BROMATE FORMATION DURING WATER TREATMENT WITH PULSED CORONA DISCHARGE PLASMA

Lappeenranta–Lahti University of Technology LUT

Bachelor’s Program in Chemical Engineering, bachelor's thesis

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Examiners: Post-Doctoral Researcher, Kinga Skalska-Tuomi

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ABSTRACT

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Keywords: advanced oxidation processes, wastewater treatment, bromate, pulsed corona discharge plasma, diclofenac, sustainable wastewater treatment.

This bachelor's thesis investigates the use of pulsed corona discharge plasma (PCD), an advanced oxidation process (AOP) in wastewater treatment. It investigates the PCD process parameters and their effect on elimination of diclofenac and formation of bromate. It also looks at the different pathways pharmaceutical waste and bromide end up in the wastewater treatment system. The experimental part explores these parameters further looking at how pH, pulse frequency and initial bromide concentration affect the purification process and the formation of bromate. From these experiments pulse frequency had the biggest impact on bromate formation followed by bromide concentration. By changing the parameters, it is important to keep bromate and diclofenac under the accepted limit set in the new EU-directive. In summary PCD- treatment is an attractive method of wastewater treatment when treatment time is kept low with a low pulse frequency mitigating the negative side reactions.

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LUTin insinööritieteiden tiedekunta

Kemiantekniikka

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Bromaatin muodostuminen veden puhdistuksessa pulssitetulla koronapurkaus plasmalla

Kemiantekniikan kandidaatintyö

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Avainsanat: Kehittyneet hapetusprosessit, jätevedenkäsittely, bromaatti, pulssitettu koronapurkaus plasma, diklofenaakki, kestävä jätevedenkäsittely.

Tämä kandidaatintutkielma käsittelee pulssitetun koronapurkaus plasman (PCD) käyttöä jätevedenpuhdistuksessa, joka on yksi edistyneistä hapetusprosesseista (AOP). Tutkielmassa perehdytään PCD prosessin parametreihin, ja miten niiden muuttaminen vaikuttaa diclofenaakin hajoamiseen ja bromaatin muodostumiseen. Lisäksi selvitetään, millä eri menetelmillä lääkejäte ja bromidi päätyvät jätevedenpuhdistusjärjestelmään. Kokeellisessa osassa tutkitaan tarkemmin parametreja ja sitä, miten pH, pulssitaajuus ja alkuperäinen bromidipitoisuus vaikuttavat puhdistusprosessiin ja bromaatin muodostumiseen. Kokeiden perusteella pulssitaajuudella oli suurin vaikutus bromaatin muodostumiseen, ja toiseksi merkittävin tekijä oli alkuperäinen bromidipitoisuus. Prosessin parametrejä säädettäessä on tärkeää, että bromaatin ja diklofenaakin pitoisuudet pysyvät uuden Euroopan unionin direktiivin hyväksytyn raja-arvon alapuolella. Kaiken kaikkiaan PCD-reaktori on kilpaileva vaihtoehto jätevedenpuhdistukseen, kun käsittelyaika pidetään lyhyenä ja pulssitaajuus matalana, jolloin haitalliset sivureaktiot minimoituvat.

SYMBOLS AND ABBREVIATIONS

Roman characters

P	Power	kW
t	time	h
V	volume	L
E	Energy delivered	kWh / m^3

Abbreviations

AOP	Advanced oxidation processes
PCD	Pulsed corona discharge
WWTP	Wastewater treatment plant
DOC	Dissolved organic carbon
HPLC	High performance liquid chromatography
PPS	Pulses per second
IC	Ion chromatograph

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1 Introduction

The need for different wastewater treatment methods has never been more relevant than today. As the European Union (EU) strives to cut down on pollution and greenhouse gas emissions, the revised urban wastewater aims to improve water quality through stricter water treatment directives (Directive (EU) 2024/3019, 2024). This law especially tackles pharmaceuticals and other pollutants such as bromide. The problem that arises when treating water which contains bromide is the formation of bromate (BrO_{3-}) during the oxidation process particularly when using advanced oxidation processes (AOPs). There are several treatment options that use AOPs that have been established and operated at large scale such as ozonation and UV-radiation (Miklos et al., 2018). This thesis investigates one of the newer methods in wastewater treatment pulsed corona discharge (PCD) oxidation and the formation of bromate during the treatment process.

Previous studies have been conducted on several methods for minimizing bromate formation during ozonation using different process parameters or chemical additions, for example by adding NH_3 the amount of bromate decreased by 42-73% (Morrison et al., 2023). To help the assessment of AOPs electrical efficiency figures of merit have been developed to help the comparison of different AOPs by Bolton and his coworkers (Miklos et al., 2018). This method has been accepted by the International Union of Pure and Applied Chemistry as the main way to access electrical efficiency (Bolton et al., 2001). Taking these factors into consideration, a study conducted by Sgroi, Snyder and Roccaro found that ozonation was the most energy efficient process calculated according to (Bolton et al., 2001) for wastewater treatment compared to UV based alternatives like UV/H_2O_2 or UV/CLl_2 (Sgroi, Snyder and Roccaro, 2021).

Keeping energy efficiency in mind and considering the new European Union regulations requiring the removal of 80% of pharmaceutical waste, it is essential to identify process parameters that meet both criteria. It was also found that different AOP process parameters, chemical additions like H_2O_2 or the change in pH increase or decrease the amount of bromate formed. Taking this into consideration the parameters used in this study will consist of different process conditions like pH, pulse frequency, initial concentration and initial water matrix conditions using diclofenac as the waste that is being purified.

With these parameters this bachelor's thesis aims to investigate the formation of bromate during the water purification process. Additionally, it aims to examine the ways in which bromide and diclofenac end up in wastewater purification process and a brief look at the advanced oxidation process used in the PCD-reactor purification process. The research aims to answer the following questions:

Q1: How much bromate is formed during PCD process under different process conditions?

Q2: How is bromate formation dependent on its initial concentration in treated water?

Q3: How does pH affect the formation of bromate?

With these questions the research aims to provide data and options for further PCD-reactor use in wastewater management. This thesis consists of a theory part and laboratory analysis report.

2 Sources of Bromide, bromate and diclofenac in wastewater

This section covers different ways that bromide, bromate and diclofenac end up in wastewater treatment cycle. It also discusses the permitted concentrations levels of bromate bromide and diclofenac in treated- and untreated wastewater.

2.1 Bromide and bromate sources

Bromide is a naturally occurring bromine-ion that has natural and anthropogenic sources. Volcanic eruptions, geothermal streams and seawater are the most prominent natural sources of bromide (Leri et al., 2024). Anthropogenic sources consist of waste incineration, pulp and paper industry, pharmaceutical industry, farming industry and flame retardants (Leri et al., 2024). There are multiple different anthropogenic ways bromide and bromate end up in the water making it all the way to households (Fig.1).

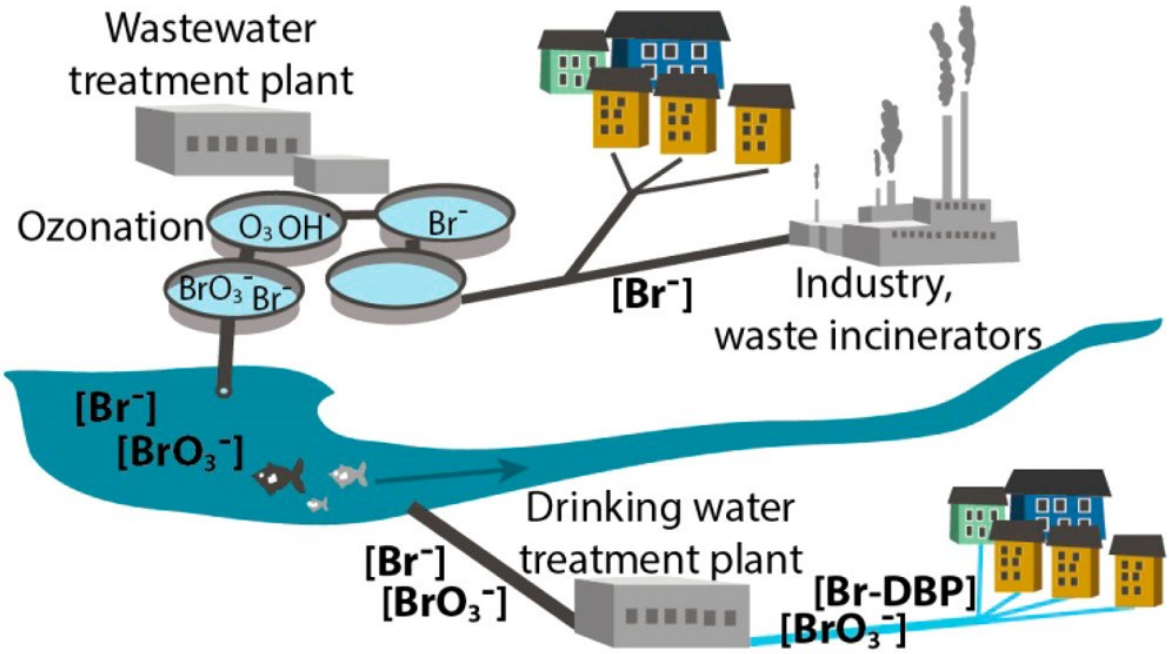

Figure 1. Anthropogenic sources of bromate and bromate in surface and drinking water (Soltermann et al., 2016)

A survey conducted in 2014 in Switzerland found that the industrial sector accounted for 83% of total bromide emissions, making it the highest contributor (Tab. 1) (Soltermann et al., 2016).

Table 1. Bromide sources measured in Weil am Rhein in 2014 (Soltermann et al., 2016)

Bromide sources	%
Chemical industry	52
Municipal waste incinerators	18
Special waste industry	13

This indicates that water discharges from factories, especially pharmaceutical and chemical factories, make up a huge proportion of the measured bromide. Furthermore, it is possible that the Finnish waters follow the same trend since a lot of the pulp and paper factories discharge wastewater into lakes. One study conducted in 2017-2021 by the Finnish Environment Institute (Syke) found that one potential bromide source comes from plastic and fabricated metal products, but the specific concentration in surface water was not evaluated in HAZBREF 2.2 (Finnish Environment Institute (Syke), 2017-2021). Furthermore, another vector that leads to contamination is stormwater runoff since it collects road salt and fertilizers. It is a small percentage of all emissions, but runoffs are usually not treated, leading to further contamination.

2.1.1 Allowed concentrations and occurrences

Bromide contamination in surface waters fluctuates from as low as 20 µg/l to as high as 400 µg/l the concentration are highly dependent on anthropogenic factors. Wastewater treatment plants had significantly higher concentrations of bromide when situated near chemical industries or waste incineration plants (Soltermann et al., 2016). For example, in the US bromide concentration varied from 64 µg/L to 2.7 mg/L (median = 234 µg/L) in industrial wastewater and was higher in untreated sources (Sharma et al., 2023). When it comes to the toxicity of bromide drinking water guidelines set by the WHO state that the daily limit for bromide is 6 mg/L for a person that weighs 60 kg. The amount is 2 mg/l for child that weighs

10 kg making bromide a substance of low toxicity and not a health concern since it occurs in low concentration in drinking water (WHO, 2017).

On the other hand, bromate a byproduct of bromide oxidation is toxic and carcinogenic in low concentrations. This makes bromide control important since the more bromide goes through the wastewater treatment process the more bromate is formed. The WHO guideline for the amount of bromate acceptable in drinking water is 10 µg/l (WHO, 2017). When it comes to limits for ecotoxicological damage The Ecotox Centre evaluates that 50 µg/l bromate can cause ecological damage both in the short and long term (Oekotoxzentrum Eawag-EPFL, 2015). Also, it has been found that certain aquatic organisms react to as low as 190 µg/l killing 50% of the test animals (Leri et al., 2024).

2.2 Diclofenac sources

Diclofenac is one of the most common pollutants in municipal wastewater. The main pathways through which diclofenac enters the environment include pharmaceutical industry, hospitals, improper disposal by consumers and effluent from wastewater treatment plants (HELCOM, 2020). The diclofenac that is passing through the wastewater treatment plants only 20-40% is broken down since the current treatment methods are unable to remove it all. Also, the amount of diclofenac going through wastewater treatment plants might play a role in this. Furthermore, diclofenac is usually used as an ointment, thus it is not metabolized in the liver if taken orally or injected (HELCOM, 2020). This leads to a lot of variability on diclofenac concentrations in surface waters thus making situation assessment harder (HELCOM, 2020).

2.2.1 Allowed concentrations and occurrences

Diclofenac can be toxic to marine life in concentrations as low as 1 µg/l. Depending on the species acute toxicity, varies between 22 mg/l – 80 mg/l on average (Vieno and Sillanpää, 2014) Bioconcentration in muscles and fish ware also recorded since diclofenac has a longer biological half-life in multiple species. Since diclofenac concentrations vary in water sources the European Union has required in the new urban wastewater treatment directive (Directive (EU) 2024/3019, 2024) that all quaternary treatment needs to remove 80 % of the twelve

selected compounds found in influent, diclofenac being one of them. Furthermore, diclofenac is placed in category one classifying it as a substance that can be easily treated. This regulation aims to cut down diclofenac released to the ecosystem inside the European Union.

3 Wastewater treatment using advanced oxidation processes

This section covers the different AOP that are used in wastewater treatment. Also, the AOP reaction mechanism and different control options for minimizing bromate formation during ozonation are covered.

3.1 Different AOP methods for water treatment

AOP are used to generate strong oxidants to oxidize organic compounds, this is why they are used in removal of pharmaceutical waste. Most of these AOP use OH-radicals but also other radicals like sulphate or chlorine are used in some of them (Miklos et al., 2018). The methods to generate these oxidants vary from the more well-known ones like ozone-based and UV-based to newer methods like PCD which falls under the physical AOP category (Fig. 2) (Miklos et al., 2018).

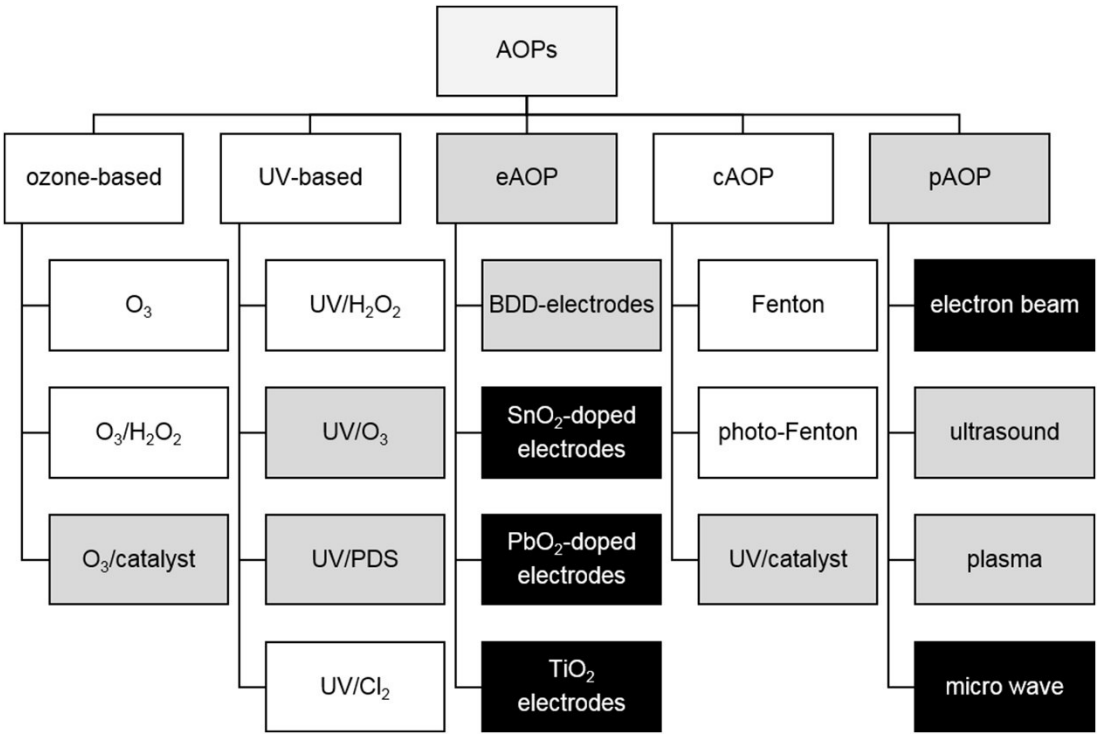

Figure 2. AOP methods for water treatment (Miklos et al., 2018)

Also, it should be mentioned that some of these methods use several processes to generate radicals like the before mentioned PCD emits UV radiation and uses ozone. For the challenges that ozone-based methods faze comes down to unwanted side reactions like bromate formation. Since at relatively high bromide concentrations in wastewater (≥100 µg/l the decomposition of ozone is faster which limits the effectiveness of the reaction (von Gunten, 2003). This leads to elevated bromate formation despite peroxide being added to combat this. The peroxide addition to the process can only decrease bromate formation by 35 % at high concentrations (U. Hübner, I. Zucker and M. Jekel, 2015) making it challenging to mitigate this problem. Despite this the positives outweigh the negatives AOPs are highly affective at removing pollutants and bacteria thus UV- and ozone-based methods are used widely.

3.1.1 AOP energy efficiency

As stated in the introduction AOP energy efficiency is calculated using figures of merit. It calculates the electric efficiency in kWh required to treat one kilogram of contaminant (Bolton et al., 2001). A study by Sgroi and coworkers (Sgroi, Snyder and Roccaro, 2021)

found that energy costs were lower in ozone based AOPs making it clear that it is the most energy efficient AOP for wastewater treatment when compared to the other methods like UV.

3.1.2 Pulsed corona discharge

There are multiple ways that plasma is used in water treatment. Plasma treatment is defined into two categories thermal plasma and non-thermal plasma. The main difference between these is that in thermal plasma constituents are in thermal equilibrium ($T_e=T_g>T_{room}$), while non-thermal plasma, known also as non-equilibrium plasma or cold plasma, are not ($T_e>>T_g=T_{room}$) (Tyczkowski, 2012). In non-thermal plasma like corona discharge uses less power to make energetic electrons collide with background molecules like N_2, O_2 and water to produce radicals (Jiang et al., 2014). PCD is one of the non-thermal plasma methods. It is using a pulsed discharge which creates strong electric fields that start chemical and physical processes (Miklos et al., 2018). The most promising PCD system is the gas phase system that enhances the production of radicals which can diffuse into the liquid phase making it most affective in water treatment applications (Jiang et al., 2014) The reactor has two main parts the pulse generator and the pulsed corona reactor. The pulse generator is used to generate high voltage between the plate electrodes while the water flows through the reactor in which the gas and liquid phase mixes. This oxidizes contaminants while UV-radiation and shock waves are generated at the same time making oxidization more efficient (Miklos et al., 2018). This method is still under laboratory trials and pilot testing and not yet adapted to industrial scale. Still PCD has shown promise in that it is an effective way to treat pollutants. In one study 25 of 27 pharmaceuticals were treated in hospital wastewater using PCD as the treatment method (Ajo et al., 2018) also the UV produced by this method has been shown to be the most effective in dealing with pathogens in AOP reactions (Sgroi, Snyder and Roccaro, 2021).

3.2 Bromate formation during ozonation

Bromate formation highly depends on the amount of free ozone molecules, since most of the ozone is used up during the oxidation of pollutants it leaves little to no ozone left to form OBr^- -ions. BrO_2^- -ions can go through a disproportionation forming bromate (Morrison et al., 2023). If hydroxyl (•OH) radicals are introduced, it can react with BrO_2^- -ions forming bromate. If hydrogen peroxide (H_2O_2) is introduced it reduces the BrO_2^- -ions back to bromide (Morrison et al., 2023) (Fig. 3).

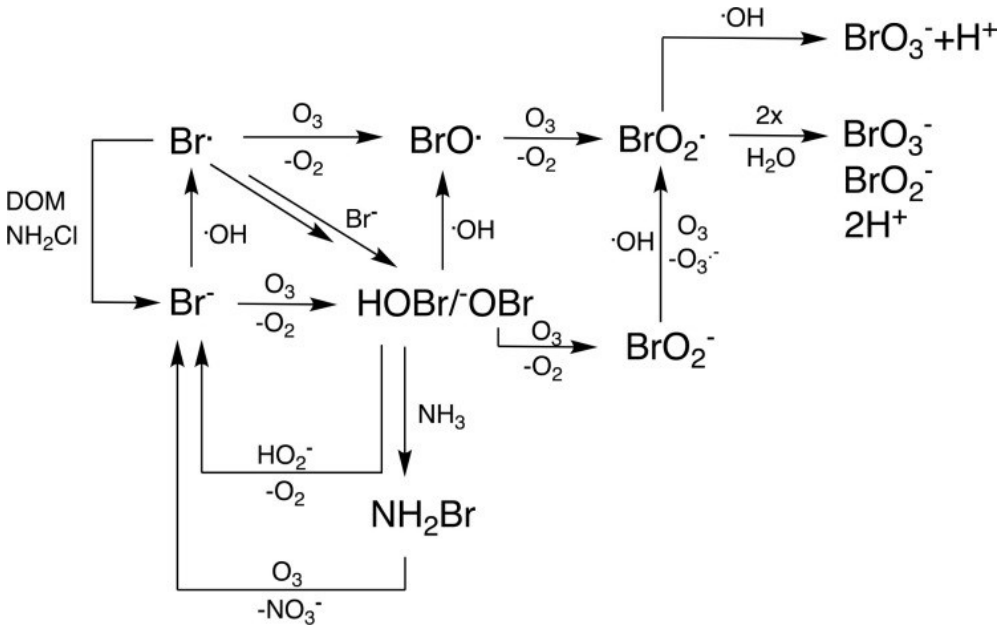

Figure 3. Bromate formation mechanism during ozonation (Morrison et al., 2023)

This demonstrates that bromate formation is a complex reaction having multiple different pathways both direct and indirect. The distribution of Br^-, OBr^- and BrO_2^- reactions with ozone or •OH radical (Fig. 4).

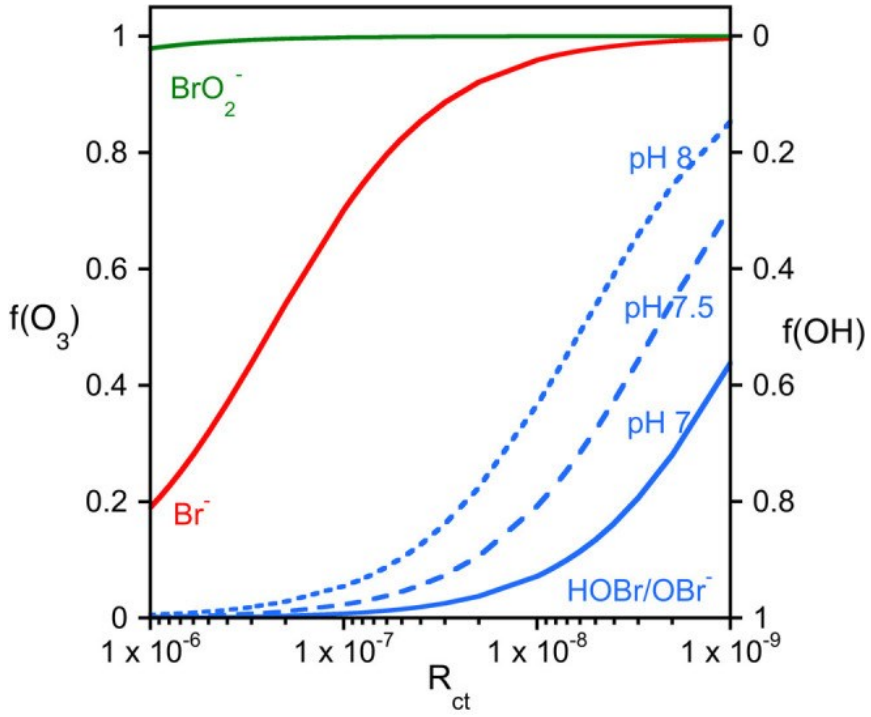

Figure 4. of Br^-, OBr^- and BrO_2^- reactions with ozone or OH as a function of ozone and OH concentrations ratio (Morrison et al., 2023).

This indicates that bromide reacts with •OH radical during the initial phase of ozonation, for later phases of ozonation oxidation happen though ozone which depends on the pH (Morrison et al., 2023). This means that with low treatment times lower pH mitigates the formation of bromate from $HOBr/OBr^-$ radicals reacting with •OH radical and boost disinfection efficiency. At longer treatment times Br^- is more effectively oxidized with ozone (Fig. 4). This would indicate that reactive species formed in the later stages of the process interact more readily with ozone. Therefore, keeping the treatment time as low as possible is important to limit the formation of bromate.

3.3 Mitigation of bromate formation

There are multiple ways to minimize bromate formation pre, during and after oxidation. Pretreatment minimization usually involves removing DOC from wastewater or bromide. During the treatment minimization happens through mostly chemical additives or by tweaking reactor parameters. After ozonation, further minimization of contaminants happens through membrane processes and filtration. However, these methods are often difficult to implement due to high cost and meeting certain water quality requirements (Fig. 5).

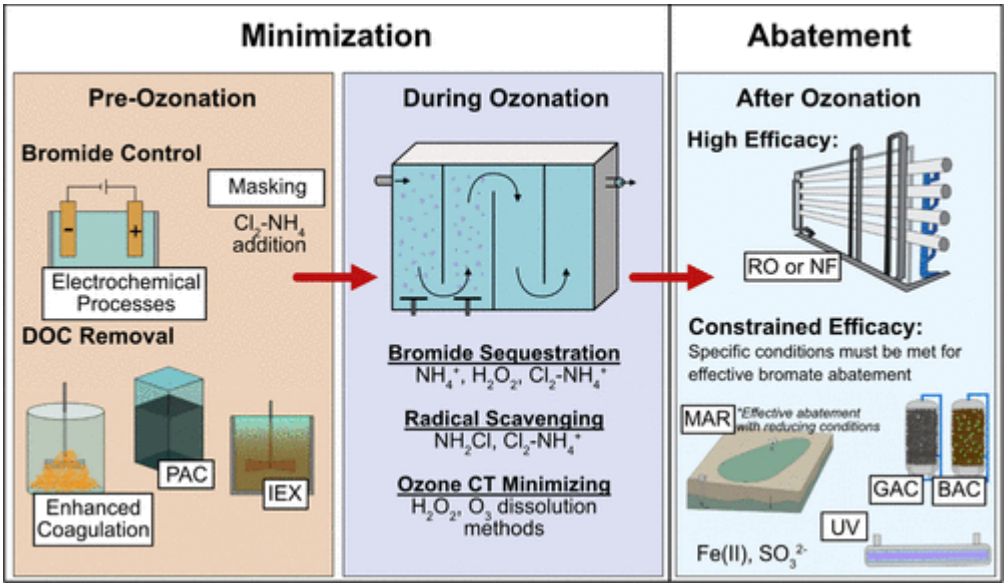

Figure 5. Bromate formation mitigation strategies (Morrison et al., 2023)

From these methods the most effective method is removing or minimizing the amount of bromide in wastewater using electrochemical processes that can remove up to 35 % of bromide. This comes at a cost of poor energy effectiveness making not optimal for upscaled systems (Morrison et al., 2023). Another bromide mitigation method is minimizing the amount of ozone needed to achieve the targeted ozone exposure by removing dissolved organic carbon (DOC) out of the wastewater. This can be achieved in multiple ways like using activated carbon 50-100 mg/l that removes up to 40 % of DOC (Morrison et al., 2023). Previous studies conducted by (Morrison et al., 2023) concluded that a decrease in pH from 8 to 6 decreases the amount of bromate formed by 50-60 % when treatment time is low. Drawback to this is cost of chemicals and disruptions in the treatment process since the pH needs to be adjusted back to neutral.

4 Laboratory tests analysis

This section covers materials and methods used in the experiments and discusses the results of these experiments.

4.1 Materials and methods

4.1.1 Chemicals

Sodium bromide (NaBr, 99%) was purchased from J.T. Baker chemicals. (Netherlands). Sulphuric acid (H_2SO_4, 96%), sodium hydroxide (NaOH, 96%) where already prepared in the laboratory as a diluted solution. Diclofenac sodium salt ($C_{14}H_{10}Cl_2NNaO_2$, 98%) was purchased from Sigma-Aldrich. (USA).

4.1.2 Analyses

Diclofenac concentration was measured using HPLC (High performance liquid chromatography) 1260 infinity made by Agilent Technologies (USA) using a Poroshell 120 EC-c18 3,0x50mm 2,7-micron column (Agilent Technologies, USA). Anions were analyzed using an anion chromatograph Dionex ICS-1100 made by Thermo Scientific (USA) using a an Dionex Ionpac AS22 column. pH and conductivity were measured using a C3210 multi-parameter analyzer made by consort (Belgium).

4.1.3 Experimental set-up

The PCD-reactor setup has a 15 L water tank, pulse generator and a pump that pumps five liters of water per minute through the reactor thus making one full cycle last three minutes (Fig. 6).

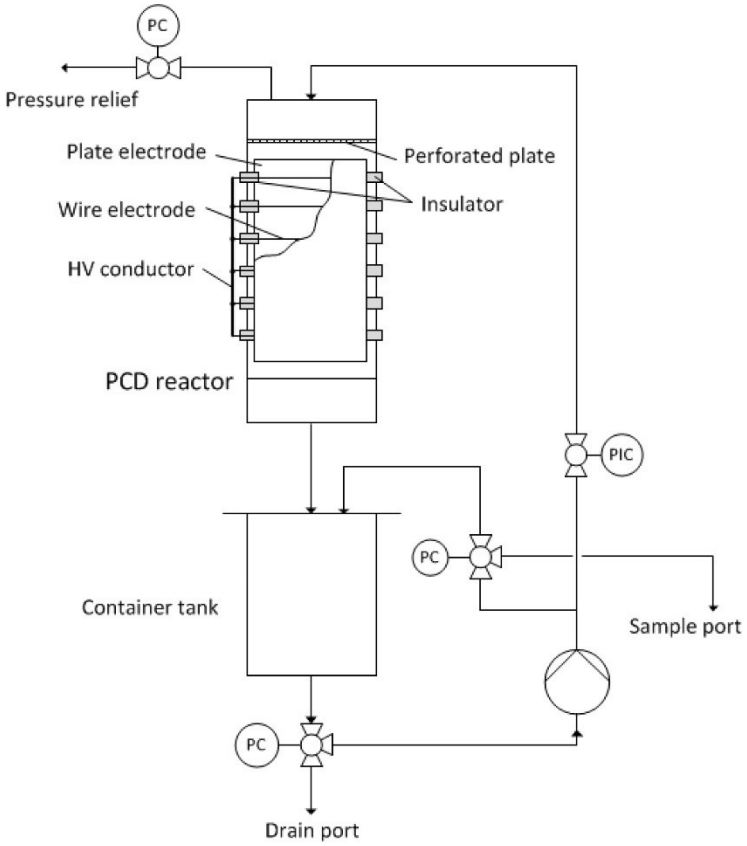

Figure 6. PCD-reactor setup (Ajo, Kornev and Preis, 2015)

The pulse generator pulses per second (pps) and power delivered (W) are listed in Table 2.

Table 2. Pulse generator setting

Pulses per second (pps)	Power delivered (W)
50	6
200	24
300	36
500	60
664	80
833	100

With these parameters the energy delivered can be calculated using equation 3

$$E = \frac{P*t}{V} \left(\frac{J}{L}\right) \quad (3)$$

4.1.4 Experiments

Bromide and diclofenac standards were prepared beforehand with a concentration of 1 mg / L in a 25 ml volumetric flask for diclofenac and 50 ml volumetric flask for bromide. Bromide was dissolved in distilled water while diclofenac had 50/50 mixture of methanol and distilled water. Before the pulse generator started, diclofenac and bromide were spiked directly into the water tank and then mixed well. The samples were treated for 13.8 minutes at 200 pps. Zero samples were collected after the spiked mixture cycled through the reactor twice and after that a sample was collected in 3.6-minute cycles. After each experiment pressurized air was pumped into the reactor chamber for 15 minutes to flush out all the excess ozone. Also, water was cycled twice through the reactor to clean the pumps and pipes between the experiments. Pulse frequency had the same setup besides 833 pps and 50 pps where the treatment time was 24 minutes for 50 pps and 6 minutes for 883 pps. The temperature of the solution stayed stable before and after the treatment at 25 ± 1 °C. Summary of experiment parameters evaluating the effect of pH, pulse frequency, initial bromate concentration on bromate formation (Tab. 3).

Table 3. Experiment parameters

Experiment parameters: Pulse frequency changes						
Initial bromide concentration (mg/L): 10		Temperature (°C): 25		Diclofenac concentration (µg/L): 100		Reactor volume (L): 15
Pulse frequency (pps)	50	200	300	500	664	833
Experiment parameters: Initial bromide concentration changes						
Pulse frequency (pps): 200		Temperature (°C): 25		Diclofenac concentration (µg/L): 100		Reactor volume (L): 15
Initial bromide concentration (mg/L)	1	5	10	20	50	100
Experiment parameters: pH changes						
Pulse frequency (pps): 200		Initial bromide concentration (mg/L): 50		Temperature (°C): 25	Diclofenac concentration (µg/L): 100	Reactor volume (L): 15
pH	10		3		7	

4.2 Results and discussion

4.2.1 The impact of pulse frequency

The removal efficiency of PCD-reactor is quite efficient when oxidizing diclofenac with 90% removed with as low 216 J/L. The increase of pulse frequency shows that the amount of time to oxidize over 90% of diclofenac decreases as pulse frequency increases since the delivered energy increases. The treatment time difference between 50 pps and 833 pps is 6 minutes (Fig. 7). Also, the decrease in treatment time can be seen as the pulse frequency is increased but this can lead to higher oxidation rates. A study by Petrochenko and Preis also found little to no difference between 200 pps and 880 pps when oxidizing bromide (Petrochenko and Preis, 2024). This would indicate that the difference between 200 pss and 833 pps difference is also small when oxidizing diclofenac since the treatment times don't vary that much from each other after 200 pps. Also 200 pps would be the preferred pulse frequency since the energy usage is much lower than 833 pps (Tab. 4) (Fig. 8).

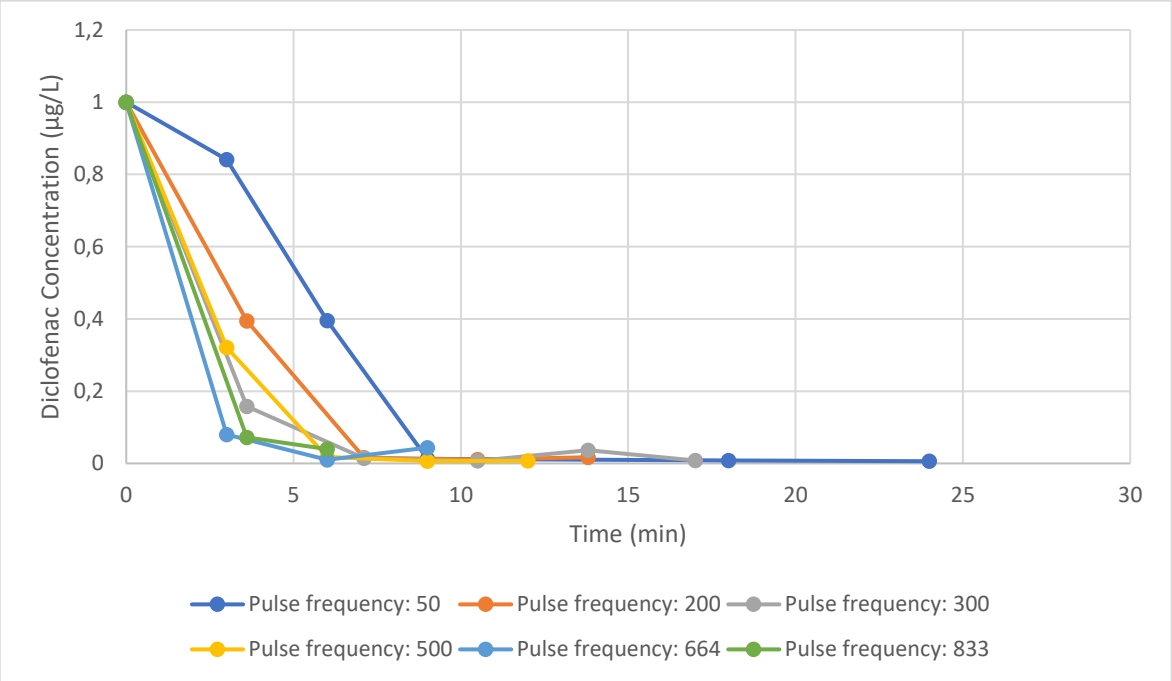

Figure 7. Diclofenac concentration as a function of time: pulse frequency 50,200,300,500,664,844, pH neural and starting bromide concentration 10 mg / L 100% removal is assumed when concentration of diclofenac is under the detection range.

Table 4. Energy delivered to achieve 90% removal of diclofenac

Pulse frequency	Delivered energy (J/L)
50	216
200	682
300	1022
500	1440
664	1920
833	2400

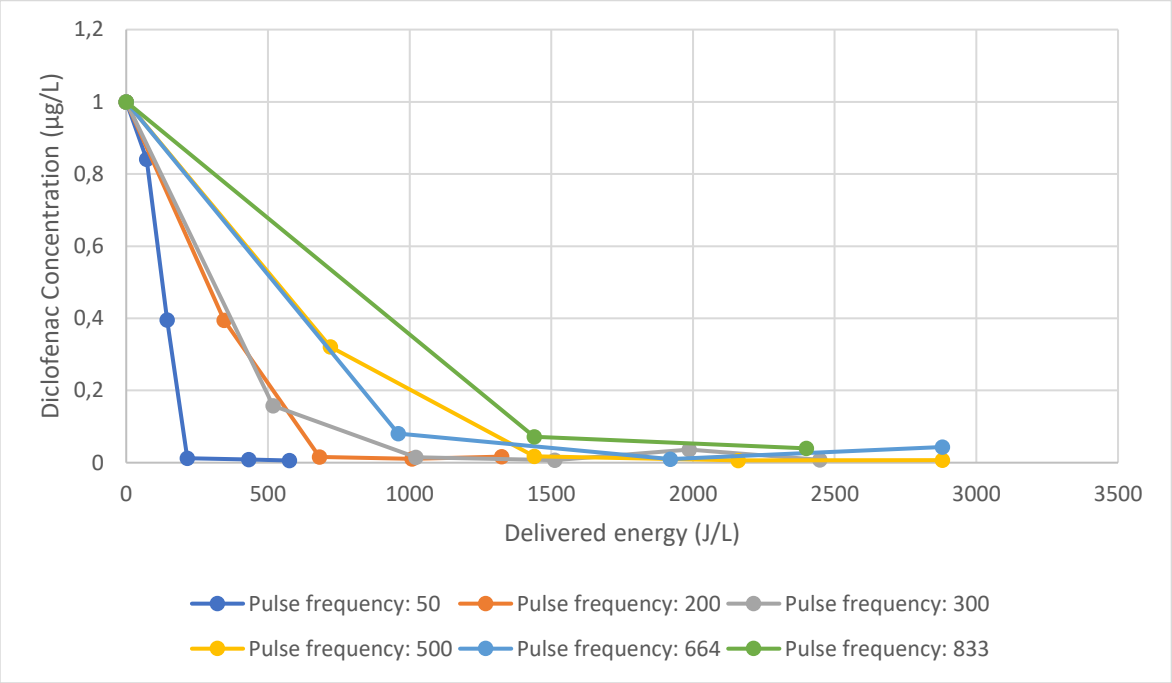

Figure 8. Diclofenac concentration as a function of delivered energy: pulse frequency 50,200,300,500,664,844, pH neural and starting bromide concentration 10 mg / L 100% removal is assumed when concentration of diclofenac is under the detection range.

During the experiment bromide concentration did not change significantly (Fig. 9). The change in bromide concentration in the 664 pps experiment is residual waste from the previous experiment. This is entirely possible that the bromide concentration doesn't change since Petrochenko and Preis found that bromide oxidation is quite slow, taking at least 30 minutes of treatment time at 200 pps and at bromide concentration of 10 mg / l (Petrochenko and Preis, 2024). From the experiments we can also see that bromate concentration only comes up in a couple of places. Since bromide oxidation takes a long time, this is not surprising since the highest treatment time was 24 minutes at 50 pps. The two changes in bromate concentration at 0 minutes are also residual waste since it is possible that water from

previous experiments was still present. All this indicates that keeping the treatment time as low as possible is a key aspect of getting the lowers amount of bromate formation.

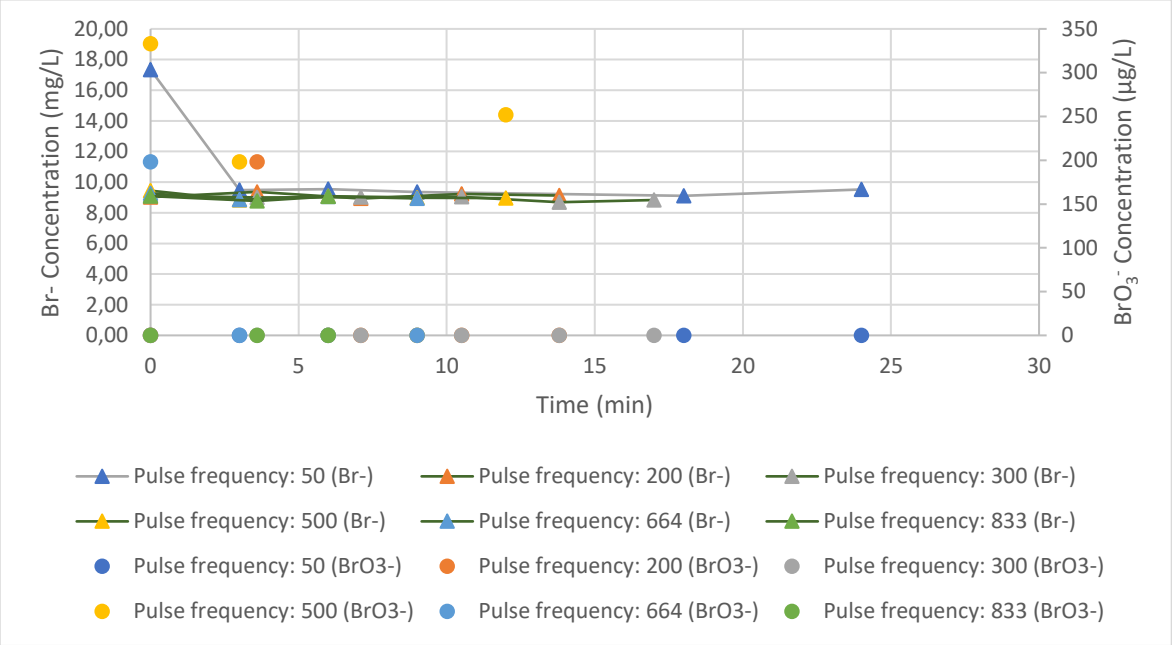

Figure 9. Bromate concentration as a function of time: pulse frequency 50,200,300,500,664,844, pH neural and starting bromide concentration 10 mg / L

On the other hand, the concentration of hypobromite changed every experiment (Fig. 10). While it is possible that some of these concentrations are false flags since the area given by the ion chromatograph peak is so low, in some cases it could be considered under the detection range. Still the experiment suggests that hypobromite is present in all the experiments. Hypobromite ozonation happens earlier in bromate formation thus making it appear more often with lower run times (Fig. 3).

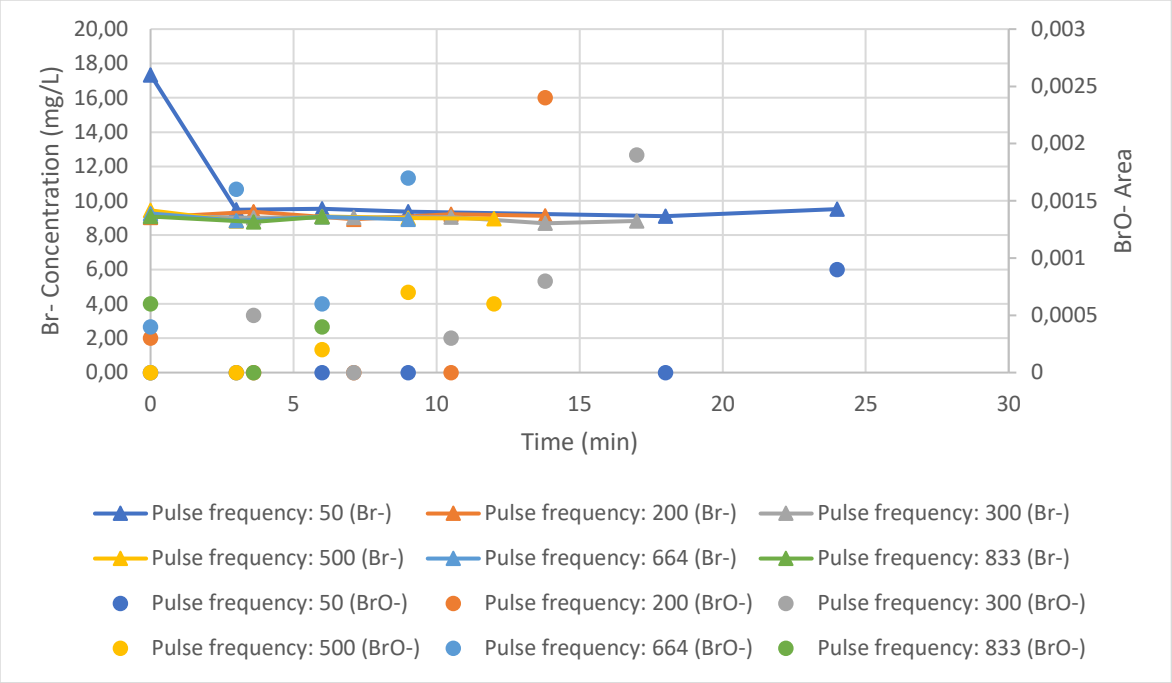

Figure 10. Hypobromite concentration as a function of time: pulse frequency 50,200,300,500,664,844, pH neural and starting bromide concentration 10 mg / L

The peaks of all the anions are numbered in numerical order (Fig. 11). This numerical order is present in every experiment chromatograph. Also, the areas of hypobromite and bromide are low indicating that the concentration of these anions are low.

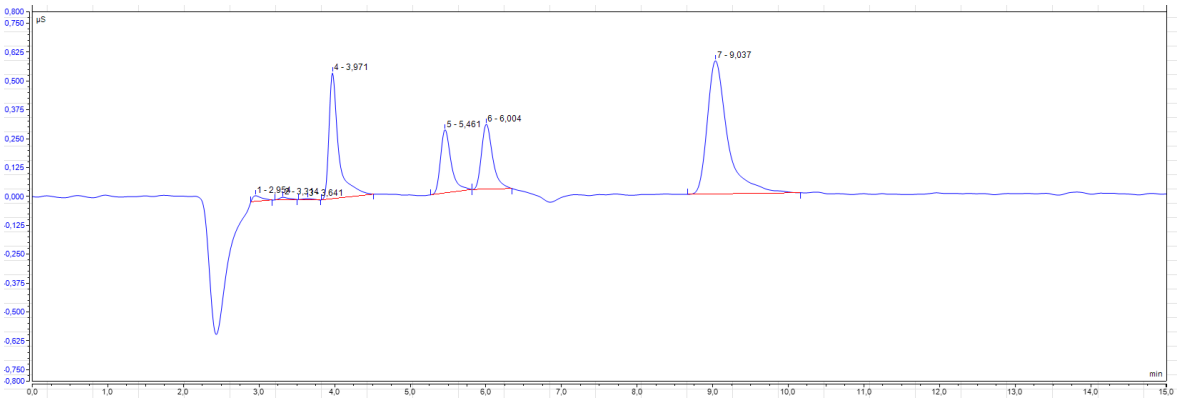

Figure 11. IC chromatogram of the treated wastewater: experiment parameters: pulse frequency 500, pH neutral, diclofenac concentration 100 (µg/L) and starting bromide concentration 10 mg / L. Peaks in numerical order 1. Fluoride 2. Hypobromite 3. Bromate 4. Chorine 5. Bromide 6. Nitrate 7. Sulfate

4.2.2 The impact of bromide concentration

The time it takes to oxidize 90% of diclofenac stays the same from 3.6 to 7.1 minutes since the pulse frequency and treatment time stay the same throughout all the experiments (Fig. 12). The oxidation rate could be underestimated because the HPLC detection limit is 5.2 µg/l; any concentrations below this threshold is considered undetectable and thus treated as zero.

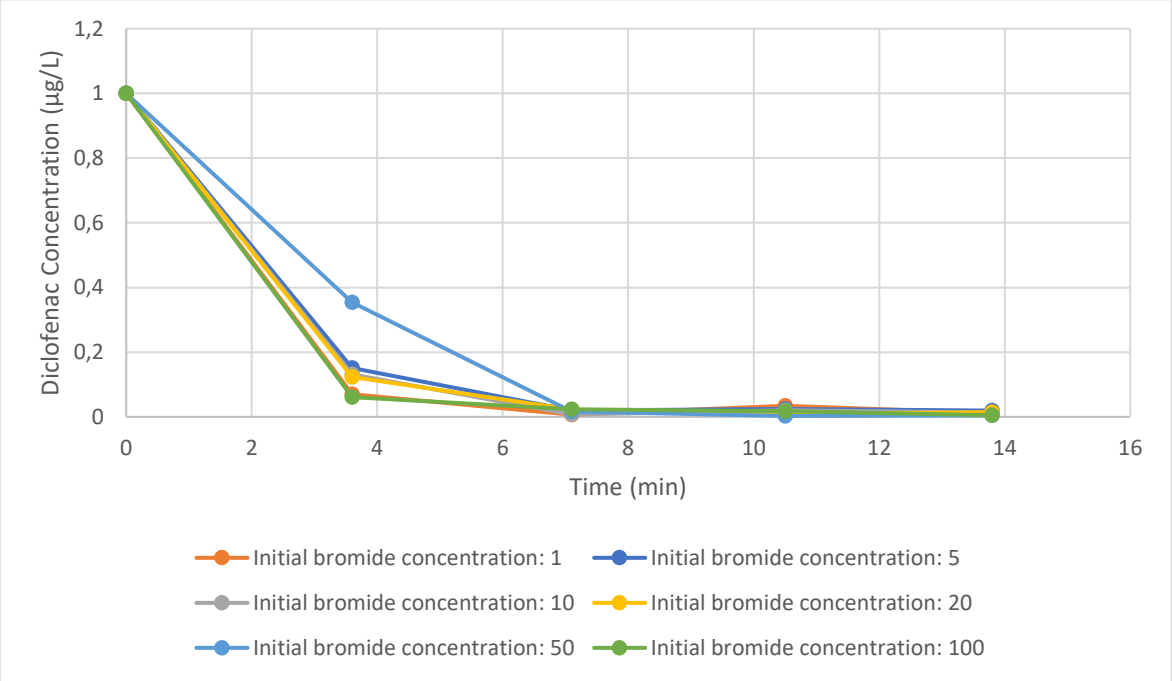

Figure 12. Diclofenac concentration as a function of time: Bromide concentration 1,5,10,20,50,100 mg / L, pH neural and pulse frequency 200 pps

The concentrations of bromide did not change significantly in this experiment either except for 100 mg/L initial concentration which increased (Fig. 13) (Fig. 14). This should not happen since no bromide was added in any tests. It most likely is residual waste again inside the pipes mixing with the new water inserted inside the water tank which leads to the increase of bromide. Another possibility is that the initial spiked water that was inserted into the tanks was not properly mixed. The bromate concentration increased by 2 mg/l from when the initial bromide concentration increased from 50 mg/l to 100 mg/l. This clearly goes over the new EU-directives of the allowed concentration of bromate in treated wastewater. However, wastewater effluents typically contain lower concentrations of bromide <0.05 mg/L especially om areas with little to no anthropogenic sources (Soltermann et al., 2016). It is

hard to say how much the initial bromide concentration increased the formation of bromate since the data is spotty. This problem comes from the fact that the samples needed to be diluted for IC analysis. Since the concentration of bromate is so low dilution makes it harder to analyze, thus IC method might not be the most effective for this type of analysis. From the concentrations of bromate that have been detected it could be said that the initial concentration of bromide increases the formed bromate. Petrochenko and Preis also found that the formation rate almost doubles when initial bromate formation goes up from 1 mg/L to 5 mg/L the difference is that the pH changed form 9->3 during the experiment (Petrochenko and Preis, 2024). Thus, the conclusion that can be drawn from this data does somewhat support this.

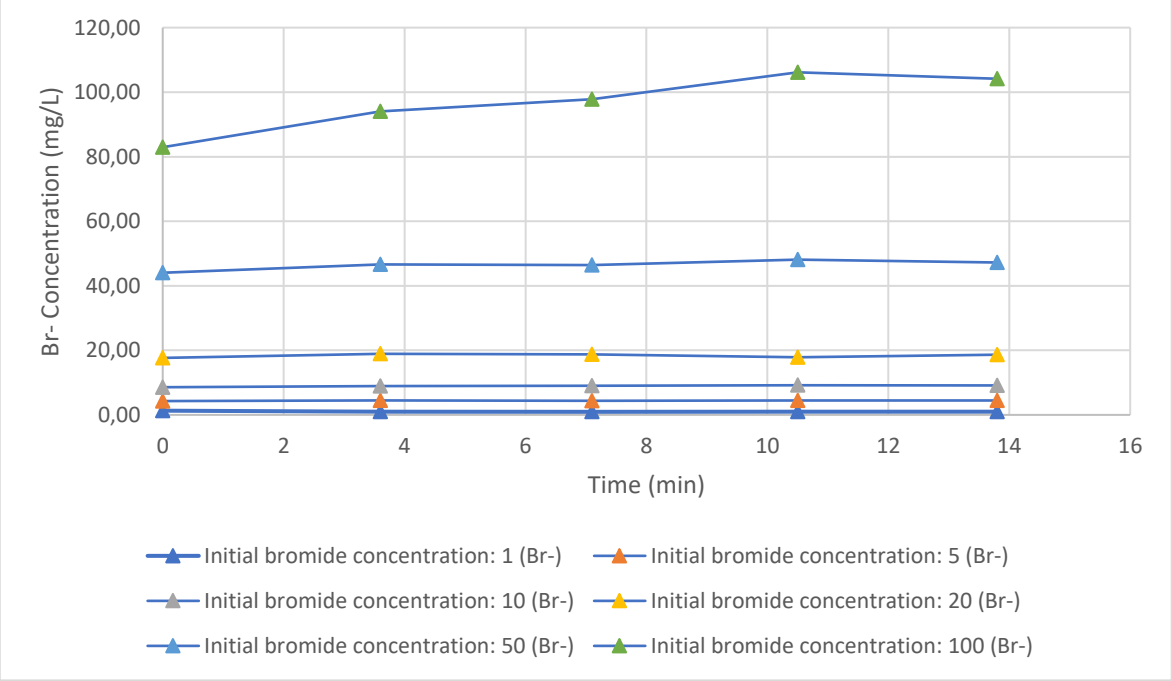

Figure 13. Bromide concentration as a function of time: Initial bromide concentration 1,5,10,20,50,100 mg / L, pH neural and pulse frequency 200 pps

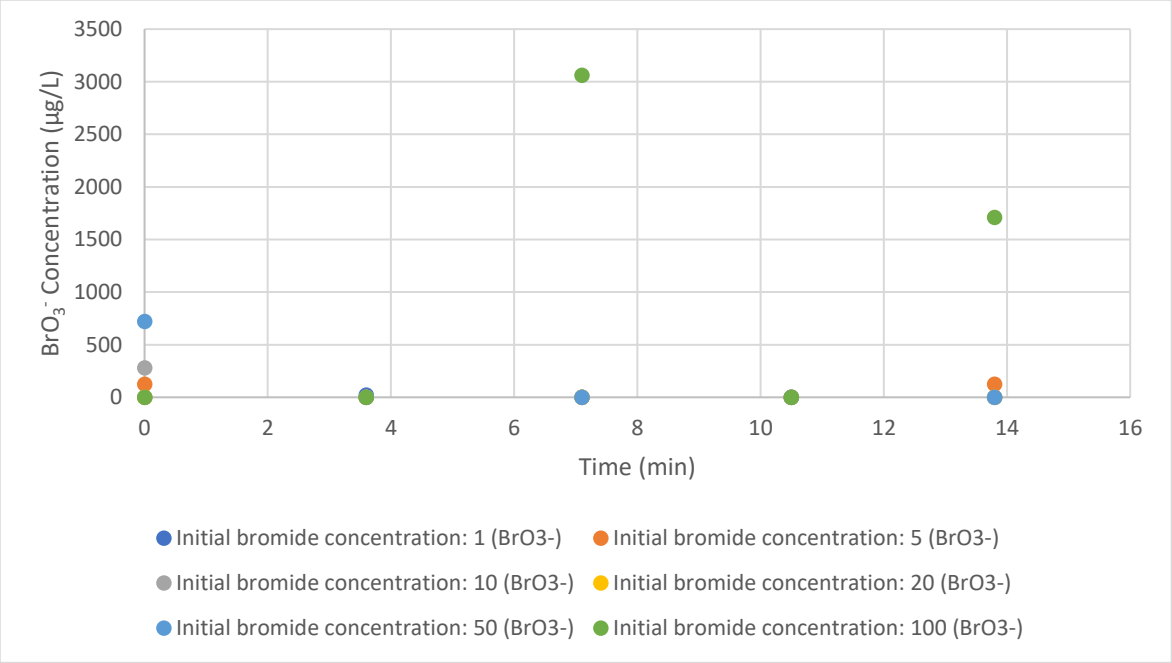

Figure 14. Bromate concentration as a function of time: Initial bromide concentration 1,5,10,20,50,100 mg / L, pH neural and pulse frequency 200 pps

The bromide concentration also increases the amount of hypobromite formed (Fig. 15) (Fig. 16). Making it important to minimize the amount of bromide in wastewater.

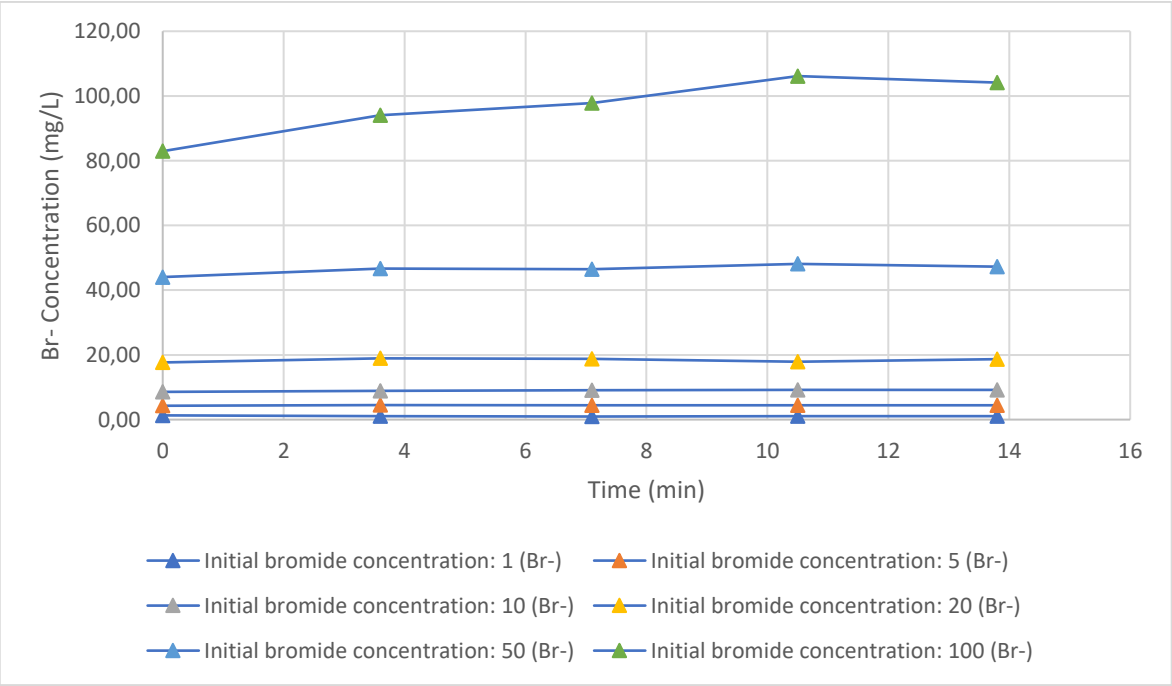

Figure 15. Bromide concentration as a function of time: Initial bromide concentration 1,5,10,20,50,100 mg / L, pH neural and pulse frequency 200 pps

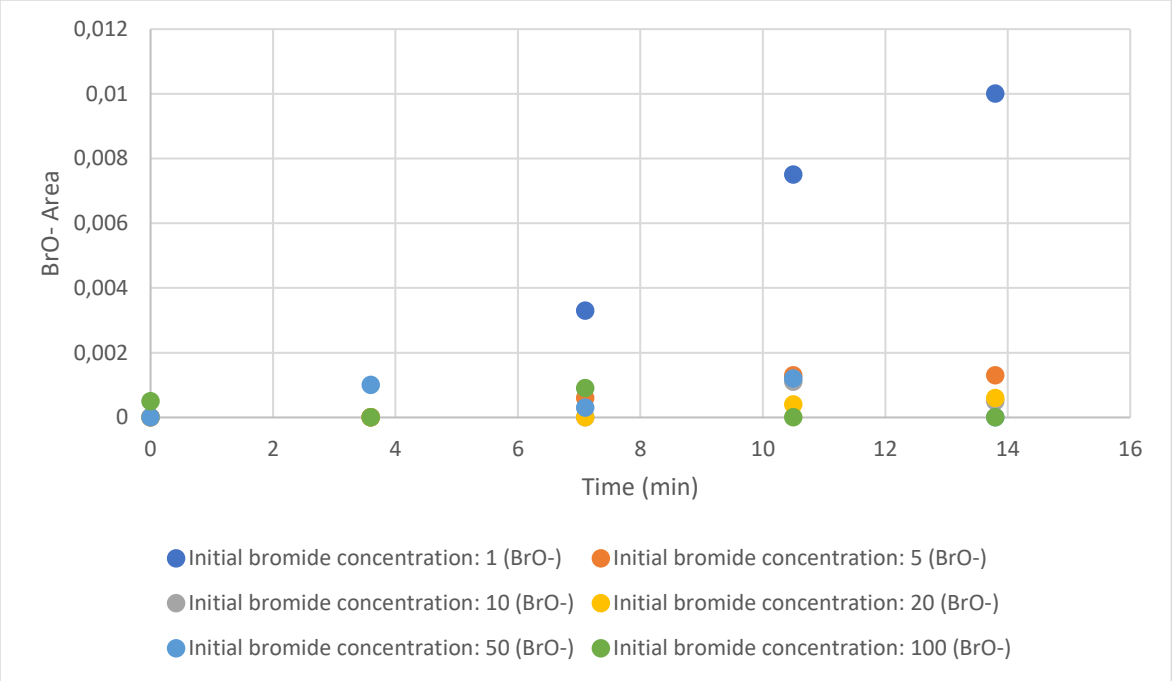

Figure 16. Hypobromite concentration as a function of time: Initial Bromide concentration 1,5,10,20,50,100 mg / L, pH neural and pulse frequency 200 pps

4.2.3 The impact of pH

The pH change did not affect the oxidation of diclofenac substantially since 90% oxidized at about the same time as previous experiments (Fig. 17). The diclofenac concentration of pH 3 experiment is not accurate because the HPLC was using water, methanol and acetic acid as an eluent making it react differently to high acidity.

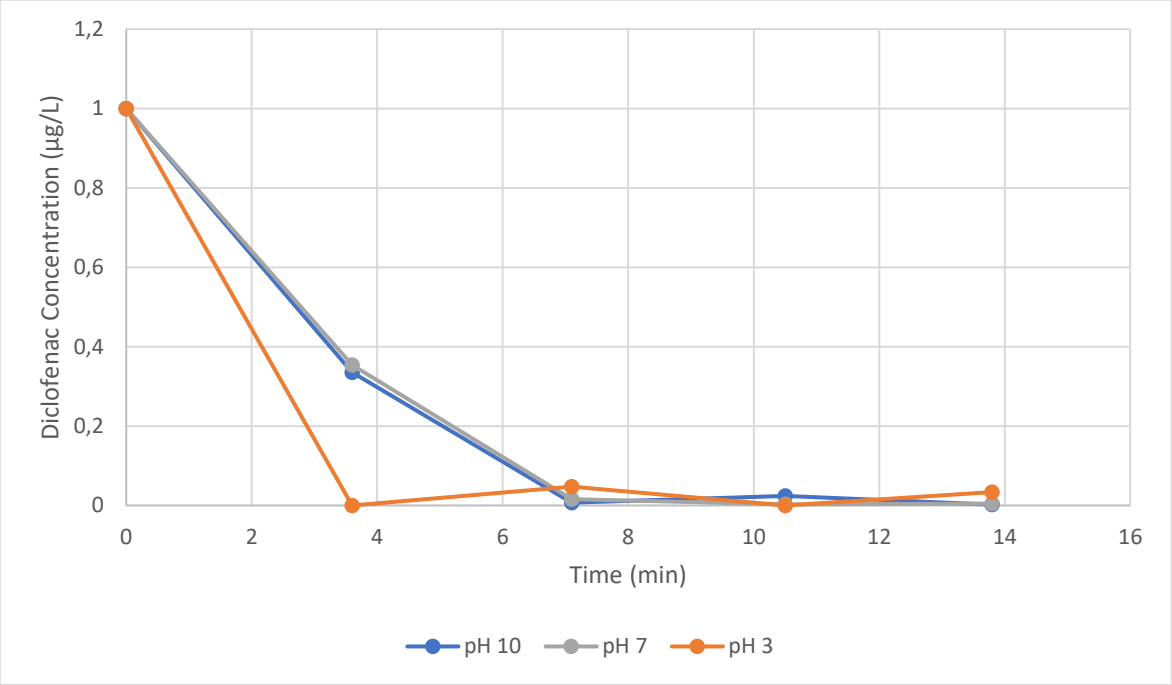

Figure 17. Diclofenac concentration as a function of time: pulse frequency 200, pH 3,10,7 and starting bromide concentration 50 mg / l

The bromate concentration did somewhat respond to the change in pH (Fig. 18). Lowering the pH value should lead to higher concentration of bromate formed with high treatment times according to (Petrochenko and Preis, 2024). There is a noticeable drop in bromide concentration when pH was 3 while pH 7 and 10 concentrations don't fall that much. However, only one bromate concentration can be seen at 11 minutes at a conversion rate from Br- to BrO^{3}- of 3%. This makes it hard to make conclusions, but the bromide concentration drop would indicate that oxidation is more efficient at pH 3 which would be consistent with the observation made by Petrochenko and Preis.

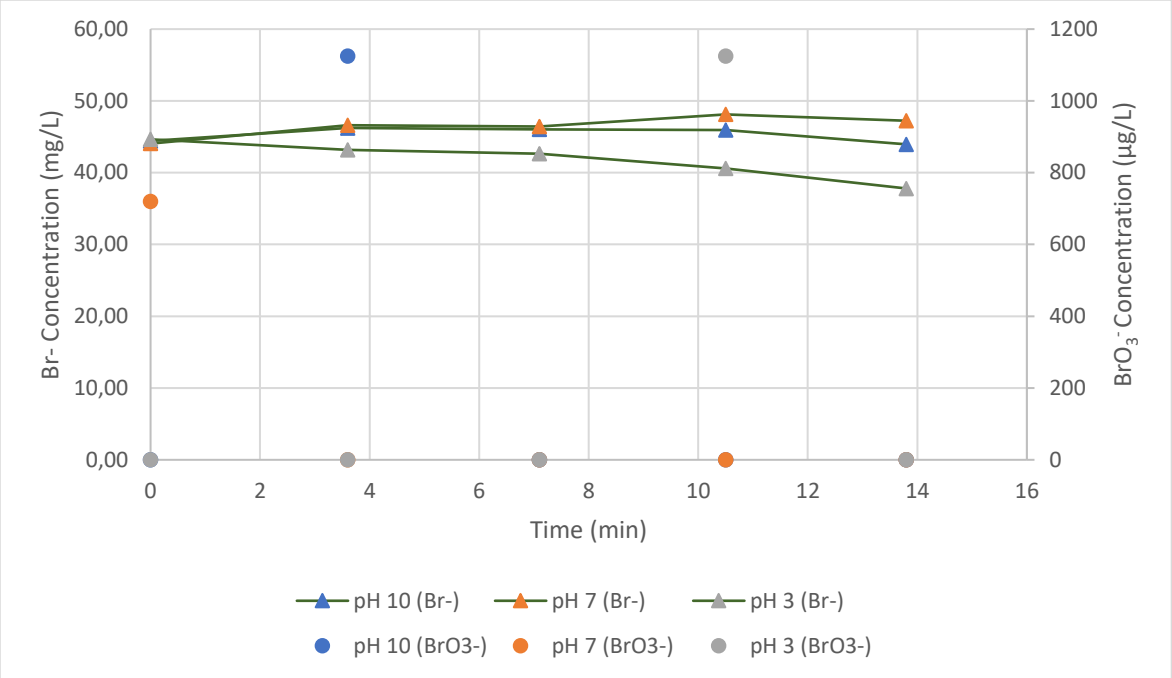

Figure 18. Bromate concentration as a function of time: pulse frequency 200, pH 3,10,7 and starting bromide concentration 50 mg / l

It can also be seen that hypobromite did react to the change of pH since the hypobromite concentration is higher at pH 3 but, the lack of hypobromous acid at pH 3 is unusual, this could be due to the low power delivered at 368 J/L. Also, at pH 10 the concentration decreases. In both cases only 3 to 4 data points make it hard to draw conclusions, but it would suggest that lower pH leads to higher concentrations of hypobromide (Fig. 19).

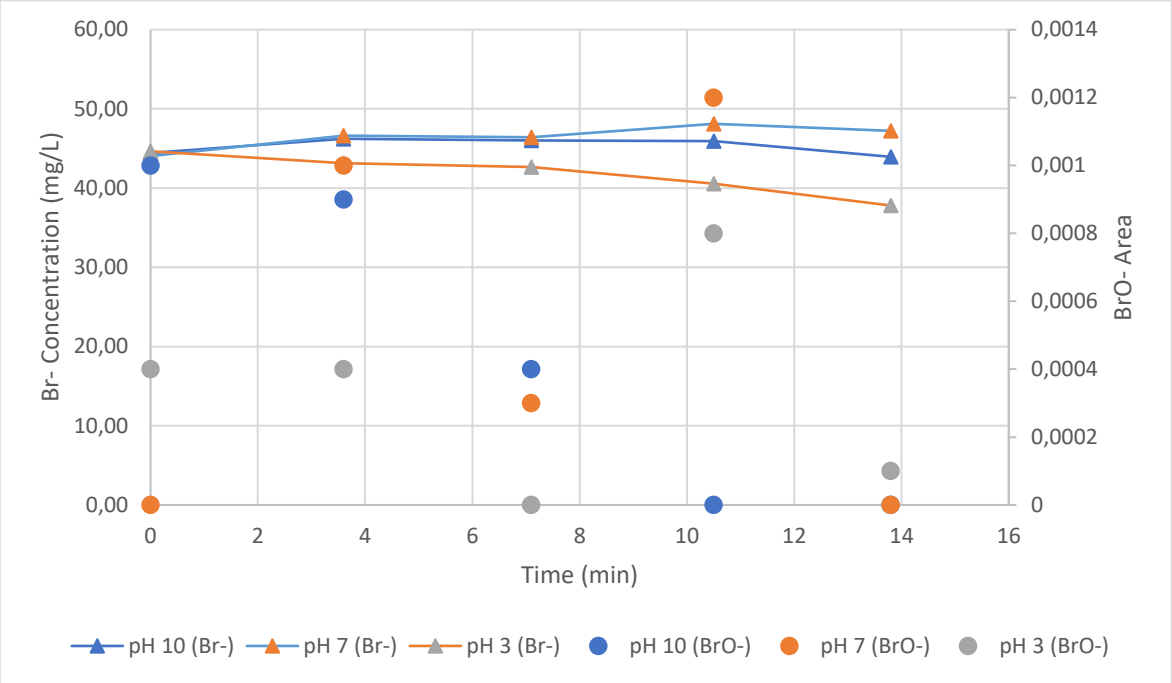

Figure 19. Hypobromite concentration as a function of time: pulse frequency 200, pH 3,10,7 and starting bromide concentration 50 mg / l

5 Conclusions

This bachelor's thesis investigated the use of the PCD process in wastewater treatment. Specifically, the parameters were investigated regarding how the initial concentration of bromide, pulse frequency and pH affect the diclofenac removal and the formation of bromate. Using the data available the main goal was to find ways to minimize the formation bromate. The importance of this comes down to the new EU-directive concerning urban wastewater treatment stating that treated water in the future needs to have significantly lower concentrations of pharmaceutical waste (<80%) and a maximum 50 µg/l of bromate.

From the experimental data, due to analytical challenges it is hard to say which parameter had the biggest effect on bromate formation. The data should indicate that higher pulse frequency raised the rate at which bromate forms but there are not enough data points to draw that conclusion. The initial concentration of bromide should also increase rate at which bromate is formed. When it comes to pH low levels should be avoided since (Petrochenko and Preis, 2024) shows that bromate formation almost doubled at low pH levels which could

be somewhat seen in the decrease of bromide concentration. In these experiments pure oxygen was not needed, and it is recommended to use air if nitrate formation does not cause problems. For further research it is recommended that if samples are analyzed using IC dilution might affect the result since it becomes almost impossible to detect small amounts of bromate making it hard to draw conclusions. Still all these factors in mind, PCD-treatment show considerable promise as wastewater treatment option thus further research should investigate upscaling this technology to industrial levels to find out if any problems arise.

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Appendix 1. Ion chromatograph standards

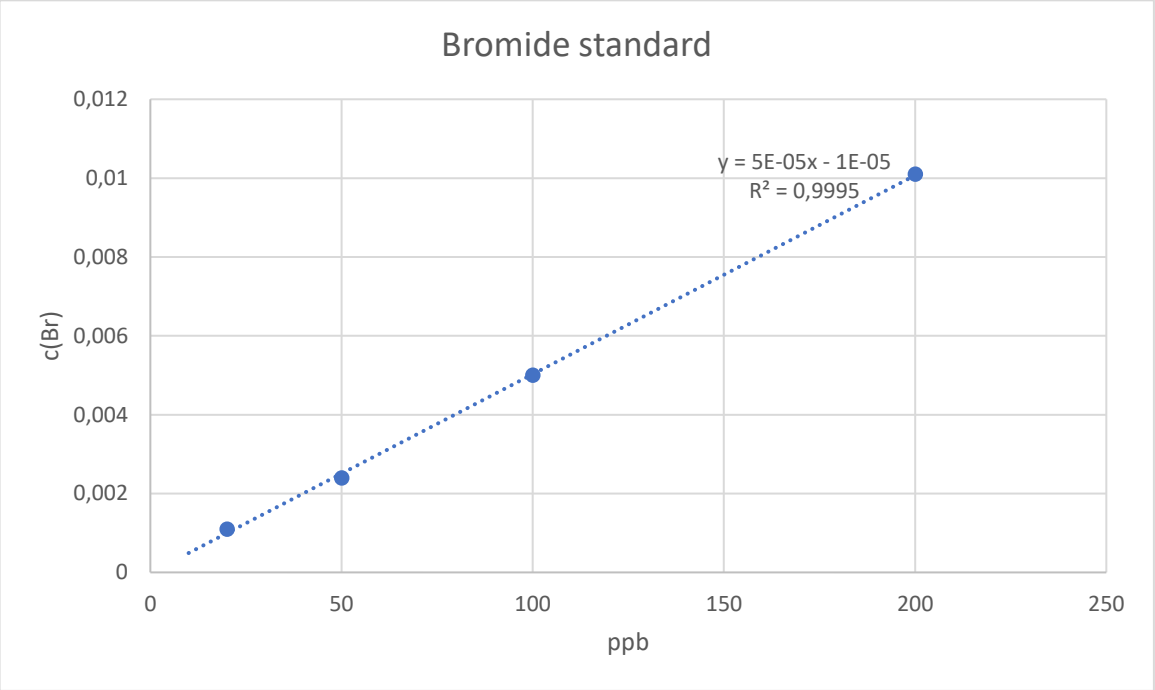

Figure 1. IC bromide standard

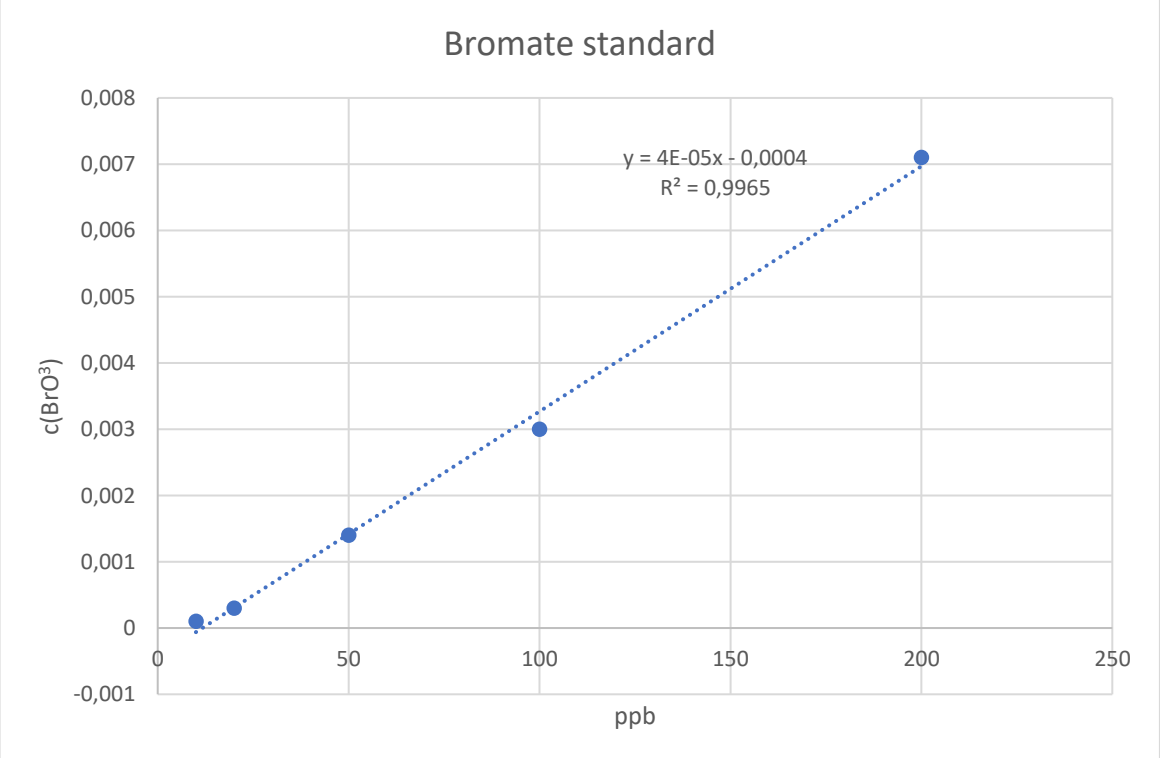

Figure 2. IC bromate standard