Degradation of Methylene Blue and 1, 4-Dioxane from Groundwater by Pulsed Discharge Non-Thermal Plasma Reactor

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DEGRADATION OF METHYLENE BLUE AND 1, 4-DIOXANE FROM GROUNDWATER
BY PULSED DISCHARGE NON-THERMAL PLASMA REACTOR

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ABSTRACT

Plasma generated by strong electric field has been studied for almost 100 years. The plasma-liquid system discharge presents new and interesting applications in the fields of environmental science, material processing and analytical chemistry. Extensive research has focused on exploring the potential application of plasma treatment of organic compounds in wastewater such as phenol, organic dyes, and TCE. The reactor electrode configurations ranges from point to point, point to plate and wire cylinder. Power supplies include DC, AC, pulsed, and microwave.

The goals of the present work were to explore the role of oxygen in a water-film plasma reactor for dye degradation and to combine this non-thermal gas-liquid plasma reactor (NTPR) with a bioreactor to treat 50ppm 1,4-dioxane in groundwater. Two types of power supply were used including an automobile ignition coil driven by DC power supply with a function generator and a nanosecond pulser. No significant additional degradation of methylene blue was detected by adding oxygen into the inlet gas compared to the pure argon case although significant ozone was produced and measured in the gas phase. This is explained by the short gas residence time and low rate of mass transfer preventing the generated ozone to transfer from gas phase into liquid phase as well as by the high reaction rate between OH radical and MB in comparison to the ozone reaction rate.

A 50ppm 1,4-dioxane synthetic media was pretreated in the NTPR at five different liquid flowrates (2,5,15,20mL/min). The combined scenario of using plasma treatment at 2ml/min and 1-month microorganism treatment was able to reduce dioxane to below 1μg/L and TOC to below 4 mg C/L

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Plasma

In nature, there are three common phases of matter including solid, liquid and gas. Each of these phases have unique characteristics which are listed in Table 1.1. However, the study of plasma as “the fourth state of matter” began around 100 years ago. Plasma is normally generated by providing energy (thermal heat, electric fields, electron beams) to a neutral gas causing the process of ionization. The ionization is the process by which an atom or a molecule gains a negative or positive charge by acquiring or losing electrons to form ions, usually in company with chemical changes [1]. Under the condition of high temperature and high pressure, electrons are stripped from orbit around the nucleus leaving a positively charged ion behind. The resulting mixture of neutral atoms, free electrons, and charged ions is called a plasma [2]. The most common method applied in generating plasma is by supplying a strong electric field which cause the process of electric breakdown. If the electric field is sufficiently high, the neutral gas can be switched from being a dielectric to a conducting gas due to the formation of charge carriers (positive charged ions and negative charged electrons). These charge carriers are accelerated by the electric field and collide with neutral atoms and molecules in the gas, which makes the field of gas discharge plasma applications widely expanded [3].

<table>
<thead>
<tr>
<th>Phases</th>
<th>Volume</th>
<th>Molecular forces</th>
<th>Fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid</td>
<td>fixed volume</td>
<td>strongest</td>
<td>no</td>
</tr>
<tr>
<td>Liquid</td>
<td>fixed volume</td>
<td>weak</td>
<td>yes</td>
</tr>
<tr>
<td>Gas</td>
<td>volume of container</td>
<td>very weak</td>
<td>yes</td>
</tr>
<tr>
<td>Plasma</td>
<td></td>
<td>electro-magnetic forces</td>
<td>yes</td>
</tr>
</tbody>
</table>

Although there are various sources of plasma, a general classification of plasma can be made based on: (i) the density of particles inside of plasma; (ii) the temperature of electrons [3].
However, a common classification is made between thermal equilibrium plasma and non-thermal equilibrium plasma (most of the laboratory generated plasmas). Precisely, all the species are at the same temperature (around 4000K-20000K) in thermal equilibrium plasma whereas average electron temperature is quite higher than heavier particles (atoms, ions, molecules) in non-thermal plasma [4].

1.2 Classification of Electric Discharge System

In general, different types of discharges can be classified by the electrode configuration and the phase distribution. Various electrode configurations that have been studied include point to plane, point to point, and wire cylinder geometry in gas, liquid, and gas-liquid systems [5]. The properties of plasma may also depend on the types of power supplies including DC, AC, pulsed, radiofrequency (RF), and microwave, and the electrode materials, gas composition, liquid properties (pH, conductivity and temperature). Generally, the types of discharge system can be classified into two categories: conventional gas phase plasma and plasma that interacts with a liquid [5].

1.2.1 Gas Phase Electrical Discharge

The origin of gas phase electrical discharge derived from the trial in which two electrodes are embedded in a glass cylinder filled with air and attached to a power supply. The applied voltage continuously accumulates under a high voltage electric field. At some critical value, the breakdown period occurs, which typically lasts from 0.01 to 100μs [6]. At breakdown the neutral gas switches from being non-conducting into conductive and generates a variety of plasma.
1.2.2 Plasma-Liquid System Discharge

Electrical discharge plasma generated in a gas phase in contact with liquid is very comparable with discharged plasmas formed directly in the pure gas phase. The general means for electrical discharge plasmas formed in a gas phase in contact with liquid are significantly different from plasmas generated directly in the liquid where both electrodes are submerged. Since the liquid density is $10^3$ times larger than the gas, the breakdown voltage at 1 atm is generally much less than that inside the liquid [5].

In most plasma-liquid systems, the discharge is generated in the gas phase where electrical breakdown takes place, consequently, the discharge interacts with the liquid surface. Consequently, the reactive species are quite distinct from those formed in gas phase plasma [7]. However, it is the presence of the liquid functioning as an electrode that causes the primary difference between gas-phase discharge and a discharge in gas phase over or in contact with liquid. It is the interactions between gas-phase-generated plasma and liquid that makes the system become an increasingly important topic.

Compared with gas phase electrical discharge, plasma-liquid system discharge presents new and interesting physics and chemistry and is becoming more and more important in the field of multidisciplinary applications such as environmental science, material processing and analytical chemistry [8]. The history of plasma-liquid system discharge is believed to date back to 1785. Around 40 years ago, the spotlight on plasma-liquid system discharge is glow discharge electrolytic action as well as the breakdown of dielectric liquids [8][10]. These studies presented the potential application of plasma-liquid interactions in the field of environmental remediation. Therefore, a series of environmental driven researches followed these studies and revealed the fact that plasma-liquid systems are rich sources of highly oxidant species including hydroxyl radical, hydrogen peroxide, UV radiation [9].
There are many reactors with various electrode configurations in plasma-liquid system. Nonetheless, these systems can be classified into three sorts (also see Figure 1): Direct discharge in liquids; Discharges in the gas phase over liquid; Discharge in gas phase.

![Figure 1.1 Classification scheme of plasma discharge: (A) Direct discharges in liquid. (B) Discharges in the gas phase over a liquid. (C) Gas phase generated plasma](image)

Increasingly investigations have been made to understand the plasma-liquid system and answer two main challenges in this field: (1) chemical interactions at the interface; (2) Environmental applications of plasma technology. Each of these topics is studied in different research fields [8].

### 1.3 Species Transport At The Interface

In the plasma-liquid system, chemical reactions commonly occur in the bulk liquid and gas phases, and at the interface accompanied with species transport [8]. For example, a very simple reaction:

\[
2 \cdot OH \rightarrow H_2O_2
\]  

(1.1)
can take place in the gas, liquid and at the interface by:

\[
2 \cdot OH_{(g)} + M \rightarrow H_2O_2_{(g)}
\]  

(1.2)
\[ 2 \cdot OH_{(aq)} \rightarrow H_2O_2_{(aq)} \]  
\[ 2 \cdot OH_{(int)} \rightarrow H_2O_2_{(int)} \]  

(1.3)  
(1.4)

The reaction occurring at the interface is also followed by species transport [8]

\[ H_2O_2_{(int)} \rightarrow H_2O_2_{(aq)} \]  

(1.5)

Various theories have been utilized to analyze the gas-liquid interface ranging from simple relationships such as Henry’s law (the limits of ideal gas solubility in liquid), Fick’s theory, and adsorption to kinetic processes, surface science and mechanical equilibrium [8]. Increasingly efforts have been made to incorporate the reaction and transport processes into computational simulation and compare the results with experimental data. For instance, the simulation is not consistent with experimental results in calculating the concentration of ozone, oxygen [8]. The gas phase free energy of these species is significantly higher than that in the liquid phase. Simulations predict the concentration difference between gas and bulk liquid phase. Whereas, for other species (i.e, hydroxyl radical, hydrogen peroxide), calculated free energy profile shows that they are more stable in the liquid phase [8].

1.4 Advanced Oxidation Processes

Groundwater quality and EPA’s drinking water regulations are leading to the need for the development of more efficient, innovative water treatment technologies. Conventional water treatment methods include bioremediation, chemical techniques, air stripping and activated carbon adsorption. More and more organic pollutants are non-biodegradable, in addition to the fact that bioremediation is a technique requiring long time frames for pollutant degradation, limits the potential application of this method. The disadvantage of air stripping is that it is only applicable to volatile organic compounds and has limitations due to the vapor-liquid equilibrium.
However, advanced oxidation processes (AOP’s) have been widely used in waste water treatment due to their advantages such as short reaction times, efficient degradation, non-selectively, and removal of toxic compounds. The primary mechanism of AOP’s is considered to be degradation through highly oxidative species, including common reagents (e.g. hydrogen peroxide and ozone), direct reactions with highly oxidative radicals (e.g. hydroxyl radical), UV irradiation, Fenton’s reaction, and non-thermal plasma. The advanced oxidation process by non-thermal plasma reactors is capable of producing highly reactive species such as hydroxyl radicals (•OH), hydrogen peroxide, and ozone. These species have strong oxidation potentials. It is required that oxidation potential should be 2.4V or higher in order to surpass the bonding energy of many organic compounds such as reflected in the energy of the bond in C-C [10]. Table 1.2 shows that hydroxyl radicals have the highest oxidation potential of most common and useful chemical oxidants (2.8V) [10]. AOPs generated by electrical discharge plasma have been widely studies in previous work including for the destruction of trichloroethylene [11], methyl tert-butyl ether [12], phenol degradation in a hybrid-series reactor [13], pulsed corona discharge for degradation of methylene blue [14], methylene blue degradation in flowing water film plasma reactor [6].

Table 1.2 Oxidation potential comparison among different species [10]

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxidation potential [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>2.80</td>
</tr>
<tr>
<td>O</td>
<td>2.42</td>
</tr>
<tr>
<td>O₃</td>
<td>2.07</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>1.78</td>
</tr>
<tr>
<td>HO₂</td>
<td>1.70</td>
</tr>
<tr>
<td>Cl₂</td>
<td>1.36</td>
</tr>
</tbody>
</table>
CHAPTER 2

EXPERIMENTAL MATERIALS AND METHODS

2.1 Power Supplies

The overall experimental setup and water film reactor configuration are depicted in Figure 2.1 and Figure 2.2, respectively. The power supply utilized in Methylene blue degradation experiment includes a DC power supply (BK Precision 1740B 0-60V, 0-4 A), a function generator (BK Precision 4010A, 2MHz ) and an automobile ignition coil. While the Nanosecond Pulser NSP-120-20 (Eagle Harbor Technologies Inc) was used in the experiments combing plasma and bioreactor to degrade dioxane in groundwater. The EHT low power series of nanosecond pulser NSP-120-20 is a completely integrated design, no external DC voltage input or pulse generator is required. It contains a DC power supply providing DC voltage for the nanosecond pulser, an energy capacitor, and a pulse charging circuit (control the charging energy and a pulse generating circuit). Compared with the ignition coil, the nanosecond pulser has several advantages: (1) the ability to treat solutions with a very high conductivity (up to 40 ms/cm), (2) the current and voltage waveforms measured with the oscilloscope aren’t as noisy as the system using ignition coil, and (3) the system is able to run for a longer treatment time (continuously up to two hours).

2.2 Reactor Configuration

As the overall experimental setup depicted in Figure 2.1, the liquid solution (deionized water, methylene blue or dioxane synthetic media) was introduced to the system with a reciprocating pump. Argon and oxygen were set to pressures of 60 psi, 80 psi, respectively. Both gas and liquid phases met at the mixing zone (Swagelok® T-joint). The high pressure mixture of gas and liquid was then introduced into the enclosed cylindrical discharge reactor. The power supply delivered a pulsed DC voltage at the top nozzle. Two stainless capillary tubes served as the inlet and outlet to the discharge region, and they also functioned as the anode and cathode for the
discharge. The discharge voltage was measured with a high-voltage probe (Tektronix P6014A, 1/1000) connected to the electrodes.

The combination of a flowing gas region with a flowing liquid film is a key feature of the plasma reactor used in this study. As Figure 2.2 depicted, the plasma discharge propagated along the interface between the two phases, and some of the products formed near the plasma channel immediately dissolve into the liquid film [15]. The inlet stainless nozzle has an inner diameter of 0.5 mm and the diameter of cylindrical discharge region is 3 mm. A well-mixed radial spray was emitted from the inlet capillary and enters the reactor chamber [15]. This spray rapidly contacted the reactor wall, and separated into a liquid film region along the reactor wall with a high velocity gas flow region in the center of the reactor. The inlet and outlet nozzles were positioned to give a 4-mm gap between the top and bottom nozzles [15].
2.3 Chemicals and Analysis

All chemicals and reagents have been utilized are obtained from manufacturer. The major feed chemicals are 0.1mM methylene blue with a liquid conductivity of 187μs/cm, 50ppm dioxane synthetic media (Ω=600μs/cm) and deionized water with a conductivity less than 5μs/cm. Hydrogen peroxide, sodium persulfate, phosphoric acid, potassium hydrogen phthalate and indigo reagent (Ω=150μs/cm) were also used as reagents. For Total Organic Carbon (TOC) measurements, sodium persulfate, phosphoric acid and potassium hydrogen phthalate were used as oxidizer, acid and total carbon standard solutions. To prepare the oxidizer, 60g of sodium persulfate and 15ml of phosphoric acid (85%) were dissolved in purified water, and brought to the total volume of 500ml. The persulfate solution was refrigerated for 24 hours before use. 100ml of phosphoric acid (85%) was mixed with purified water, brought to the total volume of 500ml and used as acid. The phosphoric acid solution is stable for around one month when stored in the refrigerator. 2.125g of
reagent grade potassium hydrogen phthalate was accurately weighed and then dried at 105-120°C for about one hour and cooled in a desiccator. Finally, the reagent was transferred to a 1L volumetric flask and dissolved in zero water. The carbon concentration of the solution corresponds to 1000mg C/L [16, 17]. The indigo stock solution was made following the standard procedures (4500-O₃). 500ml of distilled water and 1ml of concentrated phosphoric acid were added to a 1L volumetric flask. With stirring, 770 mg potassium indigo trisulfonate C₁₆H₇N₂O₁₁S₃K₃ was added into the flask. Then the flask was filled to the indicator mark with distilled water. The 1:100 dilution indigo stock solution exhibits an absorbance of 0.2 cm at 600nm [17]. 40ml indigo stock solution, 10g sodium dihydrogen phosphate and 7ml concentrated phosphoric acid was added into a 1-L volumetric flask to prepare the indigo reagent [17, 18]. The synthetic bacterial growth media used in this study for the dioxane experiments was obtained by modifying nitrate mineral solution [19]. The components of one liter of modified growth media are listed in Table 2.2 (Appendix A.1). The following stock solutions (Appendix A.2) were added to the 1000mL volumetric flasks and diluted to 1L with DI water.

2.3.1 Colorimetric Technique for Hydrogen Peroxide and MB Measurement

According to Lambert-Beer law, the concentration of hydrogen peroxide and MB were determined by measuring the absorbance using a UV/Vis spectrometer (Perkin Elmer Lambda 35). 1mL Titanium oxy-sulfate (TiOSO₄) was added into the test tube to measure hydrogen peroxide. Though hydrogen peroxide doesn’t exhibit an absorbance, it reacts with Ti⁴⁺ (equation 2.1) and exhibits a yellow tint at 410nm wavelength. A calibration curve for hydrogen peroxide was made between absorbance and H₂O₂ concentration, which yield a slope of 2.1661. Equation (2.2) was used to
calculate the concentration of species being analyzed. The wavelength for MB and hydrogen peroxide won’t interfere with each other [18]. An absorption peak for MB was observed near 660nm. Another calibration curve (figure 2.3) was developed by correlating the absorbance at the apparent wavelength with the known concentration of MB.

\[
\text{Ti}^{4+} + H_2O_2 + 2H_2O \rightarrow TiO_2H_2O_2 + 4H^+ \tag{2.1}
\]

\[
C_i = A \times D_f \times K_c \tag{2.2}
\]

\(A\) is the absorbance observed from UV/Vis, \(D_f\) is dilution factor, and \(K_c\) is the slope of calibration curve (2.1661 for hydrogen peroxide, 0.0139 for MB).

### 2.3.2 Ozone Measurement

Standard Indigo colorimetric method (4500-O_3) was used to measure ozone concentration in effluent gas products. In acidic solution, ozone rapidly decolorized indigo. The interferences resulting from hydrogen peroxide and organic oxidant were negligible since the reaction between \(H_2O_2\) and indigo is very slow. The decrease in absorbance is linear with increasing concentration of ozone. The absorption peak for indigo reagent is near 600nm. Equation 2.3 was used to calculate the ozone concentration [18].

\[
O_3 \left[ \frac{mg}{L} \right] = \frac{100 \times \Delta A}{f \times b \times V} \tag{2.3}
\]

Where \(\Delta A\) is the difference in absorbance between the sample and the blank, \(b\) is the path length of the cell in centimeters, \(V\) is volume of sample in mL, \(f\) is a sensitivity factor which equals to 0.42. Two gas washing bottles in series were prepared to measure the decolorization of indigo reagent. The first gas washing bottle contained 250mL indigo reagent while the second contained 25mL [20].
The effluent gases were bubbled through two gas washing bottles for three minutes in total. Ozone reacts with the indigo reagent causing decoloration. The absorbance of the indigo reagent in both bottles were measured at 600nm and compared to that of the original indigo solution at the same wavelength. Total ozone concentration was obtained by adding the ozone concentration in both bottles. It should be noted that the reaction time depends on the concentration of ozone. As the indigo reagent is consumed by the reaction with ozone, the concentration decreases, and the possibility that ozone escapes the gas washing bottle without reacting with indigo increases [20]. Accordingly, the longer the amount of time that the indigo reagent is treated by the effluent gas, the less accurate results would be [20].

![Figure 2.3 Calibration curve for methylene blue](image)

\[
y = 0.0139x + 0.0004 \\
R^2 = 0.9982
\]
2.3.3 Gas Chromatograph-Mass Spectrum for Dioxane

1,4-dioxane was analyzed by gas chromatography (Hewlett-Packard GC 5890 series II) coupled with mass spectrometry (GC/MS). 75µm carboxen-polydimethylsiloxane (CAR/PDMS) and 100 µm polydimethylsiloxane (PDMS) fibers (Supelco, Bellefonte, USA) were used for extracting 1,4-dioxane. 1 mL of standard or sample was transferred to a 20-mL vial that contained 9 mL deionized water. 1,4-dioxane-d8 was also added as internal standard. The vial was then sealed and the solution was magnetically stirred (400 rpm) at 65°C, with the fiber immersed in the solution for 20 min. After extraction, the fiber was thermally desorbed for 5 min at the injector (225°C). The initial oven temperature (40°C) was maintained for 2 min, then increased (15°C/min) to 225°C and held for 3 min. The detector temperature was 280°C.

2.3.4 Total Organic Carbon (TOC) Analysis

Total organic carbon (TOC) of species (MB, dioxane) was measured with a TOC analyzer (Shimadzu TOC-Vws; Kyoto, Japan) in order to quantify the amount of species (MB, dioxane) that were fully degraded to complete mineralized products (e.g., carbonates). In the TOC-Vws analyzer, the carrier gas (nitrogen) flows through the TC (total carbon) reactor at a 200mL/min flowrate. The TC reactor consists of a UV lamp and a heater. Mixtures of analyzing sample and oxidizing reagent were injected into the TC reactor (heated up to 80°C), where the sample was totally mineralized to carbon dioxide. This carbon dioxide was swept via the carrier gas from reactor to the cell of a non-dispersive infrared detector (NDIR), where the CO₂ was detected. The detection signal of the NDIR forms a peak. And the integrated area under the peak signal can be correlated to the concentration of carbon. The IC reactor detects the amount of inorganic carbon including carbonates, hydrogen carbonates and dissolved carbon dioxide using an acidic solution.
which converts all of the inorganic carbon to dissolved carbon dioxide. All the carbonates produce carbon dioxide according to the following reaction [16]

\[
Me_2CO_3 + H_3PO_4 \rightarrow CO_2(g) + 2MeCl + H_2O
\]

\[
MeHCO_3 + H_3PO_4 \rightarrow CO_2(g) + MeCl + H_2O
\]

It should be noted that TOC employs two methods for TOC analysis: TC-IC method, NPOC (non-purgeable organic carbon analysis). For these experiments, the NPOC method was used to measure the total organic carbon since sample contains non-volatile organic substances. The NPOC is a two-steps method. All the inorganic carbon was purged off from sample in IC reactor at first step. The remaining solution was then take to the TC reactor and reacted with oxidizing reagent to from carbon dioxide. Based on the assumption that all of the carbon left after the acidification process is organic the total organic carbon equals to the signal detected from NDIR.
CHAPTER 3

OZONE PRODUCTION EXPERIMENTS

Many studies have proved that adding oxygen into gas mixture is benefit for degrading dyes because of the generation of ozone as a strong oxidizer (equation 3.4-3.7). For example, the degradation efficiency of AO7 by pulsed high-voltage hybrid gas-liquid discharge with different bubbling gases increased in the order: nitrogen < argon < oxygen [21]. Methylene blue is one of the well-investigated dyes in the field of organic compound degradation by plasma treatment due to its concentration is easy to be measured by UV-Vis. The influence of the gas introduced on MB degradation was studied. For the same amount of input power, percentage of MB degradation were 40% in the air, 60% in the argon and over 90% in oxygen after 10 minutes treatment [14]. The lowest MB degradation in air resulted from a part of input energy was lost by the dissociation of nitrogen. However, hydroxyl radical can be generated by dissociation of water by excited argon atoms if argon is introduced [14]. In order to improve MB degradation and explore the role of oxygen in the water-film plasma reactor, different percentage of oxygen was added into argon as a gas mixture introduced.

Key reactions in non-thermal plasma reactor include the following [6, 14]:

Dissociation of water: \[ H_2O + e^- \rightarrow H \cdot + OH \cdot + e^- \] (3.1)
Hydrogen peroxide generation: \[ OH \cdot + OH \cdot \rightarrow H_2O_2 \] (3.2)
Decomposition of hydrogen peroxide: \[ OH \cdot + H_2O_2 \rightarrow HO_2 \cdot + H_2O \] (3.3)
Oxygen dissociation: \[ O_2 + e^- \rightarrow O \cdot + O \cdot + e^- \] (3.4)
Ozone formation: \[ O_2 + O \cdot \rightarrow O_3 \] (3.5)
Oxygen dissociation by \( \cdot O \): \[ O_2 + 2O \cdot + e^- \rightarrow 2O_2^* + e^- \] (3.6)
Oxygen dissociation: \[ O_2 + O_2^* \rightarrow O_3 + O \] (3.7)
MB decoloration: \[ C_{16}H_{18}ClN_3S + OH \cdot \rightarrow C_{16}H_{18}ClN_3S^+ - OH + Cl^- \] (3.8)

MB fully mineralized by -OH:
\[ C_{16}H_{18}ClN_3S + 51OH \cdot \rightarrow 16CO_2(g) + H_2SO_4 + 3HNO_3 + HCl \] (3.9)

MB degradation by ozone:
\[ C_{16}H_{18}ClN_3S + O_3 \rightarrow \text{Products} \] (3.10)

3.1 Ozone Generation and MB Degradation

High pressure mixture of gas (argon set at 60 psi, oxygen set at 80 psi) and liquid meet at the mixing zone (Swagelok® T-joint) and then are introduced into the enclosed cylindrical discharge reactor. A DC power supply (BK Precision 1740B 0-60V, 0-4 A) and a function generator (BK Precision 4010A, 2MHz) were used to drive the automobile ignition coil and generated high-voltage pulse. The conditions remained constant during the experiment (Table 3.1).

<table>
<thead>
<tr>
<th>Power Parameters</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Voltage</td>
<td>14</td>
<td>V</td>
</tr>
<tr>
<td>Frequency</td>
<td>500</td>
<td>Hz</td>
</tr>
<tr>
<td>Duty Cycle</td>
<td>40</td>
<td>%</td>
</tr>
</tbody>
</table>

In these experiments, the initial concentration of MB (figure 3.1) was 0.1mM at 2.0mL/min liquid flow rate. The original MB solution pH was 6.67 before being treated by non-thermal plasma reactor. Figure 3.2 shows that the liquid pH decreased after plasma treatment due to the formation of acids. Inlet oxygen concentration didn’t affect the formation of acidic substances because the pH of solution did not change with the different percentages of oxygen in the inlet gas. Figure 3.3 shows the effluent liquid conductivity increased from 187µs/cm to 500µs/cm after plasma
treatment in pure argon suggesting the generation of mineralized MB products which contributed to total liquid conductivity.

![Chemical structure of methylene blue](image)

**Figure 3.1 Chemical structure of methylene blue[6].**

![Graph showing pH response](image)

**Figure 3.2 Effluent liquid pH response to increasing O2 in the inlet gas phase for 0.1mM MB (initial conductivity=187µs/cm), the gas flow rate is 0.59L/min, liquid flow rate is 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, inlet nozzle diameter=0.01 inch.**

Effluent liquid conductivity decreased to 400 µs/cm and began to level off as the oxygen was introduced to the gas mixture suggesting mineralized MB products reacted with oxygen or ozone.
Figure 3.4 shows that ozone was generated when introducing oxygen into gas mixture. The concentration of ozone in the effluent gas was measured by Standard Indigo colorimetric method (4500-O$_3$). It can be seen that introducing MB into DI water has a dramatic effect on ozone production rate. This can be explained by the change in liquid conductivity. In order to determine the effect of feed conductivity on ozone generation, a KCL solution which has the same conductivity as the solution of 0.1mM MB was used as the liquid phase. Figure 3.4 indicates that the addition of MB affects ozone generation in a manner similar to that of added salt.

Figure 3.3 Effluent liquid conductivity response to increasing O$_2$ in the inlet gas phase for 0.1mM MB (initial conductivity=187µs/cm), the gas flow rate is 0.59L/min, liquid flow rate is 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, inlet nozzle diameter=0.01 inch.

The maximum ozone production rate in the case of using 0.1 mM MB or KCL solution was 0.005 µmol/s (Figure 3.5), which was about 20 times less than that in DI water. The concentration of H$_2$O$_2$ was also measured at different percentages of oxygen for the cases of a) DI water, b) 0.1mM MB and c) KCL solution with the same initial conductivity with 0.1mM MB.
Figure 3.4 Ozone production rate response to increasing O₂ in the inlet gas phase for DI water, 0.1mM MB (Ω=187µs/cm) and KCL solution (Ω=190µs/cm), the gas flow rate is 0.59L/min, liquid flow rate is 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, inlet nozzle diameter=0.01 inch.

Figure 3.5 Ozone production rate response to increasing O₂ in the inlet gas phase for 0.1mM MB (Ω=187µs/cm) and KCL solution (Ω=190µs/cm), the gas flow rate is 0.59L/min, liquid flow rate is 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, inlet nozzle diameter=0.01 inch.
Figure 3.6 H$_2$O$_2$ production rate response to increasing O$_2$ in the inlet gas phase for DI water, 0.1mM MB (Ω=187µs/cm) and KCL solution (Ω=190µs/cm) at 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, the gas flow rate is 0.59L/min, liquid flow rate is 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, inlet nozzle diameter=0.01 inch.

Figure 3.6 indicates that conductivity also has a dramatic effect on hydrogen peroxide production rate. The higher the liquid conductivity, the lower the H$_2$O$_2$ production rate. The H$_2$O$_2$ production rate decreases with increasing oxygen concentration in the gas mixture and levels off at high O$_2$ concentration. Small amounts of oxygen added into the gas mixture will change the properties of plasma. For example, previous work found that plasma temperature increased dramatically when oxygen was added into the system[6]. Despite the low production rate of ozone in the case of using MB in the liquid phase, 0.1mM MB decoloration percentage was measured at different oxygen concentrations in order to explore the role of oxygen.
The percentage decoloration of MB is shown in Figure 3.7. While the MB decoloration was approximately 95% with pure argon carrier gas, there was no significant additional decoloration detected after adding oxygen into system even though ozone is formed when oxygen is added. Three possible hypotheses were made to explain this problem: Firstly, MB is more susceptible to hydroxyl radical reactions which makes the reaction between MB and ozone not competitive as MB with hydroxyl radical. Secondly, it is possible that ozone favors the reaction with MB mineralized products which makes the generated ozone oxidized intermediates rather than MB. Thirdly, the residence time of gas is too short (2.7 ms) to allow the generated ozone to transfer from the gas phase into liquid phase. In this case, most of ozone formed in the gas phase dissipated in the effluent gas. To test the first hypothesis, indigo dye (more likely to react with ozone) was added to the liquid phase. Figure 3.8 shows that the addition of oxygen into the gas mixture doesn’t significantly affect the indigo dye decoloration. However, this result can only prove the validity of first hypothesis after testing the third hypothesis. If the mass transfer of ozone from gas phase into
liquid phase is too small, the reaction between ozone and indigo dye would be limited even indigo is more likely to react with ozone.

Figure 3.8 Indigo dye decoloration response to increasing O$_2$ concentration in the inlet gas phase the gas flow rate is 0.59L/min, liquid flow rate is 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, inlet nozzle diameter=0.01 inch.

Figure 3.9 1mM MB TOC removal% response of oxygen concentration, the gas flow rate is 0.59L/min, liquid flow rate is 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40% inlet nozzle diameter=0.01 inch.
The validity of the second hypothesis was tested by measuring total organic carbon. If plasma treatment is capable of decomposing MB into fully-mineralized products CO₂, TOC can be used as an indication of the extent of reaction between ozone and intermediates. TOC% removal is 40% with pure argon gas. The majority of TOC removal resulted from MB degradation. Hydroxyl radical attack MB molecule and destroy the chromophores. The addition of oxygen doesn’t have an effect on TOC removal. The data indicates that second hypothesis isn’t correct either.

3.2 Estimated Calculation of Liquid Ozone Concentration

The validity of the third hypothesis was tested by calculation. Figure 3.10 shows the simplified diagram of ozone transfer. \( P_G \) and \( P_i \) represent ozone partial pressure in bulk gas phase and at interface, \( C_i \) and \( C_L \) represent ozone concentration at interface and bulk liquid phase, \( \delta_G \) and \( \delta_L \) are the thickness of gas and liquid film. OH radical and MB, indigo reagent reactions have very fast reaction rates. Reactions in both the bulk and film are much faster than mass transfer in the film so that substrate is depleted in the film before reacting with bulk, while ozone reaction happen in the bulk liquid phase. The reaction between ozone and MB are liquid phase homogeneous reaction. Interphase area is another difference. In OH mass transfer case, the interface is plasma-liquid interphase since most OH is generated in plasma and transfer to liquid phase. However, the interface is gas-liquid interphase in ozone mass transfer case since ozone is generated in gas phase and transfer to liquid phase. Assuming all reactions of MB (initial concentration is 0.1mM) are due to hydroxyl radicals for the case with pure argon. As Table 3.4 shows, the effluent MB concentration was 0.008mM. Then 0.092mM of MB was decolored. At 2 mL/min liquid flowrate, this gives \( 3 \times 10^{-9} \) moles/s MB reacted. Assuming one mole of OH to one mole of MB (Equation 3.8), then at least \( 3 \times 10^{-9} \) moles/s of hydroxyl radical should come across from the plasma to the liquid to react with MB(equation 3.11).
It is worth noting that this is a lower limit of OH formation since some TOC was also degraded and hydrogen peroxide formed (equation 3.2).

OH molar flow:

\[
\text{OH molar flow} = \left(\frac{0.008 - 0.092}{1000}\right) \times \frac{mol}{L} \times \frac{2\text{mL}}{min} \times \frac{L}{1000\text{mL}} \times \frac{min}{60s} = 3 \times 10^{-9} \frac{mol}{s} \quad (3.11)
\]

Maximum ozone concentration in the liquid phase was calculated by Henry’s law. As figure 3.10 shows, the gas phase is assumed to be well-mixed. So ozone concentration in the gas phase equals to the effluent ozone concentration $0.05 \times 10^{-6} M$ (table 3.4) when the inlet oxygen concentration equals to 41%. Since the effluent gas phase ozone concentration was known in table 3.4, the partial pressure of ozone can be calculated by equation 3.12:

\[
P_{O_3} = \frac{C_{g,O_3}}{C_{ig}} \times 1\text{atm} = 1.25 \times 10^{-6} \text{atm} \quad (3.12)
\]
Where $C^{lg} = 0.04M$ represents the concentration of ideal gas at standard pressure and temperature. Once the partial pressure of ozone is calculated, dissolved ozone concentration in equilibrium with gas phase ozone can be calculated by equation 3.13:

$$C^*_{O_3}(l) = \frac{P_{O_3}}{H} \times C^l_{H_2O} = 1.7 \times 10^{-8} \text{mole/L}$$ (3.13)

The liquid is assumed to be a dilute solution, dissolved ozone concentration equals to the mole fraction of ozone times the molarity of water $C^l_{H_2O} = 55M$. The reaction between ozone and MB is a liquid phase homogeneous reaction. The reaction rate is calculated by equation 3.14:

$$r_2 = k_2[MB][O_3]_{0.5} = 1.4 \times 10^{-4} \frac{M}{S}$$ (3.14)

The reaction constant $k_2$ is $1.34 \times 10^5 \text{ L/mole/S}$ (Table 3.4). Ozone molar flow is calculated by multiplying liquid volume (table 3.8) and reaction rate.

Ozone molar flow (without mass transfer resistance): $r_2 \times V_l = 9.5 \times 10^{-11} \text{mol}$ (3.15)

Again, equation 3.15 gives the maximum ozone molar flow without considering mass transfer resistance. Comparing the molar flow of OH and ozone, the molar flow of hydroxyl radical is 32 times larger than ozone molar flow. If considering ozone mass transfer resistance, ozone molar flow is calculated by equation 3.16:

$$k_c \times A \times \left( C^g_{O_3} \times R \times \frac{T}{H} \times 55 - 0 \right) = 7.6 \times 10^{-14} \text{mole/s}$$ (3.16)

$k_c = 0.013 \text{cm/s}$ represents the ozone mass transfer coefficient. This value is derived from ethanol experiments [6]. $A$ represents the gas-liquid interface area (Table 3.6). In this case, the molar flow of hydroxyl radical is 40119 times larger than ozone molar flow. We assume that the reaction rate is proportional to species molar flow rates. Then the relative reaction ratio between
(OH+MB) and (O₃+MB) without considering mass transfer resistance is 32. The relative reaction ratio between (OH+MB) and (O₃+MB) with mass transfer resistance is 40119.

We can apply the same procedure to the indigo reagent reaction. Table 3.5 shows the effluent gas phase ozone concentration and the effluent indigo concentrations response to increasing O₂ in the inlet gas phase for 0.0389mM indigo. The effluent indigo concentration was 0.0304mM. Then 0.0085mM of indigo was decolored. At 0.5 mL/min liquid flowrate, this gives 6.3x10⁻¹¹ moles/s indigo reacted. Assuming one mole of OH to one mole indigo (second order reaction), then at least 6.3x10⁻¹¹ moles/s of hydroxyl radical should come across from the plasma to the liquid to react with indigo (equation 3.17).

\[
\text{OH molar flow: } \frac{(0.0389-0.0304)}{1000} \frac{mol}{L} \times \frac{0.5mL}{min} \times \frac{L}{1000mL} \times \frac{min}{60s} = 6.3 \times 10^{-11} \text{mol/s}
\] (3.17)

Ozone partial pressure is calculated by equation 3.18:

\[
P_{O_3} = \frac{c^g_{O_3}}{c^{i,g}} \times 1 \text{atm} = 0.5 \times 10^{-6} \text{atm}
\] (3.18)

Dissolved ozone concentration in equilibrium with gas phase ozone equals to:

\[
C^*_O_3(l) = \frac{P_{O_3}}{H} \times C^i_{H_2O} = 6.8 \times 10^{-9} \frac{\text{mole}}{L}
\] (3.19)

Ozone reaction rate with indigo dye is calculated by equation 3.20 as following:

\[
r_3 = k_4[indigo][O_3] = 2.09 \times 10^{-6} M/\text{S}
\] (3.20)

The reaction rate constant \(k_4\) is 10⁷ L/mole/S (Table 3.2). Effluent ozone concentration, 0.02 × 10⁻⁶ M, and effluent indigo concentration, 0.0304 × 10⁻³ M, are shown in Table 3.5. Ozone molar flow is calculated by multiplying liquid volume (at 0.5mL/min liquid flowrate) and reaction rate \(r_3\) (equation 3.21).

\[
\text{Ozone molar flow: } r_3 \times V_l = 3.56 \times 10^{-12} \text{mol/s}
\] (3.21)

Again, equation 3.21 gives the maximum ozone molar flow without considering mass transfer resistance. Comparing the molar flow of OH and ozone, the molar flow of hydroxyl radical is 18
times larger than ozone molar flow. If considering ozone mass transfer resistance, ozone molar flow is calculated by equation 3.22:

\[ k_c \times A \times \left( C_{O_3}^g \times R \times \frac{T}{H} \times 55 - 0 \right) = 3.58 \times 10^{-14} \frac{\text{mole}}{s} \]  

(3.22)

In this case, the molar flow of hydroxyl radical is 1768 times larger than ozone molar flow.

Assuming that the reaction rate is proportional to species molar flow rates then the relative reaction ratio between (OH+indigo) and (O3+indigo) without considering mass transfer resistance is 18.

The relative reaction ratio between (OH+indigo) and (O3+indigo) with mass transfer resistance is 1768.

<table>
<thead>
<tr>
<th>Table 3.2 Rate constants</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid-phase Reaction</strong></td>
</tr>
<tr>
<td>MB + •OH ( \rightarrow ) products</td>
</tr>
<tr>
<td>MB + O(_3) ( \rightarrow ) products</td>
</tr>
<tr>
<td>indigo + •OH ( \rightarrow ) products</td>
</tr>
<tr>
<td>indigo + O(_3) ( \rightarrow ) products</td>
</tr>
</tbody>
</table>

Table 3.3 Ozone production rate response to increasing O2 in the inlet gas phase for DI water, the gas flow rate is 0.59L/min, liquid flow rate is 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, inlet nozzle diameter=0.01 inch

<table>
<thead>
<tr>
<th>percentage of oxygen%</th>
<th>0</th>
<th>4.75</th>
<th>11.51</th>
<th>19.89</th>
<th>29.89</th>
<th>41.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas phase ozone production rate/μmol/s</td>
<td>0</td>
<td>0.0050</td>
<td>0.0070</td>
<td>0.0090</td>
<td>0.0102</td>
<td>0.0110</td>
</tr>
<tr>
<td>gas phase ozone concentration/μmol/L</td>
<td>0</td>
<td>0.5495</td>
<td>0.6870</td>
<td>0.9348</td>
<td>1.0398</td>
<td>1.1248</td>
</tr>
</tbody>
</table>

Table 3.4 Ozone production rate, effluent MB and H2O2 concentrations response to increasing O2 in the inlet gas phase for 0.1mM MB, the gas flow rate is 0.59L/min, liquid flow rate is 2mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, inlet nozzle diameter=0.01 inch

<table>
<thead>
<tr>
<th>percentage of oxygen%</th>
<th>0</th>
<th>4.748</th>
<th>11.507</th>
<th>19.886</th>
<th>29.885</th>
<th>41.504</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas phase ozone production rate/μmol/s</td>
<td>0</td>
<td>0.00019</td>
<td>0.00021</td>
<td>0.00038</td>
<td>0.00040</td>
<td>0.00049</td>
</tr>
<tr>
<td>gas phase ozone concentration/μmol/L</td>
<td>0</td>
<td>0.019</td>
<td>0.02175</td>
<td>0.03918</td>
<td>0.04047</td>
<td>0.04969</td>
</tr>
<tr>
<td>effluent MB concentration/mM</td>
<td>0.0083</td>
<td>0.006</td>
<td>0.0073</td>
<td>0.0058</td>
<td>0.0075</td>
<td>0.007</td>
</tr>
<tr>
<td>H2O2 concentration/mM</td>
<td>1.37</td>
<td>0.23</td>
<td>0.10</td>
<td>0.11</td>
<td>0.05</td>
<td>0.41</td>
</tr>
</tbody>
</table>
The reaction rate between MB and hydroxyl radical is 32 times higher than that between MB and dissolved ozone. While the reaction rate between indigo and hydroxyl radical is 18 times higher than that between indigo and dissolved ozone.

Table 3.5 Ozone concentration, effluent indigo concentrations response to increasing O2 in the inlet gas phase for 0.0389mM indigo, the gas flow rate is 0.59L/min, liquid flow rate is 0.5mL/min, input voltage=14V, frequency =500Hz, duty cycle=40%, inlet nozzle diameter=0.01 inch

<table>
<thead>
<tr>
<th>Percentage of oxygen%</th>
<th>0</th>
<th>4.748</th>
<th>11.507</th>
<th>19.886</th>
<th>29.885</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas phase ozone concentration/µmol/L</td>
<td>0</td>
<td>0.013</td>
<td>0.014</td>
<td>0.019</td>
<td>0.02</td>
</tr>
<tr>
<td>effluent indigo concentration/mM</td>
<td>0.0305</td>
<td>0.03005</td>
<td>0.0321</td>
<td>0.035</td>
<td>0.0304</td>
</tr>
</tbody>
</table>

Table 3.6 Determination of gas and liquid residence times at different liquid flow rates, inlet nozzle diameter=0.01 inch, argon pressure set at 60 psi [24]

<table>
<thead>
<tr>
<th>Liquid flow rate (mL/min)</th>
<th>Average argon flowrate (L/min)</th>
<th>Average area of interface (mm²)</th>
<th>Volume of gas (mm³)</th>
<th>Volume of liquid (mm³)</th>
<th>Liquid residence time (s)</th>
<th>Gas residence time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.90</td>
<td>40.54</td>
<td>26.57</td>
<td>1.7</td>
<td>0.20</td>
<td>0.00177</td>
</tr>
<tr>
<td>2.5</td>
<td>0.49</td>
<td>37.3</td>
<td>22.37</td>
<td>5.9</td>
<td>0.14</td>
<td>0.00272</td>
</tr>
<tr>
<td>4.5</td>
<td>0.27</td>
<td>32.66</td>
<td>17.61</td>
<td>10.66</td>
<td>0.14</td>
<td>0.00390</td>
</tr>
<tr>
<td>6.5</td>
<td>0.18</td>
<td>30.5</td>
<td>15.48</td>
<td>12.79</td>
<td>0.12</td>
<td>0.00521</td>
</tr>
</tbody>
</table>

In both case, OH radicals play a more significant role in decolorizing the organic compounds. This explains the reason that no significant additional degradation was detected after adding oxygen into the system. Indigo estimation proves that first hypothesis isn’t correct either. Although indigo is more likely to react with ozone compared with MB, the OH radical attack is fast and dominant in terms of organic compounds degradation. This simple estimate proved the validity of the third hypothesis.
CHAPTER 4

ANALYSIS OF THE PROCESS OF COMBINING PLASMA AND BIOREACTOR FOR 1,4-DIOXANE DEGRADATION

4.1 1,4-Dioxane Factsheet

1,4-dioxane (C₄H₈O₂) is classified as an ether. It is widely used as a stabilizer for chlorinated solvents, especially for trichloroethane (TCA) to prevent chlorinated solvents from being degraded [25]. The mixture of 1,4-dioxane and chlorinated solvents are used in industries for vapor degreasing of metal parts. Besides its massive use as a solvent stabilizer, 1,4-dioxane can also be used as a wetting and dispersing agent in textile industry.

1,4-Dioxane is highly unstable at high temperature and highly flammable. It is a colorless heterocyclic organic compound with a faint pleasant odor (Figure 4.1). The physical and chemical properties of 1,4-dioxane are summarized in Table 4.1. Contradictory to that 1,4-dioxane is highly unstable at high temperature and highly flammable, it is very resistant in natural waters which will be further explained in following chapters.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>88.11</td>
</tr>
<tr>
<td>Water Solubility</td>
<td>Miscible</td>
</tr>
<tr>
<td>Boiling point (°C) at 1 atm</td>
<td>101.2</td>
</tr>
<tr>
<td>Vapor pressure at 25 °C</td>
<td>38.1</td>
</tr>
<tr>
<td>Octanol-water partition coefficient (log K_{ow})</td>
<td>-0.27</td>
</tr>
<tr>
<td>Organic carbon partition coefficient (log K_{oc})</td>
<td>1.23</td>
</tr>
<tr>
<td>Henry’s law constant at 25°C</td>
<td>4.8×10⁻⁶</td>
</tr>
</tbody>
</table>
4.2 Environmental Impacts of 1,4-Dioxane

Dioxane may be released to air, water and soil during its production, the processing of other chemicals and its use as a stabilizer [27]. The distinct chemical properties (e.g. high water solubility and low sorption) makes it quickly dissolve into groundwater and stick to soil particles, therefore giving the contaminant an easy route to groundwater. On the other hand, the Henry’s law constant of dioxane is quite low, which makes it volatilize at a moderate rate from water and soil surface. There were around 57 metric tons of 1,4-dioxane released from manufacturing facilities to atmosphere; 26 metric tons of 1,4-dioxane to surface water; and less than 1 metric tons to soils in 2007[27].

4.3 Health Effects of 1,4-Dioxane

Common routes of exposure include inhalation, ingestion of contaminated food and water, as well as dermal contact [26]. 1,4-dioxane toxicity tests were done on lab rats by feeding them with contaminated water. The results indicated 1,4-dioxane can lead to damage even failure of liver and kidneys. Meanwhile, lab rats were exposed to 1,4-dioxane via inhalation to analyze carcinogenic effects. Cancer were detected in nasal and abdominal cavities. Besides, benign tumors were observed in livers. Humans are highly susceptible to the negative effects of dioxane, even though generally humans are exposed to trace amounts of dioxane on a daily basis. Acute
effects of dioxane poison include, but are not limited to: skin, eye, nose, throat, and lung irritation, coughing, drowsiness, headaches [27]. Some of the more serious effects have been found to be: vertigo, vomiting, anorexia, comatose state, and even death. From a reported 1,4-dioxane incident, the victim was diagnosed edema of brain, liver and kidney damage. It should be noted that certain ailments remain vague due to limited number of samples lack of long term duration studies.

### 4.4 Current Status of Dioxane Regulation

As an emerging drinking water contaminate, no federal maximum contaminant level (MCL) has been established yet. However, 1,4-dioxane has been listed on the third drinking water contaminant candidate by Environmental Protection Agency in 2009 [26]. Since then 1,4-dioxane has been widely concerned by public. For example, EPA set a residential soil screening level (SSL) of 4.9 mg/kg, a residential air screening level of 0.49 μg/m³, a screening level of 0.67 μg/L dioxane in tap water [26]. Several states also established some drinking water and groundwater guidelines (Table 3.2). These current standards suggest that the future allowable concentration limit for 1,4-dioxane may be very low (0.3-1 μg/L).

Table 4.2 Guidelines for 1,4-dioxane in drinking water and groundwater [26]

<table>
<thead>
<tr>
<th>State</th>
<th>Guidelines</th>
<th>Concentration (μg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>California</td>
<td>Notification level for drinking water</td>
<td>1</td>
<td>CA EPA, 2016</td>
</tr>
<tr>
<td>Colorado</td>
<td>Interim ground water quality cleanup standard</td>
<td>0.35</td>
<td>CDPHE, 2012</td>
</tr>
</tbody>
</table>
4.5 Various Techniques for 1,4-Dioxane Removal

It is not effective to remove 1,4-dioxane via common water treatment methods including air stripping, carbon adsorption, due to its high water solubility and low Henry’s constant [28]. In addition, conventional biological treatment typically results in poor 1,4-dioxane removal because of its high resistance to biodegradation [28]. The biochemical oxygen demand of 1,4-dioxane can be ignored in incubations with wastewater micro-organisms for one month [29]. Besides, study shows that 1,4-dioxane could not act as carbon and energy source for 180 aerobic and 100 anaerobic cultures derived from a contaminated aquifer [30].

However, advanced oxidation process have been proved to be effective for 1,4-dioxane removal in many studies. AOPs are known for their effectiveness in mineralizing a variety of organic compounds by generation of highly reactive species, with a combination of oxidation agents (e.g. ozone or hydrogen peroxide), irradiation (e.g. Ultraviolet (UV) or ultrasound), and catalysts (e.g. metal ions or photocatalysts) [31]. For example, Kwon et al. (2012) investigated the effectiveness of different ozone-based AOPs (\(\text{O}_3\), \(\text{O}_3/\text{UV}\) and \(\text{O}_3/\text{H}_2\text{O}_2/\text{UV}\)) and found \(\text{O}_3/\text{H}_2\text{O}_2/\text{UV}\) showed the highest dioxane degradation rate (94%) after 90 min at an \(\text{H}_2\text{O}_2/\text{O}_3\) ratio of 0.5 [32]. Research group presented laboratory and field experiments on the destruction of 1,4-dioxane, TCE, MTBE and NDMA (N-Nitrosodimethylamine) in contaminated groundwater by a novel Hydro-Non-Thermal-Plasma (HNTP) system [33]. This study is the first pilot-scale HNTP destruction of 1,4-dioxane from a contaminated groundwater and demonstrated high level of degradation (>90%, ) for 1,4-dioxane [33]. The disadvantages of AOPs in treating organic compounds are high capital and operation costs including costs for chemicals, electric power, and UV lamp replacement [28].
In order to develop a 1,4-dioxane degradation process that is cost effective, easy to operate, and capable of achieving a total/near-total mineralization, an AOP combining NTPR and bioreactor was proposed.

4.6 Experimental Procedures

A synthetic groundwater containing 50mg/L dioxane was pre-treated in a non-thermal plasma reactor (NTPR) in five scenarios, which differed at hydraulic retention time (HRT=0, 0.013, 0.026, 0.05, 0.13 seconds). The diameter of inlet stainless nozzle is 0.02 inch. The non-thermal plasma reactor based on a cylindrical region with a diameter of 3 mm, height of 4 mm, and a total volume of 28.27 mm$^3$. For each set of scenario, 900ml volume of sample was treated. The liquid flow rates were set at 2, 5, 10, 15 ml/min. The hydraulic retention times were calculated by using high speed camera and Matlab in Table 4.3 [15].

<table>
<thead>
<tr>
<th>Liquid flow rate (mL/min)</th>
<th>Gas flow rate (L/min)</th>
<th>Gas to liquid flow ratio</th>
<th>Volume of liquid in reactor (mL)</th>
<th>Volume of gas in reactor (mL)</th>
<th>Liquid residence time (ms)</th>
<th>Gas residence time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.258</td>
<td>2128.978</td>
<td>0.004</td>
<td>0.024</td>
<td>128.22</td>
<td>0.338</td>
</tr>
<tr>
<td>5</td>
<td>3.656</td>
<td>731.24</td>
<td>0.004</td>
<td>0.024</td>
<td>51.288</td>
<td>0.394</td>
</tr>
<tr>
<td>10</td>
<td>2.71</td>
<td>270.991</td>
<td>0.004</td>
<td>0.024</td>
<td>25.644</td>
<td>0.531</td>
</tr>
<tr>
<td>20</td>
<td>1.928</td>
<td>96.421</td>
<td>0.004</td>
<td>0.024</td>
<td>12.822</td>
<td>0.747</td>
</tr>
</tbody>
</table>

A nanosecond pulser was utilized as the power supply under following conditions: 20ns pulse width, 10 kHZ frequency and 20kV input voltage. The change in liquid conductivity, concentration of dioxane, Dissolved organic carbon and hydrogen peroxide were measured after plasma treatment. Since the proper H$_2$O$_2$ concentration range for micro-organisms growth is less than
0.025mM, the five sets of pretreated groundwater were stored in a stirring post-plasma reactor at room temperature for two days to allow further reaction between hydrogen peroxide and dioxane and then transferred to five sets of biological batch reactor that contained activated sludge. Each individual scenario have one duplicate sample. Dissolved organic carbon (DOC, measurement of intermediates) and concentration of dioxane were measured continuously during one month. The bioreactors are continuously operated. A continuous recirculation control experiment was made to compare the case with sole plasma treatment.

### 4.7 Results and Discussions

#### 4.7.1 Non-thermal Plasma Reactor (NTPR) Treatment of Dioxane

The purpose of this experiment is comparing the efficiency of combining plasma and bioreactor treatment process with sole plasma treatment as well as sole biomass treatment process. The liquid flow rates were determined by dioxane degradation. Dioxane degradation were anticipated to be around 25%, 50%, 75% and 95% right after non-thermal plasma treatment at different flow rates. Figure 4.2 shows the percentages of dioxane degradation are 96.5%, 82%, 58% and 27% right after plasma treatment at 2, 5, 10, 20 ml/min liquid flow rates, respectively. Liquid conductivity changed from 599μs/cm to 626μs/cm after treatment while the change in pH was negligible due to pH buffer solution addition. Considering hydrogen peroxide toxicity on biomass, concentration of hydrogen peroxide was also measured after plasma treatment 48 hours (figure 4.3). Results show that post-plasma reaction between dioxane and hydroxyl radical was able to reduce hydrogen peroxide concentration to below 0.025mM. Dissolved organic carbon concentrations were also measured after plasma treatment 0 hour and 48 hours (figure 4.4).
Figure 4.2 50ppm dioxane removal% and dioxane concentration at different liquid flow rate after plasma treatment 0 hour and 48 hours, pulse width=20ns, frequency=20kHz, input voltage= 20kV.

Figure 4.3 H2O2 concentration at different liquid flow rates after plasma treatment 0 hour and 48 hours, pulse width=20ns, frequency=20 kHz, input voltage= 20kV.
Most of the TOC removal right after plasma treatment resulted from degradation of dioxane. Non-thermal plasma treatment is able to produce large amounts of hydroxyl radical as the oxidant which contribute to substantial reductions in 1,4-dioxane. In other research groups, OES spectra was used for the analysis of the liquid products. The emission line intensity of C (247.9nm) significantly increased during plasma treatment. And some bands and lines due to the CH* and C₂* species could be observed clearly [34]. The presence of intermediate species such as C, CH* and C₂* in plasma can be seen as a proof of 1,4 dioxane decomposition into hydrogen and carbon-containing species [34]. The chemical structure of 1,4-dioxane results in high water solubility and high resistance to biodegradation [28]. A significant increase in the biochemical oxygen demand was also been observed suggesting the formation of biodegradable oxidation products [34]. By combining AOP of using non-thermal plasma reactor and microorganism bioreactor, the biodegradable products from plasma reactor can be further oxidized in bioreactor, which significantly reduce the costs.
4.7.2 Bioreactor Treatment

Although 1,4-dioxane is highly resistant to biodegradation, fourteen microorganism have been found to be able to degrade dioxane via metabolism [32]. Pseudonocardia dioxanivorans CB1190 was one of the most well-studied bacteria strain which are capable of mineralizing dioxane to CO₂ directly while others are capable of co-metabolizing dioxane [32]. Bacteria take dioxane or other mineralized substrates (TOC) as carbon source in order to obtain energy for cellular components synthesis. In catabolism, bacteria gain energy for cell synthesis and maintenance through oxidation of intermediates and dioxane. In this experiment, the microorganism were derived from sludge in sewage treatment plant.

4.7.3 Sole Plasma Treatment With Recirculation

In order to compare the case where sole non-thermal plasma treatment is utilized to achieve 99% dioxane removal, a control experiment is designed by recirculating the effluent liquid back. The liquid flowrate is set as 2mL/min. Both TOC and dioxane concentration in the final solution were measured (Figure 4.5). Compared with the case where dioxane solution was only run through the reactor once without recirculation (number of recirculation=0, HRT=0.13seconds), concentration of TOC, dioxane and hydrogen peroxide were significantly reduced when the number of recirculation increased to 3. The result also shows that there is a limit on the influence of recirculation on dioxane degradation. The concentration of hydrogen peroxide, TOC and dioxane change insignificantly from three-time recirculation to nine-time recirculation. Dioxane and intermediates (i.e., DOC) were removed to below 1 μg C/L and 4 mg C/L respectively when the number of recirculation is set to nine. The discharge power was measured simultaneously with a high voltage probe and oscilloscope (table 4.4)
Table 4.4 Summary of power measurement

<table>
<thead>
<tr>
<th>Liquid flow rate (mL/min)</th>
<th>Breakdown Voltage (KV)</th>
<th>Energy per pulse (mWs)</th>
<th>Power (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.42</td>
<td>0.21</td>
<td>2.11</td>
</tr>
<tr>
<td>5</td>
<td>3.39</td>
<td>0.22</td>
<td>2.22</td>
</tr>
<tr>
<td>10</td>
<td>3.24</td>
<td>0.23</td>
<td>2.25</td>
</tr>
<tr>
<td>15</td>
<td>3.22</td>
<td>0.23</td>
<td>2.28</td>
</tr>
</tbody>
</table>

4.7.4 Combined Process Results

Dissolved organic carbon and dioxane concentrations in the biological reactor were monitored during the one-month experiment (Figure 4.6). The eleven bioreactors were continuously operated. Case 1 represents the control experiment (sole NTP treatment) where dioxane solutions were recirculated for nine times. Case 2 to case 5 represent the combined processes at flow rates 2, 5, 10 and 20 mL/min. Case 6 is the sole bioreactor treatment process.
As shown in figure 4.6, dissolved organic carbon continuously decreased in bioreactors. However, dioxane concentration only slightly decreased in bioreactors (case 5 and case 6) and almost kept constant in case 2, 3 and 4, which suggests the competition between intermediates and 1,4-dioxane in terms of biodegradable ability. Obviously, the microorganisms in bioreactor tend to oxidize intermediates (i.e., DOC) rather than 1,4-dioxane. Although the intermediates in the bioreactor were not analyzed in this study, 2-hydroxyethoxyacetic acid (HEAA) was detected to be accumulated during the biodegradation process by strain ENV478 in Vainberg’s study [36]. To remove dioxane to below 1 mg C/L and intermediates (i.e, DOC) to below 4 mg C/L, the sole NTP treatment process used 1.17 seconds (case 1) and the combined process used a NTP treatment time of 0.13 second and a biological treatment time of 25 days in one of the 4 scenarios (case 2). The sole biological process only reduced less than 10% of dioxane in one month (case 6). Therefore,
we expect that the sole biological process would use a treatment time much longer than one month. The combined processes saved significant energy compared to the sole non-thermal plasma process and significant treatment time compared to the sole biological process.
CHAPTER 5

CONCLUSION

The objective of this study was to explore the potential application of water-film non-thermal plasma reactor for water treatment. It was desired to investigate the effect of oxygen on MB degradation, hence different percentage of oxygen was added into argon as inlet gas mixture. Another objective was to design the process of combining non-thermal plasma and microorganism treatment to decompose 1,4-dioxane from groundwater.

The ozone production experimental results show that in spite of a small amount of ozone generated in the gas phase, no significant contribution of ozone on organic dye (MB) degradation was detected. The mass transfer of ozone from gas into liquid is too small. Meanwhile, MB liquid residence time (~0.14 second) is too short to allow dissolved ozone reacting with MB. Oxygen doesn’t affect hydrogen peroxide formation, which provides insight into the mechanisms of hydrogen peroxide formation. It seems that ozone, oxygen, and atomic oxygen species are not participating in reactions that produce $\text{H}_2\text{O}_2$ and it would seem that this supports the idea that the $\text{H}_2\text{O}_2$ is formed at or in the liquid-gas interface where OH and water vapor are more important.

The addition of MB in DI water has a dramatic effect on ozone and hydrogen peroxide concentrations since conductivity of solution plays a significant role in discharge initiation. Although adding oxygen doesn’t contribute to organic compounds degradation, plasma temperature increases as oxygen concentration increases.

The novel approach of combining plasma and bioreactor for 1,4-dioxane degradation results show the high efficiency of this process. Compared to the combined process, the sole biological process only reduced less than 10% of dioxane and 7% dissolved organic carbon in one month. This result is as expected since conventional microorganism treatment needs a long time
period. To remove 1,4-dioxane to below 1 mg/L (98% removal) and TOC to below 4 mg C/L (86% removal), the combined process used a non-thermal plasma treatment of 0.13 second and a biological treatment time of 25 days. The combined process is more cost effective than sole plasma treatment and time efficient compared to sole bioreactor treatment.
APPENDIX A

THE COMPONENTS OF ONE LITER NMS

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Dosage (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃</td>
<td>11.76</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>1.28</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>0.15</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
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</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>0.08</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>3.9</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>6.1</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>0.002</td>
</tr>
<tr>
<td>MnCl₂·4H₂O</td>
<td>0.002</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0.002</td>
</tr>
<tr>
<td>CoCl₂·6H₂O</td>
<td>0.004</td>
</tr>
<tr>
<td>Na₂MoO₄·2H₂O</td>
<td>0.004</td>
</tr>
<tr>
<td>CuCl₂·2H₂O</td>
<td>0.001</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>0.001</td>
</tr>
<tr>
<td>Na₂WO₄·2H₂O</td>
<td>0.001</td>
</tr>
<tr>
<td>Na₂SeO₄·5H₂O</td>
<td>0.001</td>
</tr>
<tr>
<td>KI</td>
<td>0.001</td>
</tr>
</tbody>
</table>
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BIOGRAPHICAL SKETCH

SKILLS
- Background in analytical chemistry, Chemical Engineering and environmental science
- Skilled in laboratory equipment such as TOC analyzer, UV-Vis, Digital pH meter, Electrical conductivity meter, oscilloscope
- Proficient in MS Word, Excel spreadsheet, PowerPoint, Matlab and Latex
- Knowledge of Chemical Extraction, analytical instrumentation like GC and GC-MS

EDUCATION
Florida State University
Master of Engineering in Chemical Engineering
Overall GPA: 3.4/4.0
August 2015 – December 2016

China University of Petroleum
Bachelor of Engineering in Chemical Engineering
Overall GPA: 90/100
September 2011 – July 2014

EXPERIENCES
Department of Chemical & Biomedical Engineering, Florida State University, FL
May 2016 – Present
Research Assistant
- Compile and review scientific data in the context of water quality standards
- Prepare technical reports related to water quality and bioassessment field samples
- Achieve the EPA standard of decomposing 1,4 dioxane from ppm to ppb

Department of Chemical & Biomedical Engineering, Florida State University
August 2015 – Present
Research Assistant
- Analyze samples concentration using UV-Vis and provide information on compounds or quantities of compounds present. Make calibration curve based on standard solution and absorbance
- Maintain, calibrate the performance of TOC analyzer. Test and compare the TOC in pre-treatment and after-treatment sample. Perform routine samples preparation in TOC analyzer
- Explain the role of oxygen in system and mechanism of degradation by combining experimental and Matlab simulation results

Department of Chemical & Biomedical Engineering, Florida State University
March 2015- May 2015
Project team leader
- Teamed in four people to design a new “50,000 Tons/year methanol Production Facility Process”
- Simulated two reactors in series, columns and heat exchangers using Aspen Plus and Matlab
CERTIFICATE

Six Sigma Green Belt   FE