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Department of Chemical Engineering  
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**FORMATION OF NITRATES IN WATER IN PRESENCE OF FORMATE AND  
OXALATE TREATED WITH PULSED CORONA DISCHARGE (PCD)**

Bachelor thesis

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Tavallisten hapetusmenetelmien sijasta kehittyneitä hapetusmenetelmiä (AOP) on kehitetty yhä enemmän, jotta hapetusprosessista tulisi kannattavampi, tehokkaampi, ympäristöystävällisempi ja sitä voitaisiin hyödyntää laajalti eri paikoissa. Uusi teknologia, joka käyttää otsonia ja hydroksyyliiradikaalia sähköimpulssien kanssa, on yksi mahdollinen tehokkaampi vedenkäsittelymenetelmä. Kyseistä menetelmää kutsutaan pulsed corona discharge (PCD) -menetelmäksi, joka käyttää prosessissa muodostuvia otsonia ja hydroksyyliiradikaalia hapettavina tekijöinä.

Tässä työssä tutkittiin nitraatin muodostumista vedessä, kun vettä käsiteltiin PCD-laitteessa ja, kun oksalaatti- ja formaatti-ioneja oli sekoittuneina veteen. Nitraatteja muodostuu PCD-laitteessa veteen, kun ilman typpi reagoi hapettimina toimivien otsonin ja hydroksyyliiradikaalin kanssa. Aiemmissä tutkimuksissa nitraatin muodostumisen on todistettu parantuvan, kun karboksyylihapot muurahais- ja oksaalihappo ovat sekoittuneina veteen. Tässä tutkimuksessa tarkoituksena oli tutkia, miten formaatti- ja oksalaatti-ionien, joiden pitoisuudet olivat 0 ppm, 50 ppm ja 100 ppm, läsnäolo vedessä vaikuttaa nitraatin muodostumiseen. PCD-kokeista saadut näytteet analysoitiin ionikromatografilla.

Kyseisessä tutkimuksessa nitraatin muodostuminen oli samansuuruista jokaisessa kokeessa hapetusajan kasvaessa samalla, kun otettujen näytteiden pH-arvot laskivat. Tuloksena voitiin pitää sitä, ettei formaatti- tai oksalaatti-ioneilla ollut vaikutusta nitraatti-ionien muodostumiseen.

## **Abstract**

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Instead of using common oxidation in wastewater treatment advanced oxidation processes (AOPs) have been developed for making the oxidation more cost-effective, environmentally friendly and useful in different places. New technology using ozone and hydroxyl radicals with electric discharges is one possible way to improve water treatment. This specific method is called pulsed corona discharge (PCD) and it utilizes formation of ozone and hydroxyl radicals to oxidize compounds in water.

In this study formation of nitrate in water in the presence of oxalate and formate when the water is treated with PCD was examined. Nitrates are formed in PCD when the nitrogen from air reacts with ozone and hydroxyl radicals. In previous studies carboxyl acids, formic and oxalic acids, have been discovered to have enhancing influence in formation of nitrates. In this study formation of nitrate was examined using low concentrations of 0, 50 and 100 ppm of formic and oxalic acid. Samples from PCD experiments were analyzed using ion chromatograph.

As result formation of nitrate remained the same in every experiment when oxidation time was increased and at the same time when pH of samples was decreased. As conclusion in these conditions formate and oxalate did not have significant effect on the formation of nitrate.

## Symbols

E	Energy delivered, kWh/m <sup>3</sup>
P	Power, kW
t	Time, h
V	Volume of treated water, m <sup>3</sup>
$\Delta c$	Concentration difference between different samples, g/m <sup>3</sup>
$\varepsilon$	Energy efficiency, g/kWh

## Abbreviations

AOP	Advanced oxidation process
CH <sub>3</sub> OH	Cyclohexanol
·CH <sub>2</sub> OH	Cyclohexanol radical
(COOH) <sub>2</sub>	Oxalic acid
e <sup>-</sup>	Electron
Fe <sup>2+</sup>	Iron(II)
Fe <sup>3+</sup>	Iron(III)
Fe(OH) <sup>2+</sup>	Iron(II)hydroxide
HCOOH	Formic acid
HNO <sub>3</sub>	Nitric acid
H·	Hydrogen radical
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
hν	High voltage
NaOH	Sodium hydroxide

NO	Nitric oxide
NO <sup>2-</sup>	Nitrite
NO <sup>3-</sup>	Nitrate
NO <sub>2</sub>	Nitrogen dioxide
N <sub>2</sub> O <sub>3</sub>	Dinitrogen trioxide
O <sub>2</sub>	Oxygen
O <sub>3</sub>	Ozone
O·	Oxygen radical
OH·	Hydroxyl radical
PCD	Pulsed Corona Discharge
TiO <sub>2</sub>	Titanium dioxide
UV	Ultraviolet radiation

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## 1. INTRODUCTION

Advanced Oxidation Processes (AOPs) have been investigated and developed more in last decade as one process step in wastewater treatment processes. AOPs can be utilized in the disinfection step of wastewaters, where microorganisms are killed and made unable to regrow by oxidation. Advantages obtained using AOPs are environmentally friendly and cost-effectively working process. In AOPs used oxidant is hydroxyl radical. Hydroxyl radicals have significantly higher oxidative character than many other oxidants. This leads to the effective killing of microorganisms. (Andreaozzi et al. 1999)

Pulsed corona discharge (PCD) can be used in wastewater treatment and it is one of the AOPs utilizing electrical discharge. PCD has been proven to be a significantly efficient method to form ozone and hydroxyl radicals to oxidize compounds in water. PCD utilizes electrical discharges to form ozone which then forms hydroxyl radicals. (Lukes 2001)

Nitrate formation in waters is a serious issue due to the toxicity of nitrate for human nature and also nitrates can cause damage to environment because nitrates are nutrients thus they can enhance eutrophication. Eutrophication decreases amount of oxygen in waters which leads to the death of other organisms which means that nitrates should not be forming in wastewater treatment. (EPA 2014) However nitrates are formed in PCD due to the reaction of nitrogen in air with oxidants ozone and hydroxyl radical. (Kornev et al. 2013)

Carboxylic acids formic and oxalic acid might be factors affecting nitrate formation by enhancing the formation. The theory is based on the fact of formate and oxalate reacting with ozone can regenerate hydroxyl radicals. This leads to the expected increasing formation of nitrate. (Yapsakli & Can, 2004)

### 1.1. Objective

In this current study the objective was to study if nitrate formation, which occurs when water is oxidized by PCD method, is enhanced, when carboxylic acids, formic and oxalic acid, are present in water in low concentrations. Concentrations of acids where 0,

50 and 100 ppm and the experiments were done separately for both acids. Conditions in experiments were defined to be alkaline.

## 2. ADVANCED OXIDATION PROCESS

Oxidation is used in treatment of potable water to kill and make the bacteria, viruses and pathogens unable to grow. In advanced oxidation processes hydroxyl radicals are the main oxidative agents. To study AOPs ozone is generally also taken into account.

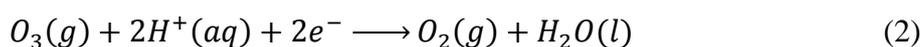
### 2.1. Ozone

Ozone  $O_3$  is an allotrope of oxygen. It is poisonous and it can be easily recognized by smell even in small quantities. (McMurry & Fay 2008) Ozone consists of three oxygen atoms and the ozone molecule is gaseous but very unstable. This means ozone reacts spontaneously forming oxygen. Ozone is highly soluble in water even more than oxygen and the solubility is affected by temperature. Solubility of ozone in water decreases when temperature is increased. (von Sonntag & von Gunten 2012)

When oxygen is treated with an electrical discharge it forms ozone. Reaction of oxygen to ozone is endothermic and this formation of ozone is shown in reaction 1. (McMurry & Fay 2008)



Ozone is used in oxidation processes because it has significant oxidizing character. It is more efficient in oxidizing than for example hydrogen peroxide or chlorine. Ozone's oxidation potential is 2.07 V when chlorine has 1.36 V and hydrogen peroxide 1.77. (Kirschner 2000) This is why it is commonly used in water treatment where it kills bacteria and pathogens. Oxidation of ozone is shown in reaction 2 where reaction products are water and oxygen. (McMurry & Fay 2008)



When ozone reacts with some organic compounds such as amines, hydroxyl radicals are formed as products of side reactions. This means when ozone is utilized in wastewater treatment hydroxyl radicals are always formed. (von Sonntag & von Gunten 2012)

In wastewater treatment processes ozone is utilized as disinfectant. In disinfection step ozone destroys bacteria, helminths, protozoa and viruses which may cause serious diseases such as cholera spread by the *Vibrio cholera* bacteria organism (EPA 1999). Ozone is first generated with electrical discharge. Then ozone is led to flow through a wastewater chamber where it flows in small bubbles disinfecting the wastewater. Ozone can be utilized also as covering agent of odor. (von Sonntag & von Gunten 2012)

Reasons for why rather ozone would be better factor in disinfection than for example chlorine is that ozone has extremely spontaneous character. In gaseous form ozone has to be post-treated but in PCD, for instance, the reactor is a closed system removing the requirement. Also after ozonation microorganisms are unable to regrow in the system. (von Sonntag & von Gunten 2012, Kirschner 2000)

## 2.2. Hydroxyl radical

Hydroxyl radical is a free radical and it has an unpaired electron (Winkler et al. 1999). Hydroxyl radical is highly oxidizing and it is even more oxidizing than ozone having oxidation potential 2.8 V (Dorfman & Adams 1973). Also reaction rate constant of hydroxyl radical explains the reactive character having the rate constant of  $10^6 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for many ozone refractory organic compounds (Andreozzi et al. 1999). Hydroxyl radical (OH) is more like weak than strong acid from its properties. When OH is ionized it forms  $\text{O}^-$  ions.  $\text{O}^-$  ions do not react in the same way as hydroxyl radicals. (Dorfman & Adams 1973)

Hydroxyl radicals can be formed in both biological and chemical reactions. In aquo-organic systems, which include hydroxylation and oxidation reaction steps, hydroxyl radicals can be formed. Also in reaction steps of oxidation reactions of inorganic ions and ion complexes and in the beginning of polymerization hydroxyl radicals will form. (Dorfman & Adams 1973)

The main reaction where hydroxyl radical is formed in biological reactions is radiation biology. This is because water is the main component in all kind of cells so when biological damage is happening it may be consequence of oxidative character of hydroxyl radical. (Dorfman & Adams 1973)

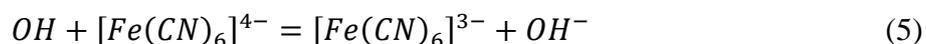
There are four main reactions of hydroxyl radical in water: addition, hydrogen abstraction, electron transfer and radical interaction. These reactions are all chemical reactions. In addition reaction a free radical is formed when either aliphatic or aromatic compound is led to react with hydroxyl radical. (Dorfman & Adams 1973)



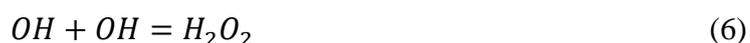
In equation (3) a cyclohexadienyl radical is formed. In hydrogen abstraction for example one hydrogen is separated from methanol when it reacts with hydroxyl radical. Products are water and a free radical. (Dorfman & Adams 1973)



In electron transfer hydroxyl radical reacts with mononegative ion which leads to forming ions in a higher valence state, an atom or a free radical (Dorfman & Adams 1973).



When two hydroxyl radicals are led to react together they can form hydrogen peroxide (Dorfman & Adams 1973).



The formation of hydroxyl radical from water is presented in equation (7) (Dorfman & Adams 1973).



## 2.1. Advanced oxidation processes

Advanced oxidation processes (AOPs) have been developed and discussed more due to their more effective oxidative character and harmless end products (Grote 2012). AOPs have been used not only in wastewater treatment but also in other fields such as soil remediation, odor control and volatile organic compound treatment (Comninellis et al. 2008). However AOPs have not been used widely in wastewater treatment in a large scale due to the costs of chemicals and the possibility of hydroxyl radicals to oxidize less effectively if specific chemicals are in water for example carbonate or bicarbonate (Grote 2012).

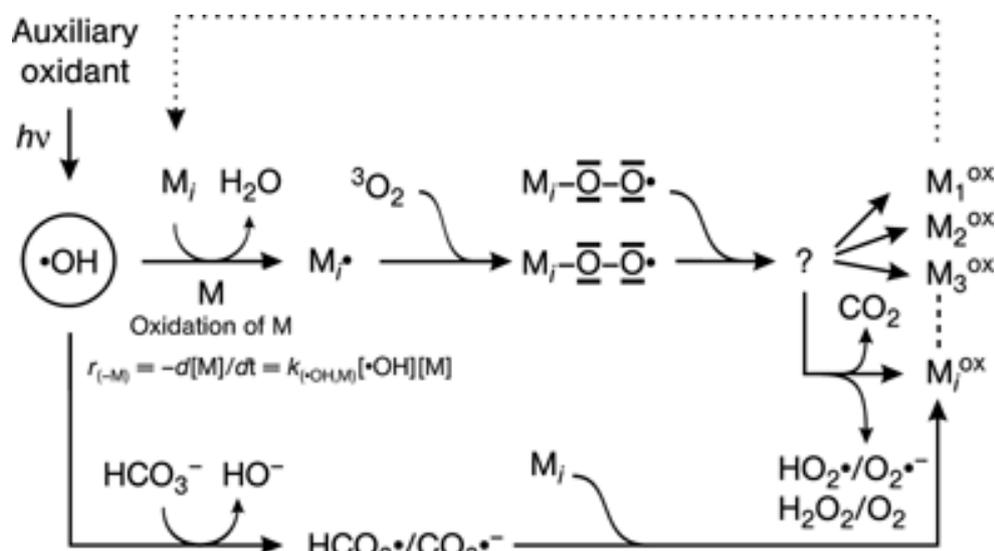
Process steps in AOP include the formation of hydroxyl radical, which as mentioned earlier has the highly oxidative character, and the reaction between hydroxyl radicals and the compounds to be destroyed. In AOPs combinations of methods using UV, ozone, hydrogen peroxide and titanium dioxide can be used to enhance the oxidation process. (Grote 2012)

AOPs are known for their huge amount of energy consumption because production of radicals requires energy. This has led to the development of electrical discharge methods which can be utilized in water treatment. (Lukes 2001) Different methods using electrical discharges are, for instance, PCD, which is the method used in this research, spark discharge in gas bubbles, PCD over a water surface, flash corona over a water surface and PCD in water aerosol. (Kornev et al. 2013) Other AOPs, which utilize different methods than electrical discharge, are, for instance, photochemical and electrochemical oxidation, UV photolysis, Fenton-type reactions, TiO<sub>2</sub> photocatalysis and wet oxidation. (Lukes 2001)

### 2.1.1. Photochemical and electrochemical oxidation

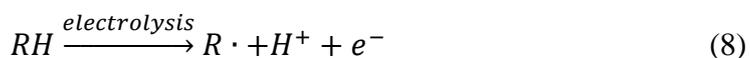
In photochemical oxidation organic molecules are oxidized by first either separating hydrogen by hydroxyl radicals or forming carbon-centered radicals by adding hydroxyl

radicals to C=C bonds. After oxidation mineralization of molecules will occur, when carbon radicals are scavenged and will form peroxy radicals which mineralize organic molecules. The oxidation and mineralization reactions in photochemical oxidation are shown in figure 1. (Pfoertner & Oppenländer 2012)



**Figure 1.** Oxidation and mineralization of organic molecules in photochemical oxidation method using hydroxyl radical as oxidant. (Pfoertner & Oppenländer 2012)

In electrochemical oxidation pollutants can be oxidized on anodes either having hydroxyl radical or oxygen in oxide lattice as oxidizing agents (Chen 2004). After electrolysis where electron from a molecule is transferred to the electrode radical cation is formed (Lukes 2001).



Electrodes such as Pt/IrO<sub>2</sub>, Ti/Pt and SnO<sub>2</sub>/Ti can be utilized to prevent the possible recombination or ions and radicals which are deteriorating oxidation (Lukes 2001).

### 2.1.2. Ultraviolet photolysis

Photolysis using ultraviolet light oxidizes organic compounds by formation of radicals. The organic compound is first excited by ultraviolet light and, when the excited compound reacts with oxygen, electrons are transferred thus making organic compound and oxygen grounded. Radical ions which are reacting with oxygen in the

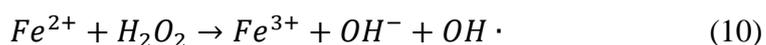
final step are being formed by recombination, hydrolysis or homolysis. (Legrini et al. 1993)



By using ultraviolet photolysis hazardous wastes can be removed from wastewaters, for instance, chlorinated and nitrated aromatics, phenols, halogenated aliphatics and oil (Legrini et al. 1993).

### 2.1.3. Fenton's process

Fenton's process is an old process but it has been developed to be utilized in wastewater treatment as one of the AOPs. In Fenton's process a reagent called Fenton's reagent is forming hydroxyl radicals when the reagent is led to react with hydrogen peroxide as follows. (Andreozzi et al. 1999)



With Fenton's reagent phenols and herbicides can be destroyed in wastewaters. Chemicals used in this process are not environmentally harmful thus it has been considered to be a viable process. However it requires some specific conditions such as specific pH range. (Andreozzi et al. 1999)

Fenton's reagent can be used also with UV-VIS light. In this case  $Fe^{2+}$  can be regenerated as follows (Andreozzi et al. 1999).

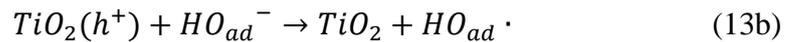
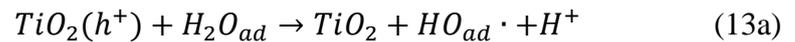


#### 2.1.4. TiO<sub>2</sub> photocatalysis

In process called photocatalysis oxygen is the oxidant when a semiconductor metal oxide is present. From these metal oxides TiO<sub>2</sub> is considered to be the most effective one. In the initial step of photocatalysis electron-hole pairs are formed as shown in equation (12). (Andreozzi et al. 1999)

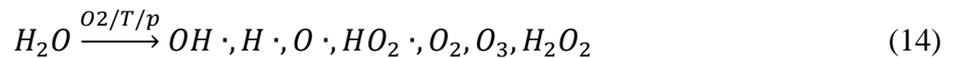


After formation of electrons superoxide anion can be formed and H<sub>2</sub>O and HO<sup>-</sup> can be oxidized to form hydroxyl radicals (Andreozzi et al. 1999).



#### 2.1.5. Wet air oxidation

Wet air oxidation is used to oxidize pollutants by using oxygen or air in high temperatures and pressures (Andreozzi et al. 1999). Commonly used temperature is in range of 175 and 325 °C and the pressure between 4 and 20 MPa. By having high temperature and pressure conditions more oxygen will be transferred from gas phase into liquid phase and also these conditions will speed the reaction between oxygen and pollutants. Some additional metal ions can be added thus making all the following products be able to form to oxidize compounds in water. (Lukes 2001)

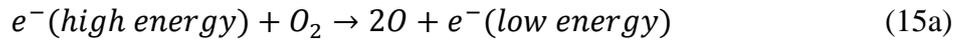


#### 2.1.6. Pulsed Corona Discharge

Pulsed corona discharge is one of the developed Advanced Oxidation Processes. PCD utilizes high voltage pulses to lead electric discharge through a substance. In this case the substance is a gas phase from where water is dispersed through in the form of droplets. This treatment of water forms ozone and hydroxyl radicals which can then

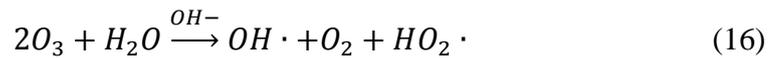
oxidize compounds. High voltage pulses are short corona discharges which form plasma. Presence of plasma produces chemical and physical phenomena, for instance, high electric field, intense ultraviolet radiation, overpressure shockwaves and it also forms substances which will react with compounds in water. These substances are reactive radicals  $\text{OH}\cdot$ ,  $\text{H}\cdot$ ,  $\text{O}\cdot$ ,  $\text{HO}_2\cdot$ . (Lukes 2001, Kirschner 2000)

Reaction where ozone is formed in PCD is as follows



Oxygen is led to react with free electrons which have high energy. Then oxygen molecules and atoms will react forming ozone. Substance Z can be either nitrogen or carbon dioxide in gaseous form. Amount of oxygen in the feed gas and corona power density are the factors affecting amount of formation of ozone. (Kirschner 2000)

When ozone decomposes in PCD hydroxyl radicals are formed (Lukes 2001).



### 3. NITRATE FORMATION WITH PCD IN PRESENCE OF FORMATE AND OXALATE

Nitrates and nitrites are formed in PCD due to the presence of nitrogen in air. Formation of nitrate in PCD has been studied because of nitrate and nitrite anions are not desired to be present in treated wastewater. However nitrate and nitrite anions can be utilized in some other treatment methods, for instance, process solutions and synthesis of nitro-compounds. (Kornev 2013)

### 3.1. Nitrate

Nitrate in potable water may cause some serious diseases. The amount of nitrate in water is controlled to avoid problems in human health. In human body nitrate converts to nitrite. For infants nitrite causes blue baby syndrome in which the hemoglobin can't anymore carry enough oxygen. If people are exposed to nitrate by drinking water long enough they will come unwell and in worst cases even die. (EPA 2014)

Air is available to lead in to PCD which means nitrogen is present in the experiments. Nitrogen can react with ozone and hydroxyl radicals which leads to formation of nitrites and nitrates. When nitrogen reacts with ozone and hydroxyl radicals first primary reaction occurs. Nitrogen oxides (NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>) are formed and they will react as follows. (Kornev et al. 2013)



With high concentrations of ozone N<sub>2</sub>O<sub>5</sub> is mainly formed and it will react with water forming nitrites (Kornev et al. 2013).



When nitrites are able to react with ozone nitrates are formed (Kornev et al. 2013).



After treatment with PCD almost all of nitrites have reacted completely forming nitrates. Some nitrogen can be left in the solution but amount of nitrates is the largest. (Kornev et al. 2013)

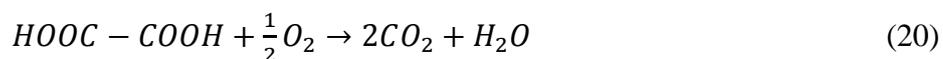
### 3.2. Oxalate

In this study oxalate is used in form of oxalic acid (COOH)<sub>2</sub> and the molecular weight of oxalic acid is 90.04 g/mol. The molecular weight of oxalic acid dihydrate is 126.07

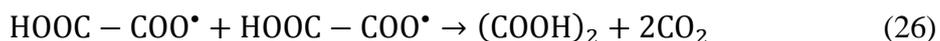
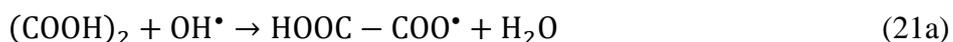
g/mol and it is most commonly used form of oxalic acid. Oxalic acid is one of the polyprotic acids which means that it has at least one proton that can be removed. Because these acids have more than one proton the polyprotic acid will degrade in many steps. Oxalic acid has some poisonous character for example in rhubarb. (McMurry & Fay 2008) Oxalic acid is also a strong acid and in this study oxalic acid is used as oxalic acid dihydrate. From its solubility properties oxalic acid is soluble in many alcohols and acetone for instance. (Riemenschneider & Tanifuji 2011)

One source from where oxalic acid is formed, for instance, is when carbohydrates are not fully oxidized in plants. Common methods where oxalic acid is used are metal treatment, textile treatment, chemical uses and it has been used also as bleaching agent. (Riemenschneider & Tanifuji 2011)

When oxalic acid is reacting with oxygen they form carbondioxide and water (Riemenschneider & Tanifuji 2011).



When oxalic acid is oxidized by OH<sup>•</sup> radical or by ozone it reacts as in following reactions (Aristova et al, 2002).



It is possible to oxalic acid to enhance the nitrate formation due to its regeneration of hydroxyl radical (Andreozzi et al. 1999).

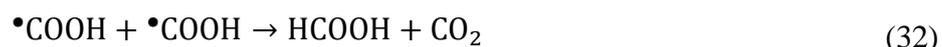
### 3.3. Formate

Anion in formic acid is formate and its formula is  $\text{HCO}_2^-$ . Formic acid ( $\text{HCOOH}$ ) itself is strongly oxidizing and the molecular weight of formic acid is 46.03 g/mol. Formic acid is corrosive and it is harmful for human health. Formic acid is formed as a by-product for instance in acetic acid production. Besides producing formic acid as by-product in acetic acid production formic acid can be also produced by different methods such as methyl formate hydrolysis, oxidation of hydrocarbons, hydrolysis of formamide and preparation of free formic acid from formates. (Bull 2010, Reutemann & Kieczka 2011)

Due to the strongly acidic character of formic acid it has been used in leather and textile industries. In addition to this formic acid is used also in controlling of pH when natural and synthetic fibers are being dyed. (Reutemann & Kieczka 2011)

Formic acids may end up in waters from different industries due to the use as pesticides, antibacterial agent or material in textile industry. Environmental impact of formic acids are negligible because formic acid biodegrades after it has been spread into water and soil. (Bull 2010)

In following reactions formic acid is lead to react with hydroxyl radical and ozone (Aristova et al, 2002).



As well with oxalate also formic acid has a possibility to enhance the nitrate formation due to the regeneration of hydroxyl radical when formate ion has reacted with ozone (Yapsakli & Can, 2004).

## **4. MATERIALS AND METHODS**

Experimental part consists of preparation of samples and used materials, operation and experiments with PCD device and final analyses using ion chromatograph to examine the formed amount of nitrate in water.

### **4.1. Materials**

Water used in PCD experiments was normal tap water. Formate used in experiments was used in a form of formic acid and oxalate in a form of oxalic acid. To prepare solutions 50 and 100 ppm liquid 80 m-% formic acid was diluted with water. Hydrous oxalic acid was dissolved also in water to get 50 and 100 ppm concentrations. For faster dissolution an ultrasonic bath was utilized.

The standard solutions for analysis of nitrate, oxalate and formate were made by diluting already made solutions each containing nitrate, formate or oxalate. Concentrations of solutions for calibration were 10 ppm, 20 ppm, 30 ppm, 50 ppm and 100 ppm. Also ion exchanged water was used during calibrations to get sample without any nitrate, formate or oxalate.

During the PCD experiments the solutions had to be alkaline due to the required knowledge of examination of the oxidation in alkaline conditions. pH has proven to have effect on formation of nitrates and nitrites thus requiring the determination of pH range in experiments (Kornev et al. 2013). Sodium hydroxide was added to the PCD device storage tank before starting the generator. pH was determined to be over 11. 99-% sodium hydroxide granules were diluted first in water and then they were added in to the tank.

### **4.2. Operation with PCD**

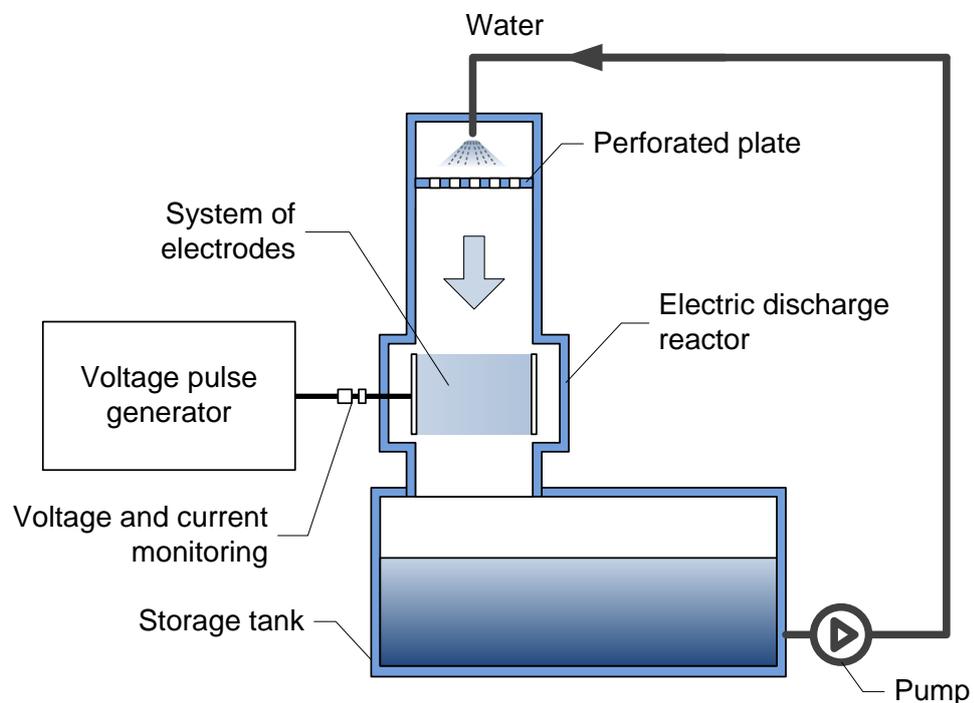
Water was pumped through PCD device from tank to upper section of the device. By dividing water stream into smaller streams and droplets with perforated plate in the

upper section of the PCD device water was supposed to react efficiently when it was passing through the electrodes. A voltage pulse generator was connected to the system and it was giving electrical pulses to the system of electrodes. An oscilloscope was placed to monitor voltage and current which came from the generator. While the water was passing through the electrodes hydroxyl radicals and atomic oxygen would begin to form. Water flow came out from the device back to the tank and at the bottom of the tank was a sampling port from where the samples were taken.

Experiments were done in room temperature and pressure. The amount of nitrate was examined when water containing either formate or oxalate was oxidized in experiments with PCD device.

### 4.3. Experiments with PCD

In figure 2 the process chart of PCD device used in this study is presented.

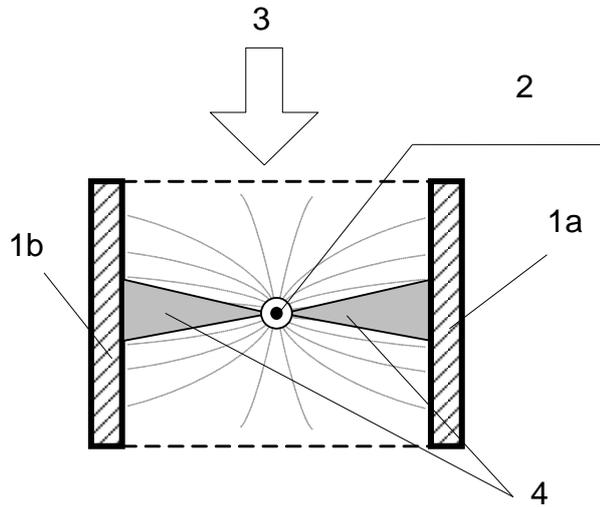


**Figure 2.** The process chart of the PCD device. (Kornev et al. 2013)

Water is pumped to the inlet which is on top of the device. Water is then led to flow first through the perforated plate where it is being dispersed and then through the electric discharge reactor which includes the system of electrodes. Voltage pulse

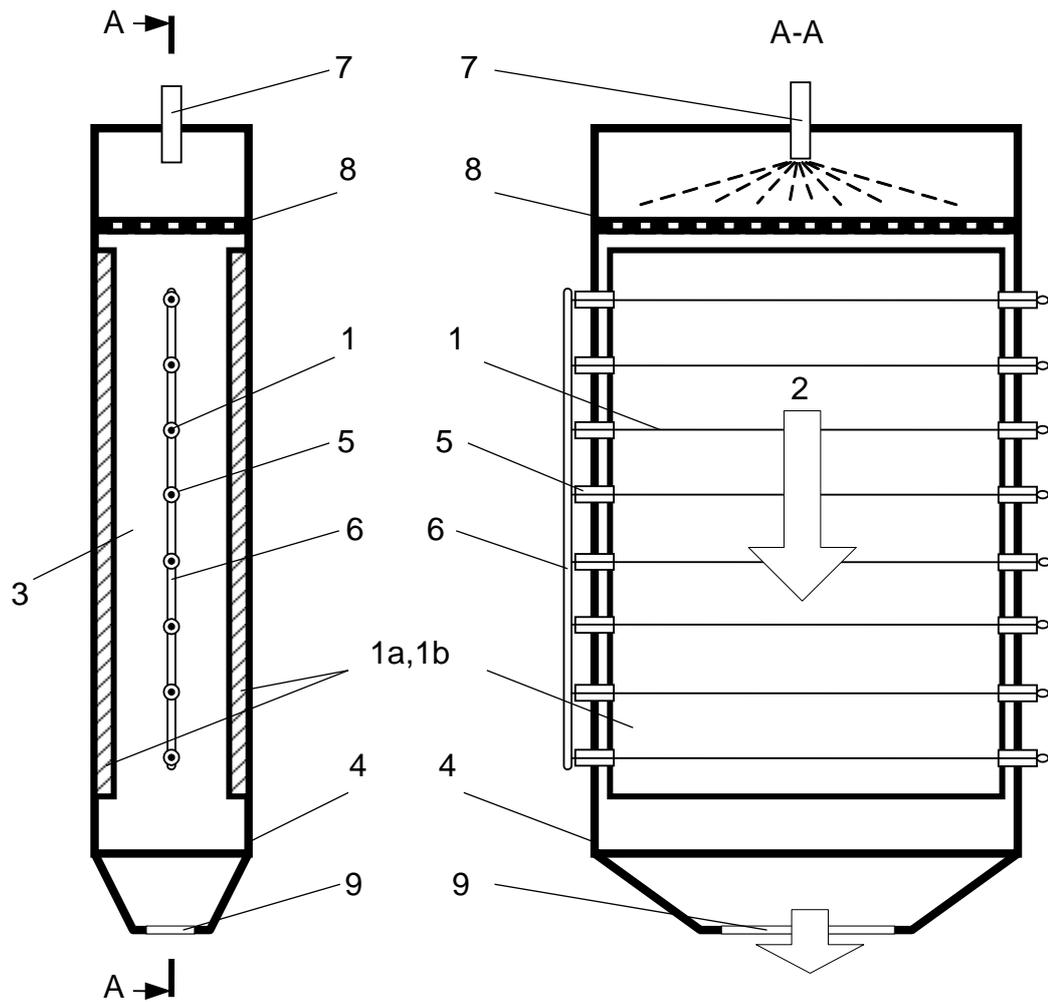
generator is producing high voltage pulses into the device. Water is then flowed back to storage tank.

In figure 3 is presented the side profile for upper section of PCD device where water is pumped to flow downwards the device and through the perforated plate.



**Figure 3.** PCD device from the side. 1a and 1b walls of chamber, 2. high voltage electrode, 3. water inlet, 4. electrical discharge.

In figure 4 parts of the reactor section of PCD device are described.



**Figure 4.** Reactor part of PCD device. 1. electrode line, 2. water flow, 3. PCD chamber, 4. lower part of the chamber, 5. electrode, 6. generator cord 7. inlet of water flow 8. perforated plate 9. sampling port.

Electrodes are connected with electrode lines in the reactor part. They are also connected to the pulse generator by a cord. In the bottom of the reactor part is the sampling port.

Total number of experiments was 12 because experiments with formate and oxalate were done separately and in every concentrations 0 ppm, 50 ppm and 100 ppm. Experiments were repeated for having more reliable results. After the oxalate and formate solutions were made, PCD device storage tank was filled with tap water up to 40 L. Then either oxalate or formate solution was added and finally sodium hydroxide was added also in to the tank. The tank was filled with water up to 50 L. Pump was turned on and water was led to flow throu the device 10 minutes without starting the

generator. After running 10 minutes pump was turned off and pH was measured. If it was over 11 the experiment could be started, if not more sodium hydroxide was added.

Before starting the generator the first sample was taken with the pump on. After sampling the generator was started and the next samples were taken after 5, 10, 20 and 30 minutes. Generator was producing electrical pulses 840 per second. Every time the time ended generator was turned off and liquid was led to flow through the device for 10 minutes so that concentrations were equal in every part of the liquid. Finally sample was taken from the sampling port and generator was turned on again.

#### **4.4. Analyses**

To analyze the amounts of nitrate, formate and oxalate Dionex ISC – 1100 ion chromatograph was used. The column in ionic chromatograph was AS22 and the pre-column AG22. The eluent in chromatograph was a solution of sodium carbonate and sodium bicarbonate and the applied flow rate was 1.2 L/min. Used suppressor was ASRS\_4mm and the suppressor was set at 31 mA current. Before starting experiments the standard solutions were analyzed with ionic chromatograph to establish a calibration line. After experiments were done with PCD device all the samples were analyzed and compared to the calibration lines.

Samples were analyzed undiluted due to already suitable initial concentrations. However everytime analyses were done, solutions containing exact concentrations of 50 ppm and 100 ppm of nitrate, formate and oxalate were also analyzed as control samples.

## **5. RESULTS**

Results are presented by using delivered energy dose and energy efficiencies to show the formation of nitrate and oxidation of formates and oxalates against energy consumption. Behavior of pH is also taken into account against energy consumption.

### 5.1. Energy

As mentioned earlier the used pulse frequency was 840 pps and the discharge power was 250 W. Formation of nitrate was determined by examining delivered energy dose. Energy dose was calculated from

$$E = \frac{P \cdot t}{V} \quad (35)$$

where	E	energy, kWh/m <sup>3</sup>
	P	power, kW
	t	time, s
	V	volume, m <sup>3</sup>

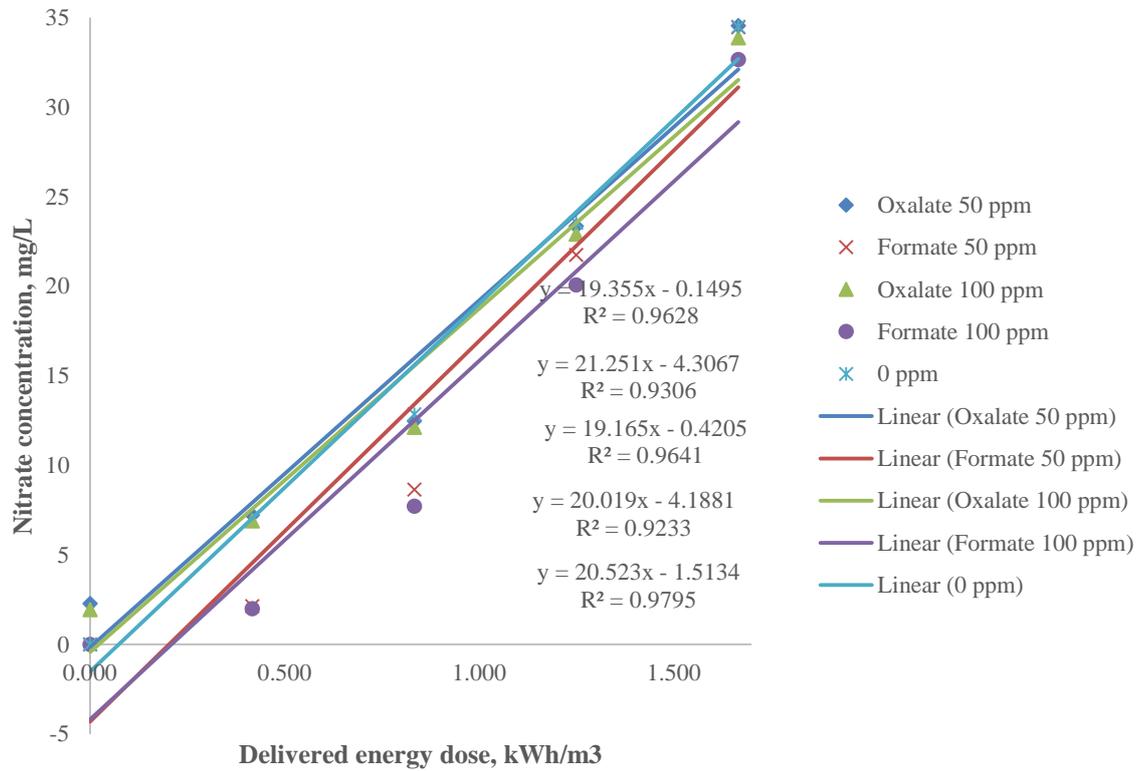
Energy efficiencies were calculated as follows

$$\varepsilon = \frac{\Delta c}{E} \quad (36)$$

where	$\varepsilon$	energy efficiency, g/kWh
	$\Delta c$	concentration change between time points, g/m <sup>3</sup>

### 5.2. Nitrate formation

Results for medium concentrations of nitrate formation calculated with equation (35) are in figure 5.

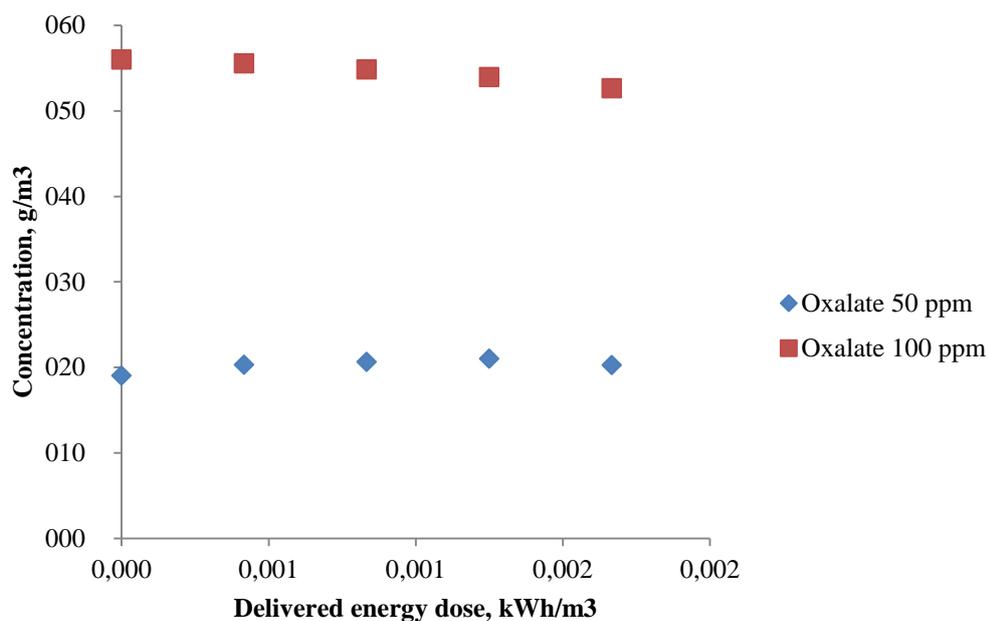


**Figure 5.** Nitrate formation during PCD experiments with concentrations of 0, 50 and 100 ppm of oxalate and formate.

As seen from figure 5 nitrate concentrations increase when delivered energy dose increases. Slopes for nitrate formation with different concentrations are nearly equal compared to each other. Nonetheless there are some differences between oxalate and formate. Nitrate concentrations with formate are lower than with oxalate or with pure water.

### 5.3. Oxidation of formate and oxalate

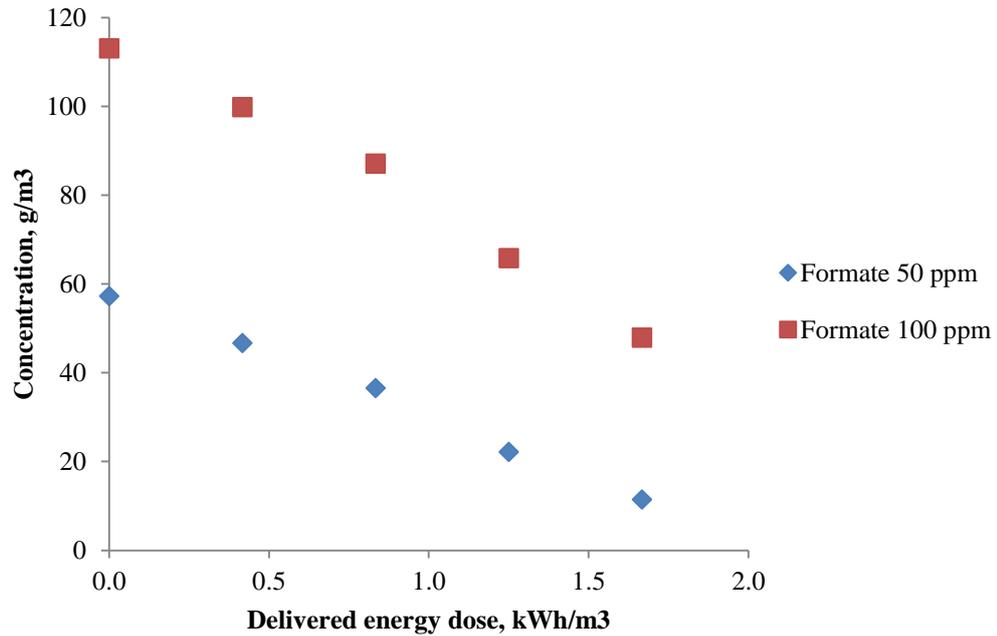
In figure 6 are results for medium oxalate concentrations during oxidation experiments.



**Figure 6.** Oxidation of oxalate during experiments with PCD device described by average oxalate concentrations of repeated experiments and delivered energy dose.

From figure 6 can be seen the barely nonexistent decomposition of oxalate and the significantly lower initial concentration of oxalate than it was set to be. Concentrations remain nearly equal for initial concentration of 50 ppm which in real is around 20 ppm concentration. For initial concentration of 100 ppm values are actually below 60 ppm and they decrease almost down to 50 ppm.

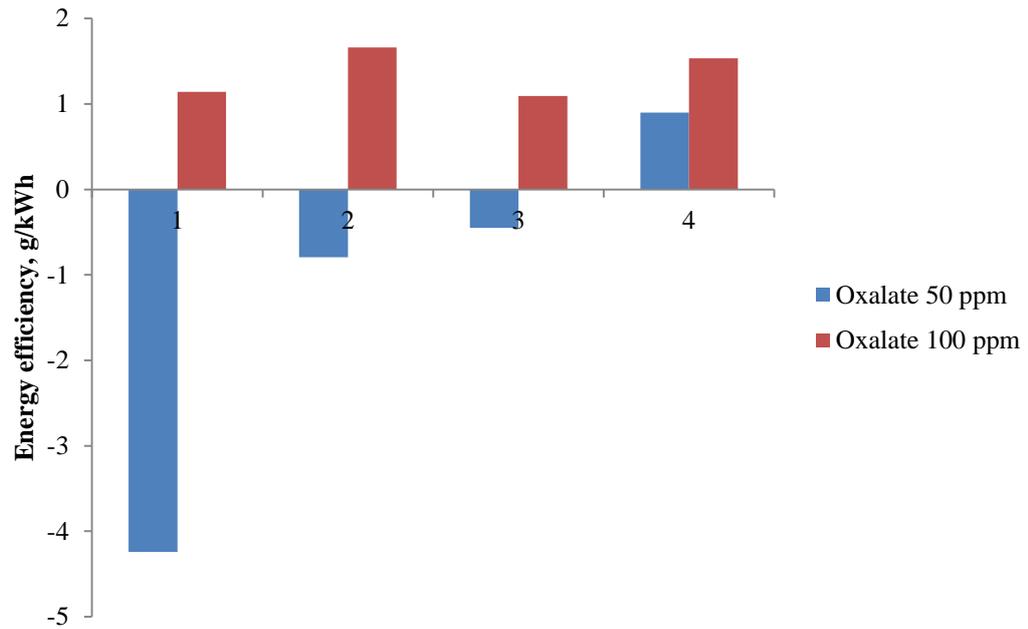
Results for average formate concentrations during oxidation experiments are presented in figure 7.



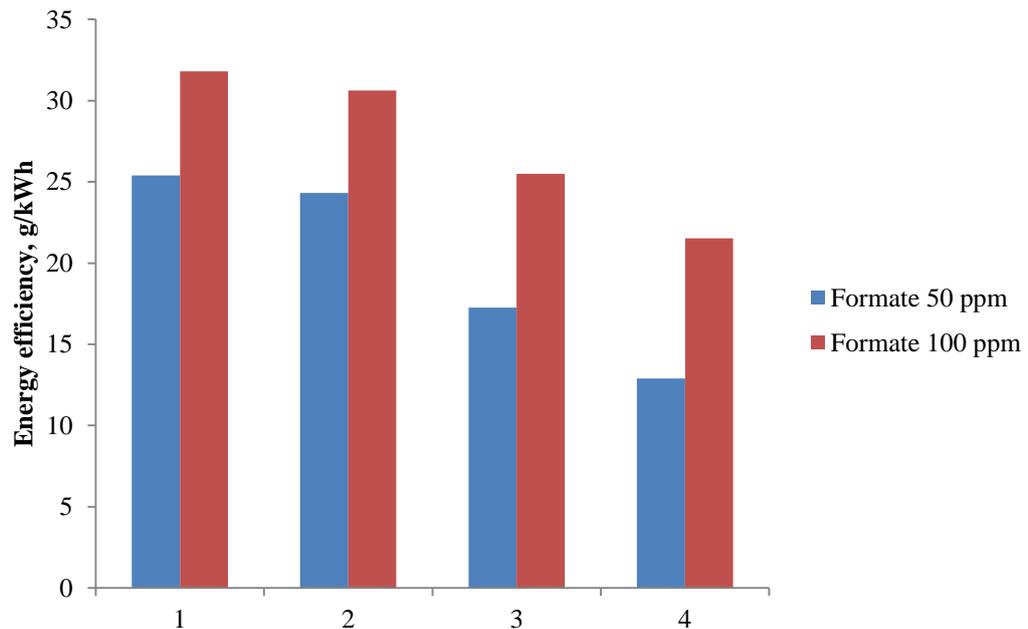
**Figure 7.** Oxidation of formate during experiments with PCD device described by average formate concentrations of repeated experiments and delivered energy doses.

Formate concentrations decrease linearly and for initial concentrations are near to the desired values. For initial target concentration of 50 ppm real concentration is below 60 ppm and for initial target concentration of 100 ppm real concentration is around 110 ppm.

In figures 8 and 9 are energy efficiencies for oxalate and formate samples calculated using equation (36)



**Figure 8.** Average energy efficiencies for oxalate samples. All efficiencies have the same loaded power 250 W but increasing time value. First pillar has time value of 5 min, second 10 min, third 20 min and last one 30 min.



**Figure 9.** Average energy efficiencies for formate samples. All efficiencies have the same loaded power 250 W but increasing time value. First pillar has time value of 5 min, second 10 min, third 20 min and last one 30 min.

Average energy efficiencies for oxalate do not give reasonable results. Energy efficiency should decrease but energy efficiency for oxalate in concentration of 50 ppm increases from below zero to almost 1 g/kWh. Values for energy efficiencies for oxalate in concentration of 100 ppm vary between 1 and 1.5 g/kWh, respectively. For formate the decrease in energy efficiency values is nearly equal for both concentrations of

formate. With 50 ppm of formate values decrease from 25 g/kWh down to 13 g/kWh and with 100 ppm values decrease from 32 g/kWh down to 22 g/kWh, respectively.

#### 5.4. Effect of pH

Experiments were done in alkaline conditions. In figures 10 and 9 are shown the measured pH values during experiments with PCD.

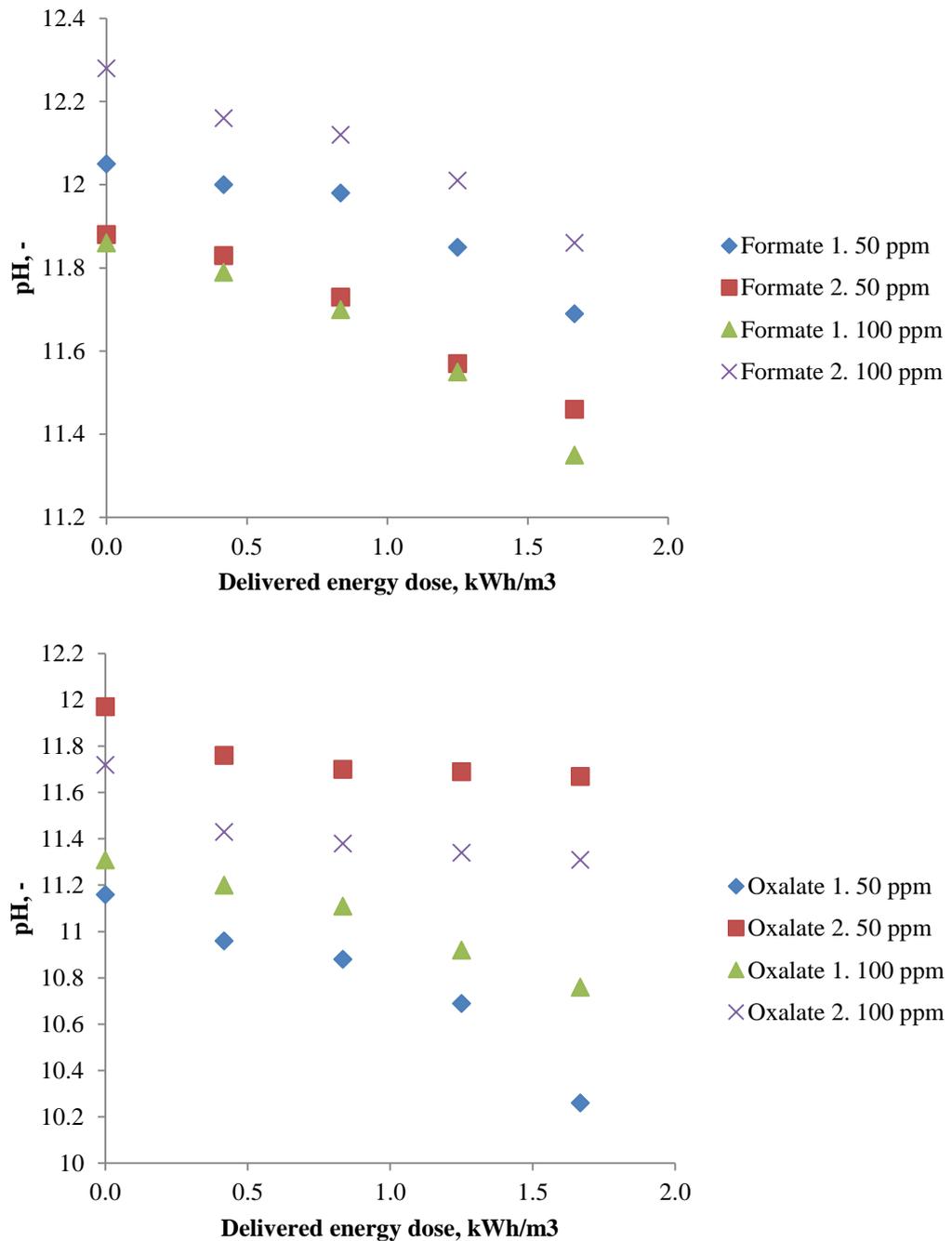


Figure 10. pH during PCD experiments with formate and oxalate.

As seen from figures 9 and 10 the pH values decrease during every experiment whether formate or oxalate was included. pH values may have decreased more if duration of one experiment was longer. Initial values are 11.8 and 12.3 with formate and values decrease during experiments down to 11.3 and 11.9, respectively. For oxalate initial values are 11.1 and 12.0 and they decrease down to 10.2 and 11.7, respectively.

## 6. CONCLUSIONS

In this research the formation of nitrate in water was examined when water was oxidized with pulsed corona discharge method in presence of carboxylic acids, formic and oxalic acid. Experiments were done separately for oxalate and formate with pulsed corona discharge device and analyses were made with ionic chromatograph. Conditions during experiments were alkaline and pulse repetition rate was chosen to be 840 pps.

Formation of nitrate was nearly equal in every experiment whether there was 0, 50 or 100 ppm of formate or oxalate. Also with pure water nitrate was formed the equal amount in every sample. Concentrations differed only slightly between formate and oxalate experiments: nitrate values with formate were lower compared to oxalate. This leads to the conclusion that presence of oxalate and formate in these concentrations and conditions does not enhance formation of nitrate in water significantly.

Equal formation of nitrate can be consequence of formate and oxalate not being able to react with ozone for regenerating hydroxyl radical thus enhancing the formation of nitrate. Also oxalate was not decomposed entirely as seen from figure 6 where the concentration of oxalate remained roughly the same. This can explain the oxalate not able to react with ozone.

Irregular decomposition of oxalate can be due to the slow oxidation of oxalate. Reliable results from ionic chromatograph are obtained when concentrations of samples are above 5 ppm. The sampling times were short thus oxalate does not have enough time to be oxidized. Furthermore sample intervals are small and oxalate cannot be decomposed as quickly as formate. This leads to the higher required amount of delivered energy.

Further experiments are needed for increasing the duration time of one experiment and the time between samples to get total decomposition of oxalate.

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