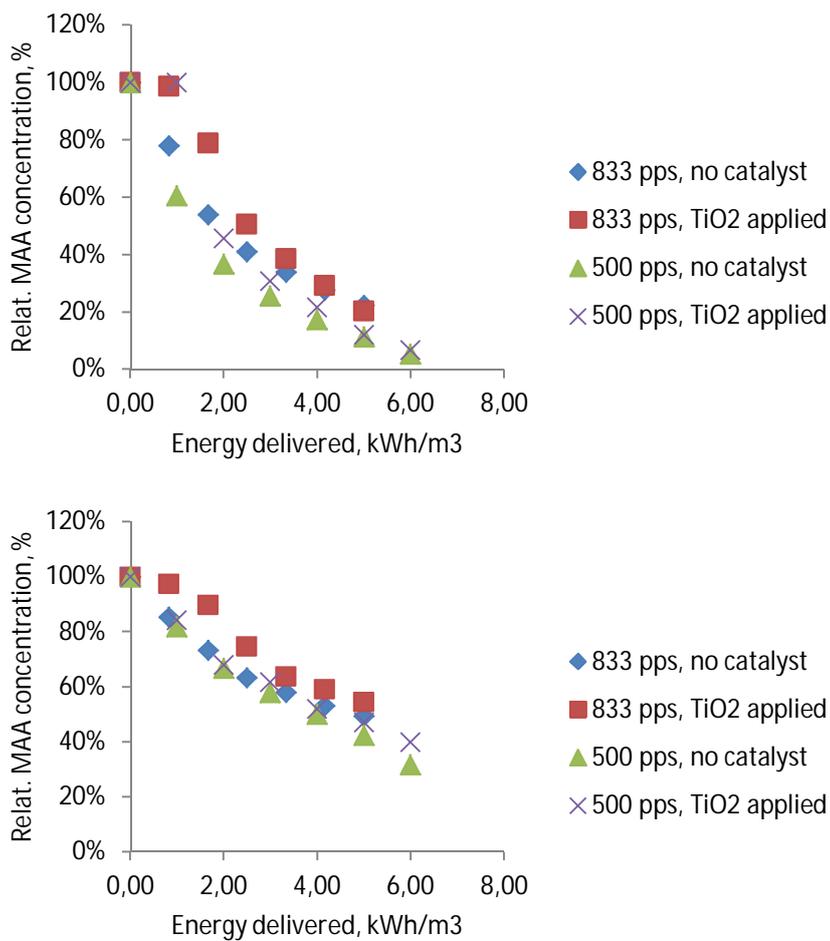
Figure 22. Oxidation of MAA with initial concentrations of 100 ppm (above) and 300 ppm (below). The values represent average results of repeated experiments.

Comparison between the results of non-catalytic and catalytic experiments is presented in Figures 21 and 22. One can see in Figure 22 that the curves resulting from different frequencies are nearly identical, but that the lower frequency curves have a tendency of settling just below those of higher frequency. For this reason, there is probably some, yet very fine contribution of the longer-living oxidants that have more time to react between pulses. From Figure 21, one can see that the energy efficiency for 30-% degradation of MAA is increased with higher initial concentration. This is explained by the probability of oxidant and pollutant collision, which is increased with higher substrate concentration.

Similarly to the results obtained from oxalate degradation, the applied catalyst cannot be observed to attribute any improvement to the process. Indeed, as one can see from Figure 21, the poorer efficiency of catalytic treatment against non-catalytic for 30-% degradation of the target substance is even clearer with MAA than with oxalate. For the initial concentration of 300 ppm, the catalytic oxidation at 833 pps experienced lag during the first kWh/m^3 delivered, which is clearly visible in Figure 22. The slow oxidation rate in the beginning logically resulted in poor efficiency determined for the 30-% reduction of MAA with the used parameters. From the comparison to the non-catalytic reference (Fig. 21) one can see that the efficiency for the non-catalytic oxidation of 300 ppm MAA solution at 833 pps is over twice that of the catalytic one. This may be due to problems that were contemplated earlier in chapter 4.2 regarding the catalyst presence.

5 CONCLUSIONS

Degradation of aqueous oxalate was expectedly slow, achieving 3.9 g/kWh efficiency for 30-% degradation at best in alkaline solution at 500 pps. However, at higher frequency of 833 pps, better oxidation rate was observed with acidic than alkaline solution as respective 80-% and 50-% oxidation rates were achieved. This is because for some, so far inexplicable reason, the oxidation in alkaline solutions with 833 pps seized after 12.5 kWh/m^3 of energy was delivered, remaining at 50-% level. To explain this phenomenon, further studies are required on the effect of pH to the process, and its complex interaction with other process parameters. Overall oxidation efficiency of oxalate showed its dependence on pulse frequency, giving clearly better overall results with lower frequency.

This is considered to be mostly due to the contribution of longer-living oxidants, like ozone, that have more time to react with the target pollutants between the discharge pulses, during which short-living species like hydroxyl radical prevail.

Degradation of aqueous MAA with PCD is overall efficient. Highest efficiency of 50 g/kWh for 30-% removal was achieved with 300 ppm concentration of the substrate at low pulse repetition frequency of 500 pps. Overall results with MAA indicated that the oxidation efficiency of the substance shows little, yet some dependence on pulse repetition frequency as lower frequency resulted in somewhat better efficiency. Meglumine acridone acetate is therefore suggested to be readily degradable along introduction of both powerful short-living oxidants and ozone that are rapidly consumed. From a practical aspect, treatment of water containing compounds like fast-reacting MAA could be considered to benefit from high pulse repetition frequency: the convenience of shorter treatment time over the modest improvement in energy efficiency might prove remarkable. Further studies for PCD use of the present configuration in field conditions and with real life solutions with e.g. industrial origin, are therefore recommended.

With both oxalate and MAA, pH of alkaline solutions decreased to acidic during treatment. This is considered to be the result of nitric acid and nitrates that were produced in the process from atmospheric nitrogen. The yield for nitrate formation showed small but consistent difference for non-catalytic and catalytic treatment with respective 11.8 g/kWh and 11.2 g/kWh rates. Further studies are required to explain the mechanism and possible catalytic effect resulting in the different yields.

Commercial TiO_2 photocatalyst Degussa P25 that was used to coat the grounded plate electrodes of the PCD device attributed no enhancement in oxidation rates of either oxalate or MAA. Moreover, in several occasions the results for catalytic treatment indicated lower efficiency than the corresponding non-catalytic ones, which may, regarding the accuracy of measurements, be explained by the alteration of discharge conditions by the presence of the catalyst. Ultra-violet radiation may also not be sufficient in the experimental conditions to attribute notable photocatalytic activity. Further studies are recommended for different ways to introduce the catalyst to the present configuration, e.g. means to locate the catalyst

directly into the plasma field. Additional areas for further studies could include possible combinations of PCD with different water treatment methods, electrode material abrasion, and residual toxicity or secondary pollution.

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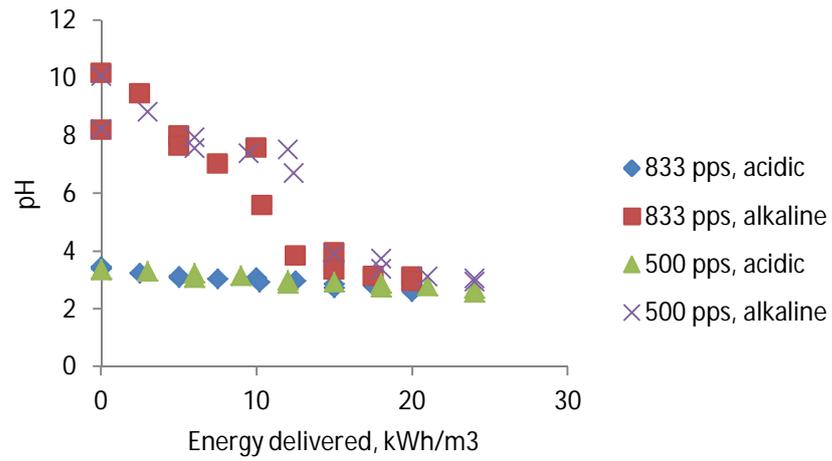
**Figure A1.** pH development in oxalate solutions during non-catalytic treatment.
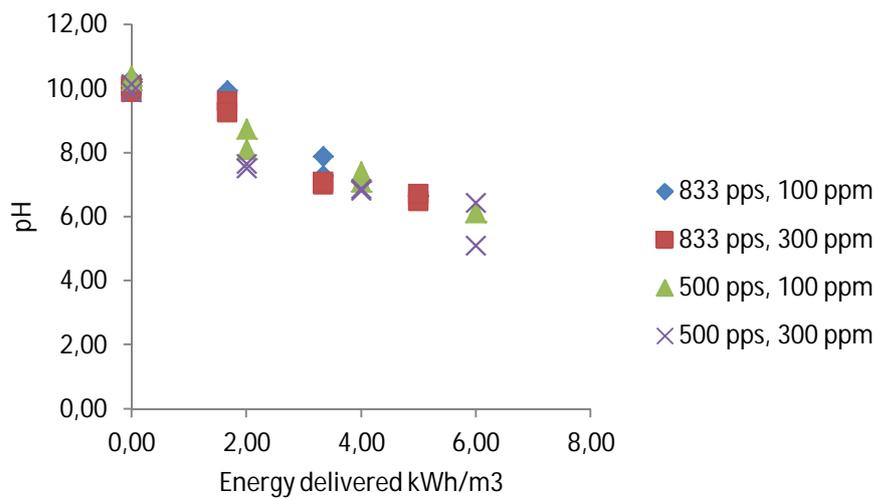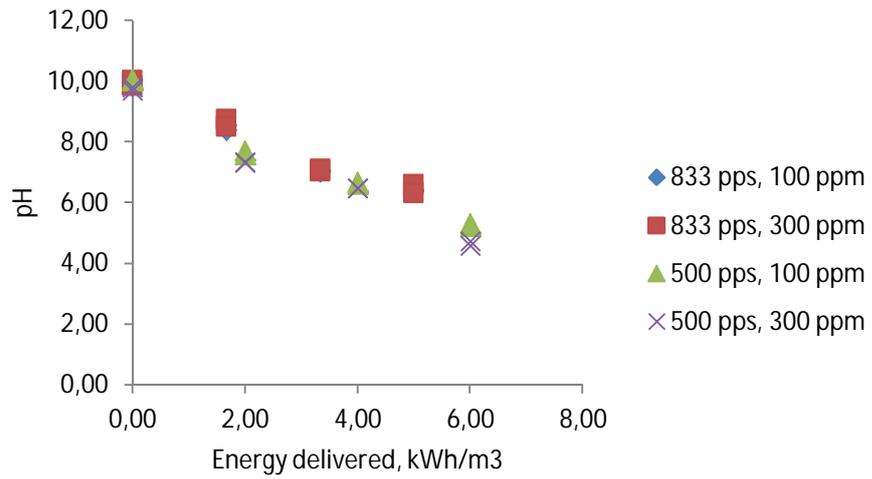
Figure A2. pH development in MAA solutions during non-catalytic (above) and catalytic (below) treatment.
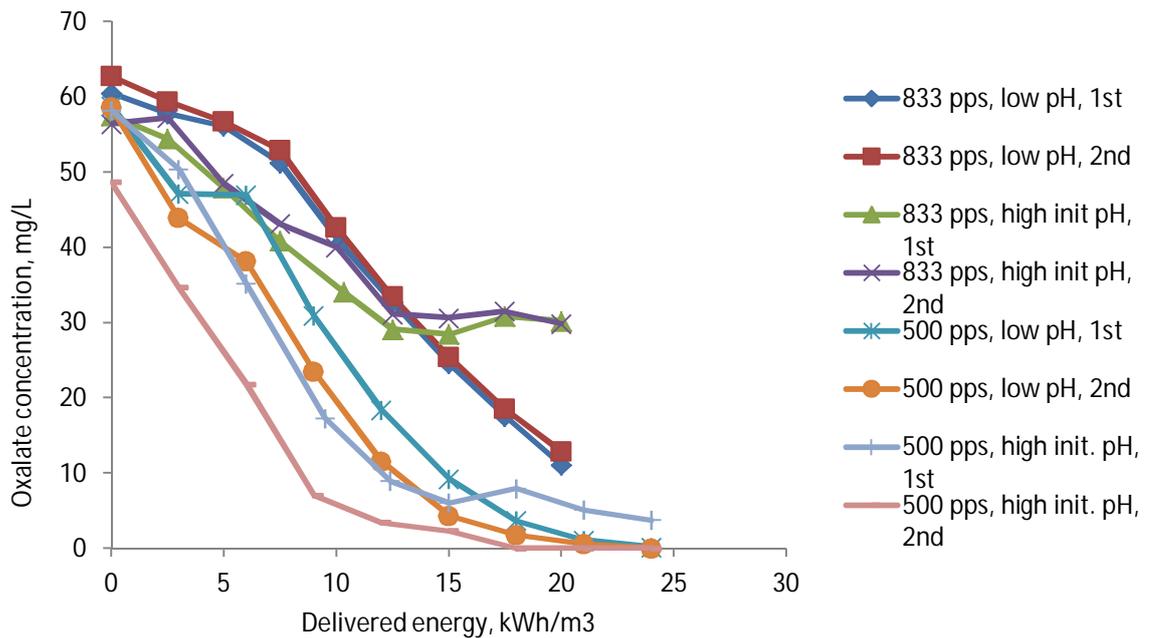
Figure A3. Non-catalytic oxalate oxidation. Initial pH values of 3.5 (low) and 10 (high) and the pulse frequencies of 833 pps and 500 pps. 1st and 2nd stand for first and repeated experiments under same conditions.
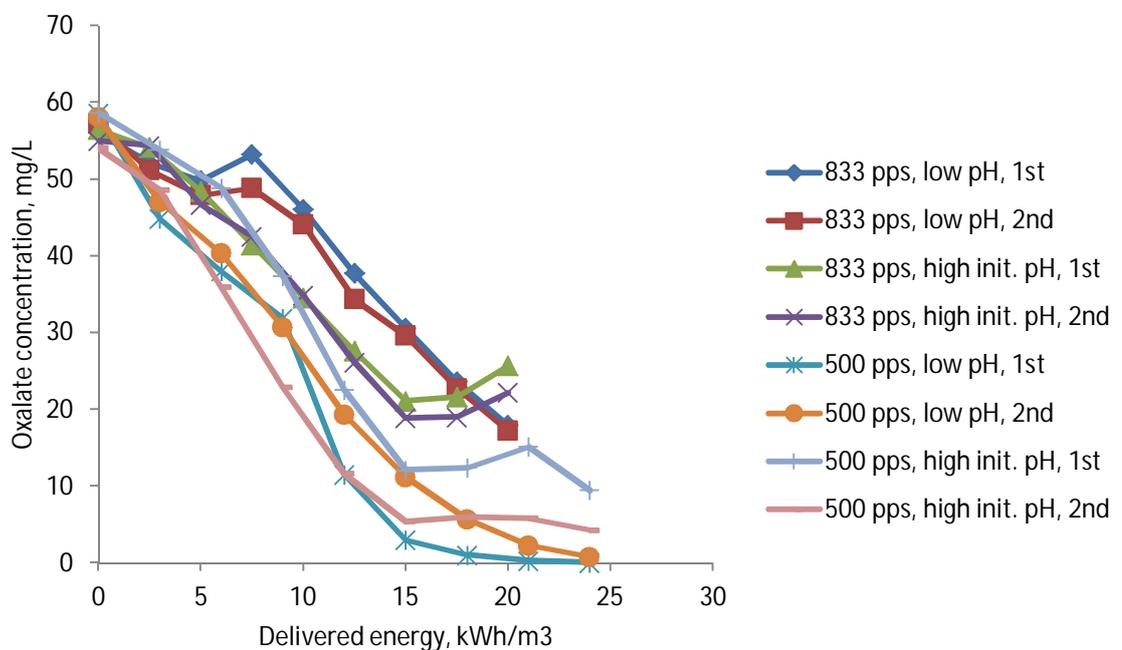
Figure A4. Catalytic oxalate oxidation. Initial pH values of 3.5 (low) and 10 (high) and the pulse frequencies of 833 pps and 500 pps. 1st and 2nd stand for first and repeated experiments under same conditions.