Reductive treatment of drinking water contaminants and disinfection by-products using aqueous phase corona discharge.

REDUCTIVE TREATMENT OF DRINKING WATER CONTAMINANTS AND DISINFECTION BY-PRODUCTS USING AQUEOUS PHASE CORONA DISCHARGE.

BY

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Abstract

With increasing global population comes an increase in the need to safe and clean drinking water. Contaminants can arise in drinking water either naturally, or by the interaction of disinfection chemicals with naturally occurring materials, or simply due to by-products of the disinfection mechanism itself. Due to the oxidative nature of our disinfection treatments, these species are in highly oxidized states, and in some cases require chemical reduction to become less harmful.

The present work demonstrates the capabilities of aqueous phase corona plasma in reductive treatment of oxidized contaminants found in drinking water. This study focuses on the treatment of the nitrate ion, bromate ion, chlorate ion and monobromoacetic acid, all of which can be found in typical drinking water systems.

The second and third chapters within this thesis establish the optimal water matrix conditions for the treatment of bromate, chlorate and nitrate. These experiments investigate the influence of pH, temperature, presence and types of oxidative scavengers, dissolved gases and by-products that are made by this treatment process with these compounds. The main conclusion of these works is that aqueous phase corona discharge is capable of producing chemical compounds with sufficient energy to chemically reduce the nitrate, bromate and chlorate anions. Acidic conditions, under low dissolved oxygen scenarios facilitated the highest amount of reduction of the target contaminants, as well as having the presence of oxidative species scavengers. It was also observed that the anoxic environment could be obtained by introducing alcohols into the contaminated solution which generated sufficient cavitation and bubbling to strip the oxygen from solution. Through a comparison of various carbonaceous compounds as oxidative species scavengers, it was determined that the volatile alcohols provided a better performance than other soluble carbon sources, due to the decrease in dissolved oxygen.

The fourth chapter considers different methods of introducing argon, oxygen and nitrogen into the test solution for the effect they would have on the treatment of solutions containing the bromate anion or monobromoacetic acid. The optimal pH for the treatment of monobromoacetic acid was also established, where again the acidic conditions prevailed. Tests were conducted to consider the effect of having the solution pre-saturated with the test gas, continually sparged, or with the gas passing through a hollow discharge electrode. The tests in which gas was blown through the discharge electrode greatly surpassed all other treatment regimes, where nitrogen provided the best removal for both contaminants under acidic conditions for bromate and under acidic and basic conditions for monobromoacetic acid.

The fifth chapter provides conclusions for the overall thesis and recommendations for future work.

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Preface

This thesis has been prepared for McMaster University following the guidelines set for thesis prepared for academic submission to journal articles. The material presented is co-authored by Vickram Lakhian and Dr. Sarah Dickson. The contributions of each are listed below.

Chapter 2

Article title:	Reduction of Nitrate Ions using Aqueous Phase Corona Discharge
Authors:	Vickram Lakhian and Sarah E. Dickson

The experimental apparatus was made by V. Lakhian. The experiments were prepared and conducted by V. Lakhian. The analysis of the samples was done by V. Lakhian, as well as the interpretation of the results. The manuscript was written by V. Lakhian and edited by S. E. Dickson

Chapter 3

Article title:	Reduction of bromate and chlorate contaminants in water using aqueous phase corona discharge
Authors:	Vickram Lakhian and Sarah E. Dickson

All of the experiments were prepared and conducted by V. Lakhian. The analysis of the samples and interpretation of the results was done by V. Lakhian. The manuscript was written by V. Lakhian and edited by S. E. Dickson

Chapter 4

Article title:	Influence of gases on the removal of bromate and monobromoacetic acid using aqueous phase corona discharge
Authors:	Vickram Lakhian and Sarah E. Dickson

The experimental setup was done by V. Lakhian. The preparation and execution of the experiments were done by V. Lakhian. The sample analysis and interpretation was conducted by V. Lakhian. The manuscript was written by V. Lakhian and edited by S. E. Dickson.

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Chapter 1

Introduction and Problem Statement

The access to clean drinking water is a very real concern for urbanized city centres. Since the early 1900s , disinfection by chlorination has been at the forefront of protecting drinking water from microorganisms that are present in natural ecosystems. The introduction of chlorination caused a rapid decrease in the number of outbreaks of cholera, typhoid and diarrhea [1]. This oxidative treatment has had tremendous success and provided an enormous contribution to the improvement of public health; however, there are also shortcomings which need to be addressed. For example, the use of chlorination in drinking water also leads to the formation of trihalomethanes and haloacetic acids when organic compounds are present in the source water being treated [2]. Other alternatives, such as ozonation and chloramination of drinking waters, both can in some cases lead to the introduction of further disinfection by-products such as bromate for the former and halo/nitrosamine for the latter [2, 3]. The benefits of oxidative treatment cannot be ignored, especially when historical data demonstrates the significant decrease in outbreaks in harmful diseases. There remains a need to mitigate the production of these compounds either through alternative treatments or in determining a method to remove these compounds from our drinking water streams and dispose of them in a safe and responsible manner. The focus of this thesis is to explore the reductive capabilities of aqueous phase corona discharge and its ability to destructively remove contaminants and disinfection by-products from simulated tap water. There has been a significant amount of work done by others who have been investigating the physical nature of the discharge and the effects of various physical characteristics of the discharge process itself [4–10], while other work has looked into the different methods of generating the high voltage discharge in water and types of electrodes and reactors [10–14]. As such, the scope of this work is limited to focussing specifically on changing features and characteristics of the water matrix to achieve chemical reduction of oxidative contaminants using aqueous phase corona discharge.

This thesis is split into three studies considering specific compounds which are found in drinking water or are generated in drinking water sources through oxidative treatment. The first study focuses on nitrate, a common contaminant found in all natural water systems originating from the decay of organic matter. This study was meant to provide a proof of concept for the system in its ability to provide reductive treatment of a real-world contaminant for drinking water. In this study the effect of solution pH, electrolytic conductivity, temperature and concentration of methanol were considered and the improvement on the level of reduction achieved was noted. A by-product analysis of the reaction was also performed, in order to elucidate on the mechanisms of treatment.

The next study builds upon the confirmation that aqueous phase corona discharge is capable of performing chemical reduction by focussing on two disinfection by-products, bromate and chlorate. Bromate and chlorate are compounds generated by the oxidative treatment of waters either through ozonation or chlorination. This study utilized the same equipment as the previous study and considered the implications of pH, temperature, methanol concentration, dissolved oxygen, and various carbonaceous species as oxidative species scavengers, and again a by-product analysis was performed to search for by-products generated from the treatment process.

The final study further explored the influence of dissolved gases in the water matrix and the effect they can have on treating bromate and monobromoacetic acid, both disinfection by-products. In this study, gas was introduced in multiple ways and its effect on the treatment of the contaminated solution was investigated. The solution was either pre-sparged by bubbling a gas through a 2 micron filter, saturating the solution with that gas and stripping all others; sparged continuously with gas through the filter a distance away from the discharge electrode; or finally testing the influence of gas flowing directly through the hollow high voltage electrode . In this experiment, the three gases tested were argon, diatomic nitrogen and diatomic oxygen. The influence of pH was also tested for monobromoacetic acid.

The objectives of this study are as follows:

- To establish the ability of aqueous phase plasma to reduce a naturally occuring contaminant in drinking water, the nitrate ion. Determining optimal water matrix characteristics for achieving reduction as well as considering the use of methanol as an oxidative species scavenger to increase the rate of reduction are some of the main investigations of this work. Determination of potential by-products is also explored in order to determine the feasibility of this treatment method.

- To expand upon the reductive capabilities of aqueous phase plasma and explore the reduction of two drinking water disinfection by-products, bromate and chlorate. The optimal water matrix characteristics for these compounds is also investigated. Expanding upon the previous work, the different physical effects that methanol can have on the dissolved gas concentration is investigated as well as testing the efficacy of different materials as oxidative scavengers. Tests are also conducted in conditions approximating real world to establish real world implications of this treatment.
- The final objective is to investigate the effect of argon, nitrogen and oxygen can have on the treatment of monobromoacetic acid and bromate. These two compounds are again disinfection by-products and the efficacy of this technology in treating waters contaminated with these compounds is worth pursuing. The goals of this work are to study the effect of different ways of introducing these gases into the test solution (either pre-saturation, continuous sparging or directly into the discharge zone) has on the treatment of these two target compounds. The results of this study can allude to how this technology could be implemented in the most effective manner.

The combined contributions of the studies performed in this thesis demonstrate that aqueous phase corona discharge is a technology capable of not only performing advanced oxidation processes, which the literature has largely focussed upon, but also advanced reduction processes. This work demonstrates that the system can be optimized towards reductive processes by altering the water matrix and introduction of various chemical species. Furthermore, this work demonstrates the ability of this technology to treat multiple contaminants which have real world implications on human health.

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Chapter 2

Background Material

2.1 Current Treatment Methods

The first section of the background material will cover some of the competing technologies which are available for treatment of the compounds which will be studied in this thesis. The contaminants which were studied were the nitrate ion, bromate ion, chlorate ion and monobromoacetic acid. There are several techniques available for treatment, however none are without their drawbacks.

2.1.1 Adsorption Methods

Granulated Activated Carbon (GAC) is able to directly capture perchlorate [1]. However, perchlorate is not as easily captured in this mechanism as in ion exchange, likely due to the poor complexing of the perchlorate anion. It was demonstrated that on virgin GAC nitrate or nitro-organics are more readily secured to bonding sites upon the GAC [1]. Similarily, for the oxyhalides, bromate and chlorate are capable of being adsorbed onto the surface of the GAC for sequestration [2, 3]. Bromate, however, is capable of being reduced upon the surface of the GAC under acidic conditions, if it is possible for it to be adsorbed [3]. Haloacetic acids have also been adsorbed by biologically activated carbon from waters, though it was not able to be biologically degraded [4].

In all cases, there is significant competition for adsorption sites from the presence of other anionic substances such as phosphates, sulfates and halides and even natural organic matter. If the concentration of these compounds is high enough, it can significantly impede the uptake of the target contaminant and reduce the efficiency of removal. Furthermore, except in the case of the bromate ion which is able to be reduced under acidic conditions, these are mainly separative methods. There would be the next step of proper disposal of a concentrated brine if the GAC is regenerated, or landfill of the GAC, which could potentially result in the contaminants being re-released over the lifetime of the landfill.

These are incomplete solutions as the competition for adsorption sites is high, there is potential for recontamination from residual waste products.

2.1.2 Ion Exchange Resins

Ion exchange resins work by providing a surface which the a target ion can be exchanged for an innocuous ion. This exchange renders the target ion safely out of the drinking water stream. In some cases, the resin after all adsorption sites are full, must be regenerated, but in so doing a concentrated brine of the various anions captured is generated [5]. For most anionic ion exchange resins, sulfate and nitrate have greater affinities for exchange sites than oxyhalides,perchlorate [5, 6]. As such there is limited effectiveness in water samples where these two interfering anions are present in large concentrations. A few new hybrid technologies are being developed where there is simultaneous capture of the contaminant and the concentrated brine from regeneration is then treated using a destructive technology. For example, Gu et. al incorporate a regenerative resin which selects for perchlorate, sulfate and nitrate and destruction of these compounds occurs through elevated temperatures and pressures in combination with the addition of a ferric chloride solution in acid. There were interactions with sulfate and nitrate also being reduced which required a higher concentration of ferric chloride [6].

Even with these new advances, spent brine disposal still remains a problem. In the above example, it was destroyed but using energy intensive procedures. Another alternative option is the use of evaporation beds, where the brine is evaporated until it becomes salt. The remaining salt is collected for disposal, which again introduces a highly soluble compound into landfills where there is a potential for release into groundwater systems [5].

2.1.3 Membrane Technologies

Reverse osmosis, or permeable membrane separation incorporates the use of an ion selective permeable membrane. Hydraulic pressure is applied to a solution of ions forcing transfer of water through the membrane. The membrane pore sizes can range from 100 pm to 1 μm; small enough to retain large ions from water. As this is a size exclusion method, many ions are retained, not all of which are harmful and this can result in the creation of a concentrated brine as more water is pushed through the membrane [5]. As there is significant pressure drop over the membrane, this process is very energy intensive and requires between 3 - 10 kWh/m^3 [7].

Again, the main problem is the reduction of this concentrated brine. A hybrid technology was developed in the work by Matos et. al [8], in which one side of the permeable membrane was a bioreactor where bacteria, excess carbonaceous material, nutrients and chloride counter ions were added. The polluted water was pressed through the membrane where biological treatment of target anions, in this case perchlorate and nitrate. After this reduction further treatment was required to remove the excess nutrients, metabolic by-products and microbial cell [8]. Other technologies also exist employing chemical reduction with ferrous compounds as described above for destruction of the brine; however, again significant energy use is required to overcome the activation energy to reduce perchlorate [9].

2.1.4 Biological Reduction

Biological reduction is also a possibility as a reducing mechanism, though it also has limitations. Biological reduction requires highly tailored environments and even in such cases, oxygen, nitrate and nitrite are preferentially reduced over oxyhalides [10–12]. Also, electron donating material, such as easily accessible carbonaceous material, as well as nutrients in the form of nitrogen, phosphate and molybdate are required in order for development of the species. Typically an anaerobic environment is required for reduction of target compounds to occur, though unfortunately while organisms are able to reduce in these environments, they are not able to grow by anaerobic respiration. In order to facilitate growth and maintenance of the population, aerobic cycles must be introduced which increases the treatment time for inorganic compounds. Biological processes are also fairly slow, and therefore often found to be impractical for large scale deployment [13]. High salinity is another detrimental factor for maintaining a healthy population of reducing bacteria, limiting the ability of biological treatment for concentrated brines [12].

Mono- and di- haloacetic acids are capable of biodegradation under aerobic processes. Bacterial strains have been isolated which are capable of degrading these substances, with preference of the mono- substituted acids over the di- and tri- haloacetic acids [14, 15]. The problem lies in that haloacetic acids are found in drinking water streams, and not waste water streams, and after the disinfection step. Therefore, having a biological contactor after disinfection to remove the compounds would negate the original disinfection, and so biodegradation of these contaminants would only be useful if a separative mechanism were used to first separate and then dispose of through biological means, providing the concentrated brine could be modified to allow the bacterial population to bloom.

Though biological remediation would be very familiar, as it is already extensively used in wastewater treatment, the long treatment times, coupled with the tight controls required for selective target contaminant removal are impediments for the blanket treatment of oxidized contaminants such as those in this study.

2.2 Aqueous Phase Corona Discharge

2.2.1 Characteristics

Aqueous phase corona discharge has been the focus of many studies for its capabilities to generate energetic active species for the degradation of target contaminants. In order to fully understand why this technology has become so interesting, it is necessary to understand the processes which are occurring as a result of the electrical breakdown of water.

Pulsed corona discharge is a method of using a strong electric field to dissociate water into the hydroxyl ($OH^\bullet$) and hydrogen (H_2) radicals. It is classified as a partial discharge system, as the discharge channel does not extend fully from the discharge electrode to the ground electrode. UV radiation can be generated dependent on solution conductivity and pressure waves, though the strength of the latter is dependent on the constituents within the water matrix.

Table 2.1: Pulsed Corona Discharge Characteristics (from [16, 17])

Voltage Rise Time	10^{-9} - 10^{-7} s
Peak Current	10 - 100 A
Peak Voltage	10 - 1000 kV
Pressure wave generation	weak to moderate
UV light generation	weak to moderate
Primary Current Carriers	Ions (opposed to electrons)

Typically, a voltage pulse with a voltage rise time on the order of $10^{-9} - 10^{-7}$ s is required, though this is heavily dependent on conductivity of the water. The characteristics of corona discharge are pulse repetition rates on the order of 10 Hz - 1 KHz, with average discharge currents of 10 - 100 A and voltages on the order of 10^4 - 10^6 [16]. The voltage rise time required is a function of conductivity, but typically on the order of $10^{-9} - 10^{-7}$ s is required. A summary from the literature review paper by Locke et. al is presented in Table 2.1.

Pulse widths are dependent on the electrical systems, however, it has been noted that long pulse widths significantly decrease the efficiency of the radical production by increasing the ohmic loss generated by joule heating of the solution [18, 19]. When the water solution is subjected to an electric pulse of time width Δt, the material properties of water come into play. The electric relaxation time τ is defined as τ = $\frac{\epsilon_o \epsilon_r}{\sigma}$, where ϵ_o is the electric permittivity of free space (8.854 $\times 10^{12}$ F/m), ϵ_r is the relative permittivity of solution (for water at room temperature, $\epsilon_r \approx 80$) and σ is the conductivity of the medium, (for tap water $\sigma = 500$ μS/cm). For tap water at room temperature $\tau = 1.42 \times 10^{-8}$ s. For the situation where the $\Delta t \gg \tau$ the medium behaves resistively, and in the case of water this results in heating of solution. When $\Delta t \ll \tau$, the medium behaves as a dielectric and a sufficiently high electric field stress can be achieved to initiate dielectric breakdown of the medium and in the case of water, this results in $OH^\bullet$ and $H^\bullet$ generation [17]. It is still possible to achieve electrical breakdown in water with voltage pulses on the order of microseconds, however, in these instances breakdown requires vapour formation due to to localized heating of the liquid and then discharge occurs within the gas phase of the water vapour [20].

2.2.2 Species generated by plasma formation

One of the earliest studies in this field which focussed on the species produced by plasma formation in water was done by Clements et. al [21]. This study used a point-to-plane geometry to generate pulsed discharge in water in order to investigate the characteristics of both positive and negative polarity, the influence of flowing various gases through the electrode and the generation of species from the discharge with and without the gas flow through spectrum analysis of the optical emission. The optical emission established the existence of the generation of H_2 and that other excited species were present. By bubbling oxygen through the electrodes they were also able to identify the generation of O_3 and promote the decolorization of an anthraquinone dye [21].

In the work by Sun et. al, an optical study of the various species generated from pulsed corona discharge in water was undertaken. In this study the effects, of pH, conductivity and gas flow through the electrode as well as physical characteristics of the electrodes such as shape and material were studied. In this study, the optical study demonstrated the generation of various radical species such as $OH^\bullet$, $H^\bullet$, $O^\bullet$. The optical emission of the $OH^\bullet$ radical corresponds to UV light. This work also showed that an increase in the $OH^\bullet$ radical generation rate occurred when argon was blown through the discharge electrode vs. oxygen, though oxygen produced O_3. Optical emission from $OH^\bullet$ radicals was also noted to increase with increasing conductivity from 1 μS/cm to 80 μS/cm, and then diminish with

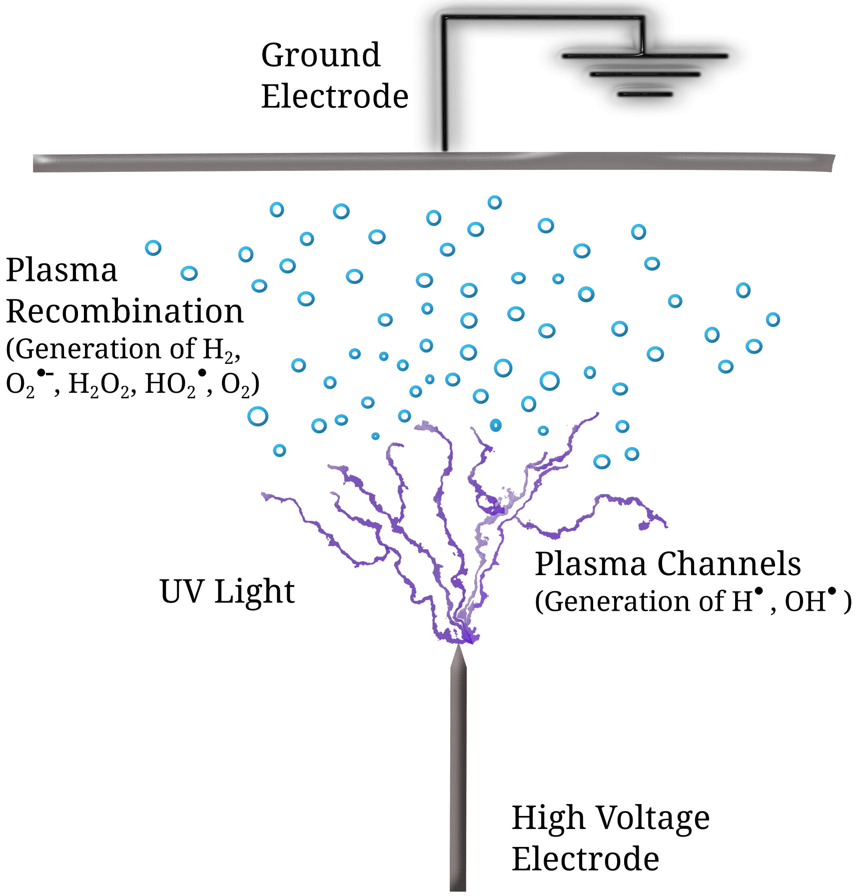

Figure 2.1: Depiction of radical generation and reaction zones for corona discharge in water

increasing conductivity of solution after that point [22].

A study performed by Kirkpatrick and Locke demonstrated that molecular species were also generated from the discharge process. Molecular oxygen (O_2), hydrogen peroxide (H_2O_2) and molecular hydrogen (H_2) are also formed from the reactions involved from the dissociation of water into the $OH^{\bullet}$ and $H^{\bullet}$ and then the propagation of these species into the bulk medium where secondary reactions can occur [23].

In work done to quantify the reductive species generated from discharge in water, Sahni and Locke showed that the species generated using aqueous phase corona discharge were capable of reducing tetranitromethane (TNM) to nitroform. This work also demonstrated the existence of the superoxide radical ($O_2^{\bullet-}$) through the use of nitroblue tetrazolium dichloride as a selective chemical probe. Different scavengers and pH regimes were tested for their influence on reducing TNM, such as varying solution pH and addition of scavenger species to facilitate reduction. Considering the pH level, it was observed that the highest conversion of TNM occured best at an elevated pH of 10. From Kirkpatrick's work it is known that corona discharge in water generates hydrogen peroxide. The hydrogen peroxide can then react with the hydroxyl radical to form the hydroperoxyl radical and water (Eqs. 2.1 and 2.2).

$$\mathrm{OH^{\bullet}} + \mathrm{H_2O_2} \rightarrow \mathrm{HO_2^{\bullet}} + \mathrm{H_2O} \tag{2.1}$$

$$\mathrm{HO_2^{\bullet}} \leftrightharpoons \mathrm{O_2^{\bullet -}} + \mathrm{H^+}, \qquad \mathrm{p}K_a = 4.8 \tag{2.2}$$

The use of various reductive and oxidative species scavengers were tested and it was determined that 0.485 M H_2O_2 outperformed 1 M 2-propanol as a $OH^{\bullet}$ scavenger and best aided the reduction of TNM.

A summary of the various compounds that are generated, and the areas where they are generated is shown in Fig. 2.1.

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Chapter 3

Reduction of Nitrate Ions using Aqueous Phase Corona Discharge

Abstract:

Nitrate is a contaminant which is ubiquitous in natural and wastewaters. This is cause for concern particularly to infants and pregnant women as it can lead to methemoglobinemia, blue baby syndrome. The current maximum acceptable concentration in both Canada and the USA is 10 ppm NO_3-N ($\sim$ 0.7 mM). The main method of nitrate removal from water sources is only found in wastewater treatment through the use of anaerobic bioreactors. A possible solution is to use aqueous phase corona discharge to generate highly energetic radicals which are able to reduce nitrate to gaseous compounds. Water molecules are excited under the influence of a rapid pulsed applied potential and are ionized into hydroxyl radicals and hydrogen radicals, which can react with other species present in secondary reactions to enhance desired effects. In this study, aqueous phase plasma is used to reduce nitrate in solution by applying pulsed high voltage to submerged electrodes to initiate the

breakdown of the water medium. Optimal water matrix characteristics were determined by varying the solution pH, conductivity, temperature and also introducing varying concentrations of methanol as an oxidative species scavenger. It was determined that the nitrogen largely escapes solution through production of gaseous by-products, leaving little residual nitrogen in solution. Over 99% removal of nitrate was achieved at a pH of 3.5 and electrical conductivity of 500 μS/cm with an initial nitrate concentration of 0.03 mM and a methanol concentration of 3 M. At higher concentrations of 0.3 mM and 3 mM, there was 0.0186 mmol and 0.0780 mmol removal, respectively, indicating higher rates of removal as concentrations increase.

3.1 Introduction

Plasma discharges in water are of great interest in modern research due to their ability to generate highly reactive species; which to date have been mainly studied for their oxidizing properties [1]. In aqueous phase plasma discharge, water is ionized into the hydroxyl radical ($OH^\bullet$) and the hydrogen radical ($H^\bullet$), while also generating ultraviolet (UV) light at various intensities dependent on the type of discharge [1–3]. The hydroxyl and hydrogen radicals, along with the UV photons can then further react outside of the main discharge zone in a radical recombination zone to form compounds and radicals. Due to the high density of liquids, this recombination zone is fairly close to the site of the original discharge. Highly oxidative radicals can be formed, such as the hydroperoxyl and oxygen radicals ($HO_2^\bullet$, $O^\bullet$) as well as oxidizing species such as hydrogen peroxide and molecular oxygen (H_2O_2, O_2) [2, 4–6]. The focus of the many recent studies has been to use the generation of these oxidizing species to bring about the decolourization of dyes, degradation of phenol and polychlorinated biphenyls, and more recently the destruction of pharmaceutical compounds [7–10]. In general, aqueous phase plasma discharges are portrayed as a method to generate the hydroxyl radical and other non-selective oxidisers for the oxidation of contaminants.

The capabilities of aqueous phase plasmas in water treatment can be expanded also to act as a generator of reducing species as well. To date there has not been as much research done to take advantage of the reductive species that are also generated from plasma discharge under water. Sahni and Locke explored the reductive capabilities of plasma by quantifying the reductive species that are generated by aqueous phase plasma. Specifically, the species such as the hydrogen radical, molecular hydrogen and superoxide ($H^\bullet$, H_2, $O_2^{\bullet -}$) are all examples of powerful reductants that can be produced directly from electrical breakdown of the water or in the radical recombination zone [11]. In the work by Sahni and Locke chemical probes specifically chosen to target reductive species to measure their generation and to minimize interactions with other compounds. The aim of this work is to expand upon their work and to facilitate the reduction of the aqueous nitrate ion (NO_3^-), a common inorganic contaminant prevalent in all natural water systems, to gas phase reaction products.

Nitrate is a ubiquitous compound in natural water systems. In the natural environment it is created by the microbial digestion of wastes containing organic nitrogenous materials; usually originating from the oxidation of animal and plant wastes [12]. However, there is a large anthropogenic impact on the nitrogen cycle, largely in the production and application of nitrates in industrial farming practices. It was determined that human practices have approximately doubled the amount of nitrogen input into the nitrogen cycle, adding roughly 140×10^9 kg through the application of chemical fertilizers and other agricultural practices, and that the rate of application is increasing [13]. Though nitrate is an essential nutrient for plant growth, excessive amounts of nitrate in water systems can result in the generation of algal blooms, which in turn can lead to anoxic dead zones. Natural systems do undergo geochemical filtration to remove nitrates, but a recent study done on the Mississippi river network has shown that these filtration mechanisms are easily overwhelmed [14].

Beyond the environmental effects, there are also human health impacts to be considered. The United States Environmental Protection Agency has mandated a Maximum Contamination Level (MCL) of 10 ppm NO_3^--N (0.71 mM), which is in agreement with Health Canada's Maximum Acceptable Concentration (MAC) for safe levels in Drinking Water. However, in the United States it has been determined that 22% of domestic wells exceed the MCL level, and in Canada, many sites have been identified as having higher than the MAC for nitrate levels with more at risk in Prince Edward Island, Southern British Columbia and Southern Ontario [15–18]. The risk posed with nitrate in drinking water originates from the fact that human saliva contains enzymes which are able to reduce it nitrate to nitrite. Nitrites in the blood stream can lead to methemoglobinemia, particularly in infants, children and those who lack the enzyme to restore tainted hemoglobin. Furthermore, nitrite under acidic conditions forms compounds capable of functionalizing amines to N-nitrosamines, which are known carcinogens [15].

The goal of this research is to take advantage of the generation of highly active radicals by aqueous phase corona discharge to chemically reduce nitrate compounds. Different characteristics are tested in order to determine the optimum water composition matrix to achieve maximum reduction by varying pH, conductivity and also concentrations of methanol as an oxidative species scavenger, as well as to consider the mechanisms for nitrate reduction and the reaction products generated by this mechanism.

3.2 Experimental Methods and Materials

3.2.1 Experimental Design

The choice of parameters centred largely about the desired electrical conductivities for experimentation. In much of the work to date, experiments have been conducted at lower electrical conductivities of 50 - 150 μS/cm [3, 5, 11]. At higher electrolytic conductivities multiple changes to the nature of the plasma discharge occur. For instance, there is an increase in discharge current and shortening of the streamer length in liquid, reducing the potential treatment zone [19]. Also, higher conductivities have been shown to reduce the amount of oxidizing species, such as the hydroxyl radical ($OH^\bullet$), which could effect the rate at which reduced species are re-oxidized, facilitating reduction [11]. To obtain a benchmark comparable to current literature the initial conductivity of 170 μS/cm was chosen, though to expand to potential future practical applications a higher electrolytic conductivity was also tested at 500 μS/cm, approximately that of tap water. Establishing the target electrical conductivities set many of the other parameters, as it set upper and lower bounds on the pH, as H^+ and OH^- ions have high electrical conductivity in solution, and the ionic strength of the solution also directly relates to the electrolytic conductivity and limits the nitrate concentration.

The pH levels that were tested were chosen to take advantage of a few factors. At low pH, there are two mechanisms which enhance nitrate reduction. The presence of ammonia, which could potentially be produced by reduction of nitrate, further facilitates nitrate removal at low pH, where dissolved ammonia takes the form of the ammonium ion (NH_4^+, pK_a = 9.25) [20]. The reduction of nitrate with ammonium is shown in Eq. 3.1.

$$5\mathrm{NH}_4^+ + 3\mathrm{NO}_3^- \rightarrow 4\mathrm{N}_2 + 2\mathrm{H}^+ + 9\mathrm{H}_2\mathrm{O} \tag{3.1}$$

The second mechanism under acidic conditions takes advantage of the fact that the nitrite anion (NO_2^-) is unstable in its protonated state (HNO_2^-) and disproportionates into nitric oxide, nitrogen dioxide and nitric acid as shown in Eqs 3.3, 3.4, 3.5 [21].

$$\mathrm{HNO}_2 \rightarrow \mathrm{H}^+ + \mathrm{NO}_2^-, \qquad \mathrm{p}K_a = 3.8 \tag{3.2}$$

$$3\mathrm{HNO}_2 \rightarrow 2\mathrm{NO}_{(g)} + \mathrm{HNO}_3 + \mathrm{H}_2\mathrm{O} \tag{3.3}$$

$$3\mathrm{HNO}_2 \rightarrow \mathrm{NO}_{(g)} + \mathrm{NO}_{2(g)} + \mathrm{H}_2\mathrm{O} \tag{3.4}$$

$$3\mathrm{NO}_{2(g)} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{NO} + 2\mathrm{HNO}_3 \tag{3.5}$$

Furthermore, there are two species generated from the pulsed corona discharge which undergo acid/base dissociation. The hydroperoxyl radical, one of the oxidizing species generated by the aqueous phase plasma discharge, also undergoes an acid-base dissociation reaction as shown in 3.6. At a pH level above 7, the hydroperoxyl radical ($HO_2^\bullet$) is completely deprotonated, leaving a residual superoxide radical ($O_2^{\bullet-}$) . This is a conversion of an oxidizing agent to a reducing agent caused by a shift in the pH [11].

$$\mathrm{HO}_2^\bullet \leftrightharpoons \mathrm{H}^+ + \mathrm{O}_2^{\bullet-}, \qquad \mathrm{p}K_a = 4.8 \tag{3.6}$$

$$\mathrm{H}^\bullet \leftrightharpoons \mathrm{H}^+ + e^-_{(aq)}, \qquad \mathrm{p}K_a = 9.6 \tag{3.7}$$

Equation 3.7 shows the dissociation of the hydrogen radical to generate an aqueous electron ($e^-_{(aq)}$) and a proton (H^+). The aqueous electron is an even stronger reducing agent with a standred reduction potential of -2.9 V, compared to -2.3 V of the hydrogen radical. This reaction has a pK_a of 9.6, and so at elevated pH above 10 the aqueous electron is present at a higher concentration than the hydrogen radical [22]. It is possible that this elevated pH will take advantage of this equilibrium reaction and enhance the reduction of nitrate. For these reasons, combined with the constraints set by the desired electrical conductivities, the various pH values were chosen to be 3.5, 7 and 10.5.

In order to facilitate the reduction of the nitrate species, methanol was added as a scavenger. Methanol (CH_3OH, MeOH) has been shown to act as a hydroxyl scavenger, preventing oxidation of other substances, and can also provide further reducing species [11, 23]. These are seen through the reactions in Eqs.3.8, 3.9. Methanol is converted into formaldehyde via a two step reaction. It is first oxidized into the methyl radical by a hydroxyl radical (Eq. 3.8), and then further oxidized by another hydroxyl radical to generate formaldehyde, a proton and the superoxide radical (Eq. 3.9). Formaldehyde and the superoxide anion can both act as reducing agents. It is also possible for the methanol to react with $H^\bullet$generated from the discharge to form H_2. Hydrogen production has been demonstrated to significantly increase with the introduction of methanol into the treatment solution [24].

$$\mathrm{CH_3OH + OH^\bullet \rightarrow CH_2OH^\bullet + H_2O} \tag{3.8}$$

$$\mathrm{CH_2OH^\bullet + O_2 \rightarrow CH_2O + H^+ + O_2^{\bullet -}} \tag{3.9}$$

$$\mathrm{CH_3OH + H^\bullet \rightarrow CH_2OH^\bullet + H_2} \tag{3.10}$$

The purpose of the elevated temperature is to simulate the steady state reaction for this system. There is natural heating of the solution from the plasma discharge through the joule heating effect. In the results shown in this work, the experiments were conducted in a water bath to ensure a constant temperature. However, in a single test to determine the steady state temperature without temperature control, the reaction vessel was operated without the water bath and achieved a steady state temperature of approximately 50^o C. Operating at this temperature has two main effects on the reaction taking place. By raising the temperature of the system, the electrical conductivity increases due to higher mobility of ions within the solution, which may negatively impact the reduction rate. However, there is also to consider the decrease in the solubility of gasses at this temperature. At a higher temperature, NO_x, NH_3 and N_2 gases become less soluble in water. Therefore, any intermediate reduced forms of the nitrate anion, other than soluble nitrite anion, are likely to be gaseous. These gases (nitrogen oxides, ammonia or diatomic nitrogen) would readily evacuate the solution at an elevated temperature and minimize the possibility of re-oxidation. Also, the increase of temperature reduces the concentration of dissolved oxygen in the system. Oxygen is a very effective scavenger of the reductive species generated, particularily the hydrogen radical, and by stripping the oxygen from system enhanced reduction may be achieved.

The experimental conditions that were tested are outlined in Table 3.1. The water matrix parameters that were altered were the concentrations of nitrate, the sample conductivity, the initial pH of the sample and also the concentration of methanol (MeOH). The physical experimental parameters consisted of changes of the solution electrical conductivity and the temperature of solution.

Table 3.1: Matrix of Test Parameters for Nitrate Tests

Parameter	Values
Sample Concentration	0.03 mM, 0.3 mM, 3 mM
Sample Conductivity	170, 500 μS/cm
Methanol Concentration	0, 0.3, 1.5, 3 M
pH	3.5, 7, 10.5
Temperature	25, 50^o C

3.2.2 Experimental Apparatus

The overall experimental design was to store a high voltage charge to a capacitor, disconnect the charging power supply and then rapidly discharge the capacitor through the reactor.

The high voltage supply consisted of a variable frequency, high voltage AC which was then used in a four stage Greinacher type voltage doubler using 1 nF ceramic capacitors and high voltage diodes. The Greinacher stages served to amplify and rectify the output voltage from the AC signal. This output was then filtered using a 10 nF ceramic capacitor. This method allowed for a variable high voltage DC power supply from 0 - 60 kV. The power delivered to the reactor was less than 5 W as was calculated by measuring the determining the energy delivered per pulse and multiplying by the pulse repetition rate. The energy delivered was measured through the current and voltage waveforms delivered to the reactor. The high voltage probe for the voltage measurement was a Tektronix P6015A and the current was measured using a current transformer (Ion Physics CM-10-MG).

The switching occurred using a rotating spark gap, which initially charged the 1 nF pulse forming ceramic capacitor, broke the charging connection, and then formed a discharging connection between the pulse forming capacitor and the reactor with the liquid sample. The rotating spark gap was created using a High Energy Ignition distributor from an automotive ignition system. Alternate posts on the distributor were used for charging

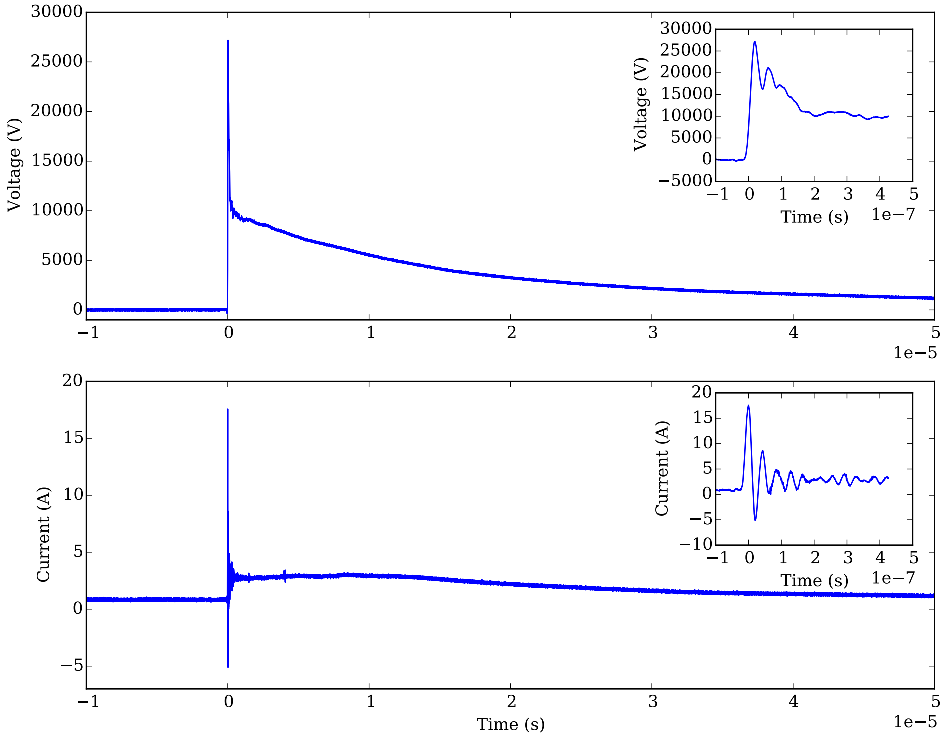

Figure 3.1: Voltage and current waveforms for a typical discharge pulse. The inset shows the transients and voltage rise time for the initial 600 ns of the pulse.

and discharging of the pulse forming capacitor to ensure that there would never be a direct short of the high voltage to the reactor. The pulse repetition rate was controlled by varying the input voltage to a DC motor which was connected via a belt to the rotating arm of the distributor. In order to minimize premature sparking and ozone formation, the head of the distributor was operated under a constant purge of dry nitrogen gas. The spark gap was operated to ensure a pulse repetition rate of 30 Hz. Voltage and current waveforms are shown in Fig. nitrate-iv. The time to achieve 90% of the peak voltage was 26 ns, as shown in the voltage inset.

The reactor itself was a standard borosilicate 3 neck flask with a volume of 100 mL.

It was placed within a water bath contained in a jacketed reactor to ensure constant temperature of the liquid. The electrodes within the reactor were made of commercially pure titanium (CP2, 98.9% pure titanium) from McMaster-Carr. The high voltage electrode was a 1.6 mm rod of titanium, with the discharge end sharpened to a point to concentrate the electric field. The sharpened tip has been shown to provide a more stable discharge over longer periods of time and less sensitive to erosion that occurs during the discharge process [6]. The ground electrode was a rectangular piece of CP2 titanium with dimensions of 12.7 mm x 6.35 mm x 38 mm. It was compression fit with a 4.7 mm rod to allow for electrical connections outside of the reactor. The distance between the high voltage electrode and the ground electrode was maintained at 35 mm. Such a large distance was used to ensure that spark discharge did not occur, especially at lower conductivities where the streamer length was longer.

One millilitre samples were taken at prescribed intervals for sampling using Suppressed Ion Conductivity Chromatography. Each time a sample was removed from the reactor, it was replaced with one millilitre of the initial solution from excess that was made at the beginning of the experiment. Analysis of nitrate concentrations, and testing for the existence of nitrite was done using Suppressed Ion Chromatography using an ion exchange column (Hamilton Company; PRP-X110S), micromembrane suppressor (Dionex; AMMS-300) and a conductivity detector (Dionex; CD-25).

Gas sampling was done using in-line colorimetric gas detection tubes for NH_3, NO, NO_2, and NO_x gases (Gastec Gas Detection Tubes; 3L, 10, 11L). The tubes are calibrated such that a 100 mL sample volume drawn into the tubes is able to yield quantification. As we were sampling headspace from an ongoing reaction in atmosphere, they were used for the detection of the presence of the gasses and a total of 1 L of sample gas was drawn over

2 minutes. The lower detection limits were as follows: the detection of ammonia (GasTec 3L) was 0.2 ppm for 500 mL of gas drawn, nitric oxide (GasTec 10) was 1 ppm for 250 mL drawn and 0.5 ppm for nitrogen dioxide with 250 mL of gas drawn.

The testing of liquid by-products for light organics from the scavenger reactions was done using headspace analysis using an Agilent 6890 gas chromatograph with a Carbowax capillary column with a film thickness of 0.50 m, ID of 0.25 mm and length of 30 m. The detector was a Waters/Micromass GCT time of flight spectrometer. The column was operated under the following temperature profile: initially hold at 50^{o}C for 3 minutes, followed by a heating ramp of 20^{o}C/min until a temperature of 240^{o}C was obtained, which was then held for 5 minutes. The column was operated under a constant flow rate of 1 ml/min of He. The injection was done in split mode with a split ratio of 2:1.

The chemicals that were used were all reagent grade or higher. The sodium hydroxide, hydrochloric acid and HPLC grade methanol were obtained from Caledon Laboratories. The sodium nitrate and sodium chloride that were used were from Sigma Aldrich. Sodium chloride was added to augment the electrical conductivity when the combined electrical conductivity of the sodium nitrate and pH was not sufficient to reach the desired levels.

3.3 Results and Discussion

3.3.1 The effect of solution pH

The results of the plasma discharge treatment to solutions of varying pH without any additives beyond the nitrate contaminant at an initial conductivity of 170 μS/cm are shown in Figure 3.2. In each test, there was a slight decrease in the nitrate concentration over time. The nitrate concentration for neutral and basic conditions initially had a higher level of reduction, however over time, nitrate was reintroduced into the system. At pH 3.5, up to 5.9% of the total nitrate in the system was reduced, while at pH 7 up to 15% was reduced, however, as time progressed nitrate was reintroduced to the system and the final value after 3 hours was 5.2% nitrate reduced. Under basic conditions, a maximum reduction of 6.8% was achieved, however again nitrate re-entered the system and a final value of only 0.66% was removed after 3 hours of treatment. The solutions were not degassed, but represented a typical situation, where at a temperature of 20^{o}C up to 1.5 mM of nitrogen gas and 2.5 mM of oxygen gas can be dissolved in solution. During plasma treatment, shockwaves and cavitation from the discharge can release these gases from solution and generate nitric acid and elevate the nitrate concentration in solution, especially in the presence of high water vapour, as has been demonstrated in the work by Burlica et. al [25]. An important note is that as the plasma treatment progresses, it generates acidity in the sample and lowers the pH, consistent with what was shown by Burlica et. al. The pH changes are outlined in Table 3.2. These pH changes are indicative of the changes that occurred in all samples that were tested in this study.

Table 3.2: Nitrate Concentrations and pH After Plasma Treatment

Initial pH	Final pH
3.5	3.3
6.5	3.5
10.5	3.8

3.3.2 The effect of methanol as a scavenger

Visually, the addition of methanol greatly increased the production of bubbles in solution and generated in a much louder pulse than observed with the absence of methanol, indicating a higher level of cavitation occurring with the addition of methanol. It is highly probably the the increased bubble formation was also due to the generation of molecular hydrogen [24], though the generation of hydrogen was not directly measured.

The results for nitrate reduction demonstrating the effect of using methanol as a scavenger are shown in Fig.3.3, which clearly shows that the addition of methanol greatly enhances the nitrate reduction process. The reaction under the low pH condition has the highest percentage removal of 86%, followed by neutral pH at 56% removal and 39% removal under basic conditions. The results show that a higher concentration of the hydronium ion facilitates higher reduction rates for nitrate, more so than the benefit of the equilibrium reaction between $HO_2^\bullet$ and $O_2^{\bullet -}$ as mentioned in Eq. 3.6.

During the plasma treatment, the pH of solution decreases due to the generation of ionized hydrogen in solution, as reported in Table 3.2, and so the benefit of this pH dependent equilibrium is diminished. The enhanced reduction capabilities of the nitrate anion under acidic conditions are likely caused by the disproportionation reactions depicted in Eq.3.3 - 3.5. These reactions would not be viable under initial basic and neutral conditions until the pH had sufficiently lowered due to the pK_a=3.4 of the nitrite anion.

The pH of the system could have been maintained by using a buffering system, however, to obtain a solution with a significant buffering capacity a solution of high ionic strength would be required and this would greatly increase the conductivity of the solution and effect the plasma discharge processes.

Conducting further tests at a pH of 3.5 demonstrates the enhanced reductive capability of plasma discharge when methanol is in solution. Fig.3.3b shows an increase in the amount of nitrate reduced with increasing methanol concentrations. This indicates that though the concentration of methanol is significantly higher than that of the nitrate, the reaction rate is greatly improved through the addition of a higher concentration of methanol.

The 3 M concentration of methanol (96 g/L) added to the solutions which were treated is fairly large, though it is shown in Fig. 3.3 that there is still a marked difference from the 0.3 M level and even 1.5 M.

The increase in the rate of reduction is likely due to two reasons. The first being the oxidative species scavenging diminished the re-oxidation of nitrogenous compounds and dissolved nitrogen into nitrates. The generation of nitrates in water has been previously observed as a means to disinfect and provide nutrients for plant growth [26]. Second, the scavenging of the hydroxyl radical by methanol generates molecular hydrogen hydrogen, in effect converting an oxidizing compound into a reducing one, which significantly enhances the reduction [24].

3.3.3 The effect of increasing solution temperature

Under an increased temperature the only pH condition which showed an increase in amount of nitrate removed was under basic conditions, relative to room temperature testing with a 3 M methanol concentration. Under acidic conditions, the amount removed remained constant and there was actually a decrease in the amount of nitrate removed under neutral pH conditions, all relative to their counterparts at room temperature with 3 M methanol. The results are shown in Fig.3.4. Under acidic conditions, again approximately 85% of the original nitrate concentration was reduced. For neutral conditions, there was a minimal decrease in the amount of nitrate that was reduced in the system, approximately 48% of the total nitrate concentration was removed. However, in the case of initial basic conditions, there was an increase in the amount of nitrate removed which also obtained 48% reduction.

It was expected that the increased temperature would enhance gas stripping from solution and enhance the rate of reduction, however there was no significant change under acidic conditions, a diminishment for neutral conditions and enhancement only demonstrated in the basic condition.

It is likely that the cavitation occurring from the discharge, especially with the addition of methanol, was sufficient to facilitate stripping, and so no significant improvement is made under acidic conditions, and a decrease in performance is demonstrated under neutral conditions.

The increase under basic conditions can be explained by the increased rate of reaction between the aqueous electron and nitrate which occurs with increased temperature [27]. At an elevated pH, the hydrogen radical ($H^\bullet$) undergoes an acid-base equilibrium reaction to produce an aqueous electron ($e^-_{(aq)}$) as in Eq. 3.7. The initial rate of reduction under basic conditions exceeds that of that of the neutral condition, and as the treatment progresses the solution acidifies and this enhancement is lost, which is seen by the change in slope.

3.3.4 The effect of solution conductivity

As the conductivity of the solution was increased from 170 μS/cm in Fig. 3.3a to 500 μS/cm, there was a decrease in the amount of nitrate reduced to 62% from 85% under acidic conditions, and a slight reduction at neutral pH to 50% from 55%. The basic condition actually showed initial improvement again, but as the solution acidified the effect was diminished, and there a small increase from 39% to 43% reduction of nitrate under initial basic conditions. The work by Sahni and Locke showed that an increase in the conductivity had minimal effect on the generation of reducing species, but had an effect on reducing the amount of hydroxyl radicals produced, but only for initial acidic and neutral conditions [11]. The reactions described in Eqs.3.8,3.9 show how the reaction of the hydroxyl radical ($OH^\bullet$) reacts with methanol (CH_3OH) in two steps to generate superoxide ($O_2^{\bullet-}$). A possible explanation for the decrease in nitrate removal under acidic and neutral conditions could be that the reduced amount of hydroxyl radicals is diminishing the secondary generation of superoxide through reactions with methanol. The increase under basic conditions suggests that the conversion of the hydroxyl radical to superoxide through methanol does not play as significant a role under basic conditions, possibly because of the existence of the aqueous electrons at the elevated pH, which would be the primary reducing agent.

3.3.5 Concentration changes and limits of reduction

The purpose of the experiments in Fig.3.6 demonstrate the level of reduction which can be obtained at levels for various real water systems. The 0.03 mM concentration level is approximately the amount of nitrate found in surface drinking water sources, while the 3 mM concentration is what would be expected in wastewater plants with high levels of influent nitrogen.

The tests shown in Fig.5a demonstrate that at the lower initial concentration of 0.03 M NO_3^- complete removal is possible at low nitrate concentration under acidic conditions over the 3 hour treatment time. In this instance there was over 99% removal, while neutral and basic conditions showed roughly equal amounts of NO_3^- removal at 39% and 40% removal, respectively. Fig.5b shows the percent nitrate removal for a similar test except at a concentration of 3 mM. In this test, we see monotonic, linear removal of nitrate in all cases, with the acidic case having the highest removal of 26% and neutral and basic conditions showing similar amounts of 22% removal.

3.4 Residual species analysis

The liquid samples after treatment were further tested to determine possible residual chemical species that could have been generated from the plasma treatment process. The gas phase was tested by drawing 1 L samples of air through Gastech tubes designed for identification of specific NO_x gases and ammonia, of which only NO was detected in all cases. The nitrate concentrations were determined by anion chromatography, and the chromatograms were inspected for the generation of nitrite which was not observed. Under acidic conditions with an initial 3 mM NO_3^- in solution (0.3 mmol NO_3^-) shown in Fig 3.6b, a total of 0.014 mmol of NH_4^+ remained at the end of testing while a total of 0.084 mmol of NO_3^- was removed. This indicates that under acidic conditions the bulk of the nitrogen is being stripped from solution as either NO or N_2 gas and not remaining as ammonium.

In the instance with no methanol, traces of hypochlorite were found, indicating that in the absence of scavengers it is possible to oxidize chloride by aqueous phase plasma.

The liquid samples were then tested using GC-MS for the generation of light organic amine compounds from the interaction of the plasma, methanol and nitrate. There was no indication of any lingering compounds in solution beyond methanol; indicating that any byproducts made were gaseous and did not remain in the water matrix. The initial concentration of 3 M methanol yielded a chemical oxygen demand (COD) of 144 g O_2/L, at the end of a three hour experiment there remained a COD of 140.4 g O_2/L.

3.5 Conclusions and future work

The results of this work show that aqueous phase pulsed corona discharge is capable of reducing the nitrate anion in solution with the presence of methanol as an oxidative species scavenger. Optimal conditions were discovered to be acidic conditions (pH 3.5) with solution conductivity of 170 μS/cm, though even a higher, more practical solution conductivity of 500 μS/cm still showed significant reduction in nitrate. The treatment operation would generate sufficient heat to operate at an elevated temperature, which in this study has been found to have minimal effect on the amount of nitrate reduced under acidic conditions, but increased the rate of reduction under basic conditions, with minimal decrease on neutral conditions. This study also incorporated the use of methanol as an oxidative species scavenger, though the concentrations of both nitrate and that of the methanol tested in this study are higher than those typically found in natural water bodies or wastewater treatment operations, it was found that the rate of removal rates greatly increased with increasing concentrations of both. This suggests that a concentrating mechanism, such as membrane filtration, could be employed to increase efficiency and retain any scavengers and undesired compounds from exiting the treatment path, generating a source of clean water with no secondary waste. This warrants further research for the utility of aqueous phase plasma as a treatment possibility for nitrate.

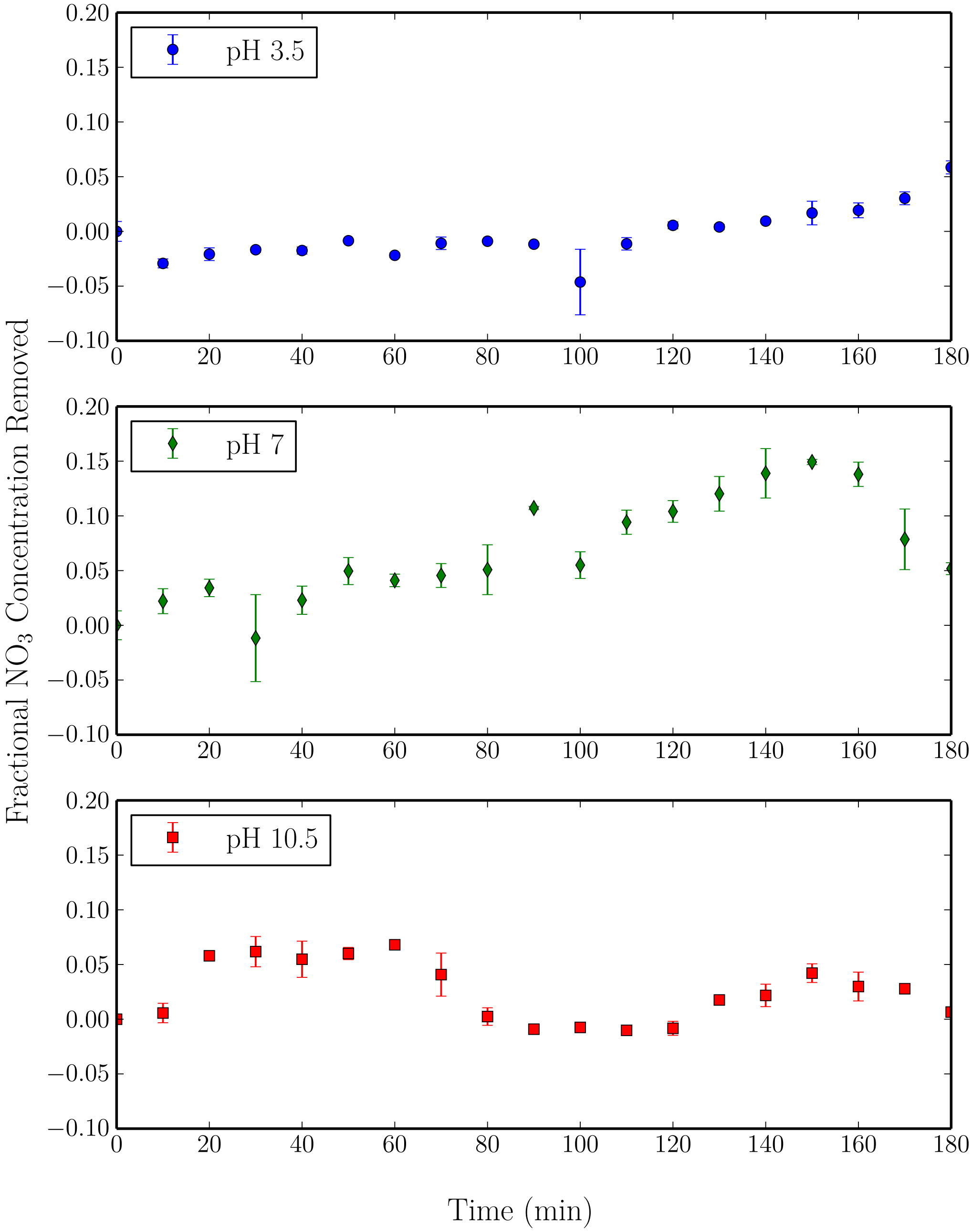

Figure 3.2: Fractional nitrate concentration of water samples with respect to time of plasma treatment of the solution. The inital concentrations of nitrate were 0.3 mM at a electrical conductivity of 170 μS/cm

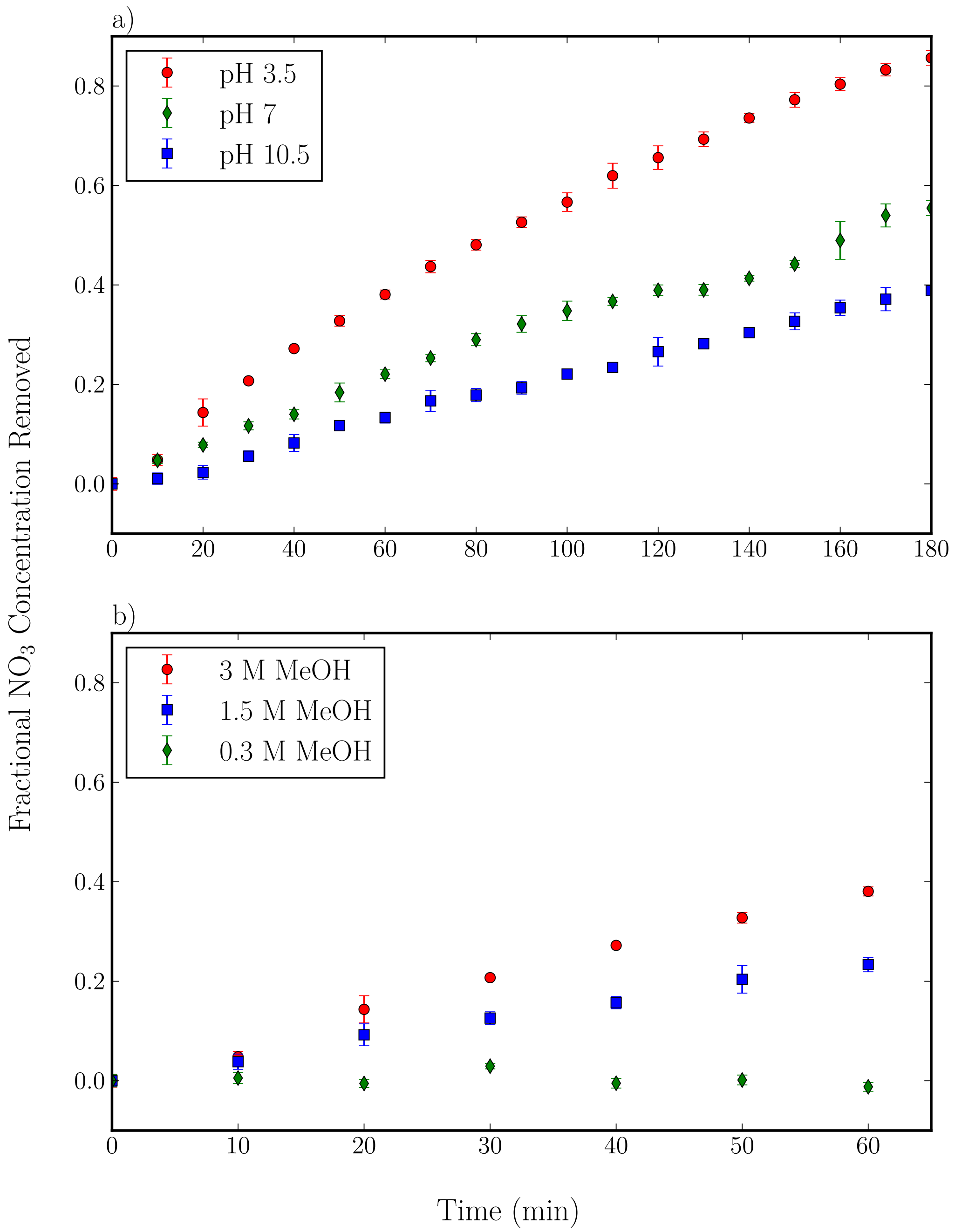

Figure 3.3: Fractional removal of nitrate concentration relative to total nitrate of water samples of various pH levels with respect to time of plasma treatment of the solution with composition 0.3 mM nitrate, 3 M methanol and electrical conductivity of 170 S/cm. b) Fractional removal of nitrate from samples with varying levels of methanol. The solution had a pH of 3.5, 0.3 mM of nitrate and an electrical conductivity of 170 S/cm. Both experiments were done under atmospheric conditions.

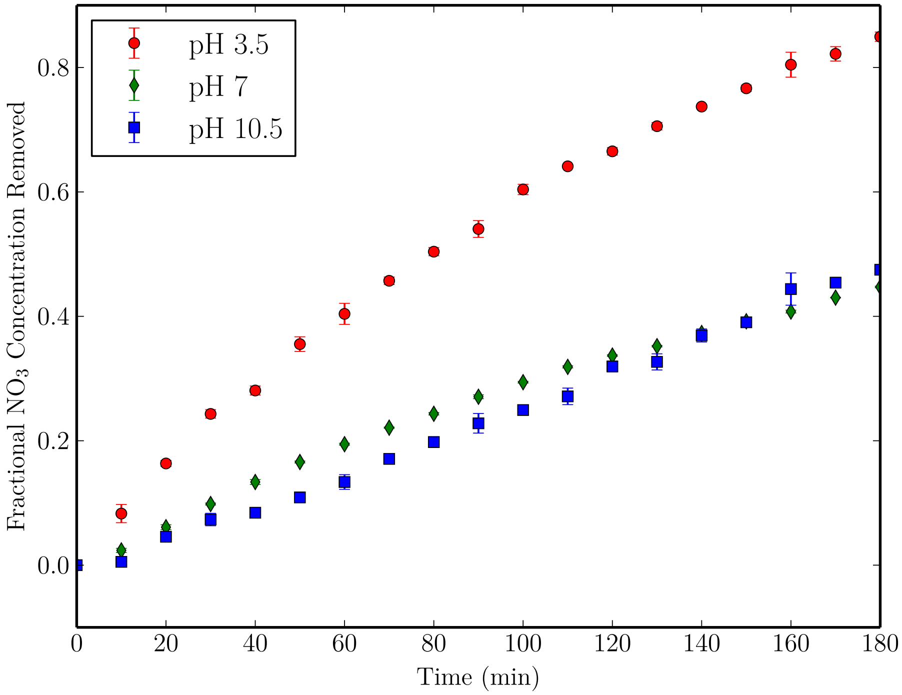

Figure 3.4: Fractional removal of nitrate relative to total nitrate of water samples with respect to time of plasma treatment of the solution. The inital concentrations of nitrate were 0.3 mM, with a methanol concentration of 3 M. The electrical conductivity of the solution was 170 μS/cm. The temperature was increased to 50^{o}C, under atmospheric conditions.

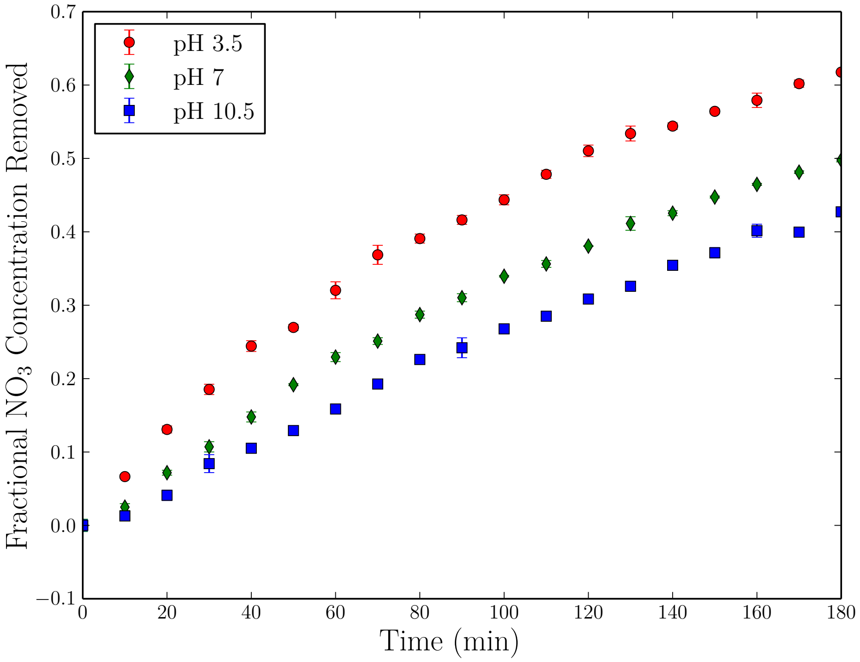

Figure 3.5: Fractional removal of nitrate relative to total nitrate in solution at various pH levels. The initial solution consisted of 0.3 mM NO_3^-, 3 M MeOH, at a conductivity of 500 μS/cm.

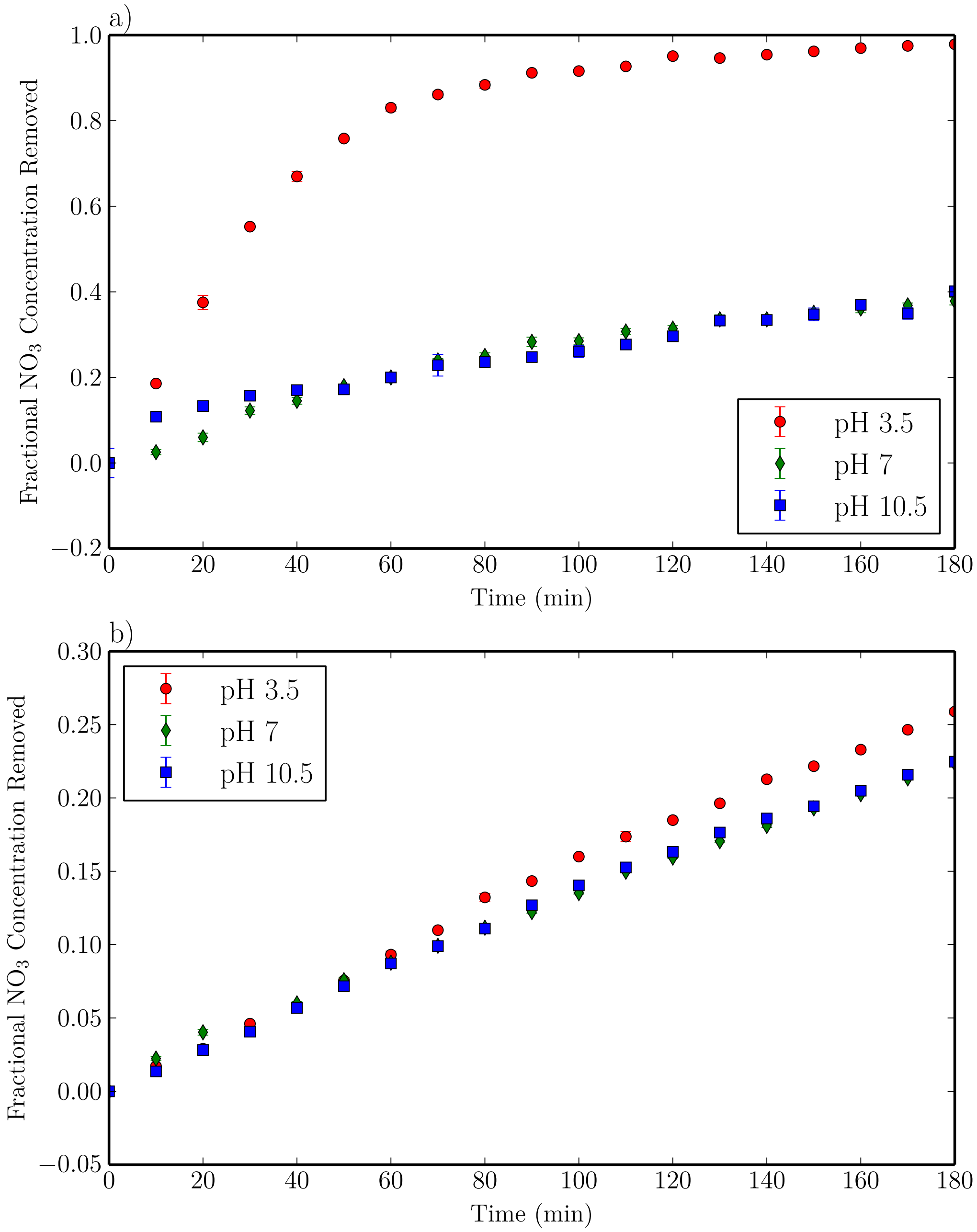

Figure 3.6: a) Fractional removal of nitrate relative to total nitrate in solution at various pH levels. The initial solution consisted of 0.03 mM NO_3^-, 3 M MeOH, at a conductivity of 500 μS/cm and temperature of 50^o C. b)Fractional removal of nitrate relative to total nitrate in solution at various pH levels. The initial solution consisted of 3 mM NO_3^-, 3 M MeOH, at a conductivity of 500 μS/cm at a temperature of 50^{o}C.

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Chapter 4

Reduction of bromate and chlorate contaminants in water using aqueous phase corona discharge

Abstract

This study demonstrates the ability for aqueous phase corona discharge to chemically reduce bromate and chlorate anions to lower oxidation states. The experiment consisted of a high voltage pulse being applied to a needle electrode to generate highly reactive oxidative and reductive species in a temperature controlled reactor containing the contaminated solution. The total power consumption was 4 W. Variation of the water matrix conditions involving changes to pH, types of oxidative species scavengers, temperature changes and also changes to dissolved oxygen content were studied in order to determine their effect on the reduction process using plasma discharge in water. Once optimal parameters were

established, the concentrations of the contaminants were varied to determine length of time required for near complete reduction. Optimal conditions were established for chlorate and bromate which concluded that under acidic pH, it is possible to achieve 70% reduction of bromate in 60 min of treatment at 3 μM. The reduction of chlorate was greatly enhanced with oxidative species scavenging, though a reduction of 15.6% removal after 60 min. at an initial concentration of 30 μM was achieved without scavenging. Under optimal conditions with the inclusion of methanol 95% reduction of 30 μM concentrations of $NaBrO_3$ and $NaClO_3$ were achieved in 50 minutes, while at 300 μM a similar level of reduction was achieved in 90 minutes for $NaBrO_3$ and 170 minutes for $NaClO_3$.

4.1 Introduction

Disinfection is an integral part of drinking water treatment throughout the world, and generally involves the use of oxidants in the form of hypochlorite, chlorine dioxide or ozone for the removal of organic compounds and inactivation of bacteria. One potential side effect of using powerful oxidants is the generation of disinfection by-products. Two examples of these are the bromate and chlorate anions (BrO_3^- and ClO_3^-) which have adverse effects towards both human health and the environment.

The bromate anion is a genotoxic human carcinogen, which affects the kidneys, peritoneum, testes and thyroid [1]. The United States Environmental Protection Agency (USEPA) has currently set a Maximum Contaminant Limit (MCL) of the bromate anion in drinking water at 10 μg/L ($\approx$ 80 nM). All fresh water systems include the bromide ion (Br^-), and so virtually any drinking water source using current oxidative disinfection techniques can potentially become contaminated through the formation of the bromate anion. Bromide concentrations typically range from 10 - 1000 μg/L in natural environments. Concentrations can be much higher when coal or potassium mining or chemical production industries are present [2, 3]. When bromide levels are less than 20 μg/L, bromate formation is not problematic, however when they increase to the 50-100 μg/L range excessive bromate can be formed [2, 4]. Furthermore, when the bromate anion is released to the environment it is not readily biodegraded and has significant ecotoxicity; some water-borne organisms and larvae have observed lethal dosages at 31 mg/L, and fish eggs exposed to bromate have developed chronic pathological disorders to the brain and spine [5]. For this reason, numerous studies have been performed to investigate the formation of the bromate anion under different scenarios in order to minimize the possibility of harming humans and ecosystems [1, 2, 6].

The formation of BrO_3^- is complex, though the largest concern originates from ozonation as the primary means of disinfection for drinking water systems containing a high concentration of bromide [2]. However, it is also possible for bromate to form by oxidation in conventional disinfection by chlorine dioxide or hypochlorite solutions [7]. Advanced oxidation techniques which involve the hydroxyl radical ($OH^\bullet$) are also able to contribute to the formation of bromate, though they are unable to oxidize bromo-oxides fully to bromate, they are capable of expediting the process by oxidizing the bromide anion to necessary preliminary stages, such as hypobromite (HOBr) [2, 6]. The formation of bromate is a multi-step approach and some of the numerous possible reactions which facilitate bromide oxidation to bromate are outlined in Eqns. 4.1-4.9 [2, 8].

$$\mathrm{Br^- + O_3 \rightarrow BrO^- + O_2} \tag{4.1}$$

$$\mathrm{Br^- + OH^\bullet \rightarrow HOBr^-} \tag{4.2}$$

$$\mathrm{HOBr \leftrightharpoons H^+ + OBr^-} \tag{4.3}$$

$$\mathrm{BrO^- + OH^\bullet \rightarrow BrO^\bullet + OH^-} \tag{4.4}$$

$$\mathrm{2BrO^\bullet \rightarrow OBr^- + BrO_2^-} \tag{4.5}$$

$$\mathrm{BrO^- + O_3 \rightarrow BrO_2^- + O_2} \tag{4.6}$$

$$\mathrm{2BrO_2^- \rightarrow BrO^- + BrO_3^-} \tag{4.7}$$

$$\mathrm{BrO_2^- + O_3 \rightarrow BrO_3^- + O_2} \tag{4.8}$$

$$\mathrm{3BrO^- \rightarrow 2Br^- + BrO_3^-} \tag{4.9}$$

Chlorate is a contaminant of concern for different reasons. Chlorate is known to cause damage to red blood cells and can also decrease iodide uptake through competitive inhibition. Decreased iodide uptake has been shown to lead to impaired thyroid activity and can result in developmental problems [9]. The current MCL for chlorate is set at 1 mg/L ($\approx$ 12 μM) by the USEPA, however, the World Health Organization (WHO) has set guidelines for a lower limit at 700 μg/L [9, 10].

Chlorate can originate from the disproportionation of hypochlorite (OCl^-) solutions or through the use of gaseous chlorine dioxide for disinfection in water treatment processes. Chlorine dioxide ($ClO_{2(g)}$) readily decomposes to chlorite anion ($ClO^-_{2(aq)}$) in solution, which is unstable except at high pH and also undergoes disproportionation to the hypochlorite and chlorate anion (analogous to Eqn. 4.7). In fact, many of the same reactions which occur for bromate (Eqns. 4.1-4.9) also occur for chlorate generation, through very similar pathways [2, 7, 11–14].

Since this reaction naturally occurs, chlorate and chlorite are present in most sodium hypochlorite solutions used for disinfection in drinking water systems [13]. For chlorine dioxide disinfection, chlorite is the primary by-product of the process, with 68% of the chlorine dioxide turning into chlorite and 9% turning into chlorate [15]. Chlorate is also generated through the ozonation process of water, in a similar pathway as bromate [11]. Both are also used in the wood pulp and paper industries, where they are used as bleaching agents [16]. Chlorate is also the primary component of most weed killers, and can enter water systems from surface run off [5, 9].

The current mitigation technique for bromate and chlorate is to minimize their production. Pre-oxidation of influent water can minimize the amount of chlorine-based disinfection for the finished water, which decreases the production of both contaminants; however the choice of pre-oxidation mechanism must be selected carefully. Bromate formation can be minimized if ozonation occurs at lower pH, though it must later be raised for distribution [2, 8, 17]. This is because the hypobromite ion is a weak acid with a pK_a of 8.7, and in its protonated form is much more difficult to oxidize [8]. This is desirable because HOBr can also act as a residual disinfectant [2]. Lowering to a pH of 6 or below minimizes the amount of BrO_3^- formed, and higher concentrations of Br^- can actually suppress BrO_3^- formation due to the scavenging action of the Br^- towards ozone to form HOBr [2].

Chlorate mitigation is performed by proper storage of hypochlorite solutions. When disinfecting using hypochlorite, proper storage of the solutions, i.e. low temperature, reduced ionic strength and stored at a pH between 11-13. This hampers the disproportionation of ClO^- to ClO_2^- and ClO_3^-[9].

The proposed methods for the removal of the bromate and chlorate anions from water include ion exchange, nano filtration and electrochemical reduction [5, 18]. UV irradiation and reduction using Fe(II) had also been studied, though doses of radiation higher than what is typically seen for oocysts and high doses of Fe(II) ($>$ 10 mg/L) were required as well as a decrease in solution pH [2]. Biological reduction of bromate and chlorate can occur, however, only in the absence of nitrates under anaerobic conditions [19]. Chlorate can also be removed by granular activated carbon though bromate is actually reduced on the surface of activated carbon, though it also requires pH modification [2, 5].

In this study, the reduction of BrO_3^- to Br^- and $ClO_3^-$to Cl^- by the use of aqueous phase corona discharge is studied. Aqueous phase plasmas have been previously studied as a means to generate high energy radicals in solution [20]. A strong electric field generated at an electrode disassociates water into the hydroxyl radical ($OH^\bullet$) and hydrogen radical ($H^\bullet$), which can further propagate into the bulk media to generate active molecular species or further radicals [20]. There have been previous studies which have considered aqueous phase plasmas for their oxidizing capabilities [21, 22], however the presence of reducing radicals have also been established which can be utilized for the reduction of oxyhalide compounds [23]. The hydrogen radical, molecular hydrogen and superoxide ($H^\bullet$, H_2, $O_2^{\bullet -}$) are examples of reducing agents that are generated through the aqueous plasma process [23]. Furthermore, with the addition of methanol into the solution, oxidizing species ($OH^\bullet$, O_2) can be converted to reductive species such as formaldehyde and superoxide (CH_2O, $O_2^{\bullet -}$) as shown in Eqns. 4.10, 4.11 [23, 24]. Also, it has been reported that with the increase in methanol in solution, significant amounts of molecular hydrogen are generated through hydrogen abstraction (Eq.4.12).

$$CH_3OH + OH^{\bullet} \rightarrow CH_2OH^{\bullet} + H_2O \tag{4.10}$$

$$CH_2OH^{\bullet} + O_2 \rightarrow CH_2O + H^{+} + O_2^{\bullet -} \tag{4.11}$$

$$CH_3OH + H^{\bullet} \rightarrow CH_2OH^{\bullet} + H_2 \tag{4.12}$$

The goal of this work is to explore the efficacy of aqueous phase plasma to reduce the BrO_3^- and ClO_3^- anions and characterize the optimal water matrix conditions for reduction. This is done by i) quantitatively comparing the reduction under various pH levels and ii) to consider the concentration of methanol as a scavenger, and compare it to other carbonaceous materials, iii) to observe the effects and roles solution temperature can play to gain insight as to how an aqueous phase corona discharge system could be employed and iv) consider simulated real world water samples and look at the products from the reaction.

4.2 Materials and Methods

4.2.1 Chemicals

Sodium bromate and sodium chlorate were obtained from Sigma Aldrich. For each test the electrolytic conductivity was augmented with the addition of sodium chloride and the pH was altered using hydrochloric acid. The methanol used was HPLC grade, and was from Caledon Laboratories Inc, as were the sodium chloride and hydrochloric acid. The

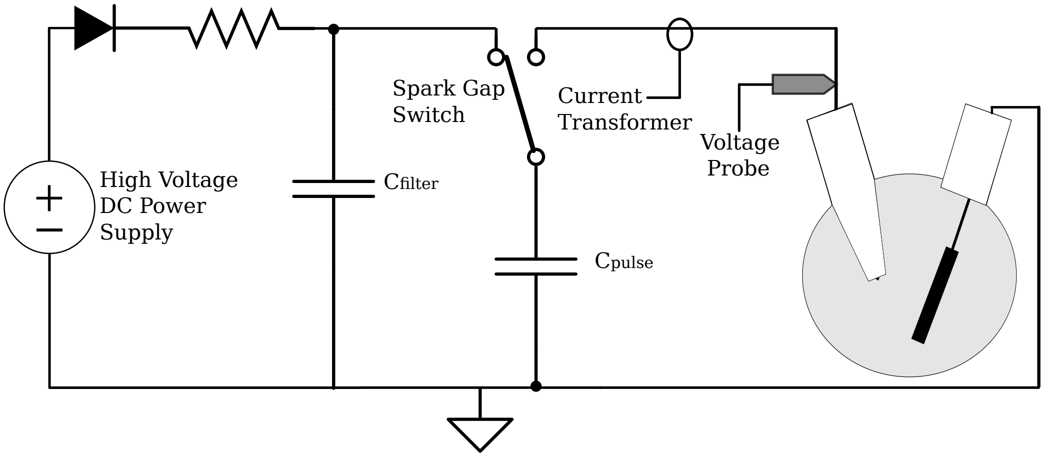

Figure 4.1: Simplified schematic of experimental apparatus.

methanol used was HPLC grade, while the ethanol used was 95% pure. The aforementioned reagents were obtained from Caledon Laboratories Inc. The sucrose, sodium bromate and sodium chlorate were obtained from Fischer Scientific. The D-sorbitol was obtained from Sigma Aldrich. All chemicals were reagent grade or higher and were used without further purification. All solutions were made using 18.2 MΩ deionized water.

4.2.2 Apparatus

A simplified schematic of the equipment used is shown in Figure 4.1. The experimental apparatus consisted of a high voltage DC power source charging a pulse forming capacitor, which was then disconnected from the supply and discharged into the reactor. The DC high voltage pulse was applied to the reactor using a rotating spark gap which alternated between charging the pulse forming capacitor and discharging into the water reactor. A 10 MΩ resistor and 10 nF filter capacitor were used as an RC filter to stabilize the output. The spark gap was operated under a dry nitrogen gas purge to minimize ozone formation and prevent pre-mature discharge. A 1 nF capacitor was used as the pulse forming capacitor and pulse repetition rate applied to the reactor was 30 Hz. The voltage measurements were taken using a Tektronix P6015A high voltage probe and the current was measured using an Ion Physics CM-10-MG current transformer. The measurements were taken using a Tektronix TDS5054B Digital Oscilloscope. The time average energy deposition rate was under 4 W, calculated by the root-mean-square average of the product of the voltage-current curves. These curves are shown in Figure 4.2. Each waveform is the average of 150 waveforms captured by the oscilloscope. The voltage rise time was 24 ns.

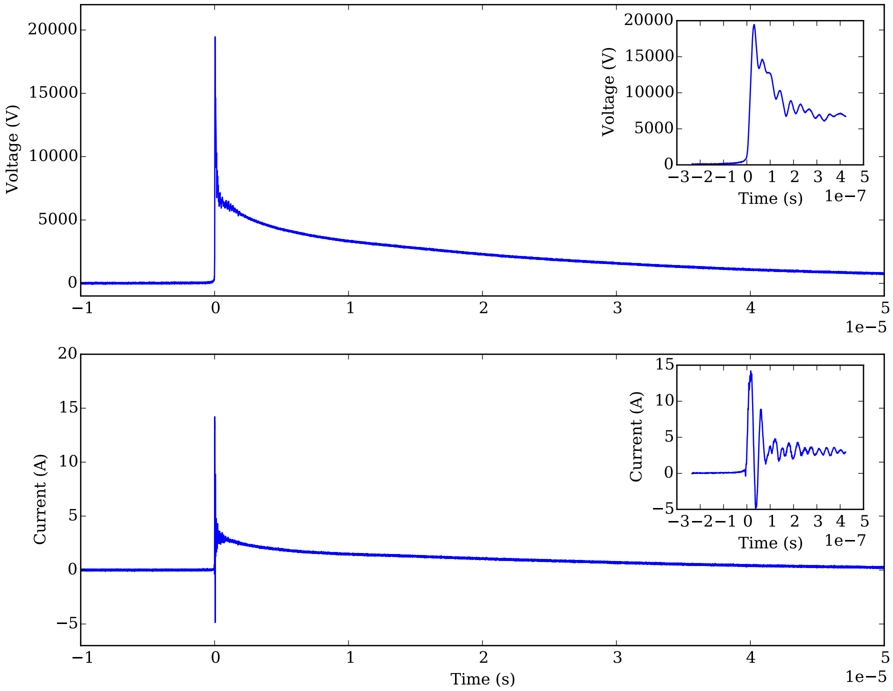

Figure 4.2: Voltage and current waveforms for a typical applied pulse to the treatment reactor. The inset in each graph shows the initial 600 ns of a typical pulse capture.

The reactor vessel was a 100 mL three necked flask made from borosilicate glass. All of the electrodes were made of commercially pure titanium (98.9% purity). The ground electrode was a 4.7 mm rod compression fit into a rectangular block with dimensions of 12.7 mm x 6.35mm x 38 mm. The high voltage electrode was a sharpened rod with diameter of 1.6 mm. The distance between the high voltage and ground electrode was maintained at 5 cm for all experiments.

4.2.3 Analytical

Ion Analysis

At the beginning of each experiment an excess of the solution to be tested was made, beyond the 100 mL volume of the test reactor. One millilitre samples were taken at prescribed intervals throughout the experiment and replaced from an excess of the original stock test solution to eliminate the effect of reducing volume. The contaminant anion concentrations were determined using suppressed ion chromatography using an anion exchange column (PRP-X110S, Hamilton Company) with a membrane suppressor (AMMS 300, Dionex) and detected using a conductivity cell (CD25, Dionex). The mobile phase consisted of 1.4 mM $NaHCO_3$ and 1.6 mM Na_2CO_3 mM buffer, with 2.5% methanol operated at a flow rate of 1.6 mL/min. The regenerant for the suppressor was 50 mN H_2SO_4 at a flow rate of 5 ml/min.

Liquid Organic Analysis

Testing for liquid organic by-products from the reaction with the plasma species, methanol and inorganic ions was conducted using headspace analysis of the liquid samples on a gas chromatography-mass spectroscopy system. The samples were heated to 80^oC and 100 μL of headspace was injected into the sample port. An Agilent 6890 gas chromatograph was used with a Carbowax capillary column with a film thickness of 0.50 m, ID of 0.25

mm and length of 30 m for the separation of compounds. A Waters/Micromass GCT time of flight spectrometer detector was used for the measurements of the mass of the species separated. The column was operated with a temperature profile of: initially hold at 50^o C for 3 minutes, followed by a heating ramp of 20^oC/min until a temperature of 240^oC was obtained, and then held for 5 minutes. The column was operated under a constant flow rate of 1 ml/min of helium. The injection was done in split mode with a split ratio of 2:1.

4.3 Results

4.3.1 Bromate and chlorate reduction in virgin samples

Initial testing consisted of treatment of virgin samples of bromate and chlorate in solution at an electrolytic conductivity of 500 μS/cm, roughly equivalent to that of tap water, and at pH levels of 3.5 and 7, depicted in Figure 4.3. The rate of reduction under acidic conditions for BrO_3^- is significantly greater than that at neutral conditions, while for ClO_3^- the difference between the rates of reduction is small. Under acidic conditions 16.6% of the initial BrO_3^- concentration was reduced, while 5.20% of the initial ClO_3^- concentration was reduced in 30 minutes of treatment. Under neutral pH conditions only 2.85% of the initial BrO_3^- concentration was reduced and 4.65% of the initial ClO_3^- concentration was reduced in the same time period. Ion chromatograms of the samples (not presented) after treatment showed a decrease in either the BrO_3^- or ClO_3^- peak and the increase of a peak corresponding to Br^-or Cl^-. In the case of chlorate, as treatment progressed a peak emerged that corresponded to the time of the ClO_2^- anion, but there was no extraneous peak observed in the case of bromate. There was a minor decrease in pH when the solution was operated at neutral pH, and no observed change under acidic conditions. The decrease under neutral

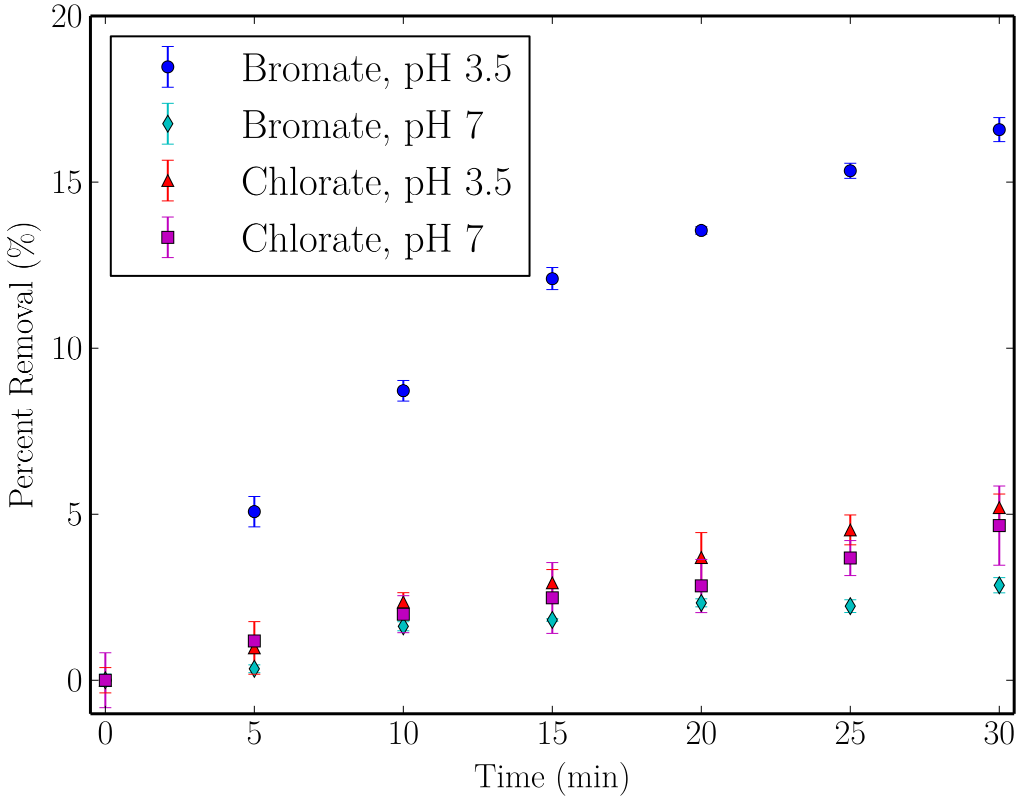

Figure 4.3: Percent removal of $NaBrO_3$ and $NaClO_3$ with time of pulsed high voltage discharge treatment applied at a pH of 3.5 and 7. The initial solution consisted of a concentration of 300 μM of $NaBrO_3$ or $NaClO_3$ at an electrolytic conductivity of 500 μS/cm and operated at room temperature and atmospheric pressure.

pH could be due to the absorption of carbon dioxide from the environment, as no buffering agent was employed in the water matrix. Any decrease in pH under acidic conditions may have been too small to be noticeable.

Simulated polluted tap water

Testing in an environment similar to heavily contaminated tap water was also conducted. Figure 4.4 shows further investigation under the same water matrix conditions, however at lower concentrations to simulate a contaminated tap water source. The concentrations were chosen to be a source heavily contaminated with BrO_3^- , roughly 30x higher than the MCL limits established by the USEPA, and only moderately contaminated with chlorate, twice the USEPA MCL for ClO_3^-. In this instance the experimental test concentrations were 30 μM $NaClO_3$ and 3 μM $NaBrO_3$ and over an increased run period of 60 minutes. The same trend of an increased rate of reduction for bromate under acidic conditions, and similar reduction levels for bromate under neutral pH conditions and chlorate under both conditions is seen as above. In this instance 70.3% of the initial BrO_3^- concentration under acidic conditions and 8.98% removal under neutral conditions were removed. For ClO_3^- the minimal affect of pH remained, where 15.6% of the initial ClO_3^- concentration was removed under acidic conditions, while under neutral conditions 14.4% of the initial ClO_3^- concentration was removed.

4.3.2 Effect of methanol as an oxidative scavenger

The introduction of methanol (MeOH) as an oxidative species scavenger greatly enhances the reduction rate of both bromate and chlorate ions and amplifies we see vast improvement between low pH and neutral pH for chlorate. The methanol concentration was varied from 0.030, 0.30 and 3.0 M (0.96, 9.6 and 96 g/L). The target contaminant was 300 μM $NaBrO_3$in a solution with an electrolytic conductivity of 500 μS/cm. The reduction over time is depicted in Fig. 4.5.

Typically when extra carbonaceous material is required for the anaerobic removal of nitrates from wastewater plants, methanol doses of 7- 15 g/L are commonly used. Thus the 0.03 M and 0.3 M concentrations are reasonable concentrations for methanol to facilitate reduction of the target ions. The 3 M concentration is an order of magnitude higher than what is typically seen in wastewater streams, however the halate concentrations studied

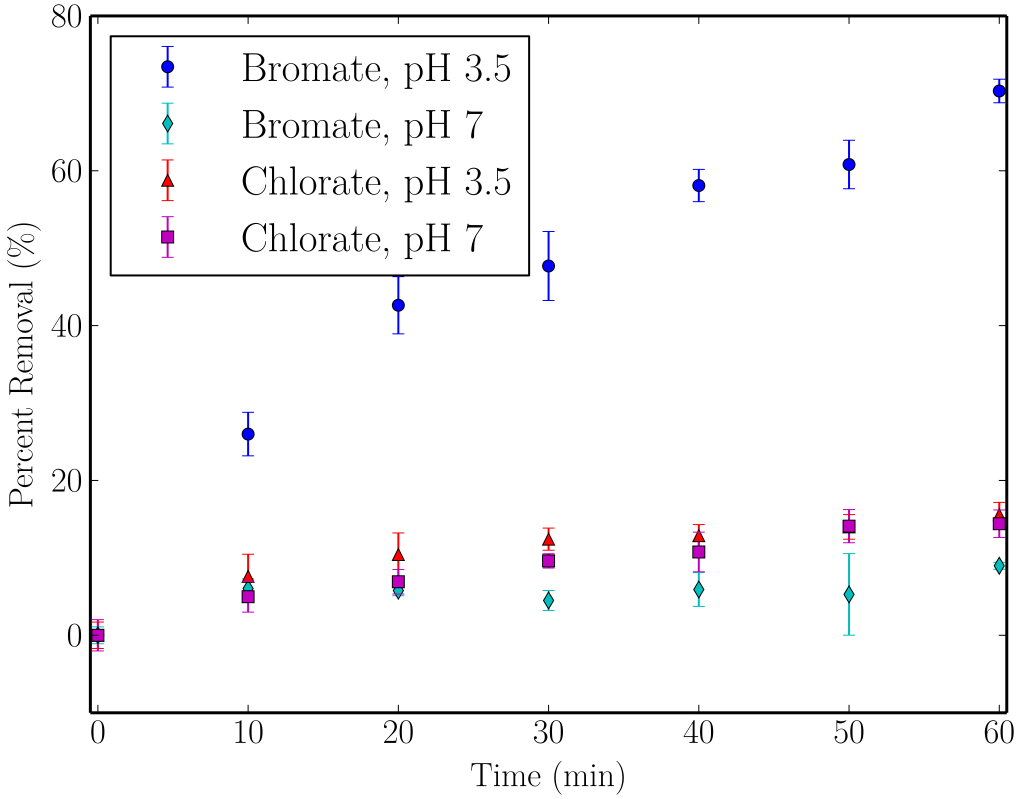

Figure 4.4: Percent removal of 3 μM NaBrO$_3$and 30 μM NaClO$_3$with time of pulsed high voltage discharge treatment applied at a pH of 3.5 and 7. The electrolytic conductivity of solution was 500 μS/cm and the experiment was operated at room temperature and atmospheric pressure.

here are also significantly higher than that which would be seen in any treated waters or industrial sources without a concentrating mechanism occurring first upstream, in which case it is reasonable to test under such a high methanol concentration.

The highest rate of reduction occurred with the highest level of methanol, 31.7% of the initial concentration of bromate was removed in 30 minutes. At the initial concentration of 0.30 M MeOH, a reduction of 26.6% of was removed and at the lowest concentration of 0.030 M MeOH 21.5% was removed in 30 minutes of treatment. Increasing the methanol concentration by an order of magnitude resulted in only an increase of approximately 5.1%

of the amount of bromate reduced in 30 minutes.

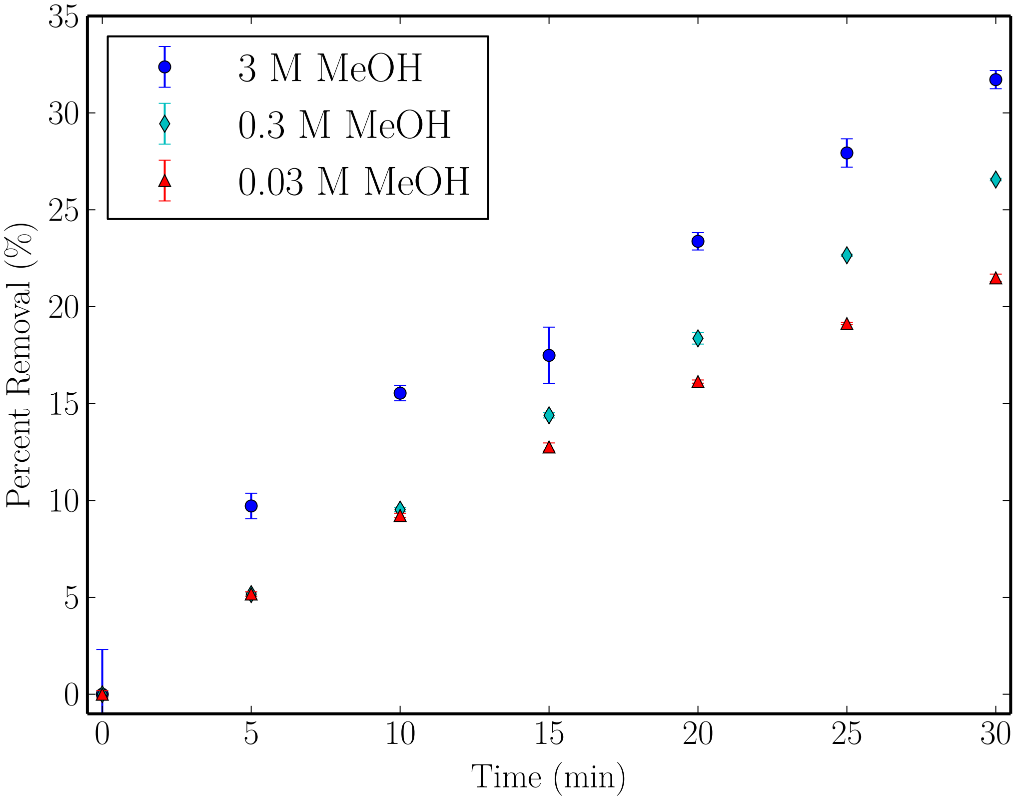

Figure 4.5: Percent removal of 300 μM $NaBrO_3$ with varying concentrations of MeOH at a pH of 3.5 and electrolytic conductivity of 500 μS/cm with time. The experiment was operated under atmospheric conditions and room temperature

The results of the experiments performed under both acidic and neutral pH conditions for both chlorate and bromate with the addition of 3 M methanol is shown in Figure 4.6. Under the acidic conditions 31.7% removal of bromate and 13.6% removal of chlorate are obtained from their initial concentrations of 300 μM. Under neutral pH conditions, 22.1% of the initial bromate concentration was removed and only 6.9% of the initial chlorate concentration in a 30 minute treatment time. The inclusion of methanol into the water matrix also greatly increased the amount of bubbles formed from the plasma discharge in solution.

Visibly, large plumes of gases were created at the tip of the electrode which propagated into the bulk of the media. This bubble formation increased the rate at which dissolved oxygen was either consumed or driven out of the solution, which may have greatly contributed to the reduction of the target ions through decreased scavenging of reductive species. There was also a small decrease in pH as plasma treatment occurred

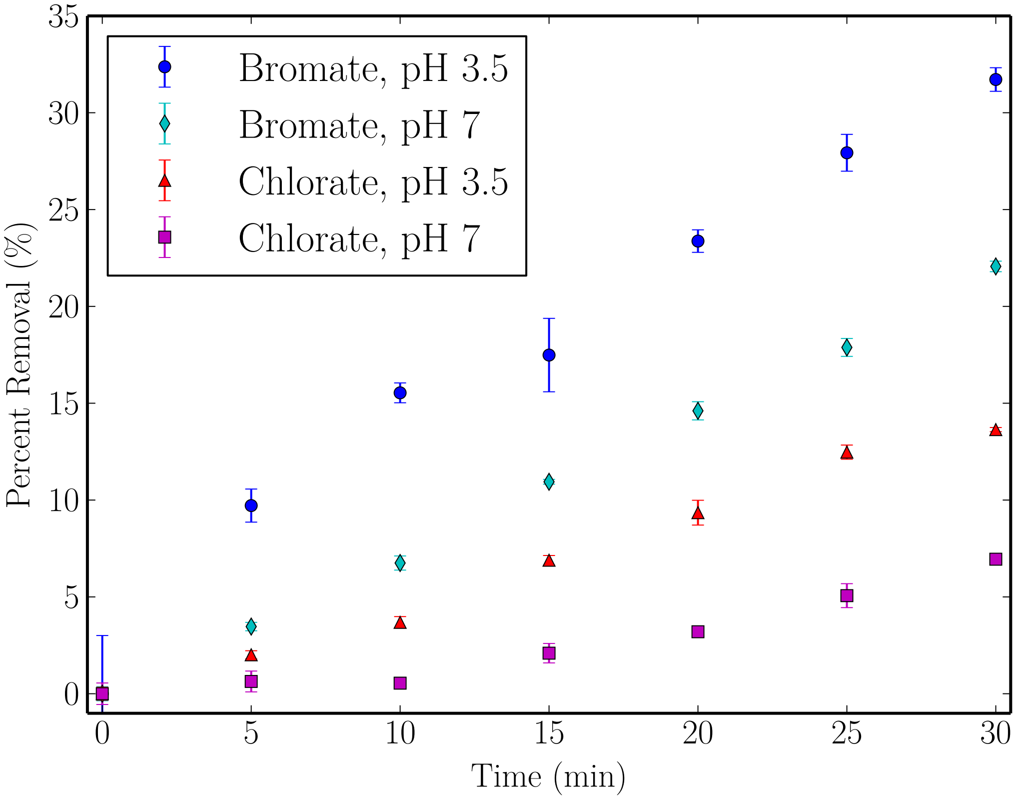

Figure 4.6: Percent removal of 300 μM $NaBrO_3$ and $NaClO_3$ and 3 M MeOH with time of pulsed high voltage discharge treatment. The tests were operated with a water matrix consisting of an electrolytic conductivity of 500 μS/cm and at pH levels of 3.5 and 7 at 25^{o}C and atmospheric pressure.

There was a pronounced effect on the dissolved oxygen content with the inclusion of methanol which is portrayed in Figure 4.7. Under virgin conditions, there is an initial, minor decrease in the dissolved oxygen content from 8.0 mg/L O_2which then levelled off and remained constant over the course of treatment with a value near 7.5 mg/L O_2. The inclusion of 3 M MeOH into the water matrix shows a dramatic decrease in the dissolved oxygen content and stabilization at a 2.5 mg/L O_2. At elevated temperatures, this effect is even more dramatic and a lower dissolved oxygen concentration is achieved of 1.9 mg/L O_2.

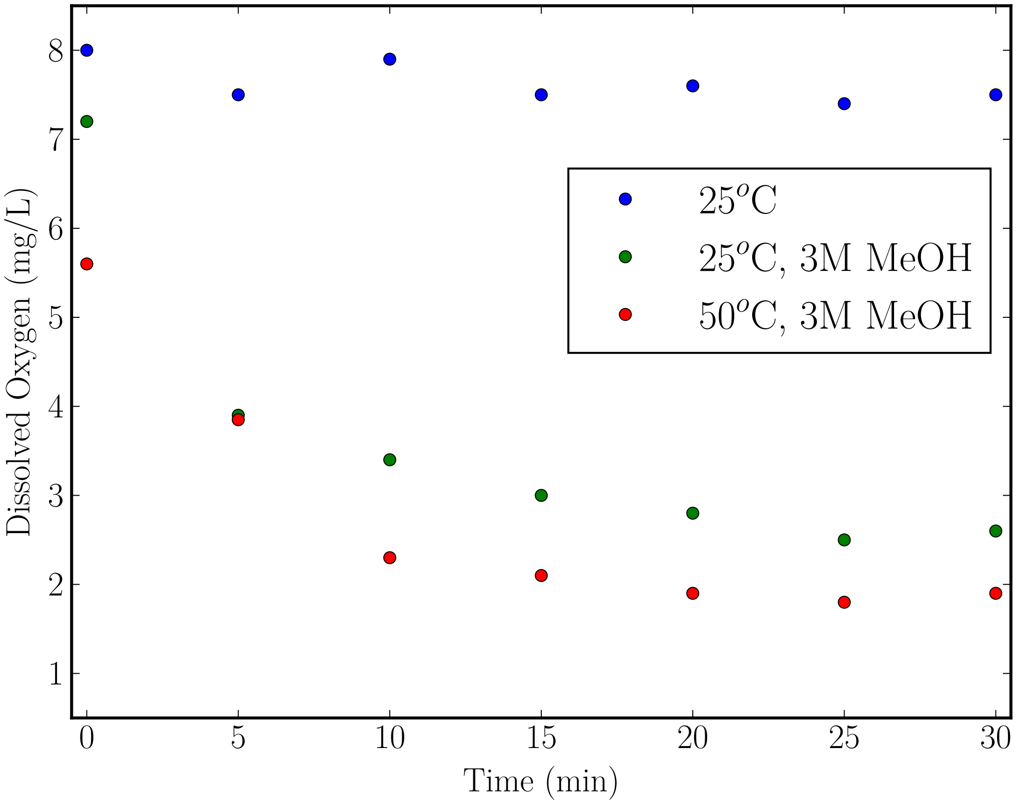

Figure 4.7: Dissolved oxygen concentration with time of plasma treatment of test solutions at differing temperatures and with or without methanol. Test conditions consisted of 300 μM $NaBrO_3$, electrolytic conductivity of 500 μS/cm and atmospheric pressure.

Organic substances other than methanol were tested as potential oxidative species scavengers, including ethanol, D-sorbitol and sucrose. Figure 4.8 illustrates how using volatile

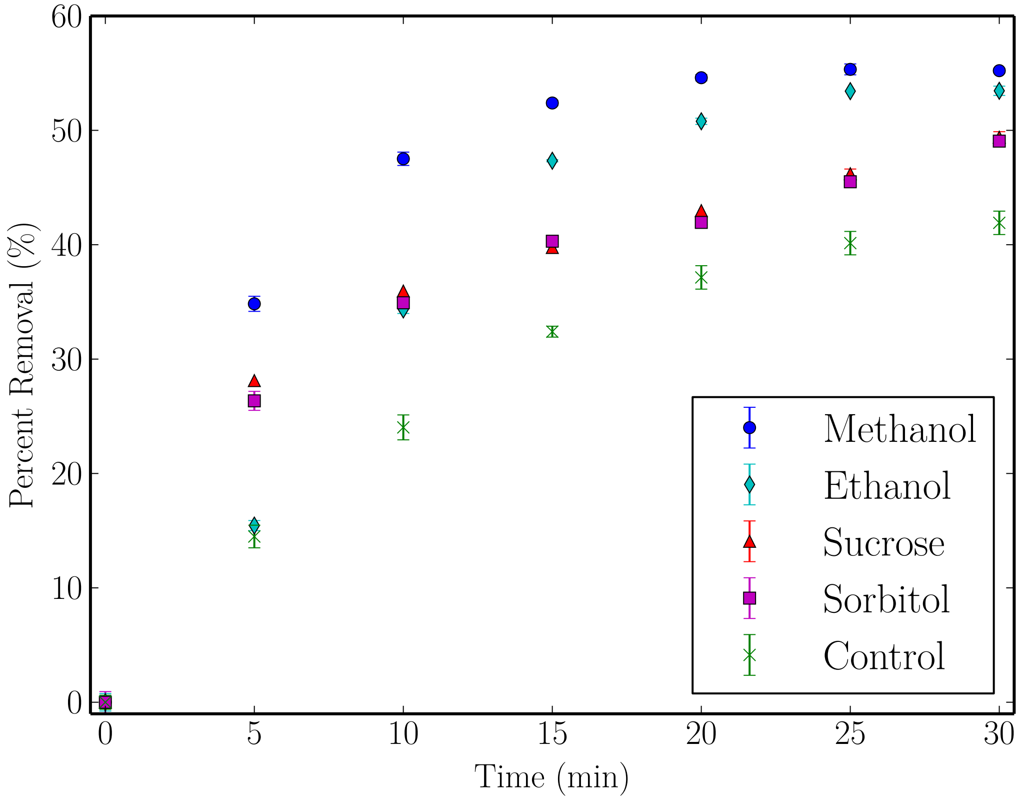

Figure 4.8: Plasma treatment of a solution contaminated with 10 μM $NaBrO_3$ with an electrolytic conductivity of 500 μS/cm with various organic constituents added for oxidative species scavengers. Experiments were conducted at atmospheric pressure and room temperature.

alcohols like methanol and ethanol improve the performance over other carbonaceous material. The concentration of the organic compound was normalized to a chemical oxygen demand of 500 mg/L-O_2, or 10 mM methanol, 5.2 mM ethanol, 2.4 mM D-sorbitol (sorbitol) and 1.3 mM sucrose. In all cases, we see a rapid reduction of the BrO_3^- ion, though the enhancement was greatest for methanol and ethanol, demonstrating the highest level of reduction after 30 minutes of 55.2% and 53.5%, respectively. Sucrose followed next with 49.4% removal, showing similar amounts of removal as sorbitol at 49.1%. This demonstrates the effectiveness of having soluble carbonaceous material in solution as an effective oxidative species scavenger which greatly improves the reduction rates, as demonstrated by comparing to a control test with no scavenger achieving only 41.9% reduction at this lower concentration. As mentioned previously, adding methanol to the solution greatly increased the bubble formation in solution while undergoing plasma treatment, which was also true for ethanol, but not for sorbitol or sucrose. This led to the drop in dissolved oxygen which assists in the reduction and is further described in Section 4.3.3.

4.3.3 Effect of temperature increase

When applied high voltage pulses last longer than the order of a microsecond, some of the energy is consumed as joule heating of the solution [22]. In this case, the pulse width is shown to be over 50 μs and heating is observed of the sample solution if operated without the water bath around the reactor. The steady state temperature under normal operation without the cooling jacket was approximately 50^oC, and so further experimentation was performed at that temperature. Figure 4.9 shows increased reduction occurring for both chlorate and bromate when the solution temperature was stabilized to 50^oC.

With the increase in temperature, rates are further improved: 41.9% of the initial $NaBrO_3$ was removed and 24.0% was removed of the initial $NaClO_3$ under acidic conditions. Under neutral pH conditions 26.8% of the initial $NaBrO_3$ and 8.4% of the initial $NaClO_3$ were removed. The likely cause for this increase in reduction is due to the minimization of the scavenging of reductive species by dissolved O_2. A further investigation involving experiments conducted with 300 μM $NaBrO_3$ and 3 M MeOH at a conductivity of 500 μS/cm at 25^oC and 50^oC but de-oxygenating the water with a 3 minute nitrogen purge prior to testing. Control tests showed no appreciable loss in mass due to stripping

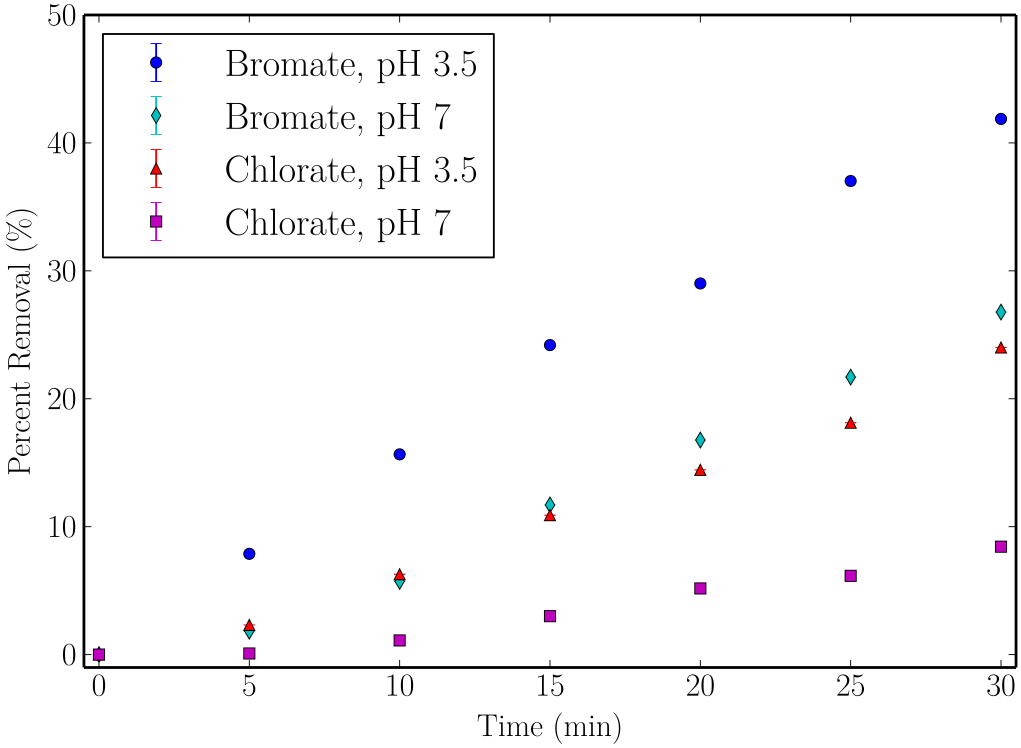

Figure 4.9: Percent removal of 300 μM $NaBrO_3$ and $NaClO_3$ and 3 M MeOH with time of pulsed high voltage discharge treatment operated at a constant temperature of 50^{o}C, and atmospheric pressure. The electrolytic conductivity of solution was 500 μS/cm.

of methanol from the purge. Figure 4.10 shows the results of this test, and the equivalence between increasing the temperature to minimize the dissolved O_2 versus stripping the solution of O_2 prior to testing. There is a small difference between the level achieved at 25^{o}C that had been deoxygenated and 50^{o}C and deoxygenated - indicating that the temperature change did indeed have a an effect, which could be a result of more rapid thermal decomposition of the $HBrO_2^-$, which will be discussed in Section 4.4

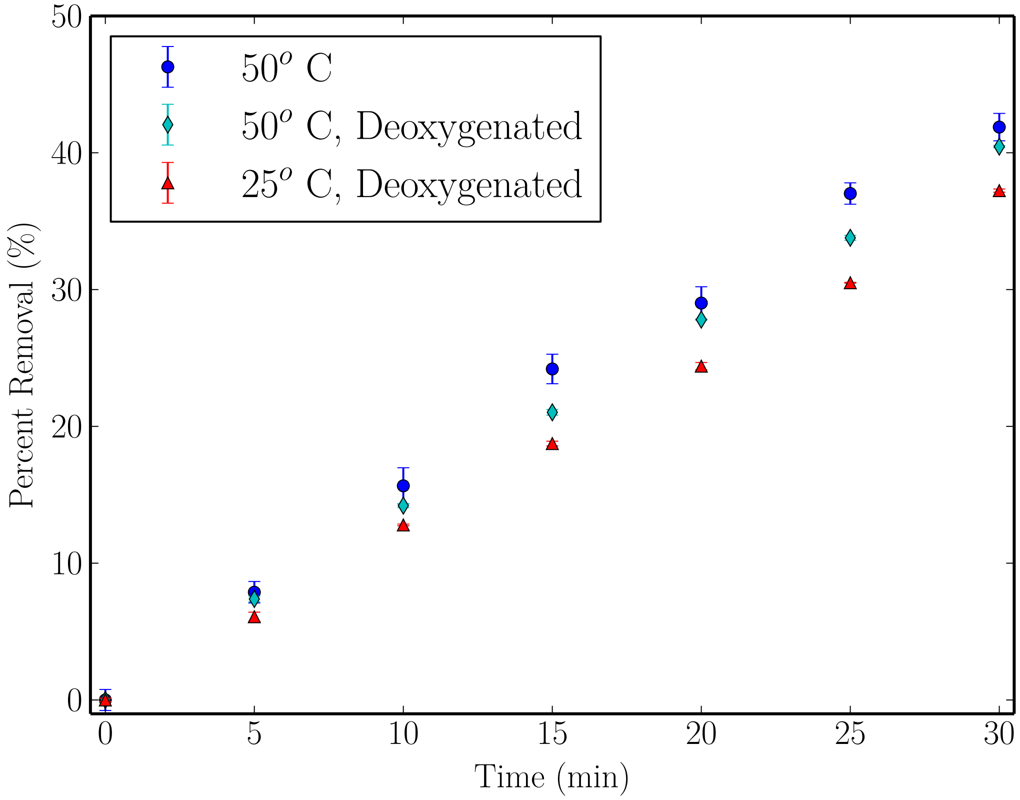

Figure 4.10: Comparison of percent removal of 300 μM $NaBrO_3$, 3 M MeOH at 25^oC and 50^oC in samples with deoxygenation pre-treatment and a sample without. The electrolytic conductivity of the samples was 500 μS/cm and the experiment was operated under atmospheric conditions.

4.3.4 Time to complete removal

From the results of the previous tests, it has been determined that operating at a pH of 3.5 with 3 M MeOH at the elevated, steady-state temperature of 50^oC of the uncooled reactor resulted in optimal reduction for both BrO_3^- and ClO_3^-. In order to determine the time to complete removal for both chemicals under these conditions, tests were conducted at 30, 300 and 3000 μM concentrations. The results of these tests are shown in Figure 4.11.

The results of this experiment show that greater than 95% (2.93 μmol) of the BrO_3^- is be removed from solution within 60 minutes at a concentration of 30 μM $NaBrO_3$ and in 90 minutes (28.4 μmol) at a concentration of 300 μM BrO_3^-. At a concentration of 3000 μM or 3 mM, we see a linear rate of reduction of BrO_3^- where 77.7 μmol (25.9%) of the initial BrO_3^- concentration has been removed in 180 minutes.

At the 30 μM concentration ClO_3^- achieved a level of level of 96% (2.96 μmol) removal after 60 minutes to achieve. To reduce 300 μM concentrations by 95% (28.5 μmol) of it's initial concentration took 150 minutes. At the 3000 μM concentration 63.7 μmol (21.2%) of the initial concentration was removed after 180 minutes.

It is interesting to note that the time required to reduce both $NaBrO_3$ and $NaClO_3$ at 30 μM is nearly identical, suggesting that the generation of the reductive species was the limiting factor in this case.

4.4 Discussion

Effect of pH on reduction rates of BrO_3^- and ClO_3^-.

The large difference between the rates of reaction between bromate under acidic conditions and all other test conditions likely is due to the oxidation/disproportionation mechanisms for chlorate and bromate and the difference in the acidity constants for bromine and chlorine in their hypohalite (XO^-) and halite (XO_2^-) forms [14]. The acidity constants are shown in Table 4.1.

Table 4.1: pK_a of Halo-oxides

	pK_a		pK_a
HClO	7.5	HBrO	8.7
$HClO_2$	1.92	$HBrO_2$	3.43
$HClO_3$	-1	$HBrO_3$	-2

Initially, XO_3^- is reduced, either directly or through a multi-step process, by either $H^\bullet$, $O_2^{\bullet-}$ or CH_2O to XO_2^-. The XO_2^- anions are less stable in their protonated form and disproportionate to the $X^- + XO_3^-$, as shown in Eqn. 4.7 for BrO_3^-[25]. The bromate anion is reduced to bromite, which at a pH of 3.5 will have nearly equal concentrations between it's protonated and deprotonated form due to its pK_a of 3.43. This is not true for chlorite, whose pK_a is 1.92, which will still be predominantly in the deprotonated form.

It is understood that disproportionation occurs even more rapidly at elevated temperatures [14], and regions of locally induced pockets of higher temperature can be generated by the joule heating effect after the initial streamer formation in the plasma discharge, especially with long discharge pulse widths [22]. Therefore, the region nearest to the plasma discharge zone is likely to have the highest density of the reduced forms of XO_3^- from radical interactions, which then can cause disproportionation due to the higher temperature disproportionation according to Eqn. 4.7 and Eqn. 4.9, generating X^-, XO^- and XO_3^-. This reaction occurs more quickly from BrO_3^- under acidic conditions because $HBrO_2$ is much more unstable and susceptible to disproportionation than it's conjugate base BrO_2^-, and this acidic form can be realized to a fair extent at a pH of 3.5 [7]. The same is true for $HClO_2$, however, with its lower pK_a value, the bulk of the ClO_2^- is in the more stable, conjugate base form so this secondary disproportionation does not occur. This explains why ClO_2^- is seen in the chromatograms of chlorate reduction from plasma treatment under all test conditions, but no BrO_2^- is observed in the chromatograms for the reduction of BrO_3^-.

From this reasoning, the instability of the BrO_2^- relative to that of ClO_2^- results in a higher rate of reduction for BrO_3^- than ClO_3^-, and in general the disproportion rates for the bromine oxoanions are more rapid than those for chlorine oxoanions [14].

Interactions with methanol

With the introduction of the methanol into the system a dramatic increase in the rates of reduction is observed for both halates under all tested conditions. Introducing methanol as a scavenger limits the amount of re-oxidation of X^- to XO^-, which is the necessary first step towards the oxidation path to XO_3^-.The scavenging of the hydroxyl radicals is very effective for methanol (rate constant $k = 9.7 \times 10^8$ L mol$^-1$ s$^-1$ [26]) and also allows for the formation of further reducing compounds such as CH_2O , $O_2^{\bullet-}$ and H_2. It is unlikely that oxidation to the halate is occuring; it has been shown that the oxidation from XO_2^- to XO_3^- does not occur by $OH^\bullet$ but by O_3 [2]. It is unlikely that O_3 is being generated by the plasma process, as this usually requires the need for gaseous oxygen to pass through the plasma discharge zone. Though there may be some dissolved oxygen present in solution, ozone generally is not observed in generation of submerged electrodes without gas passing through the electrode [27]. Furthermore, with the addition of methanol into the system, we see a substantial decrease in the amount of dissolved oxygen in the system. This decrease in dissolved oxygen is likely due to the increase in bubble formation. It has been reported in literature that plasma discharge in a solution containing fairly high concentrations of methanol generates significant amounts of H_2 gas [28]. Therefore, methanol then not only enhances the reduction by generating further reductive species, but the increase in bubble formation rapidly decreases the amount of dissolved oxygen in the system which reduces the scavenging of $H^\bullet$, a primary reducing species, by the dissolved O_2. The coupled effects of suppression of re-oxidation and dissolved oxygen with the introduction of more reductive species shows a much higher rate of decrease under both test conditions for both chlorate and bromate. In the instance of ClO_3^- reduction, there was a very small difference between the the two pH levels tested, though when methanol was introduced there was a marked distinction between the pH of 3.5 and pH of 7, suggesting that there may also be a pH dependent reaction with methanol occuring which facilitates reduction.

Effects of temperature increase

Increasing the temperature also improved the rates of reduction in all cases. As explained previously, it is believed that this is caused by scavenging of reductive species by dissolved oxygen (for example: $H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$, $k = 2.1 \times 10^{10}$ [26]). Therefore, improved reaction rates can occur if this oxygen has been stripped from solution. One method to remove dissolved gases from solution is to subject it to cavitation while heating, which is precisely what occurred for the experiments in Section 4.3.3. It is known that pulsed corona discharges in water do cause cavitation [20], and so by bringing the temperature of solution up to reduce the solubility, a lower dissolved oxygen content can be achieved and a higher rate of XO_3^- reduction can be obtained. The lower rate observed in the deoxygenated sample at 25^{o}C (Figure 4.9) is likely due to the constant mixing conditions at lower temperature allowing some O_2 to re-enter solution throughout the test at room temperature.

The increase in reduction rates for both halate species under elevated temperatures are likely a factor of disproportionation occuring more rapidly, causing the species to move from the hypohalite and halite forms to the halate and halide forms. Then, with the presence of methanol, the re-oxidation to the hypohalite form is suppressed. This populates the lower oxidation state of halides, as there is active reduction of the upper oxidation levels by the generation of reducing compounds and enhanced disproportionation.

Liquid Analysis

The liquid samples were analysed for by-products: anions by using ion chromatography, and low molecular mass organic compounds using gas chromatography - mass spectroscopy (GC-MS). The only anions that were detected through for the reduction of BrO_3^- were Br^- , while for ClO_3^- increases in the Cl^- concentration were observed, as well as the introduction of a new ClO_2^- peak. Total mass balances of the Br and Cl atoms in inorganic compounds showed 98% ± 3% conservation of these ions. Testing for halogenated organic compounds in solution using the GC-MS showed no traces under either neutral or acidic conditions for ClO_3^- reduction or BrO_3^- reduction. The gases escaping from the reactor were not tested or captured, and as such if any of volatile halogenated organics were created, they were likely lost.

4.5 Conclusion

The results of this work show that aqueous phase corona discharge is capable of reducing the bromate and chlorate anions into bromide and chloride respectively. Reduction is favoured under acidic conditions compared to neutral pH and the efficiency of the process is improved with the addition of methanol to scavenge any oxidative species and minimize re-oxidation of reduced species, reduce the dissolved oxygen in solution and also to generate further reductive species from radicals generated from the plasma discharge. Other organic compounds such as ethanol, sorbitol and sucrose also are effective in increasing the rate of reduction of the target contaminants, however, those which aid in decreasing the dissolved oxygen concentration through increased cavitation show significant improvement over other organic compounds. An increase in temperature, brought upon either by heating the solution with an external source or by the discharge itself, served to minimize the dissolved oxygen content within the reactor to stop reductive species scavenging further increasing the rate of reduction. Treatment times of 60 minutes is sufficient to reduce greater than 95% of the 30 μM concentrations of both bromate and chlorate under optimal conditions, and greater than 95% removal is achieved within 90 minutes for the bromate anion and 150 minutes for the chlorate anion at a concentration of 300 μM. A linear rate of reduction was seen for both BrO_3^- and ClO_3^- at the higher concentration of 3000 μM after 3 hours of treatment yielding a 25.9% removal of BrO_3^- after 180 minutes of treatment and 21.2% removal of the initial ClO_3^- concentration after 180 minutes of treatment.

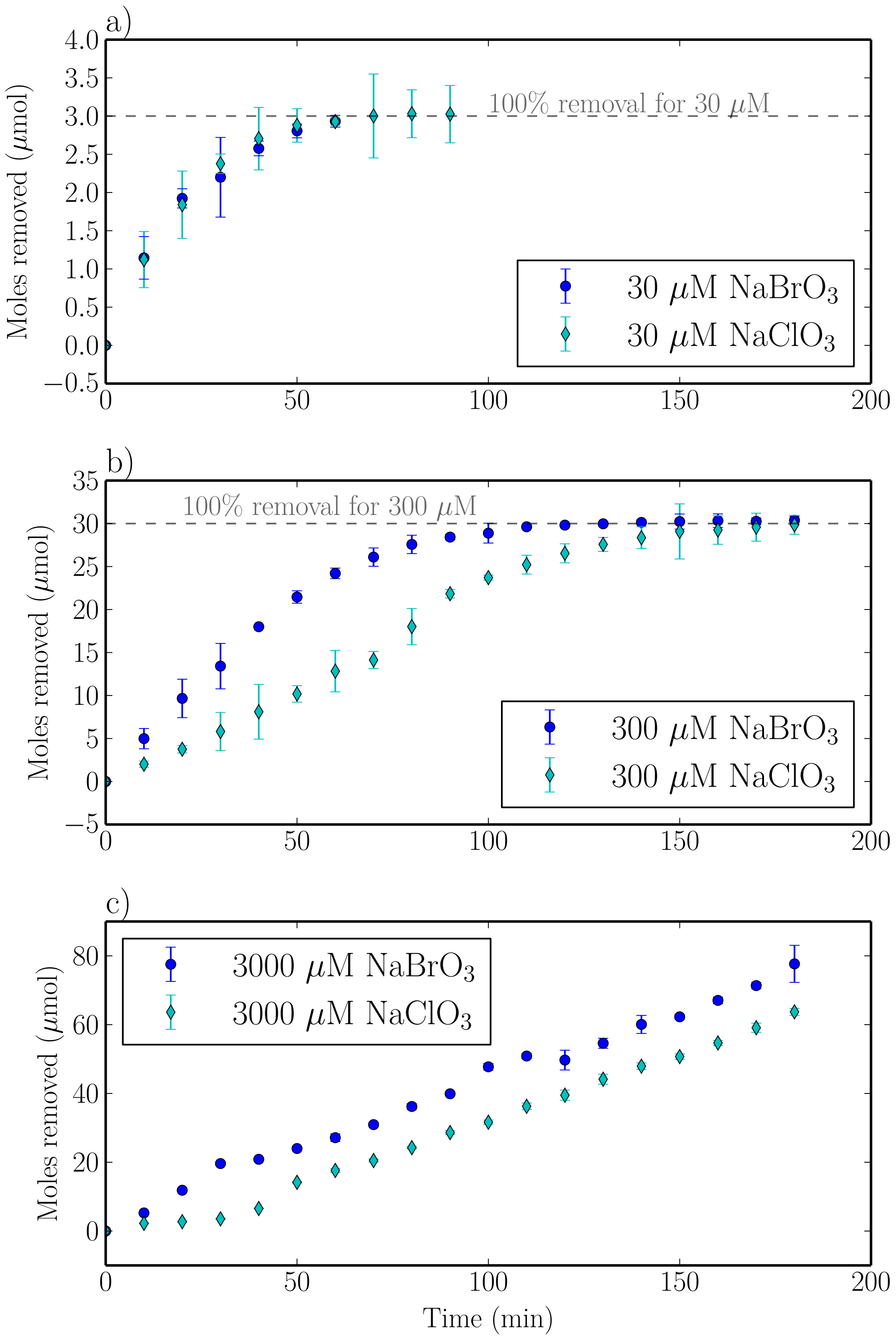

Figure 4.11: Time series tests for samples at a pH of 3.5, containing 3 M MeOH and at an electrolytic conductivity of 500 μS/cm for concentrations of a) 30 μM and b)300 μM and c) 3000 μM of $NaBrO_3$ and $NaClO_3$

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Chapter 5

Influence of gases on the removal of bromate and monobromoacetic acid using aqueous phase corona discharge

Abstract

This paper investigates the effect of introducing gases into solution in three different methods while using aqueous phase pulsed corona discharge for the degradation of the bromate ion and monobromoacetic acid. Treatment of the bromate ion and monobromoacetic acid were tested at a pH level of 3.5, while monobromoacetic acid was also tested at a pH of 10.5. The test solution is either pre-sparged and saturated with the test gas, continuously bubbled with the test gas a distance away from the discharge electrode, or bubbled directly through a hollow discharge electrode. The gases tested were Ar, N_2 and O_2. This experiment shows that in the pre-sparge conditions where the test solution is saturated with the

test gas, bromate reduction occurs preferentially in anoxic conditions, while constant bubbling of the solution causes a decrease in the levels of reduction of bromate. For monobromoacetic acid, a solution saturated with Ar had the highest level of removal while solutions saturated with N_2 or O_2 resulted in similar effects on the treatment with the plasma discharge under acidic conditions. When continually sparging the solution with the test gases, Ar actually hindered the removal rate while N_2 and O_2 showed improvement under acidic conditions. Under basic conditions for monobromoacetic acid, all gases behaved similarly in both cases of pre-sparging and continual sparging, with a slight improvement when the solution was continuously sparged. When gases were passed through a hollow electrode it was shown that N_2 caused a very large improvement in all test cases for both compounds, followed by Ar and with O_2 demonstrating the poorest performance, indicating a preference over reductive methods of treatment versus oxidation.

5.1 Introduction

Disinfection has become a fundamental part of drinking water treatment around the globe. The dramatic decrease in pathogen induced maladies since its introduction in the early 1900s has spoken volumes on its benefit to human health. However, as methods of improving the disinfection process have developed, and similarly as detection methods for contaminants have increased, there has been a marked rise in the number of instances where harmful disinfection by-products have been detected in water in use for being delivered to humans through drinking water or recreational use [1–3]. The widespread use of chlorination in municipal drinking water containing organic matter can result in the generation of haloacetic acids [1, 2]. Chlorination oxidizes bromide in waters to form bromine which readily interacts with organic humic and fulvic acids to generate haloacetic acids [1]. Disinfection by ozonation and chlorination also facilitates the oxidation of bromide to the bromate ion (BrO_3^-), which is another harmful contaminant found in treated waters [4, 5].

Unfortunately, these compounds are harmful to human health. The bromate ion is a genotoxic carcinogen, and is capable of damaging the kidneys, peritoneum, testes and thyroid gland when ingested [6]. A maximum contaminant limit has been set by the United States Environmental Protection Agency (USEPA) at a concentration of 10 μg/L (approx. 80 nM) in drinking water. Monohaloacetic acids are cytotoxic, genotoxic mutagenic and teratogenic, with monobromoacetic acid being much more harmful than monochloroacetic acid. Monohaloacetic acids were shown to have a functional association with oxidative stress, inflammation and cancer on human intestinal epithelial cells [7]. The USEPA has set a MCL of 60 μg/L for monohaloacetic acids in drinking water; approximately 430 nM for monobromoacetic acid.

In this study, aqueous phase corona discharge will be used to remove these contaminants from water. Treatment methods using corona discharges in water have been studied previously for their ability to treat a wide variety of organic compounds. For example, experiments have been conducted which have shown the degradation of phenol, chemical warfare agents, antibiotics and endocrine disruptors using corona discharge in water [8–12]. This widespread variety of contaminants is able to be treated due to the non-selective nature of the radicals that are formed from corona discharge in contact with water.

Aqueous phase corona discharge is known to dissociate water molecules (H_2O) into hydroxyl ($OH^\bullet$) and hydrogen ($H^\bullet$) radicals [13, 14]. These radicals then propagate out into the bulk solution where they can encounter other molecules and undergo secondary reactions, such as the formation of $O^\bullet$, $O_2^{\bullet -}$, $HO_2^\bullet$ radicals and also molecular species such as H_2O_2, H_2, and O_2 [14, 15]. Many of these species are highly reactive and capable of oxidizing or reducing contaminants. In order to facilitate one mechanism over the other, it is necessary to alter the conditions of the water matrix in order to scavenge the species corresponding to the undesired reaction. For example, alcohols are known to scavenge the hydroxyl radical which would make oxidation more difficult, but would result in the generation of aldehydes and further reductive species [15]. Alternatively, having a high dissolved oxygen content can cause the hydrogen radical to be scavenged by the oxygen molecules and result in a decreased rate of reduction [16]. Furthermore, the pH of solution has direct impacts on the species involved. For example, the hydrogen radical ($H^\bullet$) undergoes an acid base dissociation to generate a proton and an aqueous electron ($e^-_{(aq)}$), which is a more potent reducing species with a standard reduction potential of -2.7 V as compared to -2.3 for the hydrogen radical. These reactions are depicted in Eqs.5.1-5.3 [15, 16].

$$\mathrm{H}^\bullet \leftrightharpoons \mathrm{H}^+ + e^-_{(aq)}, \qquad \mathrm{p}K_a = 9.6 \tag{5.1}$$

$$\mathrm{H}^\bullet + \mathrm{O}_2 \rightarrow \mathrm{HO}_2^\bullet, \qquad k = 2.1 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}} \tag{5.2}$$

$$\mathrm{HO}_2^\bullet \leftrightharpoons \mathrm{H}^+ + \mathrm{O}_2^{\bullet -}, \qquad \mathrm{p}K_a = 4.8 \tag{5.3}$$

The bromate ion (BrO_3^-) and monobromoacetic acid ($CH_2BrCOOH$) are depicted in Figure 5.1. The bromate ion is a highly oxidized form of the bromide ion and requires chemical reduction in order to become the less harmful bromide ion. Monobromoacetic acid is a saturated, aliphatic organic compound, which could potentially be oxidized and mineralized to CO_2, H_2O and Br^-, or reduced by stripping of the Br^- from the compound and form acetate radical and bromic acid, as depicted in Eq. 5.4 [16].

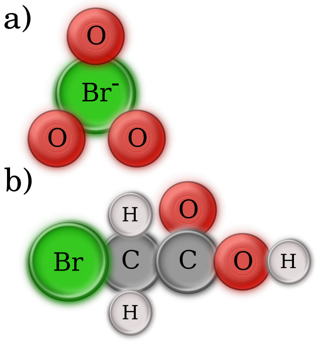

Figure 5.1: a) Bromate ion, b) Monobromoacetic acid

$$H^{\bullet} + CH_2BrCOOH \rightarrow HBr + CH_2COH_2^-, k = 3.3 \times 10^8 \text{ L mol}^{-1}\text{s}^{-1} \tag{5.4}$$

Typically, oxidation is sought after for target organic compounds due to the non-selectivity of the hydroxyl radical and the potential for complete mineralization of the compound. However, the main method of attack by the hydroxyl radical is in hydrogen abstraction for saturated aliphatic compounds [16, 17]. This would not result in the liberation of the Br^- ion from the compound, and successive oxidation to finally mineralize the brominated organic compound would likely be slow.

The test parameters will involve the addition of gas into the test reactor in three different methods, by i) sparging the solution before treatment to saturate the test solution with the gas; ii) continuous sparging of the test gas while the treating the solution and iii) flowing the test gas through a hollow electrode placed at high voltage. The gases to be tested are argon (Ar), diatomic nitrogen (N_2) and diatomic oxygen (O_2). The inclusion of oxygen allows to test whether generating an environment more favourable to oxidation or reduction results in a more rapid decrease in the monobromoacetic acid.

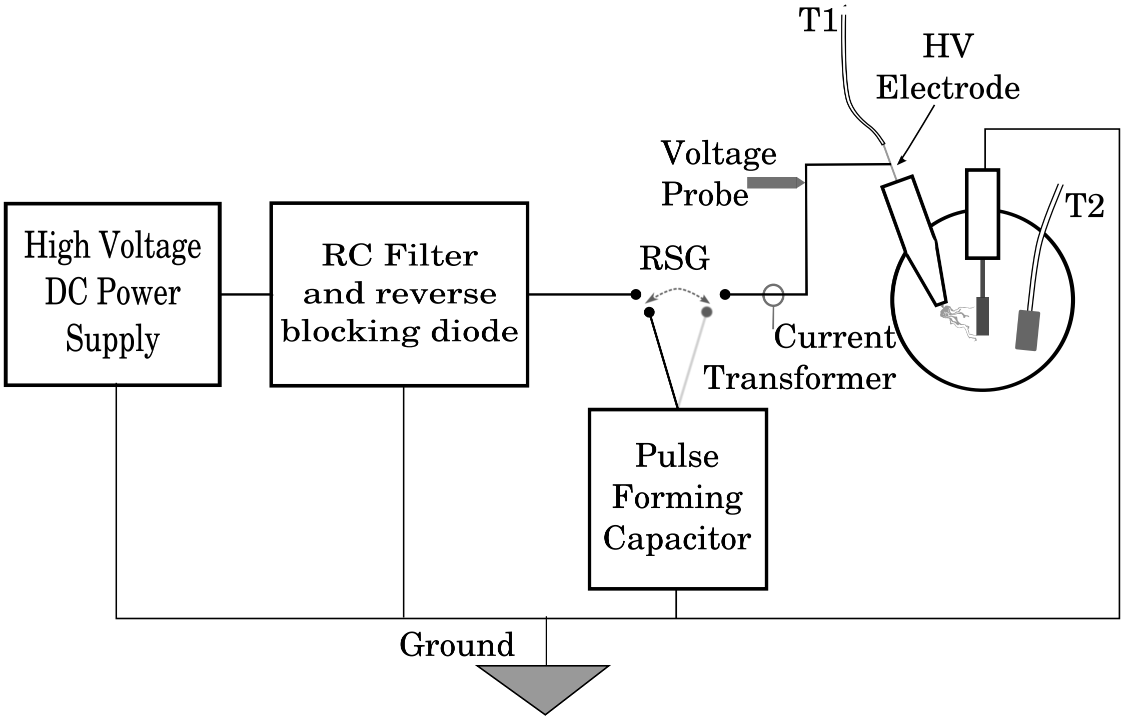

Figure 5.2: Schematic of experimental apparatus. The equipment consisted of a high voltage DC power supply whose output was filtered through a low-pass RC filter. The output of the filter was switched using a Rotating Spark Gap (RSG) to a pulse forming capacitor (1 nF) which was then switched, also through RSG to discharge into the reactor. T1 and T2 are tubes used to supply gas to the reactor either through the electrode or through the stainless steel filter which acted as a sparger.

5.2 Experimental Methods

The overall block diagram for the experimental apparatus is depicted in Figure 5.2. An in-house built high voltage DC power supply was used which consisted of a high frequency, high voltage AC source powering a 4-stage Cockroft-Walton type voltage multiplier which provided rectification and voltage amplification. This system was considered to be the High Voltage DC Source. The output from this source was then filtered with a low-pass RC filter consisting of a 10 nF ceramic capacitor and a 10 MΩ resistor bank connected to the rotating spark gap (RSG). The rotating spark gap consisted of a modified High Energy Ignition distributor from automotive purposes. The central post was connected to the pulse forming capacitor (1 nF) while the outer terminals alternated between charging, from connection to the filtered output of the high voltage dc supply, or discharging, connected to the submerged electrode in the reactor. The high voltage discharge electrode was either a solid electrode or hollow one to allow gas flow through the electrode. The solid electrode consisted of CP2, commercially pure titanium (98.9% purity) which was sharpened to a point, to concentrate the electric field at the tip, and then slightly rounded to minimize erosion. The second electrode was a hollow 316 stainless tube, with an interior diameter of 0.635 mm. In both electrodes the exterior diameter was 0.813 mm. The ground electrode was a piece of CP2 titanium with dimensions of 12.7 mm x 6.35 mm x 38 mm, press fit into a 4.7 mm diameter cylindrical rod also of CP2 titanium.

The reaction vessel was a 100 mL three neck flask with custom made PTFE holders for the ground and high voltage electrode. The contents were constantly mixed using a magnetic stir bar. The entire vessel was immersed in a temperature controlled bath to ensure a constant temperature of 25^{o}C throughout the experiment. The gases were introduced to the reactor either by being passed through to the hollow stainless steel high voltage electrode or to a stainless steel filter. The stainless steel filter had a pore size of 2 μm and was used to sparge the solution and saturate with the desired gas. The gases used in this experiment were medical grade nitrogen and oxygen (99.0% purity) and 99.997% pure argon.

The electrical measurements were taken using a Tektronix P6015A high voltage probe and an Ion Physics CM-10-MG current transformer. The output of these probes were measured using a Tektronix TDS5054B Digital Oscilloscope which had a 500 MHz bandwidth and was capable of 2 gigasamples/second. The waveforms were averaged over 150 pulses to ensure an accurate representation of the average current and voltage which were delivered to the system.

The concentrations of the compounds after treatment were analysed using suppressed ion chromatography. A Varian Pro-Star 230 SDM was used as the pump for mobile phase delivery while the sample was introduced using a Varian 410 auto-sampler with 100 μL sample loop and detected using a Dionex CD-25 conductivity detector. The chromatography column was a Hamilton PRP-X110S column with dimensions of 4.1 mm x 150 mm. A Dionex AMMS-300 micromembrane suppressor was used to suppress the mobile phase conductivity and provide sample acidification which yielded in a signal boost and decreased lower detection limits. The mobile phase was run isocratically and was a solution of 1.4 mM $NaHCO_3$ and 1.6 mM Na_2CO_3 mM with 2.5% methanol by volume operated at a flow rate of 1.6 mL/min. The regenerant for the suppressor was 50 mN H_2SO_4 at a flow rate of 5 ml/min.

The water matrix characteristics such as conductivity and pH were measured using a Mettler-Toledo SevenMulti bench-top pH and conductivity probe. Dissolved oxygen was measured using a YSI-5000 dissolved oxygen probe.

The electrolytic conductivity of each test solution was fixed at 500 μS/cm, approximately that of tap water. To prepare for each experiment, 150 mL of the required test solution was prepared, with 100 mL being used in the reactor. Regular sampling occurred every 5 minutes by drawing 1.5 mL of the treated solution and replacing with 1.5 mL from the excess which was prepared.

Previous work has shown that optimal reduction for the bromate ion occurs with decreasing pH, and as such the bromate reduction tests were conducted at a pH of 3.5. Monobromoacetic acid ($CH_2BrCOOH$) has a pK_a of 2.9, and as such was tested at pH 3.5 and pH 10.5. The pH of 3.5 was set due to constraints imposed by limiting the electrical conductivity of the solution to within drinking water levels and also to maintain the pH within reason in regards to future applicability. The basic pH was set to test treatment efficacy at an elevated pH where the monobromoacetic acid would be in its deprotonated form, and the electrolytic conductivity would be similar to that of pH 3.5 without adding excessive chloride as compared to the pH 3.5 test, as chloride is a known scavenger of $OH^{\bullet}$ radicals and can effect secondary reactions [18].

5.3 Results and discussion

5.3.1 Results from Pre-sparged Experiments

The experiments presented in Figure 5.3 consisted of saturating the solution with the desired gas prior to treating the solution with the plasma discharge. This was done by purging the solution with 50 ml/min of one of the three gases being tested: argon, oxygen and nitrogen through the 2 μm stainless steel filter. In order to ensure a complete saturation of the solution, the dissolved oxygen content was measured. In the case of argon and nitrogen it was ensured that the dissolved oxygen content had dropped to 0.0 mg/L, which was the lower limit of detection for the equipment, and for the tests involving sparging with oxygen prior to treatment, it was ensured that the concentration of dissolved oxygen in solution was saturated at 8.2 mg/L. The sparging lasted over 5 minutes, ensuring that 2.5 test volumes of gas had passed through the solution.

Figure 5.3a shows that under acidic conditions, very similar rates of reduction occur for the bromate ion under anoxic conditions of saturating the solution with argon or nitrogen, achieving 20.4% and 22.1% reduction respectively. Under oxygenated conditions there is a

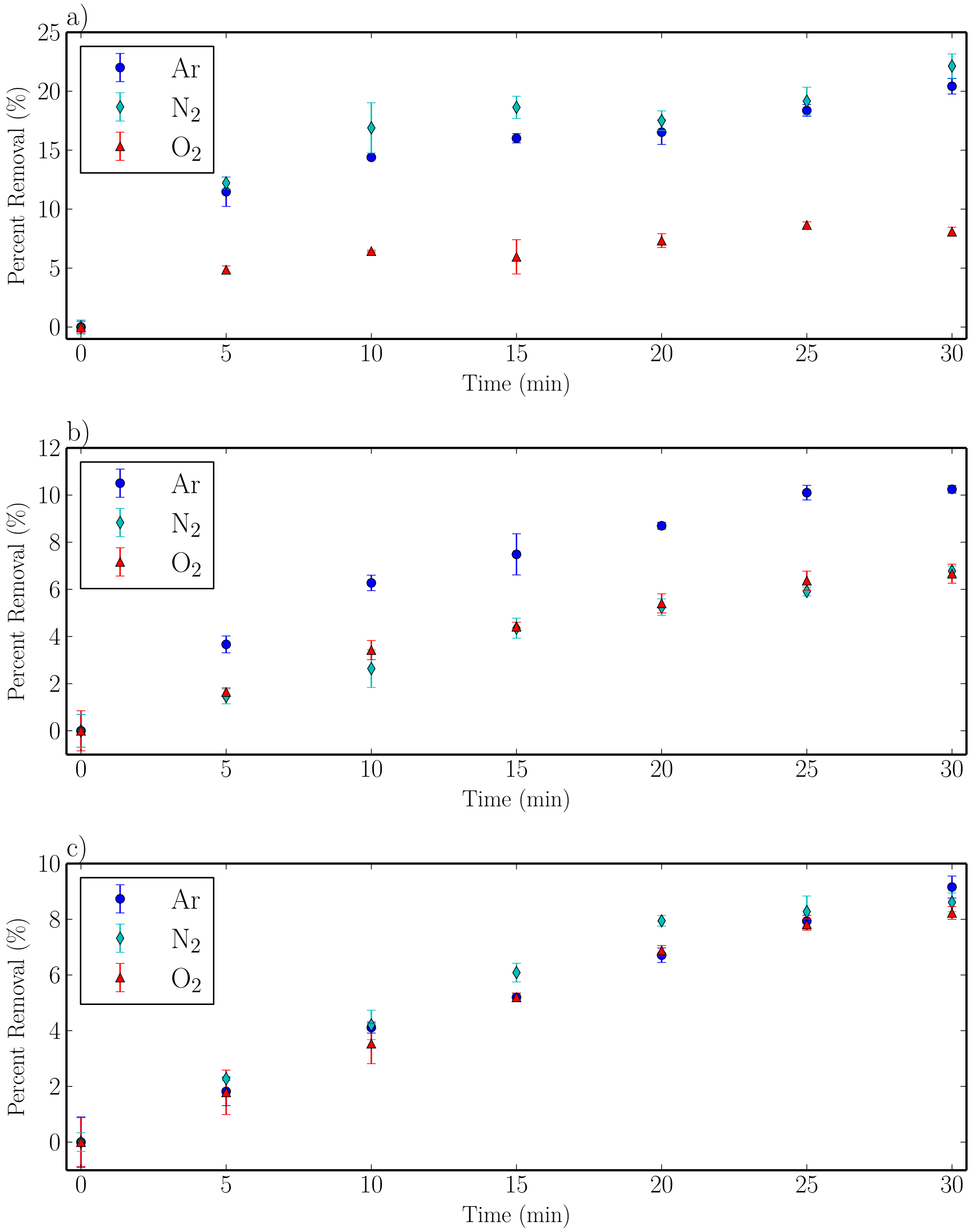

Figure 5.3: Time series results for the pre-sparged gas experiments. The results shown are for tests for treating a solution contaminated with a) 10 μM $NaBrO_3$ at a pH 3.5, b) 10 μM $CH_2BrCOOH$ at a pH of 3.5 and c) 10 μM $CH_2BrCOOH$ at a pH of 10.5. The results of each figure are shown with the changing test parameter of the dissolved gas: argon, nitrogen and oxygen.

marked difference, where only 8.09% of the total amount of bromate is reduced. This result can be explained by the high rate of scavenging of the hydrogen radical by dissolved oxygen. This reaction converts the reducing species of $H^\bullet$, into the oxidizing species of $HO_2^\bullet$ which diminishes the total amount of reducing species and hence suppresses the reduction of bromate.

In Figure 5.3b a different trend is observed where having the acidic test solution (pH 3.5) saturated with Ar increases the total amount of monobromoacetic acid decomposition in solution compared to that when the solution is saturated with either N_2 or O_2. The amount of monobromoacetic acid decomposed in saturated Ar is 10.2%, while in N_2 saturated solution it was 6.78% and in O_2 saturated solution it was 6.66%.

There is a significant difference between the results of the Ar saturated solution and the N_2 and the O_2 saturated solution, which are nearly equivalent. This suggests that the dominant form of removal of the monobromoacetic acid at lower pH is not dependent on the hydrogen radical, though it is appears to be responsible for significant reduction of the bromate ion.

Figure 5.3c shows slightly lower levels of removal when the solution is basic for the removal of monobromoacetic acid. When the solution was saturated with Ar a removal of 9.16% of the initial monobromoacetic acid was achieved. Fairly similar results were also achieved when the solution was saturated with N_2 and O_2; 8.61% removal was achieved with N_2 saturation and 8.23% removal when the solution was saturated with O_2. As in the previous case in Figure 5.3b, a comparable level of removal is observed when the test solution is saturated with either O_2 or N_2, indicating again that the $H^\bullet$ is not playing a significant role in the removal.

In the basic pH level scenario all three gases behave equally, again indicating that the role of the hydrogen radical is not as prevalent as it is for bromate reduction. In this instance a different mechanism is at work due to the fact that at a pH level above 10 the hydrogen radical undergoes a deprotonation reaction to generate a hydrated electron ($e^-_{(aq)}$). This electron then is able to abstract Br^- from the $CH_2BrCOOH$ in the following reactions [16]:

$$\mathrm{H}^\bullet + \mathrm{OH}^- \leftrightharpoons e^-_{(aq)} + \mathrm{H_2O}, \qquad \mathrm{p}K_a = 9.6 \tag{5.5}$$

$$\mathrm{CH_2BrCOOH} + e^-_{(aq)} \rightarrow \mathrm{CH_2COOH}^\bullet + \mathrm{Br}^- \tag{5.6}$$

As the species involved is the hydrated electron, and not the hydrogen radical, the type of dissolved gas does not have a distinctive effect on the removal rate during the pre-sparged/saturated gas tests.

5.3.2 Results from Continual Sparging Experiments

In these experiments, the solution was first sparged for 5 minutes with the test gas, and then continuously sparged throughout the experiment at a volumetric flow rate of 50 ml/min. The placement of the sparging filter was some distance away from the high voltage electrode, however with the continual mixing bubbles were still present in the vicinity of the high voltage discharge electrode. The constant bubbling also ensured that the headspace of the reactor was shielded from the atmosphere and only the test gas was present during the experiment. The results are shown in Figure 5.4.

The introduction of constant gas bubbling into the system hampered the rate of bromate removal in the case of nitrogen and argon, but surprisingly increased the rate of reduction with oxygen. Figure 5.4a shows that a level of 12.9% reduction was achieved when the

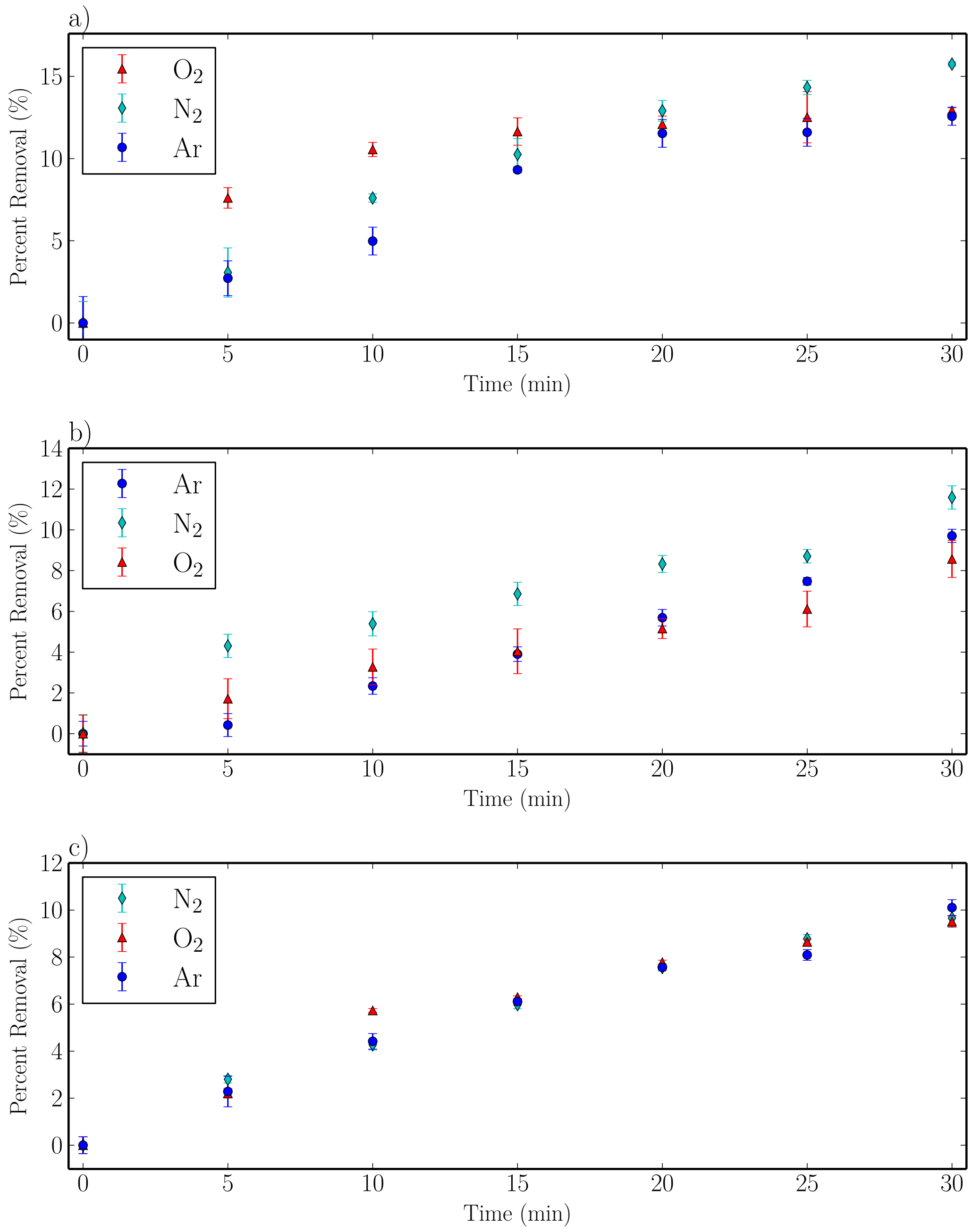

Figure 5.4: Time series results for continually sparged experiments. The results shown are for tests for treating a solution contaminated with a) 10 μM $NaBrO_3$ at a pH 3.5, b) 10 μM $CH_2BrCOOH$ at a pH of 3.5 and c) 10 μM $CH_2BrCOOH$ at a pH of 10.5. The results of each figure are shown with the changing test parameter of the sparging gases: argon, nitrogen and oxygen.

solution was bubbled with Ar and when bubbling with N_2 a 15.7% reduction level was achieved, a decrease of roughly 7% in both instances. In the case of O_2 bubbling, the initial rate of reduction is more rapid than either Ar or N_2, though the rate decreases as the experiment progressed and a steady state concentration was achieved near the 20 min. mark with small changes in the concentration of the bromate ion. The bubbling of O_2 increased the total of amount of the bromate ion reduced compared to the previous test of pre-saturation of the the solution was with O_2 prior to beginning the treatment. The continual sparging showed an 12.6% removal of BrO_3^- where originally only 8.09% had been removed, a 4.5% increase.

A small decrease in the overall removal of monobromoacetic acid was also observed for the conditions involving Ar, however an increase was shown for both N_2 and O_2. When continuously sparging the pH 3.5 solution with Ar a removal of 9.71% was achieved, a decrease of 0.5% from the pre-saturation condition. When N_2 was continuously sparged into solution a removal of 11.6% was achieved, an improvement of 4.81%, while for O_2 sparging there was an increase of nearly 2% to 8.57% removal.

Under basic conditions for monobromoacetic acid, again very similar results were achieved for all test cases along with a slight improvement from the pre-sparged experiments conducted. In this instance, continuous sparging with Ar demonstrated a total removal of 10.1%, while sparging with N_2 resulted in a removal level of 9.66%. Continuous sparging with O_2 resulted in 9.51% removal.

The odd behaviour of a decrease in the level of removal for bromate and a slight increase in the removal of monobromoacetic acid is odd, though explained by the literature. In the work of Shih and Locke, it was observed that by bubbling argon near the discharge electrode a decrease in the formation of hydrogen peroxide was observed as compared to still water [19]. From this it was inferred that there was a decrease in the amount of radical species that were generated. It was observed that in bubbled water the plasma preferentially propagated within the low density bubbles over the liquid water. The plasma bubbles then consisted or a partial mixture of ionized steam and the gas, as opposed to a bubble fully formed of ionized steam. While this caused an observable reduction in the initiation energy required to form the discharge channels, it also decreased the generation rates of the $OH^{\bullet}$ and H_2O_2 in that study [19]. This is likely also the case for the reductive species, and hence the diminished removal levels of the bromate ion. The steady-state behaviour of the reactor when oxygen bubbles were introduced were likely a result of the initial reduction of the bromate ion to bromide, however when the discharge passed through the oxygen bubbles ozone was likely generated. The ozone could then interact with the bromide ion to reform bromate [5].

The slight increase for monobromoacetic acid under both acidic and basic conditions as compared to the pre-saturation condition, while a decrease in the rate of reduction of bromate, also compared to the pre-sparge condition is likely due to the nature of the species involved, and not the generation of chemical compounds by the plasma discharge. The bromate ion is a highly stable ion, which does not decompose under atmospheric conditions within the normal temperature ranges of liquid water. Monobromoacetic acid, however, does degrade thermally through hydrolysis at 65^{o}C [20]. Though the temperature of the reaction vessel was maintained at 25^{o}C, the plasma discharge is capable of generating species at much higher temperatures; plasma temperatures within the streamers have been reported to be greater than 2000 K [21, 22]. As mentioned previously, in the work of Shih and Locke plasma preferentially propagates through the lower density bubbles over that of the higher density liquid. As the density of the bubble is significantly lower than that of water, the excited species generated, though lower in number, may be excited to significantly higher temperatures due to the longer mean free path between collisions caused by the lower density within the gases. As such, it is possible for energized species to be excited to sufficient levels where upon collision with monobromoacetic acid would result in imparting enough kinetic energy for the molecule to undergo hydrolysis (Eq. 5.7) with the surrounding water molecules and form glycolic acid.

$$\mathrm{BrCH_2COOH + H_2O \rightarrow CH_2OHCOOH + Br^- + H^+} \tag{5.7}$$

5.3.3 Results from Hollow Electrode Experiments

The hollow electrode experiments consisted of using a hollow stainless steel tube which was the same diameter as the solid titanium electrode through which gases could flow into the reactor at the same flow rate of 50 ml/min as in the continual sparging experiments. The gas flowing through the hollow electrode allowed the plasma to ignite within the much lower density gas phase and at a lower breakdown voltage. Due to the lower density, the mean free path of the excited species is longer and the species can be excited to higher energies before collisions, ensuring a higher level energy of ionization and a higher probability of successive secondary ionizations. Figure 5.6 also demonstrates a higher discharge current resulting from flowing the gas through the discharge electrode, indicating that a larger amount of ionized species were generated in this method than the previous two.

Figure 5.5 shows significant improvement over Figure 5.3 and Figure 5.4 in all test cases. For the reduction of the bromate ion as shown in Figure 5.5a, the influence of Ar through the electrode resulted in 42.3% reduction, while nitrogen showed a much higher

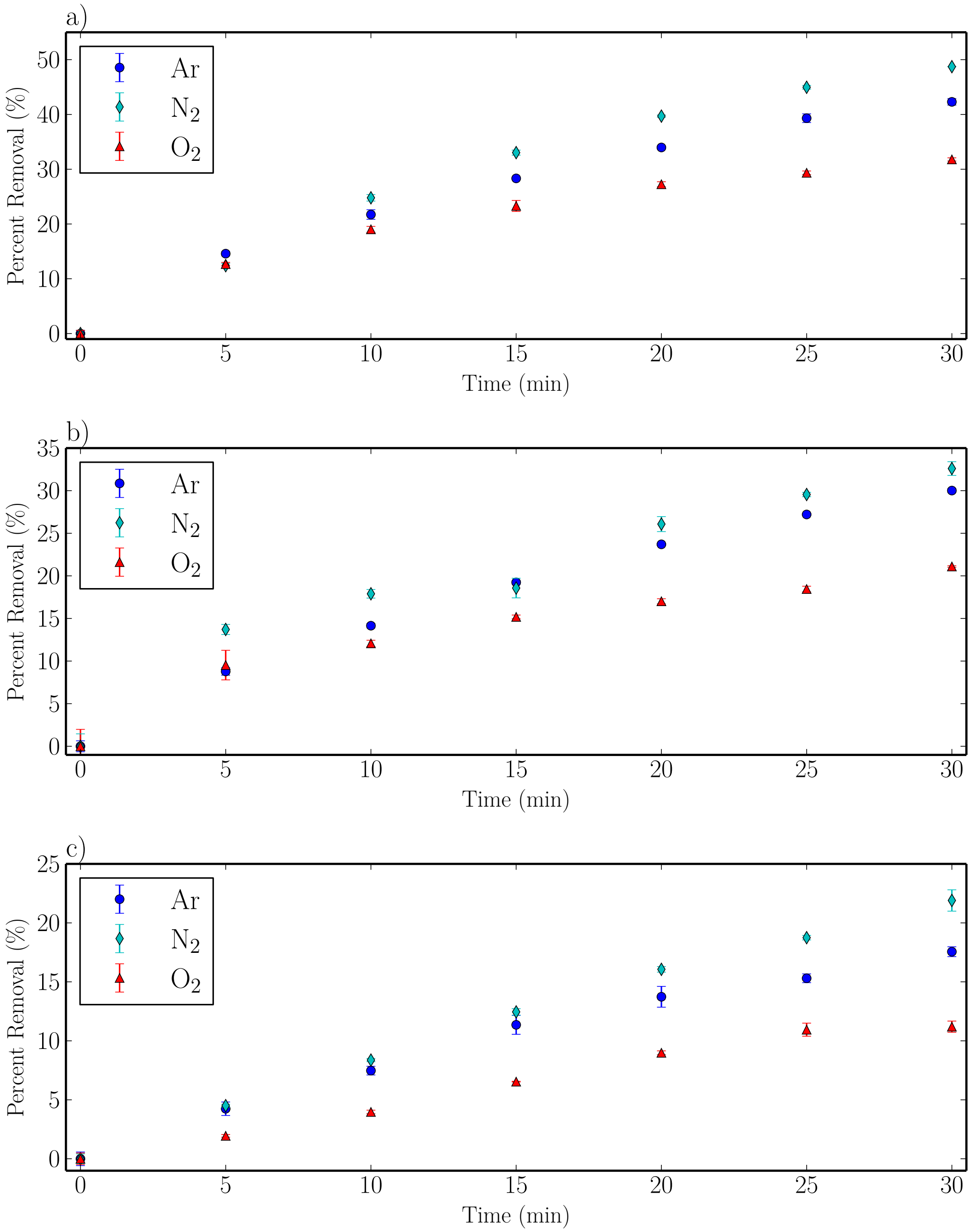

Figure 5.5: Time series results for experiments conducted by flowing the test gases through the hollow high voltage electrode. The results shown are for tests for treating a solution contaminated with a) 10 μM $NaBrO_3$ at a pH 3.5, b) 10 μM $CH_2BrCOOH$ at a pH of 3.5 and c) 10 μM $CH_2BrCOOH$ at a pH of 10.5. The results of each figure are shown with the changing test parameter of the sparging gases: argon, nitrogen and oxygen.

improvement, surpassing Ar and achieving 48.7% reduction. Passing O_2 through the high voltage electrode resulted in the lowest level of reduction, achieving only 31.8% reduction.

Treating monobromoacetic acid under acidic conditions resulted in a similar trend where N_2 generated a higher level of removal over Ar or O_2. Figure 5.5b shows that when Ar was passed through the hollow electrode 30.0% removal of the contaminant was achieved in 30 minutes, though this was less than that when N_2 was passed through the electrode, where a level of 32.6% was removed. When O_2 was passed through the hollow electrode, a decreased level of removal of 21.1% was achieved.

Figure 5.5c shows the data when the same experiment for monobromoacetic acid was conducted at the elevated pH of 10.5. In this instance the removal rate when N_2 is passed through the hollow electrode is over double that of the Ar. When Ar is passed through the hollow high voltage electrode in the basic solution of monobromoacetic acid a 17.6% level of reduction is achieved, though when N_2 is passed through 21.9% is achieved and only 11.2% when O_2 is passed through.

The addition of flowing gas through the discharge electrode significantly improved the rate of reduction in all cases, and the supremacy of N_2 over Ar and O_2 as the preferred gas for removal of this compound is observed. By flowing low density gas through the discharge electrode the plasma can be ignited in the lower density media and generate a higher level of radicals than typically seen with direct discharge in solution. Sun et. al observed that flowing Ar or O_2 through the hollow discharge electrode generated higher emission intensities for $OH^\bullet$, $H^\bullet$ and O radicals. With Ar flowing through the hollow electrode the emission lines from the radicals were higher than those for O_2. It was also observed that the $H^\bullet$ emission intensity was the strongest when compared to the other peaks in the discharge in Ar, though in the discharge with O_2 the emission intensity from $H^\bullet$ was the lower than that of the O and $OH^\bullet$ radicals [23]. Typically, the literature concerns itself with advanced oxidation processes for the degradation of organic compounds, and N_2 is not typically tested, with the exception of some of the very first work in this field by Clements et. al, where the effect of bubbling nitrogen gas through the discharge electrode was tested for the decolorization of an anthraquinone dye [13], not for reduction of compounds.

The introduction of gas through the hollow electrode at such high volumes relative to the test reactor generates a large number of energized species which are excited to higher energies due to the lower densities and longer mean free paths. This results in more radical generation and higher removal rates. In the case of O_2 bubbling through the discharge electrode, it also results in the generation of O_3. Unfortunately, though O_3 is typically used as an oxidizing species in water treatment, it is a much more selective oxidizer than $OH^\bullet$. Ozone preferentially attacks unsaturated aromatic and aliphatic compounds and specific functional groups [24]. In the case of a saturated aliphatic compound like monobromoacetic acid and inorganic bromate ion, it is unable to react and as such offers the poorest performance of the gases.

It is postulated that the reason for the improvement of N_2 over Ar, is due to the fact that it is a diatomic molecule versus monotomic. Both gases generate an anoxic environment which facilitates reduction using the $H^\bullet$, though at the same volumetric flow rate a higher amount amount of ionized species are being generated from diatomic N_2 as from Ar. This is corroborated by considering the root-mean-square (RMS) current with hollow electrodes which are presented in Table 5.1. The table depicts the RMS value for an average of 150 waveforms for the treatment of monobromoacetic acid under acidic conditions with Ar, N_2, and O_2 flowing through the electrodes. The RMS current values for O_2 and N_2 are approximately 25% higher than that for Ar, indicating that a higher number of ionized

Table 5.1: RMS Current Values for Pulsed Discharge with Hollow Electrodes

Gas	RMS Current (A)
Argon	0.0435
Nitrogen	0.0531
Oxygen	0.0534

species are being generated. The drawback of using O_2 and N_2 is that once ionized that are significantly more reactive than Ar and can create other species like ozone or nitrogenous species, such as nitrates and nitrites, which can impede the reduction reaction, and also have potentially harmful effects to human health.

5.3.4 Electrical Characteristics

The electrical characteristics of 150 averaged waveforms are depicted in Figure 5.6 under constant input power. In all cases depicted in Figure 5.6a the peak discharge voltage is approximately 23.5 kV with a typical voltage rise time of 20 ns for the pre-sparged condition, 33 ns for the continuous sparge condition and 16 ns for the discharge through the hollow electrode. The voltage and current waveforms show ringing from the rapid pulsed discharge and long exponential decay in all cases. The voltage decay for each condition was also significantly different, which correlates with the difference in discharge currents observed. The hollow electrode undergoes a much more rapid voltage decay which is corroborated with the highest discharge current (Figure 5.6b), attaining a peak value of 30.1 A, and a much higher discharge current throughout the pulse as compared to the other tests conditions resulting in a more rapid decrease in electric potential. The constant sparge tests follows with the next most rapid decay in voltage with also a higher discharge current of 26.2 A and also a higher discharge current, than that of the pre-sparge condition. The pre-sparge condition attains a maximum current of 22.7 A, and shows the longest tailing of the

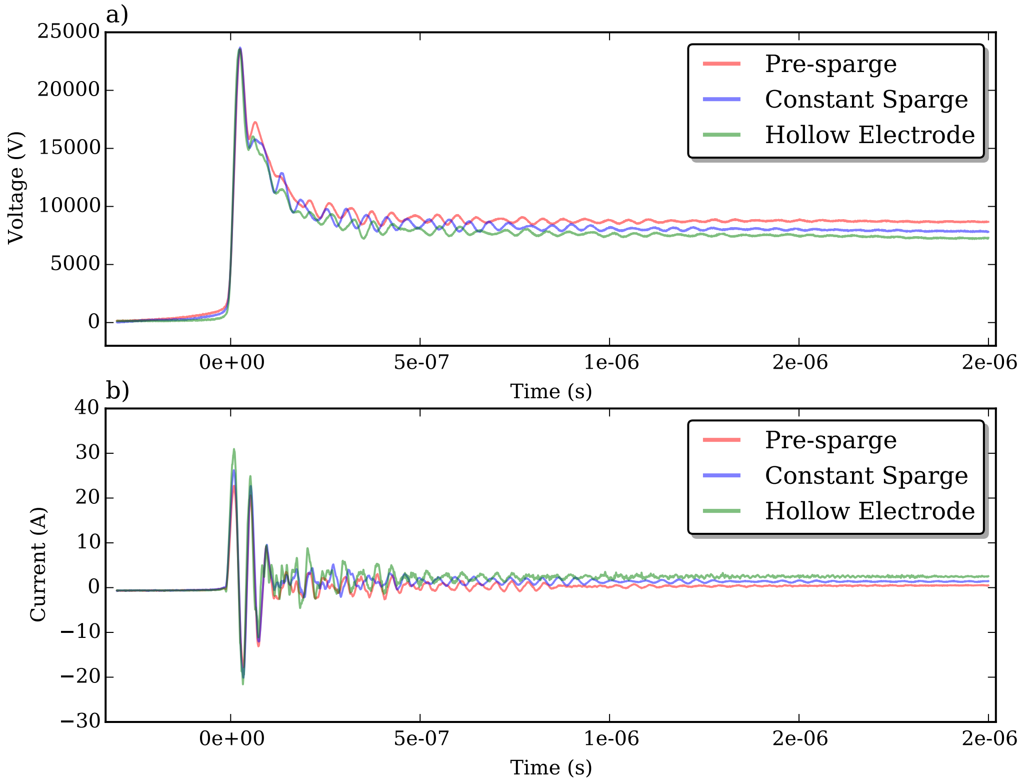

Figure 5.6: Waveforms for typical discharges into the treatment reactor when the test matrix has been saturated with the test gas, continual sparging with the test gases and when gas is being passed through the hollow high voltage electrode. (a) Voltage waveforms, (b) current waveforms.

voltage and lowest discharge current of all the conditions throughout the entire pulse.

The results here are in agreement with what was observed in the previous sections. The highest current draw is observed for the hollow discharge electrode tests indicating the highest level of radical production as was expected and described earlier. The more rapid decay voltage of the continuous sparging experiments over the pre-sparged experiments and higher discharge current are indicative of more plasma generation from the discharge, likely in the low density bubbles, though this does not necessarily result in higher levels of reduction as it introduces a further step with the interaction with the water and the generation of the active species. This additional step causes the energy from the discharge to be averaged over the surface of the bubble and likely results in lower activity of the species generated and as such the lower reduction for bromate.

5.4 Conclusion

The results of this study demonstrate that aqueous phase discharge is capable of removing both the bromate ion and monobromacetic acid at an electrolytic conductivity of 500 μS/cm and temperature of 25^{o}C. Monobromoacetic acid was tested at a pH of 3.5 and 10.5. Three different methods of introducing nitrogen, oxygen and argon into the test solution were tested for their effect on the rates of reduction of both compounds. These methods included pre-sparging of the solution to saturate with the test gases, continuous sparging of the test solution with the test gases away from the discharge electrode, and finally flowing the test gases directly through a hollow discharge electrode. For the pre-sparge tests it was observed that anoxic conditions favoured the reduction of bromate, while specifically a solution saturated with Ar generated the highest level of reduction of monobromoacetic acid under acidic conditions. Under basic conditions, all gases seemed to have the same effect of reduction on monobromoacetic acid. With continuous sparging of the test solution, a decrease in the level of reduction of bromate was observed in the cases with argon and nitrogen, though an increase was observed when oxygen was continuously bubbled. An increase from the pre-sparged conditions was observed for monobromoacetic acid under acidic and basic conditions, except in the case of argon under acidic conditions, which showed a minor decrease. It was observed that the highest rate of removal for both compounds was achieved using diatomic nitrogen flowing through the hollow discharge electrode, followed by argon. Introducing oxygen into solution resulted in the lowest rate, likely due to the scavenging of reductive compounds and generation of oxidizing species under the hollow discharge electrode scenario.

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Chapter 6

Conclusions

6.1 Contributions

This results of this work clearly demonstrate the reductive capabilities of aqueous phase corona discharge. The main points which have been explored and can be determined from the experiments contained are listed below.

- Aqueous phase corona discharge is capable of reducing nitrate to gaseous compounds, likely nitrogen oxides and diatomic nitrogen. The reactions are best facilitated under acidic conditions, with a high concentration of oxidative species scavengers to limit the amount of re-oxidation. Increased temperature does not improve the rates of reduction for NO_3^- and nearly complete reduction is obtained for typical surface water conditions. There was no nitrite generation observed from the reduction process, likely because as it was generated at a sufficiently high energy to disproportionate or was quickly reduced by the active compounds.
- Bromate and chlorate are also capable of being reduced by aqueous phase corona

discharge. In this instance, the observed by-products were bromide and chloride and hypochlorite. Again, acidic conditions prevailed in facilitating the reduction of these target contaminants, as having a high concentration of oxidative species scavengers.

- For the reduction of bromate and chlorate , an environment with no dissolved oxygen greatly expedited the removal of the target compounds from solution. This could be achieved by stripping the dissolved oxygen, addition of a volatile organic compound which produces significant amounts of bubbles during the pulsed discharge or by heating the solution. Complete removal of these compounds to benign levels is possible using this treatment method.
- Numerous carbonaceous materials can be used for the oxidative scavengers. In this work, methanol, ethanol, d-sorbitol and sucrose were tested for their ability to increase the reduction rates, and all were successful. The volatile alcohols performed better than the sugar and sugar alcohol, likely due to the increased cavitation and facilitation of oxygen stripping.
- Monobromoacetic acid is also capable of being removed from solution using aqueous phase plasma. Acidic conditions are again optimal for its removal.
- When testing the effect of different gas flow methods to treatment, it was observed that continuous bubbling of argon of nitrogen into solution decreased the overall rate of reduction for bromate as compared to a solution saturated with those same gases, while an increase was observed for oxygen.
- There was a slight increase in the amount of monobromoacetic acid which was removed by bubbling gases through the solution as opposed to a solution saturated with the gases. This was attributed the mixed phase allowing the energized species

to achieve a higher kinetic energy and initiate thermal hydrolysis of the monobromoacetic acid.

- When igniting a plasma in a hollow electrode with various gases, it was observed that nitrogen provided the highest level of treatment for water contaminated with either monobromoacetic acid or bromate. Argon followed next, then finally oxygen with the poorest performance. There was a significant improvement in using the gas flow through the discharge electrodes over plasma discharge in solely the liquid phase. A higher discharge current in this method of plasma generation is indicative of a higher amount of reactive species being produced, and the lower breakdown voltage of the gases likely yielded more energetic species as well.
- It was shown that the discharge current for diatomic nitrogen and oxygen was higher than that for argon when the gases were passed through the hollow discharge electrode. This is indicative of a higher amount of plasma generation from these gases as compared to argon, even though argon demonstrated better performance for removal of the contaminants over oxygen.

6.2 Recommendations for Future Work

Further mechanistic insight as to the specific reactions which are occuring would be highly desirable to further understand the capabilities of this technology. The work of this thesis was limited to specifically the effect of the water matrix upon reductive capabilities, however there is significant work that remains to be done, a few of which are listed below.

- A more detailed study on the mechanisms taking place through the use of optical spectroscopy. Unfortunately, this was not possible due to lack of equipment in this work. Optical emission would allow identification of excited species which would help to identify what is present and potentially what intermediate compounds are being generated from the process. Access to a higher power electrical system would also be beneficial in reducing treatment times.

- Different sources of oxidative species scavenging material could also be investigated. In this work volatile alcohols (methanol, ethanol), a sugar alcohol (d-sorbitol) and a sugar (sucrose) were tested. Other compounds of industrial relevance would be dyes, or potentially filtered/settled wastewater, which would be treating two potential problems with one solution.

- Expanding the current knowledge by considering other compounds. A large bulk of the current literature is considering other contaminants, such as pharmaceutical compounds, endocrine disruptors, pesticides and other potentially harmful compounds. These tests all occur in lab settings, and it is still largely unknown what the interactions would be with other real world species present in water such as phosphates, sulfates and even dissolved metal ions. Considering the impact of benign compounds on treatment and also by-product formation would be essential to the deployment of this technology.

- This thesis has focussed largely on attempting to reduce compounds using aqueous phase corona discharge because there has been a plethora of publications on oxidation of target contaminants. It would be interesting and highly valuable to investigate the performance on a mixed solution which contains contaminants which require oxidation to decrease in toxicity and others which require reduction, and determining treatment methods. This could be performed by sequentially changing types of gas flowing into the reactor via hollow electrodes or sequential chemical dosing of the test solution.

- Design of an optimized electrical discharge system which is capable of sub-microsecond pulses and high energy deposition. This would allow for a more efficient system for converting electrical energy into radical generation by minimizing joule heating. Some examples of this exist in literature already using different circuit topologies, such as magnetic pulse compression, semiconductor and gas-gap Marx generators and pulse forming networks. These systems still suffer from limitations and complications in dealing with reflected pulses when there is an impedance mismatch between the power supply and the water matrix, which would be variable in a practical application due to temperature and dissolved solids concentrations.

- Reactor design is another important factor. The area of effect for this treatment technology is limited to a region near the discharge zone, which makes scaling up problematic. There have been tests to change the reactor design such as coaxial flow through reactors, increasing the number of electrodes, and a porous ceramic electrodes have been considered. Given that treatment will likely require a residence time on the order of minutes, developing a proven method of scaling is necessary.

- Along with reactor design is determining a method to facilitate treatment in high conductivity brines. As the electrical conductivity of the solution rises, it becomes much more difficult to initiate breakdown and have significant radical generation due to the joule heating effect. One solution for this could be to use a porous, hollow electrode with significantly high gas flow to prevent the conductive water from interacting too closely with the solution, allowing for breakdown to occur within the gas and have the energized species propagate out for reactions in the bulk solution. Another possibility would be to have a gas electrode using gas flow through a capillary at high voltage outside of solution, and treat the surface of the water with an electrode outside of solution. The latter solution is a surface treatment, as opposed to a volume treatment, but requires significantly less energy and so a comparison of energy per volume treated would be interesting as well as the rates of reaction of the two systems.

Appendix A

Research to be submitted to Peer Reviewed Journal

A.1 Effect of Hydrodynamics and Geometry on Particle Transport in Saturated Fractures: Experimental and Simulation Results

Authors: S.P.L. Cianflone, V.Lakhian, S.E. Dickson

This work was submitted as part of Sean Cianflone's Ph.D. Thesis, though significant contributions were made by V. Lakhian. This work is in preparation to be submitted to Water Resources Research. Below is the abstract for this work, followed by a brief synopsis of the contributions made by V. Lakhian.

Abstract

An experiment to measure the transport of particles (0.046 μm and 0.55 μm microspheres) in randomly generated variable aperture fractures where variation only occurred in the xy-plane, not along the z-axis, were conducted. The fracture geometry was then used to computationally generate a fluid velocity field via the Navier-Stokes equations and optimize a random walk particle tracking (RWPT) algorithm that included hydrodynamic effects on transport, including the velocity field, shear, gravity, and diffusion. The experiments were used to optimize parameters in the RWPT model and the resulting simulations were analyzed for insight into the effects of hydrodynamics on particle transport. Results show that shear has a small but appreciable effect on the transport of particles causing an increase in dispersion. Shear represents less than 1% of the particle movement when compared to movement caused by fluid migration. Examination of fracture geometry showed that local narrowing of the fracture aperture field causes particles to shift the area of the fracture where transport occurs. More specifically, it was found that some pinch points can force particles into the center of the fracture thus eliminating any chance of collision with fracture walls, thereby 1) reducing the likelihood of retention due to adhesion to the fracture walls; and 2) increasing the mean particle velocity which results in a higher peak concentration of particles exiting the fracture. These effects depend on the local geometry and are not predictable from typical fracture characterization statistics alone (e.g. aperture mean, covariance, and correlation).

A.1.1 Synopsis of contribution

The overall experimental direction and motivation for this paper, the experimental design and construction was done in by S.P.L. Cianflone and V.Lakhian. The goal of this study

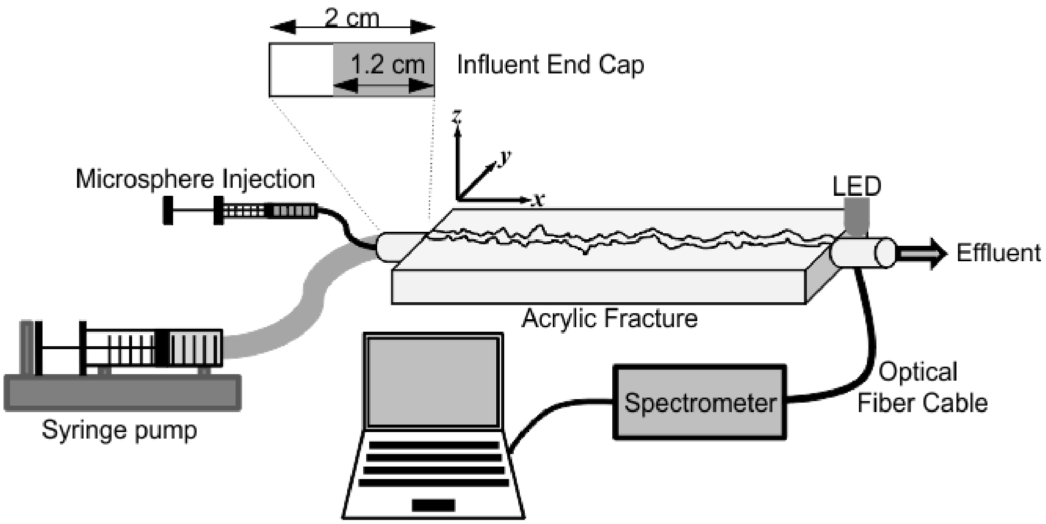

Figure A.1: Schematic of the experimental setup showing the PMMA fracture, microsphere injection site, and the optical fiber cable allowing for the measurement of microsphere concentrations using a spectrometer. Microsphere injection in the influent end cap is shown. The z axis of the fracture is invariant (aperture of 2.3 mm) in the sense that there is no aperture variation along this axis. The variation in the fracture is in the xy plane (the length of the fracture being measured along the x axis), thus producing a quasi-three dimensional fracture. (Reprinted from Cianflone, 2015 [1])

was to study how hydrodynamic forces caused by the flow field through the geometry of a simulated rock fracture affected the transport of particulate contaminants. This was done by establishing a real life model of a rock fracture as closely as possible. With an established computer model of the fracture, it was then laser cut into acrylic sheet to generate a 2.5 D fracture (variations in $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ with a fixed depth in $\hat{\mathbf{z}}$) with an accuracy on the order of 0.2 mm. The experimental apparatus consisted of this a syringe pump to provide flow to the rock fracture, the fracture itself and a detection mechanism. Detection of the contaminants consisted of coupling an LED and fiber optic Cable to monitor the outlet port of the rock fracture. This allowed real time detection of fluorescing microspheres which were used as the contaminants. A schematic of the experimental setup is shown in Fig. A.1 and is reprinted from the S.P.L. Cianflone's PhD Thesis.

References

[1] Sean Philip Leonard Cianflone. *Effects of Fracture Geometry on Contaminant Transport*. PhD thesis, McMaster University, nov 2015.