Removal of Pharmaceutical Carbamazepine Using Pulsed Corona Discharge Generated in Water

REMOVAL OF PHARMACEUTICAL CARBAMAZEPINE USING PULSED CORONA DISCHARGE GENERATED IN WATER

BY

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Lay Abstract

Pharmaceuticals are being released into the environment at an increasing rate due to population growth and a rising dependence on these compounds. Pharmaceuticals are resistant to many common water treatment methods; however, electrical discharge generated within the water to be treated (pulsed corona discharge) is an emerging water treatment technology that has been shown to successfully treat many pharmaceuticals. In the present work, pulsed corona discharge has been used to treat carbamazepine present in a relatively clean water matrix. Removal was maximized by optimizing the solution pH, solution conductivity, type of gas bubbled through the electrode, and gas flow rate. The best removal was achieved in solutions with lower pH and conductivities where oxygen was bubbled through the electrode at a relatively high rate.

Abstract

Increasing concentrations of pharmaceutical compounds and their metabolites in aquatic environment threatens both aquatic species and human health. Many pharmaceuticals are persistent in the environment and resistant to conventional water treatment; hence, alternate treatment techniques are required to remove these compounds from water. Aqueous phase electrical discharge has been demonstrated to successfully remove a range of pharmaceutical compounds from water. This technique is characterized by the simultaneous generation of highly reactive species and physical effects within the aqueous solution to be treated.

The present study investigates and optimizes the efficacy of pulsed corona discharges generated in water for the treatment of carbamazepine (CBZ) in a relatively clean water matrix by varying the solution pH, solution conductivity, gas type injected, and gas flow rate injected.

A point-to-plane reactor configuration was employed to produce plasma channel- streamers. In this geometry, the electrical discharges were produced directly within the aqueous phase to be treated by charging a 1nF pulse forming capacitor using a high voltage (25 KV) DC power supply through 10 MΩ resistor to generate discharges within the water at a 30 HZ pulse repetition rate.

Solution pH, solution conductivity, gas type, and gas flow rate were optimized to maximize the removal efficacy of CBZ removal by pulsed corona at the laboratory scale. The CBZ degradation rate (concentration decrease over time) was monitored using LC/MS/MS, with overall degradation ranging from 14-94% depending on the experimental conditions. The results demonstrate that higher CBZ removal efficiency is achieved under lower pH and conductivity conditions. Moreover, enhanced degradation efficiency is obtained when gas, and particularly oxygen, is bubbled through the high voltage hollow electrode, especially at higher flow rates.

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Abbreviations

AOP – advanced oxidation process

CBZ – carbamazepine

WWTPs – Wastewater treatment plants

DFC – diclofenac

NTP – nonthermal plasma

DBD – dielectric barrier discharge

DC – direct current

HV – high voltage

AEFS – average electric field strength

HPLC - high performance liquid chromatography

MS – mass spectrometry

GAC - granular activated carbon

Cl^- – chloride

H_2O_2 - hydrogen peroxide

O_3 – ozone

$^\bullet OH$ - hydroxyl radicals

$^\bullet HO_2$ - hydroperoxyl radical

Ar - argon gas

DI – deionized

$^\bullet H$ – hydrogen atom

$^1O_2$ - singlet oxygen

$O_2^{\bullet -}$ - superoxide

$^{\bullet}O$ - oxygen atom

UV – ultraviolet

e^{-}_{aq} - solvated electrons

CBZ-DiOH - trans-10,11-dihydro-10,11-dihydrocarbamazpine

CBZ-EP - 10,11-dihydro-10,11-epoxycarbamazepine

ClO_2 - chlorine dioxide

BDD - boron doped diamond

TOC - Total Organic Carbon

LOQ - limit of quantification

MDL – method detection limit

S/N - signal to noise ratio

Co-Authorship

This thesis has been prepared based on the “Guide for Preparation of Master’s Thesis” set by McMaster University.

Chapter 3: Carbamazepine Removal Using Pulsed Corona Discharge in Aqueous Solution

Authors: R. Pourzarea, V. Lakhian and S. E. Dickson

The optimization of influential variables on carbamazepine removal efficiency from a relatively clean water matrix was investigated. The experiential design, laboratory work, data analysis, and results interpretation were conducted by Roya Pourzarea under the supervision of Drs. S. Dickson-Anderson and V. Lakhian. The manuscript was prepared by Roya Pourzarea and edited by Dr. S. Dickson-Anderson.

Chapter 1: Introduction- Water Contamination and Treatment Issue

In recent years, there has been a significant increase in the consumption of pharmaceuticals [1]. These synthetic organic compounds are widespread in use in the modern world in both human and veterinary medicine production, aquaculture and agriculture. There are different pathways for pharmaceuticals to reach potential drinking water sources, including both surface water and groundwater [2–4]. Discharges of partially treated industrial, hospital or domestic wastewater effluents, and leakages and emergencies into the downstream surface water, contaminated runoff from manure lagoons, pastures, on-farm burial, agricultural lands, and aquaculture sites through overland flow, and interaction between surface and contaminated ground water through gaining streams can potentially transfer the pharmaceuticals into the surface water. The main sources of pharmaceuticals introduction into the groundwater include: wastewater effluents used for groundwater replenishment purposes; surface/ground water interactions; animal manure applied to the soil for agricultural purposes; leaking underground storage tanks; and, landfill leachate [2, 4, 5].

Antiepileptics is one class of pharmaceuticals, prescribed for the treatment of epilepsy, that is categorized as highly recalcitrant, non-biodegradable organics. Pharmaceuticals within this class therefore typically withstand degradation in wastewater treatment plants (WWTPs). Not surprisingly, studies have reported increasing concentration of antiepileptics, and carbamazepine (CBZ) in particular, in the environment including surface and ground water, the influent and effluent streams of wastewater treatment plants (WWTPs), and treated drinking water in a number of countries [2, 3]. Exposure to CBZ, even at the ng.L^{-1} concentration range, has the potential to cause biological harm to the ecosystem [1, 6, 7], including effects on reproduction and regeneration period, impaired digestive and blood cell function, hindered growth processes, and artificially induced endocrine disruption. [6, 8–11]. Chronic exposure to pharmaceuticals, even at low doses, also poses a threat to human health [12, 13]; fetuses, infants and people with impaired enzymes function are particularly vulnerable to long term exposure of pharmaceuticals [12]. However, more investigations are required to assess the effect(s) of exposure (the possible risks to human health) due to long-term and low level exposure via drinking water [14].

Studies have shown the incapability of conventional wastewater (including preliminary, primary, secondary, tertiary and disinfection treatments) and drinking water (consisting of coagulation by alum, ferric chloride, or polymers, flocculation/sedimentation, followed by rapid sand filtration and disinfection) treatment processes to efficiently remove recalcitrant, non-biodegradable pharmaceuticals with high polarity [5, 15]. Studies indicate 10% removal efficiency of CBZ by WWTPs [16], and 12% by conventional drinking water treatments [17]. These results also have been underscored by the detection of CBZ in WWTP effluents at concentration as high as 6.3 $\mu g.L^{-1}$ [15], in groundwater at concentration up to 610 $ng.L^{-1}$ [5], and in finished water at concentration up to 86 $ng.L^{-1}$), [18, 19]. CBZ and one of its primary metabolites (10,11-dihydro-10,11-dihydroxycarbamazepine) have also frequently been detected in Canadian wastewater effluents at concentrations up to 0.6 $\mu g.L^{-1}$, as well as in surface waters at concentrations ranging from 0.84 to 16.3 $ng.L^{-1}$ [20–22].

The ability of CBZ to resist secondary wastewater treatment can be related to its structural and chemical properties. The complex spatial structure of CBZ (a three-ring phenolic base compound) hinders its reactions with oxidants. Additionally, non-biodegradability at trace concentrations (up to $\mu g.L^{-1}$ which is the concentration of CBZ in the environment), and a very low distribution coefficient between the aqueous and secondary sludge phases, result in incomplete elimination of CBZ by conventional treatment methods [16, 23].

Water treatment methods such as membrane filtration (micro-filtration) in a hybrid system with granular activated carbon (MF-GAC) result in partial removal of CBZ (63%) [24]. This result could be further enhanced in a dual membrane hybrid system where nano-filtration is added as a post treatment to MF-GAC system, resulting in more than 80% removal of CBZ [24].

More powerful advanced oxidation processes (AOPs) have emerged as effective methods that aim for the generation of highly reactive hydroxyl radicals to fully or partially oxidize various organics, including pharmaceuticals. Ozonation (>90%) [17], direct photolysis in the presence of Fe (III) and chloride (Cl^-) species (>95%) [25], UV/H_2O_2- induced photo degradation (up to 90%) [26], and photocatalytic degradation using TiO_2 catalyst (78.4%) [27] have demonstrated successful removal of CBZ.

In spite of the effectiveness to remove CBZ, these techniques have some disadvantages, including: incomplete mineralization [28], continuous supply of ozone or hydrogen peroxide during the process [29], requiring oxygen and/or H_2O_2 storage thereby introducing long-term stability and corrosion issues [1], post treatment and removal of catalysts suspended in water to avoid their potential toxicity, and the risk of pollutant adsorption, and not degradation, on the catalyst surface [30].

To eliminate the disadvantages of these water treatment techniques, electrical discharge has recently emerged as a promising treatment technique that does not require chemical storage, subsequent separation of catalysts and contaminants, or produce a concentrated effluent requiring further treatment. This technique has received great attention in a wide variety of applications varying from the degradation of volatile organic compounds [31] and the inactivation of microorganisms in water [32].

Decomposition of pharmaceuticals have been widely investigated in different configurations (dielectric barrier discharge (DBD) and pulsed corona discharge) where the plasma is generated in air. Hijosa-Valsero et al. (2013)

investigated the degradation of organic micro-pollutants in a DBD configuration with atmospheric plasma [33]. Krause et al. (2009) investigated barrier electrodes in which corona discharge was generated over a thin water layer and 98% degradation of CBZ was achieved after 30 min [34]. Gerrity et al. (2010) studied a pilot-scale non-thermal plasma (NTP) of an electrode-to-plate configuration for the removal of CBZ [35]. The results indicated a rapid degradation for CBZ up to 90%.

The main problem with the electrical discharges generated over water is that generated species in plasma need to be diffused into the aqueous phase to initiate the reaction with pollutant [1]. Additionally, as the reaction takes place in the boundary between liquid and gas phases, this technique is mostly efficient for shallow liquid layer.

This limitation could be avoided by more efficient aqueous electrical discharge which is generated directly in water [36]. This technology generates highly reactive species directly within the water to be treated via the production of an aqueous phase plasma. It simultaneously triggers the variety of physical effects including the formation of UV radiation, pressure shock-waves, thermal effects, and chemical reactions through in situ generation of reactive radicals ($^{\bullet}OH$, $^{\bullet}H$, $^{\bullet}O$, $^{\bullet}HO_2$, $^{1}O_2$, $O_2^{\bullet -}$) and longer lived species (H_2O_2, O_3 and H_2, and UV irradiation) directly in aqueous solutions [37]. The hydroxyl radical is a powerful, non-selective oxidizing agent responsible for degradation of various organic molecules including CBZ ($E^0_{\bullet OH\,/\,H_2O}$ = 2.85 V vs. standard hydrogen electrode, pH = 0) [24]. It is able to react at diffusion controlled rates and typically allows for complete degradation of the compound to potentially safer by-products or mineralization to carbon dioxide [40]. The primary proposed biotransformation route for CBZ is oxidation of 10-11 carbon-carbon double bond in the azepine ring by oxidants such as $^{\bullet}OH$ to yield 10,11-dihydro-10,11-epoxycarbamazepine. The removal efficiency is strongly dependent on the hydroxyl radical production rate [41], which in turn is dependent on input power, reactor configuration, electrode polarity, electrode coating, solution conductivity, solution pH, residence time, gas type, gas flow rate, and initial all play key roles in removal efficacy of electrical discharge systems [37].

In a recent study done by Banaschik et al. (2015), the effect of aqueous corona discharge on removal of pharmaceuticals including CBZ has been explored [1]. In this study, discharges were generated in an extended coaxial configuration filled with spiked clean water and 90% decomposition level for CBZ has been achieved during 66 min treatment time. No parameters influencing the removal efficiency were explored in this investigation.

In the present study, we have investigated the efficacy of pulsed corona discharge generated directly within aqueous phase to be treated for the removal of CBZ in a relatively clean water matrix. The scope of the work is to focus on optimizing a range of parameters to achieve the maximum degradation of CBZ. Specifically, the effects of electrode separation distance, solution pH, electrical conductivity, gas type, and gas flow rate on the efficiency of the oxidation process were investigated at the bench-scale in a 100 mL point-to-plate reactor. CBZ was selected for the present study based on the frequency with which it is prescribed in Canada, its confirmed presence in source water, its recalcitrant nature, and its resistance to biodegradation and treatment [42].The investigations in this thesis indicate the capability of aqueous phase corona discharge technology on destruction of highly recalcitrant contaminants with potential toxicity impact on aquatic life. Furthermore, this work demonstrates the capacity of the system for optimization to achieve the maximum efficiency.

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Chapter 2: Literature Review

2.1. Electrical Discharge for Water Treatment

Electrical discharge methods have emerged as promising treatment techniques that effectively eliminate several of the drawbacks of AOPs, adsorption, and membranes as water treatment technologies. This technique has received great attention in a wide variety of treatment mechanisms varying from oxidation of volatile organic compounds [1], to the inactivation of microorganisms [2], to reduction of organic compounds dissolved in water [3].

This section covers the electrical breakdown mechanism in different phases, plasma chemistry and the generated reactive species induced by plasma. Chemical and physical effects initiated by electrical discharges will also be discussed. In addition, potential parameters influencing the discharge initiation, discharge characterization, and the degradation efficiency are covered.

2.1.1. Electrical Discharge in the Gas Phase

The discharge channel forms when a voltage exceeding the breakdown voltage is applied to the high voltage (HV) electrode. Gas-like streamers occur in the gas phase occupying the space between the discharge electrode and ground electrode.

There are two possible mechanisms for gas plasma formation. In the first pathway, generated energetic electrons attack the gas molecules. As a result of gas molecule ionization, primary electrons are generated and become a part of gas molecules through their attachment. In the second mechanism, ionization of gas molecules occurs through a photoionization reaction with irradiation, such as UV light, generated. Electron detachment from the ions with negative charges will lead to the formation of positive ions. Primary generated electrons with high speeds will result in higher electron formation through the impact ionization. The resulting large mass of electrons and positive ions develops the plasma discharges. As a result of this continuous electron generation, discharge will propagate toward the counter electrode, leading to either full electrical discharge where the discharge channel reaches the counter electrode or partial breakdown where it is not long enough to contact the ground electrode [4, 5]. This ionization process is affected by the electric field surrounding the gas molecules. More powerful electric fields result in higher ionization impacts.

In some types of gas-liquid reactors, hybrid gas-liquid reactors and reference reactors, hydrogen peroxide (H_2O_2) is formed in the liquid in the absence of gas phase discharge. There are two types of hybrid reactors: parallel reactors (Figure 2.1. a) in which the HV electrode is placed in the gas phase and the ground electrode is located at the gas-liquid interface surface, and series reactors (Figure 2.1. b) with the ground electrode in the gas phase over the surface of water. Higher formation of ozone (O_3) in the parallel reactor, compared to the series reactor has made it more applicable and efficient for destruction or removal of nitrobenzene [6] whereas series reactors are considered more useful when phenol needs to be degraded [7]. The latter occurred as a result of hydroxyl radicals (${}^{\bullet}OH$) or O_3 substitution on the benzene ring of the phenol.

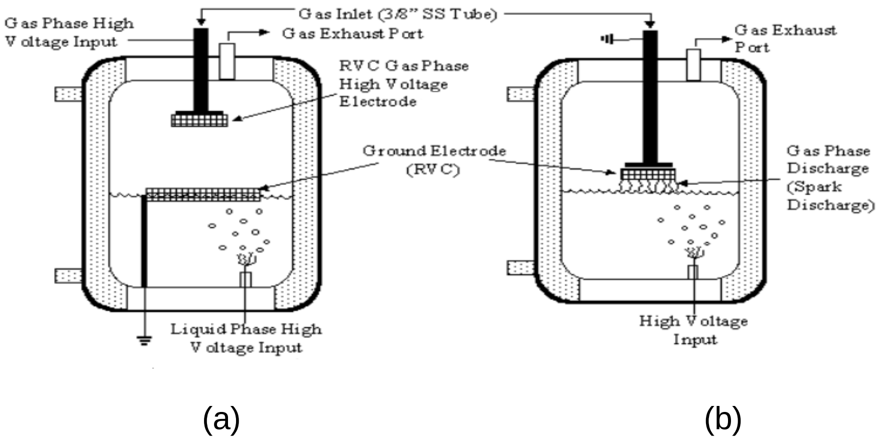


Figure 2. 1. Schematic of Reactor; a) Parallel Configuration, b) Series Configuration (Source: Appleton et al. 2002 [6])

Species Generated at the Gas/Liquid Interface

In the gas–liquid phase systems, the reactive species are generated in the gas phase and reach the liquid phase due to propulsion by the existing electric field through the interface; therefore, they can react with water molecules to create other reactive species such as ${}^{\bullet}OH$ radicals [8]. As a result of ${}^{\bullet}OH$ recombination, H_2O_2 can be formed as another reactive species. Studies have reported a high yield of ${}^{\bullet}OH$ radical formation in gas phase discharge systems [8]. This could be related to the relatively large amounts of hydrogen gas (H_2) and H_2O_2 generated in the gas phase. One hypothesis is that a reaction region forms in which the water molecules dissociate into H_2 and oxygen gas (O_2) and then form H_2O_2.

The applied current and voltage influence the H_2, O_2, and H_2O_2 yields [9]. The study of H_2O_2 formation in gas-liquid phase discharge systems have shown a similar stoichiometry for the formation of H_2 and H_2O_2 when the applied voltage and current are low. As the applied voltage is increased, the formation of H_2 and H_2O_2 increase at different rates.

The type of gas utilized in gas-liquid discharge systems affects the types of species generated. In addition, the more stable radicals can lead to secondary discharge chemical reactions in liquid-gas phase systems [9]. For example, in a gas-liquid phase point-to-plane reactor where O_2 is applied as the gas phase above the water surface gaseous $O^-{}_2$ and $O^-{}_3$ are generated, which subsequently form $^\bullet OH$ and hydroperoxyl radical species ($^\bullet HO_2$) upon contact with the aqueous phase [9]. Reactive species generated by different applied gases in the gas phase over the water surface have different results in degradation of organic compounds (such as phenol) in the liquid phase. Enhanced organic removal efficiency has been reported when O_2 is utilized as the gas phase rather than argon gas (Ar) due to the generation of O_3 in addition to $^\bullet OH$ radicals, providing more rapid and efficient removal results [10].

2.1.2. Electrical Discharge in Liquid Phase

Electrical discharges are generated directly in water to form corona-like plasma channels in the region between electrodes, but they do not reach the ground electrode (Figure 2.2. a); to generate spark discharges where the discharge channel contacts the counter electrode (Figure 2.2. b) [11].

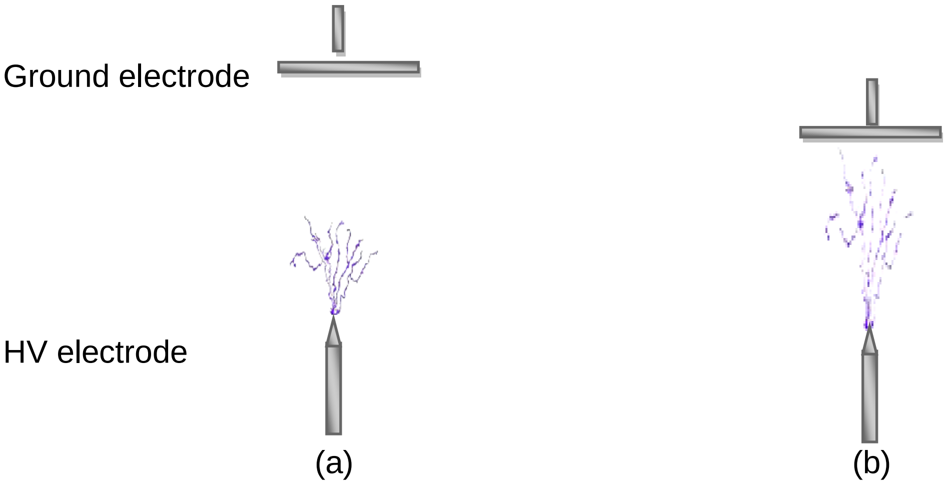


Figure 2. 2. Point-to-plane Discharge Diagram: (a) Streamer Discharge, (b) Spark Discharge

To determine the features of discharges generated in liquid, the differences in phase density and conductivity, and electrical discharge strength of both the gas and liquid phases must be considered. As the density of liquid is considerably higher than that of gas, there is no free path between the particles so they can collide and accelerate frequently. Furthermore, the liquid molecule ionization potential is higher than that of the gas phase. The substantially higher conductivity of the liquid phase with respect to the gas phase leads to a different propagation pattern of the streamer discharge. Electrical/ionization and thermal bubble formation theories can help to explain the mechanism of breakdown that occurs in the liquid phase when high voltage is applied to the point electrode (HV electrode) [12–14].

Electrical or Ionization Theory. Based on the ionization theory, the electrical breakdown initiation occurs via the direct dissociation of the atoms and molecules into ions in the absence of generated gas bubbles and also thermal effect [15]. This has been related to the bubbles short lifetime (10^{-8}s) which is required for free electrons to be produced. This result has been verified by comparison of power calculated from the voltage and current wave shapes and the required liquid vaporization power, the lower resistance of streamer discharge, and the equal velocities of streamer in both deionized (DI) and tap water. In this situation, the mobility of protons in the vapor phase can enhance the streamer propagation velocity.

Two controversies have been proposed to undermine the ionization theory [15]. The first argument disputes the electron mass evolution in the liquid, which could be concluded from strong electron dispersion in the liquid solution. In addition, electrons cannot accelerate to a large extent in dense liquid solutions. Second, the independent and free electron survival is highly unlikely in liquids as they have short life times and form solvated electrons very rapidly [16].

As a result of liquid ionization and bubble breakdown, free electrons and positive ions are generated. These components form plasma channel which is an ionized gas with the overall neutralized state (no electric charges) and thermal energy consisting of the average of all components energy except the generated free electrons. The plasma region is characterized by very high temperature and low pressure in thermal plasmas. Underwater plasma generation is also characterized by small volume of plasma generated as a result of spatial discharges propagation. The corona discharges increase the temperature of a small volume of the liquid phase and keep the bulk volume temperature approximately equal to the room temperature. This results in generation of non-thermal plasma (NTP). Non-thermal plasmas include high-pressure plasmas such as Dielectric barrier discharge (DBD) plasma, pulsed corona discharge plasma, gas-liquid hybrid discharge plasma, and microwave plasmas which, similar to thermal plasmas, are applied in environmental treatments [18–20].

NTP discharges with the advantages of ignorable thermal loss and physical damages to the reactor are able to decompose the organics, however the thermal decomposition efficiency is not high because of very small thermal region in the liquid phase. In this system, thermal effect contributes in the organic destruction through the pyrolysis of water molecules, which results in preliminary formation of reactive species [10, 21]. DBD is one of the NTP generation technique that has been greatly used in water, wastewater and air pollution treatment fields [17], [21]–[25]. Although an efficiently destructive method, DBD fails when the concentration of organic contaminants and mineral salts in the treatment solution is high. This can be explained as a result of competition of contaminants for reactive oxidant species [26]. Recent studies have shown satisfactory removal results for various organics including pharmaceuticals using NTP [20, 28–30].

2.1.2. 1. Aqueous phase corona discharge

Characteristics of Pulsed Corona Discharge

Underwater electrical discharge systems are characterized by substantial energy consumption (1 J/pulse to 1 KJ/pulse) [11]. This together with the more complicated processes of their direct formation in water phase, and therefore insufficient knowledge about liquid discharge behavior, have been considered the primary issues with this technique. Therefore, having a profound understanding about the reactions occurring due to the presence of discharges is required to fully understand this technology.

The utilization of electric fields large enough to form a low density region (gaseous bubble) on the HV electrode surface leads to the generation of electrical discharge [30]. The generated discharge channel does not reach the counter electrode (ground electrode) from the HV electrode due to its partial extension, thus it is characterized as partial discharge system. Characteristics of pulsed corona discharge listed by Locke et al. (2006) have been summarized in Table 2.1 [9, 31].

Table 2. 1. Characteristics of Pulsed Corona Discharge

Voltage rise time	10^{-9}-10^{-7} s
Peak voltage	10-1000 KV
Peak current	10-100 A
Pulse repetition rate	100-1000 Hz
UV light generation	Weak to moderate
Pressure wave generation	Weak to moderate

Species Generated by Pulsed Corona Discharge

Underwater electrical discharges lead to the formation of several species, including highly reactive, short-lived radicals and longer-lived species, which can be investigated using spectrophotometric methods such as emission spectroscopy owing to its high sensitivity and speed of detection.

As stated by bubble theory, electrical discharge inception passes the water bubbles (vapor) breakdown. As a result of water vapor breakdown through electron collision, primary radicals of $^{\bullet}$OH and hydrogen atom ($^{\bullet}$H) are formed [31]. However, the generation of reactive species is not limited to these radicals. Dolan et al. (1992) has listed 16 pathways for the generation of different species due to water bubbles (vapor) breakdown by the electron impacts with water molecules (Table 2.2) [32].

Table 2. 2. Possible Reactions of Water Vapor with Electrons

No	Reactions		Products
1	$H_2O + e^-$	→	$H_2O^+ + 2e^-$
2	$H_2O + e^-$	→	$OH^+ + H^\bullet + 2e^-$
3	$H_2O + e^-$	→	$O^+ + 2H^\bullet + 2e^-$
4	$H_2O + e^-$	→	$O^+ + H_2 + 2e^-$
5	$H_2O + e^-$	→	$H^+ + OH^\bullet + 2e^-$
6	$H_2O + e^-$	→	$H^+ + O^\bullet + H^\bullet + 2e^-$
7	$H_2O + e^-$	→	$H_2^+ + O^\bullet + 2e^-$
8	$H_2O + e^-$	→	$OH^- + H^+ + e^-$
9	$H_2O + e^-$	→	$O^- + H^\bullet + H^+ + e^-$
10	$H_2O + e^-$	→	$O^- + H_2^+ + e^-$
11	$H_2O + e^-$	→	$OH^+ + H^- + e^-$
12	$H_2O + e^-$	→	$H^- + O^+ + H^\bullet + e^-$
13	$H_2O + e^-$	→	$H^- + O^\bullet + H^+ + e^-$
14	$H_2O + e^-$	→	$OH^\bullet + H^\bullet + e^-$
15	$H_2O + e^-$	→	$O^\bullet + 2H^\bullet + e^-$
16	$H_2O + e^-$	→	$O^\bullet + H_2 + e^-$

The primary species generated in the aqueous plasma are $^\bullet OH$, $^\bullet H$, and $^\bullet O$, which subsequently recombine in the bulk solution to form other radicals such as $^\bullet HO_2$, singlet oxygen ($^1O_2$) and superoxide ($O_2^{\bullet -}$) or longer lived and stable by-products such as H_2O_2, O_3 and H_2. Depending on the solution conductivity and magnitude of the discharge energy, UV irradiation can also be produced when primary excited species return to a lower energy level state [2, 41, 42].

Studies demonstrate the generation of $^\bullet OH$ and $^\bullet H$ radical occur as a result of water molecule dissociation by excited electrons (equation 2.1) [30].

$H_2O^* + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}H + H_2O$ (2.1)

Hydrogen gas (H_2) and oxygen atom (${}^{\bullet}O$) are other possible products of this reaction. Direct ionization by electron impact also leads to radical generation, however the probability of this reaction is very low. ${}^{\bullet}OH$ radicals, subsequently, can be dissociated into ${}^{\bullet}O$ and ${}^{\bullet}H$ radicals under higher energy input [35]. These species also react with water molecules to form ${}^{\bullet}OH$ radicals and H_2 gas. ${}^{\bullet}OH$ radical has the largest standard redox potential (in the world) ($E^0_{\bullet OH / H2O} = 2.85$ V, vs. standard hydrogen electrode, pH = 0) after fluorine ($E^0 = 3.03$ V, vs. standard hydrogen electrode, pH = 0) and it is a powerful, non-selective oxidizing agent responsible for degradation of various organic molecules including carbamazepine (CBZ) [36].

Water molecule breakdown and the generated discharge channel with very high temperature also leads to thermal dissociation of water molecules as well as induced UV light decomposition, both of which result in the generation of ${}^{\bullet}OH$ and ${}^{\bullet}H$ radicals according to the equation 2.2 [31].

$H_2O \rightleftarrows {}^{\bullet}OH + {}^{\bullet}H$ (2.2)

The most likely pathway for the breakdown of water molecules is through reacting with photons. UV irradiation is dissipated over the whole electrode gap and forms the species via the following pathway (equation 2.3).

$H_2O + h\nu \rightarrow H_2O^* \rightarrow {}^{\bullet}OH + {}^{\bullet}H$ (2.3)

Generated radicals undergo subsequent recombination process to yield more stable by-products such as H_2O_2, O_2 and H_2 gases (Eqns.2.4-2.6).

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (2.4)$$

$$^{\bullet}H + {}^{\bullet}H \rightarrow H_2 \quad (2.5)$$

$$^{\bullet}OH + {}^{\bullet}O \rightarrow O_2 + {}^{\bullet}H \quad (2.6)$$

Clements et al. in 1987 investigated the effect of gas injection through the electrode in the reaction region [37]. They reported the generation of O_3 as a result of O_2 bubbling. Sun et al. (1997) conducted an optical study to investigate various species formed by underwater pulsed corona discharge. The optical emission results verified the generation of radicals such as $^{\bullet}OH$, $^{\bullet}H$, and $^{\bullet}O$. They related the optical emission of the $^{\bullet}OH$ radicals to UV light, which is increased with solution conductivity (from 1 µS/cm to 80 µS/cm) and then decreased as conductivity increased beyond 80 µS/cm [38]. In the study done by Kirkpatrick and Locke (2005), more stable species such as H_2O_2, O_2 and H_2 molecules, in addition to radicals, are generated [33]. This is due to a decrease in the discharge channel temperature, and therefore a decrease in the bubble dissociation which subsequently reach the bulk region where secondary reactions occur [33]. The results of this study demonstrate the generation of H_2O_2 by corona discharge which leads to the production of $^{\bullet}HO_2$ radical and water as a result of the reaction with $^{\bullet}OH$ radicals, as shown in the following equations (2.7 and 2.8).

$$^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}HO_2 + H_2O \quad (2.7)$$

$$^{\bullet}HO_2 \rightleftharpoons O_2^{\bullet -} + H^+ \qquad pK_a = 4.8 \quad (2.8)$$

Other studies have successfully generated other reactive species including $^\bullet O_2$, $O^{-\bullet}{}_2$, $^1O_2$; and long-lived species such as O_3 (as well as $^\bullet H$, $^\bullet O$, $^\bullet OH$, $^\bullet HO_2$, H_2O_2 and UV light) when using the O_2 for the gaseous phase [28, 30, 47–52]. $^\bullet OH$ radicals are produced during the radical formation reactions when H_2O_2 is dissociated in the liquid phase (equation 2.9) [53, 54].

$$H_2O_2 \rightarrow {}^\bullet OH + {}^\bullet OH \qquad (2.9)$$

$O_2^{\bullet-}$ radicals are created through two different pathways. The mechanism consists of either a) solvated electrons (e^-_{aq}), generated from electron contact with the bubble/liquid interface, reacting with $^\bullet O$; or b) $^\bullet H$ radicals reacting with O_2 molecules [46]. The former mechanism occurs relatively infrequently as electron occurrence in the liquid phase, and thus electron solvation, is rare [47]. $O_2^{\bullet-}$ radicals can either oxidize or reduce the species of concern.

UV light is a reactive species generated by electrical discharges, which leads to photochemical reactions. The influence of the UV light generated is affected by the amount of input energy into the liquid phase [48]. The UV light level varies by solution conductivity. Increasing the solution conductivity results in an increase in the UV light formation [49]. Another factor impacting the UV generation is the plasma power. Therefore, the spark and arc systems with the higher energy produce UV lights more efficiently than the corona streamer discharges do.

2.1.2.2. Chemical and Physical Effects Induced by Liquid Phase Electrical Discharges

Chemical Reactions

Chemical reactions are initiated by highly energetic electrons (10 eV) in the liquid phase plasma region as well as energetic photons when electrical discharges are generated in the water phase. The chemistry of the reactions is influenced by different factors such as the components of the liquid solution, electrical conductivity, and characteristics of electrodes in the liquid phase. The reactions occur differently for the different electrolytes and in the absence or presence of species quenching the radical reactions. Conductivity of the solution, for instance, impacts the electrical discharges and, subsequently, the reactive species generation. Higher solution conductivity lowers the radical generation; however, it results in a higher rate of UV light formation [49]. Moreover, the electrode material causes in different reactions in the water by changing the solution content due to the ion release.

Physical Effects

Physical degradation can occur due to UV light, thermal decomposition, shock waves, and energetic ultrasound. Studies have demonstrated the contribution of generated UV radiation in organic compounds degradation such as phenol [50]. The reaction pathway could be either direct reaction with organics or generation of reactive species which, subsequently, can react with the organic contaminants.

Fast discharge propagation in the arc system generates shock waves with the 5-20 K bar pressure [51]. The shock waves then influence the thermal decomposition of organics when the O_2 is absent (pyrolytic) and the reactions in which the radicals are participated. When pressure decreases, the generated shock waves transform to refraction waves, which, subsequently, form very short secondary shocks. However, the efficiency of shock wave formation in the liquid phase surrounding the plasma region is not high, and it is dependent on input energy to the system [52]. The reported approximate amount of shock wave formation due to electrical discharges under water phase is 8% of total energy input [53].

Influential Factors on Electrical Discharge Formation and Characteristics

This section describes the influential parameters on electrical discharge initiation and the related features in aqueous phase as the first step on the investigation of underwater discharges in organics degradation, including solution pH, solution conductivity, gas type, and gas flow rate.

Solution Conductivity. The solution conductivity is considered a very influential factor playing a key role in all discharge parameters including initiation and characterization [37]. Solution conductivity increases as the treatment time passes [9]. This has resulted from increasing the solution temperature due to formed discharges.

In more conductive solutions, electrical discharge generation is facilitated and the threshold voltage decreases. More conductivity indicates more ionic species in the solution, therefore less resistance to current flow. Higher current propagation results in water molecules being heated and vaporized more easily, resulting in easier and faster discharge formation.

The relaxation time (є/σ) is longer in distilled water than that of in conductive water (0.202 mS/cm), therefore the discharge characteristics are also changed with changing solution conductivity [9]. When the solution conductivity is low, a limited range of pulse voltages can be applied so that a sustainable streamer, but not spark, is formed [54]. Transition from corona discharge into spark discharge occurs in lower water conductivities [55]. In addition, higher conductivity results in a shorter discharge length. In higher conductivity solutions the electrical field space on the growing streamer head must be compensated more rapidly, which results in a shorter streamer length, thereby decreases the $^{\bullet}OH$ radical generation [9].

Solution pH. The electrical discharge process results in changing solution pH as treatment proceeds. Sun et al. (1999) showed a rapid decrease in pH of phenol solution with treatment time until it reached steady state within 8 min of commencing treatment [39]. They ascribed the decrease of solution pH during treatment to H_2O_2 production as well as primary organic acids such as muconic and fumuric and secondary smaller organic acids such as oxalic and formic acids. Studies indicate the dependency of reactive radicals emission intensity such as $^{\bullet}OH$, $HO^{\bullet}_2$, and $O^{\bullet -}_2$ on solution pH, however the H_2O_2 formation is independent of pH variation for solutions with conductivity of below 500 μScm^{-1} [46, 64, 65].

Application of Gas Bubbling and Gas type. Gas bubbling through the HV electrode significantly affects the generation and characteristics of the discharge in the liquid phase. According to bubble theory, electrical discharge initiation is facilitated when the solution is saturated with gases, as gas bubbles replace water bubbles, which are required for discharge breakdown, lowers the electric field required to initiate discharge resulting in less required energy input [58]. However, in the absence of gas bubbles, a large amount of energy and thus more input power is required to vaporize the water in order to generate the water bubbles. As a result, gas bubbling may improve system efficiency as it also reduces energy being contributed to water vaporization to form the bubbles, which results in less required input power. In the presence of gas bubbling, streamer branches propagate easily in all directions from the needle tip because the density of the medium in the gas bubble is much lower than the water.

In the absence of gas bubbles, corona discharges are unlikely to be generated; discharges are mainly spark, which proceed at a higher rate, with longer life spans, reaching the counter electrode. Generated sparks have the potential to destruct the electrode tips, the electrode coating, and damage the reactor due to overheating caused by spark channels. Lower applied voltages, larger electrode gaps, the use of gas bubbling, and higher solution conductivities can prevent the sparks from forming.

The type of gas employed also influences the plasma characteristics and therefore the types and concentrations of reactive species generated. Facilitated initiation of ionization and electron avalanche process impacts the formation of reactive species and reduces the joule heating loss occurred due to the vaporization. Different injected gases are, thus, anticipated as a positive influence on the removal of organic compounds from water [46, 67–69].

Gas Flow Rate. The electrical discharge generation is also influenced by the flow rate of injected gases into the reaction zone. The discharge channel initiation is facilitated when the gas flow rate is raised. The fact is that strong electric fields are required to overcome the density of water and the considerable resulting resistance in order to generate electrical discharges. Higher flow rates can defeat this resistance as it decreases the density of the medium and therefore results in easier discharge initiation. In addition, the generation and evolution of electron avalanches with increasing gas flow rates facilitates the plasma discharge formation. An upper limit to the gas flow rate exists; however, as when the solution within the electrode gap becomes too highly saturated with gas, the liquid breakdown ability is lowered.

2.2. Pharmaceutical Compound Degradation by Underwater Electrical Discharge

This section presents an overview of pharmaceutical compounds, and specifically CBZ and its metabolites, which are highly persistent compounds, its toxicity effect on ecosystem, and its treatment technologies are covered.

2.2.1. Pharmaceutical Compounds

Pharmaceuticals are classified as synthetically produced organic chemicals. A wide variety of applications, including human and veterinary medicine, aquaculture, and agriculture, have led to pharmaceutical compounds being synthesized in large volumes [55]. Additionally, as a result of growing population and ongoing progress in scientific achievements, pharmaceutical production is increasing. US IMS health reported a 5.4% increase in prescribed pharmaceuticals from 2008 to 2012 [62]. Pharmaceuticals are excreted from the body in the form of the parent compound or metabolites [63]. Many pharmaceuticals compounds are highly resistant to biodegradation and conventional treatment technologies [72, 73], and consequently their residuals have frequently been found in effluents from wastewater treatment facilities. These micropollutants have also been detected in various aquatic environments including surface water, ground water at up to low $\mu g.L^{-1}$ concentrations, and have potentially affected the ecology even at these low concentrations [74–80].

2.2.1.1. Carbamazepine and Potential Metabolites

CBZ has been important drug for treating a wide variety of diseases since 1962. It has been widely used as a strong antiepileptic (anticonvulsant) drug to treat different kinds of seizure disorders. Epilepsy or seizure disorder, caused due to neuron system malfunction, is one of the prevailing kinds of neuron disorders. It is also an efficient mood stabilizer [73] that is why it has been effectively used to treat schizophrenia disorder. Moreover, mental disorders such as bipolar disorder have been dealing with using this drug [82, 83]. CBZ also lowers sever nerve pain. In some cases, combined with other drugs, it is an effective drug for treatment of alcohol withdrawal syndrome [76]. Due to its range of applications, CBZ is prescribed often; the reported prescribed volume of CBZ in 2001 in Canada was 28 tons [77]. CBZ is absorbed by the human body at a rate of approximately 72%, and the remaining approximately 28% is excreted from the body [78]. After absorption and metabolizing by the liver, just 1% leaves the body in the parent form; the remaining 71% is excreted in urine in the form of metabolites. CBZ is a three-ring aromatic molecule with amine functional group (Figure 2.3), which creates polarity. The general characteristics of CBZ are listed in Table 2.3.

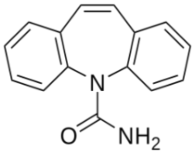


Figure 2. 3. CBZ Structure

Table 2. 3. CBZ Properties

Formula	$C_{15}H_{12}N_2O$
Molecular weight	236.26858 $g.mol^{-1}$
Water solubility	17.7 $mg.L^{-1}$ (20 °C), 20 $mg.L^{-1}$ (25 °C),
Complete solubility	ethanol
IUPAC name	5H-dibenzo[b,f]azepine-5carboxamide
pK_a	13.9

References: www.sigma-Aldrich.com, PubChem (open chemistry database)

Studies have reported 33 potential CBZ metabolites detected in urine samples collected from both rats and humans [79]. The most important CBZ metabolites include trans-10,11-dihydro-10,11-dihydrocarbamazpine (CBZ-DiOH) and 10,11-dihydro-10,11-epoxycarbamazepine (CBZ-EP) [77]. CBZ-DiOH is excreted with urine in about 30% and has been detected more frequently in wastewater samples [78]. Additionally, it is a metabolite of a CBZ derivatives called oxacarbazepine. The importance of CBZ-EP is associated to its anti-epileptic properties and pharmaceutical activity as the parent compound.

Five CBZ metabolites have been investigated in the aqueous environment using LC/MS/MS technology [80]. The primary proposed route of CBZ biotransformation is oxidation of the 10-11 carbon-carbon double bond in the azepine ring by oxidants such as $^{\bullet}OH$ to yield 10,11-dihydro-10,11-epoxycarbemazepine. Although stable, this metabolite is subsequently hydrated to 10,11-dihydro-10,11-dihydroxycarbemazepine when its epoxy ring is hydrolyzed. 10,11-dihydro-10,11-epoxyCBZ may potentially pose toxicity risk to the neuron system [89, 90]. CBZ and its five metabolites have been detected in WWTP influents and effluents and CBZ and CBZ-DiOH in surface water in Canada. Figure 2.4 shows CBZ and its five metabolites [80].

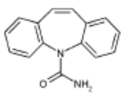
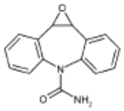
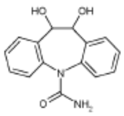
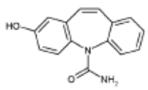
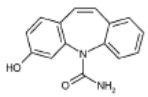
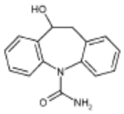
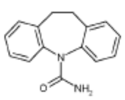
	carbamazepine	CBZ	$C_{15}H_{12}N_2O$ 236.10^a
	10,11-dihydro-10,11-epoxycarbamazepine	CBZ-EP	$C_{15}H_{12}N_2O_2$ 252.09
	10,11-dihydro-10,11-dihydroxycarbamazepine	CBZ-DiOH	$C_{15}H_{14}N_2O_3$ 270.10
	2-hydroxycarbamazepine	CBZ-2OH	$C_{15}H_{12}N_2O_2$ 252.09
	3-hydroxycarbamazepine	CBZ-3OH	$C_{15}H_{12}N_2O_2$ 252.09
	10,11-dihydro-10-hydroxycarbamazepine	CBZ-10OH	$C_{15}H_{14}N_2O_2$ 254.10
	10,11-dihydrocarbamazepine^b	CBZ-DiH	$C_{15}H_{14}N_2O$ 238.11

Figure 2. 4. CBZ and the Proposed Metabolites in Aqueous Environment (Source: Metcalf et al. 2003 [77])

Other studies have generated CBZ metabolites through UV irradiation, oxidation by chlorine dioxide (ClO_2), and oxidation by activated sludge. According to these studies, the 10,11-double bond on the CBZ molecule is the most common target for oxidative species [83]. The oxidation reaction of CBZ by $^{\bullet}OH$

radicals first produces, 10,11-dihydro-10,11-epoxycarbemazepine [84], and quinazoline derivative (BQD) is the subsequent metabolite, which results from cleavage of the epoxide ring [85]. A potential intermediate is involved in BQD generation, in which the azepine ring is contracted forming an aromatic structure (Figure 2.5), leading to production of another potential metabolite called acridine-9-carbaldehyde (X4) or acridone-*N*-carbaldehyde (X3) [48]. Transformed products will continue to be generated as a result of breaking the aldehyde bond leading to the formation of ACIN and then ACON. As there are primary chains in the CBZ structure, the second primary pathway for metabolite formation is the chain cleavage due to thermal effects or a number of oxidants [83]**.**

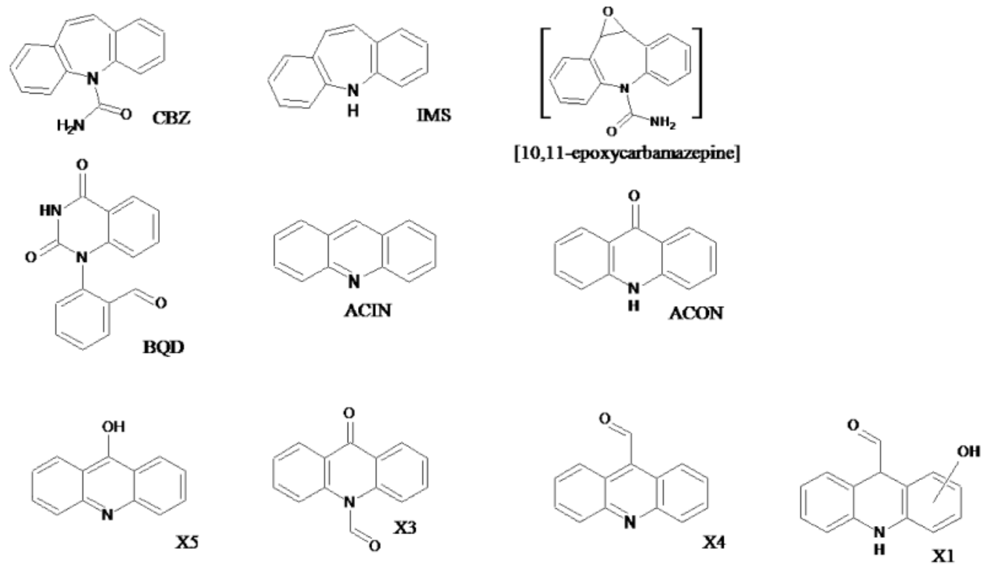


Figure 2.5. Potential metabolites resulting from oxidation by ClO_2, photodegradation by UV irradiation, and biotransformation by activates sludge (Source: Heath et al. 2009 [83])

2.2.1.2. Toxicological Effect of CBZ on Aquatic Species

Even at trace concentrations, CBZ can cause toxicological effect on aquatic species. Some examples of irreversible effects on these species are listed below.

- Alteration in phenotypic characteristics (reproduction and behavioral response) in invertebrates [86]
- Disturbance in the digestive gland enzymes function and also muscle blood cell function in bivalves [87]
- Growth hindrance in Daphnia [88]
- Inhibition of neurological enzyme activity in shrimp [89]
- Increase in regeneration length and decrease in the number of new sections generated in polychaetes [73]
- Losing the defense mechanism against the oxidation, leading to lipid peroxidation enhancement in macroinvertebrates [87]
- Reduction of membrane stability of cytoplasmic organelles, induce the activity of organs producing cytochrome p450 enzymes, and destruction of DNA in gills and hepatopancreas tissues in crab [87]
- Induction of the activity of estrogens, resulting in estrogenic activities in fish [90]

Continuous exposure to pharmaceuticals resulting from the accumulation of pharmaceutical residuals in the food chain, and regular consumption of water contaminated with pharmaceuticals, can potentially raise the possibility of risk to human health [99–101]. Infants, fetuses and people with impaired enzymes function are especially vulnerable to chronic effects from these exposures [91].

2.2.2. Existing CBZ Treatment Techniques

CBZ is not effectively removed through conventional drinking water treatment as it has a low distribution coefficient between the aqueous and secondary sludge phases [78], [94]. Ternes et al. (2002) found that coagulation using iron(III) chloride, followed by flocculation and sedimentation, resulted in only 12% removal of CBZ [64]. Additionally, the complex spatial structure of CBZ (a three-ring phenolic base compound) requires a high activation energy in order to react with oxidants. Oxidation ClO_2 did not result in any removal of CBZ [105] as it shows low reaction rate constant ($<0.015\ M^{-1}\ s^{-1}$) [95]. Treatment techniques such as membrane filtration (micro-filtration) in a hybrid system with granular activated carbon (MF-GAC) have resulted in partial removal of CBZ (63%) [96]. Dual membrane hybrid systems, in which nano-filtration is added as a post treatment to the MF-GAC system, have achieved more than 80% removal of CBZ [96]. However, the fouling issue and formation of concentrated filtrate requiring further treatment are drawbacks with these methods. A number of advanced oxidation processes (AOPs) have been employed with varying degrees of success in fully or partially oxidizing CBZ including: ozonation (>90%) [64], direct photolysis in the presence of Fe (III) and chloride (Cl^-) species (>95%) [97], UV/H_2O_2-induced photo degradation (90%) [48], and photocatalytic degradation using TiO_2 as a catalyst (78.4%) [84]. In spite of their demonstrated effectiveness for the removal of CBZ, these AOPs have some disadvantages, including: incomplete mineralization [83], required continuous supply of O_3 or H_2O_2 [98], required O_2 and/or H_2O_2 storage thereby introducing long-term stability and corrosion issues [55], required post treatment to remove potentially toxic catalysts [99], and the risk of adsorption on the catalyst surface rather than mineralization [99].

2.2.3. Application of Underwater Electrical Discharges for the Destruction of Organic Compounds

A wide variety of contaminants have been degraded by underwater electrical discharges, including organics [100] and microorganisms [2]. Example of organics treated by underwater discharge include dyes and phenolic compounds [3, 109–113]. Decolorization of a dye present in water via the reactive species generated by the process was first investigated by Clements et al. in 1987 [37]. This was a starting point for the application of electrical discharges in the purification of drinking water. Phenol has been widely utilized as a model for underwater electrical discharge treatment to understand the reaction pathways of more structurally complicated organics due to its simple structure. Furthermore, phenolic byproducts are completely known, which assists the study of by-product formation. This technology has also been applied to pharmaceutical compounds including CBZ, diazepam, ibuprofen, 17 a-ethinylestradiol, diclofenac, bisphenol A, hydroquinone, and caffeine [63, 114].

Hijosa-Valsero et al. (2013) investigated a laboratory scale degradation of organic micro-pollutants (atrazine, chlorfenvinfos, 2,4-dibromophenol, and lindane) in two atmospheric pressure nonthermal plasma reactors-conventional batch reactors and coaxial thin-falling-water-film- under DBD [26]. The samples were primary effluents collected from a pharmaceutical manufacture with the conductivity of 705 $\mu S.cm^{-1}$ and a solution pH of 7.3. Faster degradation kinetics were observed for all pollutants in batch reactor ((0.534 min^{-1} for atrazine; 0.567 min^{-1} for chlorfenvinfos; 0.802 min^{-1} for 2,4-dibromophenol; 0.389 min^{-1} for lindane) than those of in coaxial reactor (0.104 min^{-1} for atrazine; 0.523 min^{-1} for chlor- fenvinfos; 0.273 min^{-1} for 2,4-dibromophenol; 0.294 min^{-1} for lindane). Removal was achieved at lower rates when atrazine and lindane were spiked in industrial wastewater ($k = 0.117$ min^{-1} for atrazine; $k = 0.061$ min^{-1} for lindane). The removal efficiency of contaminants in pure water solutions study showed an improved degradation of parent compounds with an increase in treatment time, however generated by-products were not fully removed after 15 min of treatment time. In the study of energy efficiency, coaxial reactors were more energy efficient than the batch reactors. The energy input was 47-447 mg/KWh. As stated in this investigation, the researchers found that the effectiveness of this technology is hindered by the significant amount of consumed gas which should be taken into consideration.

Krause et al. (2009) investigated the effect of corona discharge generated over a thin water layer to degrade CBZ, clofibric acid, and iopromide from one solution. In this study, a two barrier electrode geometry has been used to treat ultra pure water and landfill leachate containing target contaminants [107]. Solutions were treated using pulsed and continuous modes. The results show improved degradation efficiency for continuous treatment of CBZ compared to pulsed treatment with the same energy input. The energy cost was 500 W. The removal efficiency of CBZ was 84% from solutions containing landfill leachate and up to 98% from ultra pure water within 30 min treatment time. An E-Screen Assay was conducted to evaluate the estrogen activity of iopromide, and the results showed no activity as a result of 99% removal during pulsed corona treatment after 15 min. They also examined the effect of different materials such as iron, iridium oxide, titanium and boron doped diamond (BDD) used in counter-electrode. BDD electrodes showed the highest degradation efficiency. In this study, pumping air and a mixture of Ar/air through the barrier electrodes showed an effective degradation.

Gerrity et al. (2010) studied a pilot-scale NTP generated by corona discharge in an electrode-to-plate configuration for the removal of pharmaceuticals such as CBZ and endocrine disrupting compounds in tertiary-treated wastewater and contaminated surface water [108]. In this study, the treatment efficacy of the process was evaluated varying water qualities. The results indicate rapid removal of all pharmaceuticals including CBZ with up to 90% degradation rate. They also examined the decomposition rate of contaminants in the batch mode and the potential treatment abilities of the technique in single-pass modes. The initial concentration of CBZ in the batch experiment was 176 $ng.L^{-1}$ and in the wastewater and spiked surface water single-pass experiments was about 219 and 1600 $ng.L^{-1}$, respectively. The degradation rate of CBZ was higher than other contaminants (reaction rate constant of 1.03 k (m^3/kWh). The energy efficiency evaluation was the other objective of this study. The required electrical energy per order of magnitude was less than 0.3 kWh/m^3-log for CBZ in surface water which is less than required amount in AOP methods (0.4-2.3 kWh/m^3-log for UV based oxidation processes).

Panorel et al. (2013) investigated the efficiency of gas phase pulsed corona discharge created along wires for the degradation of some pharmaceuticals [109]. The contaminated solution was showered in jets, droplets and films between electrodes. The effect of pulse repetition rate, the amount of energy consumed, and the O_2 gas injection as the gas phase into the reaction zone has been examined in this study to evaluate the energy efficiency of the system. The results showed a complete degradation ranging from 70-99% removal in 30 min while 500W energy was used. The degradation rate was enhanced when O_2 gas was injected in the gas phase, which was associated to generation of O_3 and $^{\bullet}OH$ radicals.

Dobrin et al. (2013) used pulsed corona discharges in O_2 over the liquid surface for the removal of pharmaceutical diclofenac (DCF) from the spiked tap water, where the discharges were generated in copper wires [27]. The solution conductivity was 250 $\mu S.cm^{-1}$ and the obtained solution pH was 6. The results demonstrated a complete removal of >99% of an initial concentration of 50 mg.L^{-1} in 15 min and the 0.76 g/kWh energy consumption. Total Organic Carbon (TOC) measurement also showed a 50% decrease after 30 min treatment. By-products study did not show any chlorinated degradation products, indicating over 95% of chlorine (Cl) present in DCF was eliminated as Cl^- ions, however carboxylic acids such as formic, acetic, oxalic, malonic, maleic and succinic were detected, leading to a possible degradation pathway of DCF.

In another study done by Sugiarto and Sato (2001), spark discharges were used to investigate the effect of discharge type on removal efficiency of phenol [101]. The results showed an enhanced degradation when spark is combined with streamer discharge compared to individual spark or streamer discharge application. The effect of O_2 bubbling into the reaction zone was also studied, which demonstrated a great influence on phenol degradation rate. This could be related to $^{\bullet}O$ and $^{\bullet}OH$ radicals produced when generated O_3 undergo the reaction with UV or energetic electrons. The study of the addition of chemicals such as H_2O_2 into the reactor showed significant degradation of phenol, which resulted from the dissociation of H_2O_2 during photolysis by UV and generation of $^{\bullet}OH$ radicals. The energy consumption in this study was 20 KV.

Sato et al. (2009) used a hybrid system consisting of underwater corona discharge and spark discharge generated in a point-to-plane configuration to decoloration of Rhodamine B [110]. Combined system was used to increase the energy efficiency compared to when only spark discharges are applied and to increase the decoloration rate compared to streamer discharge application. The spark discharges require more energy (360 J/mL energy input for 80 % decoloration); therefore, to increase the energy efficiency of the spark mode, H_2O_2 was added and 70-80 J/mL energy requirement was achieved. The increase in solution conductivity showed a decrease in streamer length which was leveled off at 0.01 $mS.cm^{-1}$ conductivity, leading to a decrease in decoloration rate. Increasing the streamer length led to the generation of spark discharge. The effect of treatment time and air/Ar/O_2 gas bubbling also was explored on the decomposition efficiency of phenol. The results showed higher degradation efficiency when treatment time increases and it was higher for O_2 application than air in the corona discharge mode. Additionally, the effect of reactor type on phenol removal showed higher efficiency for reactors containing O_2 gas than Ar gas phase. The generation of O_3 and conversion to $^{\bullet}OH$ radicals and other oxidants was likely the reason.

Malik et al. (2002) in a similar set up investigated the decoloration of methylene blue from distilled and tap water by aqueous phase pulsed corona discharge alone and combined with O_2 and O_3 bubbling [111]. A point-to-plane geometry was used to generate the electrical discharges. The results showed a decolourization of methylene blue from the DI water within 120 min as a result of treatment by corona discharge. This time was reduced to 25 min when O_2 was bubbled through the reaction region and to 8 min with O_2 and O_3 enrichment. The required treatment time for decolourization from tap water, however, was higher for all three cases: pulsed corona discharges (>210min)> pulsed corona discharges with O_2 bubbling (30 min)> pulsed corona discharges with O_2+O_3 bubbling (11 min). The different decomposition rates of contaminant in DI and tap water verified the different characteristics of corona discharge in two solutions and the effect of solution conductivity in the generation rates of reactive species. After treatment, the pollutant concentration, solution pH, and solution conductivity were also measured. Energy consumption was estimated at 41mg/KWh.

Lukes and Locke (2005) investigated a point-to-plane hybrid system consisting of over water gas phase discharge and the concurrent generation of liquid phase corona discharge for degradation of substituted phenols [7]. Ar and O_2 were used as gas phase constitutions to study the degradation mechanism. Phenols were degraded when $^{\bullet}OH$ radicals and O_3 in the presence of Ar and O_2 attack phenol ring during electrophilic substitution reactions. The degradation efficiency of 47-80% within 60 min treatment time has been achieved. The oxidation kinetics and the reactivity of phenols as a function of chemical structure were studied. The produced hydroxylated by-products from the reaction of phenols with $^{\bullet}OH$ radicals or O_3, and the generated muconic acid from the reaction with O_3 have verified the possible mechanisms of substituted phenols degradation. The energy cost was 281-457 KWh/m^3.

In a recent study done by Banaschik et al. (2015), the capability of aqueous corona discharge on removal of seven persistent pharmaceuticals (carbamazepine, diatrizoate, diazepam, diclofenac, ibuprofen, 17a-ethinylestradiol, trimethoprim) has been explored [55]. In this study, corona discharge was generated in a reactor with extended coaxial configuration filled with spiked clean water with the 30 $\mu S.cm^{-1}$ conductivity. A Marx generator has been used to apply positive high voltage pulses with peak voltage of 80KV, 20 Hz repetition rate, a pulse width of about 270-300 ns at FWHM, and a rise time of 30 ns. The recorded current waveform shows a peak current of 200 A with a pulse period of 100 ns. The volume of water was 300 mL. For most pharmaceuticals, degradation rates ranging from 45% to 99% within 15-66 min treatment time was achieved. CBZ was decomposed by 90% after 66 min. In this study, water quality parameters such as temperature, solution pH, solution conductivity, concentration of dissolved O_2 were monitored. Possible generation of nitrate and nitrite was also studied. The result of these investigations showed no notable change in pH and nitrate and nitrite concentration. The averaged energy dissipated per pulse was 1.4 J. They finally degraded phenol as a chemical probe and investigated its possible by-products. Measuring the concentration of H_2O_2 and studying the reaction mechanisms of phenol with $^{\bullet}OH$ radical, they implied that it was likely $^{\bullet}OH$ radical oxidation causing the degradation.

2.2.4. Oxidation by Reactive Species in the Liquid Phase

In the liquid phase, organic compounds are degraded when primary and secondary radicals, ions, and molecules generated by the discharges attack the target bonds. $^{\bullet}OH$ radical readily react with aromatic and unsaturated aliphatic compounds via an electrophilic addition process (radical- molecule reaction: see equation 2.10) during the oxidation process. In this reaction, $^{\bullet}OH$ radical attacks the phenolic ring as an electrophile [37, 120].

$$^{\bullet}OH + PhX \rightarrow HOPhX^{\bullet} \qquad (2.10)$$

Organics also undergo the reaction with $^{\bullet}O$ ($E^0_{O/H2O}$ = 2.42 V). As the knowledge behind the reaction mechanism of the $^{\bullet}O$ with organics is not well understood, it is hypothesized that it undergoes an electrophilic addition reaction with aromatics and unsaturated aliphatic compounds, similar to $^{\bullet}OH$ radicals [30]. $HO^{\bullet}_2$ radical as the weakest oxidative species generated by plasma ($E^0_{HO^{\bullet}2/H2O}$ = 1.44 V) also react with organic compounds via hydrogen abstraction mechanism. This radical is pH dependent and exists in an equilibrium with $O^{\bullet -}_2$ ($E^0_{O^{\bullet -}2/H2O}$ = -0.33 V) [36]. At pH = 3.5, $^{\bullet}HO_2$ possesses 95% of the equilibrated concentration while at pH = 6, it accounts for 6% of the equilibrated concentration. However, no experimental evidence has proved the degradation of organics by this radical. H_2O_2 with oxidation potential ($E^0_{H2O2/H2O}$) of 1.77 V [36] is another oxidant reacting with organic molecules either directly or indirectly through the photolysis or Fenton's reactions (equation 2.11) [113]) and production of $^{\bullet}OH$ radicals in the bulk liquid solution. In this reaction, iron salt is used to produce Fe^{2+}. Organics might also directly react with the O_3 molecule [112]. $^1O_2$ as a better electrophile than $^3O_2$ react with unsaturated organic compounds with electron donating substituents through substitution reaction [114].

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \qquad (2.11)$$

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Chapter 3: Carbamazepine Removal Using Pulsed Corona Discharge in Aqueous Solution

Pourzarea R., Lakhian V., and Dickson-Anderson S.E. Carbamazepine Removal by Pulsed Corona Discharges in Aqueous Solutions. *Will be submitted to Journal of Water Research*

Abstract

Pulsed-streamer corona discharge has been utilized for treatment of carbamazepine (CBZ) in aqueous solution. The influence of solution pH, electrical conductivity, gaseous species, and gas flow rate on removal efficiency has been investigated and the optimal conditions for achieving the highest degradation rate are determined. The results indicate that acidic condition is favorable for CBZ removal, and increase in solution conductivity to 500 µS.cm^{-1} decreases the degradation efficiency. The results also demonstrate the great influence of gas bubbling on discharge generation and, thus, the removal efficiency, which is further improved when the argon flow rate increases from 20 to 50 mL.min^{-1}. The highest removal level was achieved when oxygen gas is bubbled through the high voltage electrode (HV) into the reaction region. Treated samples were analyzed by LC/MS/MS technique to quantify the degradation level of CBZ. In the present work, CBZ has been removed from the simulated polluted drinking water samples, and degradation levels of 14 – 94% were achieved within 25 minutes of treatment, depending on the applied conditions.

Keywords- Pulsed corona discharge, Plasma, Removal rate, carbamazepine, Gas injection

3.1 Introduction

Many pharmaceuticals have been observed in the aquatic environment by researchers [1]. These synthetic organic compounds are widespread in use in human and veterinary medicine production, aquaculture, and agriculture. Discharge from insufficiently treated industrial, hospital, and domestic wastewater, runoff from agricultural land and aquaculture sites, discharge from septic systems, wastewater effluents used for aquifer storage, and landfill leachates have resulted in pharmaceuticals and their metabolites increasingly emerging in aquatic environments, often contaminating potential drinking water sources including both surface water and groundwater [2, 3].

Antiepileptics are a class of pharmaceuticals, prescribed for the treatment of epilepsy, that are categorized as highly recalcitrant, non-biodegradable organics. Pharmaceuticals within this class therefore typically withstand degradation in wastewater treatment plants (WWTPs). Not surprisingly, studies have reported increasing concentration of antiepileptics, and CBZ in particular, in the environment including surface and ground water, the influent and effluent streams of wastewater treatment plants (WWTPs), and treated drinking water in a number of countries [2, 3]. The increasing concentration of CBZ in the aquatic environment is of great concern, raising the potential for adverse effects on human and environmental health. Exposure to CBZ, even at the ng.L^{-1} concentration range, has the potential to cause biological harm to the ecosystem [4–6] including effects on reproduction and regeneration period, impaired digestive and blood cell function, hindered growth processes, and artificially induced endocrine disruption. [5, 7–10]. Chronic exposure to pharmaceuticals, even at low doses, also poses a threat to human health [11, 12]; fetuses, infants and people with impaired enzyme function are particularly vulnerable to chronic exposure to pharmaceuticals [11].

CBZ is extraordinarily persistent in aquatic environments due to its polar nature [13]. It is highly resistant to biodegradation, and therefore is not readily removed by conventional wastewater treatment processes; removal efficiencies are typically reported to be less than 10% [14]. CBZ has been observed at concentrations as high as 6.3 $\mu g \cdot L^{-1}$ in WWTP effluents [1], and up to 1.1 $\mu g \cdot L^{-1}$ in surface water [15]. In Canada, CBZ and one of its primary metabolites (10,11-dihydro-10,11-dihydroxycarbamazepine) have been detected wastewater effluents at concentrations up to 0.6 $\mu g \cdot L^{-1}$ in wastewater effluents, and in the range of 0.84 to 16.3 ng·L^{-1} in surface water [15–17]. CBZ has also been detected in groundwater at concentrations as high as 610 ng·L^{-1} [18].

CBZ is not effectively removed through conventional drinking water treatment as it has a low distribution coefficient between the aqueous and secondary sludge phases [14, 19, 20]. Ternes et al. (2002) found that coagulation using iron(III) chloride, followed by flocculation and sedimentation, resulted in only 12% removal of CBZ [13]. Additionally, the complex spatial structure of CBZ (a three-ring phenolic base compound) requires a high activation energy in order to react with oxidants. Oxidation by chlorine dioxide (ClO_2) did not result in any removal of CBZ as it shows low reaction rate constant (<0.015 M^{-1} s^{-1}) [21]. However, a number of advanced oxidation processes (AOPs) have been employed with varying degrees of success in fully or partially oxidizing CBZ including: ozonation (>90%) [13], direct photolysis in the presence of Fe (III) and chloride (Cl^-) species (>95%) [22], UV/H_2O_2-induced photo degradation (90%) [23], and photocatalytic degradation using TiO_2 as a catalyst (78.4%) [24]. In spite of their demonstrated effectiveness for the removal of CBZ, these AOPs have some disadvantages, including: incomplete mineralization [25], required continuous supply of ozone (O_3) or hydrogen peroxide (H_2O_2) [26], required oxygen and/or H_2O_2 storage thereby introducing long-term stability and corrosion issues [4], required post treatment to remove potentially toxic catalysts [27], and the risk of adsorption on the catalyst surface rather than mineralization [27].Treatment techniques such as membrane filtration (micro-filtration) in a hybrid system with granular activated carbon (MF-GAC) have resulted in partial removal of CBZ (63%) [28]. Dual membrane hybrid systems, in which nano-filtration is added as a post treatment to the MF-GAC system, have achieved more than 80% removal of CBZ [28]. These techniques, employed either alone or as hybrid systems, result in secondary wastes that require disposal or further treatment [27].

Electrical discharge methods have emerged as promising treatment techniques that effectively eliminate several of the drawbacks of AOPs, adsorption, and membranes. Specifically, it does not require subsequent separation of catalysts from the treated water, or treatment or disposal of a secondary waste stream. This technique has received great attention in a wide variety of treatment mechanisms varying from oxidation of volatile organic compounds [29], to the inactivation of microorganisms [30], to reduction of organic compounds dissolved in water [31].

The decomposition of pharmaceuticals using electrical discharge has been investigated in various configurations in which the plasma is generated in air rather than water. Hijosa-Valsero et al. (2013) investigated a laboratory scale degradation of organic micro-pollutants (atrazine, chlorfenvinfos, 2,4-dibromophenol, and lindane) from aqueous solutions in two atmospheric pressure nonthermal plasma reactors-conventional batch reactors and coaxial thin-falling-water-film reactor- under dielectric barrier discharge (DBD). Faster degradation kinetics were observed for all pollutants in batch reactor than those of in coaxial reactor. Removal was achieved at lower rates when atrazine and lindane were spiked in industrial wastewater [32]. Krause et al. (2009) employed barrier electrodes in a laboratory-scale setup to generate corona discharges over a thin layer of water, and achieved 98% degradation of CBZ after 30 min [33]. The initial concentration CBZ was 0.1 mM. Gerrity et al. (2010) investigated the removal of CBZ using non-thermal plasma (NTP) at the pilot scale and an electrode-to-plate configuration, and achieved rapid removal of CBZ, with up to 90% degradation [34]. The initial concentration CBZ was at 219 $ng.L^{-1}$ in tertiary-treated wastewater samples and at 1600 $ng.L^{-1}$ in spiked surface water samples in single-pass mode, and at 176 $ng.L^{-1}$ in batch mode. Panorel et al. (2013) investigated the efficiency of gas phase pulsed corona discharge created along wires for the degradation of some pharmaceuticals [35]. The results showed a complete degradation ranging from 70-99% removal in 30 min while 500W energy was used. The degradation rate was enhanced when O_2 gas was injected in the gas phase, which was associated to generation of O_3 and $^{\bullet}OH$ radicals. Dobrin et al. (2013) used pulsed corona discharges in O_2 over the liquid surface for the removal of pharmaceutical diclofenac (DCF) from the spiked tap water, where the discharges were generated in copper wires [36]. The results demonstrated a complete removal of >99% of an initial concentration of 50 $mg.L^{-1}$ in 15 min and the 0.76 g/kWh energy consumption.

The primary issue with generating the plasma in gas just above water, rather than within the water itself, is that the reactive species generated by the plasma must be then diffused into the aqueous phase to initiate a reaction with the pollutant [4]. Additionally, the reaction then occurs within the boundary between the liquid and gas phases, and therefore this technique can only be efficient when the liquid is present in thin layers.

These limitations are avoided when the electrical discharges are generated directly in the water to be treated [37] thereby producing an aqueous phase plasma, which simultaneously triggers a series of physical and chemical effects including: UV radiation, pressure shock-waves, thermal effects, radicals ($^{\bullet}OH$, $^{\bullet}H$, $^{\bullet}O$, $^{\bullet}HO_2$, $^{1}O_2$, $O_2^{\bullet-}$), and other reactive species (H_2O_2, O_3 and H_2,) [38]. The hydroxyl radical ($^{\bullet}OH$) radical has the largest standard redox potential ($E^{0}_{{}^{\bullet}OH / H_2O}$ = 2.85 V vs. standard hydrogen electrode, pH = 0) after fluorine (3.03 V) and it is a powerful, non-selective oxidizing agent responsible for degradation of various organic molecules including carbamazepine (CBZ) [24]. It is able to react at diffusion controlled rates and typically allows for complete degradation of the compound or mineralization to carbon dioxide [41]. The primary proposed degradation pathway for CBZ is oxidation of the 10-11 carbon-carbon double bond in the azepine ring by oxidants such as $^{\bullet}OH$ to yield 10,11-dihydro-10,11-epoxycarbamazepine. The removal efficiency is strongly dependent on the $^{\bullet}OH$ production rate [42], which in turn is dependent on input power, reactor configuration, electrode polarity, electrode coating, solution conductivity, solution pH, residence time, gas type, and gas flow rate; thus all of these factors play key roles in the removal efficacy of electrical discharge systems [38].

In the study conducted by Sugiarto and Sato (2001), spark discharges were used to investigate the effect of discharge type on removal efficiency of phenol [43]. The results showed an enhanced degradation when spark is combined with streamer discharge compared to individual spark or streamer discharge application. Sato et al. (2009) used a hybrid system consisting of underwater corona discharge and spark discharge generated in a point-to-plane configuration to decoloration of Rhodamine B [44]. The effect of treatment time and air/Ar/O_2 gas bubbling also was explored on the decomposition efficiency of phenol. The energy requirement was at 360 J/mL and at 70-80 J/mL in the presence of H_2O_2. Malik et al. (2002) in a similar set up investigated the decoloration of methylene blue from distilled and tap water by aqueous phase pulsed corona discharge alone and combined with O_2 and O_3 bubbling [45]. Energy consumption was estimated at 41mg/KWh. Lukes and Locke (2005) investigated a point-to-plane hybrid system consisting of over water gas phase discharge and the concurrent generation of liquid phase corona discharge for degradation of substituted phenols [46]. The degradation efficiency of 47-80% within 60 min treatment time has been achieved. The energy cost was 281- 457 KWh/m^3.Banaschik, et al. (2015) demonstrated the ability of corona discharges generated within the aqueous solution to be treated to remove a range of pharmaceuticals, including CBZ [4]. They achieved 90% removal of CBZ after 66 minutes of treatment using a reactor with an extended coaxial configuration filled with spiked clean water up to a concentration of 0.5 mg.L^{-1}.

The purpose of this research is to extend the understanding of the efficacy of pulsed corona discharges generated in water in treating CBZ in a relatively clean water matrix by optimizing specific parameters, including solution pH, electrical conductivity, gas type, and gas flow rate at the laboratory scale.

3.2 Materials and Methods

Experimental Apparatus. The batch reactor consisted of either a stainless steel hollow tube (0.635 mm interior, 0.813 mm exterior diameter) or a titanium solid electrode (98.9% purity, exterior diameter 0.813 mm) as the HV electrode and a titanium rod (12.7 mm x 6.35mm x 38 mm) as the ground electrode within a 100 mL borosilicate three necked flask reactor. The hollow HV electrode tip was cut between experiments to remove corrosion to ensure reproducibility of the experimental results. A temperature controlled recirculating bath was used to maintain the temperature of the solution to be treated constant at approximately 25 ^{o}C throughout the treatment process to minimize thermal degradation of CBZ. The solution was stirred constantly using a magnetic stir bar and a stirring plate.

A point-to-plane electrode configuration is utilized to generate corona discharges for as shown in Figure 3.1. A high voltage direct current (DC) power supply was used to charge a 1 nF pulse forming capacitor. The charge stored in this capacitor then discharges within the water in the reactor through a rotating spark gap switch, which alternatively rotates between the capacitor and the reactor, at pulse repetition rate of 30 Hz. In order to prevent premature discharge and O_3 formation, the spark gap region was continuously purged with dry nitrogen. The electrical characteristics were captured using an oscilloscope (Tektronix TDS 5054B Digital Phosphor, 500 MHz) to record the voltage (Tektronix P6015A high voltage probe) and current (Ion Physics CM-10-MG current transformer) values during each experiment. A large number of data points are captured in one continuous record by this real-time oscilloscope to build an entire waveform during each trigger incident. Figure 3.2 shows the ensemble averages from 150 voltage and current waveforms recorded throughout these experiments. The time-averaged, root-mean-square (RMS) power of these experiments was approximately 3.5W ±0.3. The voltage rise time was in the order of 10^{-9} - 10^{-8} s.

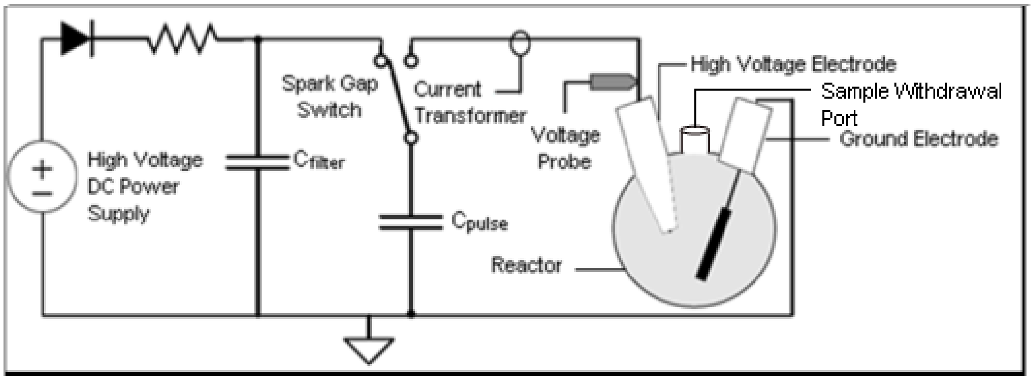

Figure 3. 1. Schematic Representation of the Power Supply and Reactor Configuration (after: Lakhian, 2016)

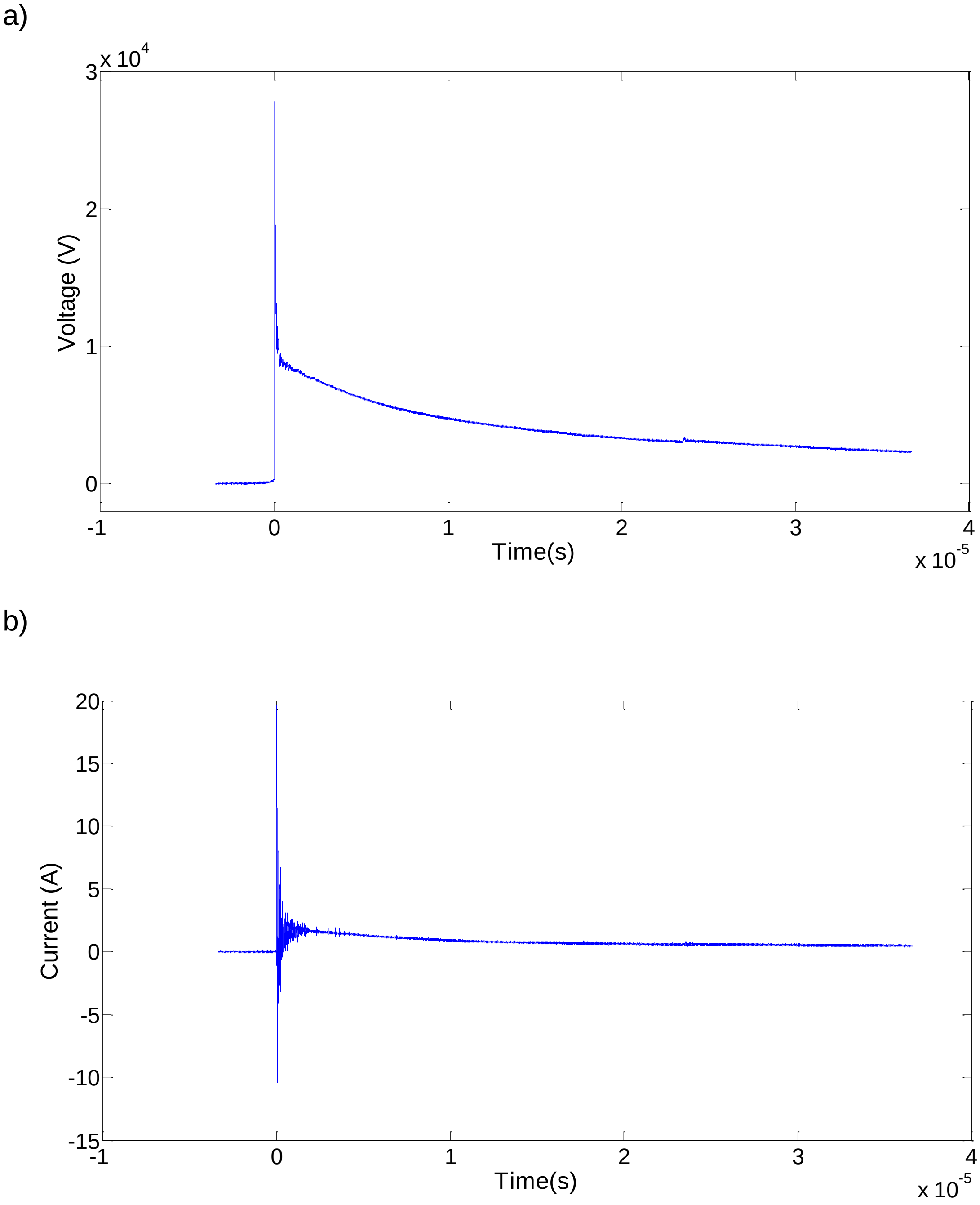

Figure 3. 2. Ensemble Averages of 150 a) Voltage and b) Current Waveforms

Chemicals and Solutions. All solutions were prepared using 18.1 MΩ/cm Milli-Q water. Conductivity was adjusted using 1 M NaCl (99%, Caledon Laboratories Inc.), and the pH was adjusted using 1 M HCl (prepared from a 11.65 M solution, Fisher Scientific Canada) and 1 M NaOH soltuion (97%, Caledon Laboratories Inc.). The CBZ employed in these experiments was 98% pure (Alfa Aesar), and diluted to stock solution with a concentration of 17.7 $mg{\cdot}L^{-1}$ using Milli-Q water. Complete dissolution of CBZ was ensured through exposing the submerged solution vessel in an ultrasonic bath for one hour. Solution conductivity was measured using a Mettler Toledo conductometer, and pH was measured using a Symphony pH meter. Solutions were stored at 4 °C to reduce environmental effects. Control experiments were conducted to ensure that neither short term storage nor ultrasonic agitation resulted in the decomposition of CBZ.

Experiments. The formation rate of the reactive species (i.e., $^{\bullet}OH$, $^{\bullet}H$, and $^{\bullet}O$) responsible for organic molecule degradation is significantly improved when oxygen or an inert gas, such as argon, is bubbled through the plasma region [47]. Sun et al. (1999) found that while the generation of radicals (OH, $^{\bullet}H$, and $^{\bullet}O$) was significantly improved in the presence an inert gas, the presence of oxygen further increased removal efficacy as it facilitates the generation of more diverse radicals (i.e., O_3, singlet oxygen ($^1O_2$) and superoxide (O_2^-)) [47]. Therefore oxygen, argon, and nitrogen were chosen as the gases to inject through the hollow HV electrode into the plasma region throughout these experiments. The gas was employed for the sole purpose of improving the generation of reactive species.

The experiments shown here focus on a subset of a larger series of influential parameters on removal efficiency. Experiments were conducted using

0.5 mg·L^{-1} CBZ at three pH levels (3.5, 7, 10.5), two solution conductivity levels (150 µS.cm^{-1} and 500 µS.cm^{-1}), three gas types (oxygen, argon, nitrogen), and three gas flow rates (20 mL.min^{-1}, 50 mL.min^{-1}, 100 mL.min^{-1}) where the electrode gap was 2 cm. Table 3.1. shows the experimental conditions. Each experiment involved exposing a CBZ solution to corona discharges for 25 minutes with a gas injected through the HV electrode for the duration of the experiment. The gas flow rate was adjusted using a rotameter. Samples (1 mL) were withdrawn for analytical purposes at five minute intervals (5, 10, 15, 20, 25 min) throughout each experiment. To decrease the possible effects on CBZ removal, the reactor volume was kept constant by adding 2 mL of the initial stock solution to the reactor after every second sample was withdrawn. Each experiment was repeated twice to ensure reproducibility.

Table 3. 1. Experimental Conditions

Solution pH	Electrical Conductivity (µS.cm^{-1})	Gas Type	Gas Flow Rate (mL.min^{-1})	Averaged Energy Deposition ×10^{3}(J)
3.5	150	Ar	50	2.8
10.5	150	Ar	50	3.3
7	150	Ar	50	2.9
3.5	500	Ar	50	3.5
3.5	500	N_2	50	3.1
3.5	500	O_2	50	3
3.5	500	N-G	---	3.4
3.5	500	Ar	20	3.2
3.5	500	Ar	100	1.3

- N-G; no gas injection

Liquid Chromatography Tandem Mass Spectroscopy. The concentrations of CBZ and its degradation products were determined using high performance liquid chromatography - tandem mass spectroscopy (HPLC/MS/MS). The instrument consisted of a Waters 2695 HPLC system equipped with a Phenomenex Luna C18 resolution column (25 × 4.6 mm, 5µm). Forty percent acetonitrile and a mixture of 0.05% formic acid (HPLC grade, Fluka-Sigma Aldrich) and 60% water were used as eluents with variable ratios as follows: 60% water, 40% ACN at time 0, 0% water, increased to 100% ACN in 10 min, kept constant for 3 min, 60% water, 40% ACN at 13.1 min, and finally re-equilibration to 60% water, 40% ACN in 5 min during the gradient elution at a flow rate of 0.2 $mL \cdot min^{-1}$. The estimated limit of quantification (LOQ) was 0.5 $mg \cdot L^{-1}$ based on the observed signal to noise ratio (S/N) of 10. Five-µL sample volumes were injected. Method detection limit for this concentration of CBZ is 0.2 $mg \cdot L^{-1}$. A mass analyzer (Waters/Micromass Quattro Ultima) was set up for multiple reaction monitoring in positive ion mode (electrospray ionization) of the transition m/z 237→194 for quantification of the target species. The mass chromatograms obtained were used to quantify CBZ and its degradation products using a calibration curve based 12 CBZ samples of known concentration ranging from 0.0024 to 5 $mg \cdot L^{-1}$ ($R^2 = 0.995$).

3.3 Results

The following sections describe the effects of solution pH, solution conductivity, gas type, and gas flow rate on the removal of CBZ using the power supply and reactor configuration described above.

Solution pH

The results show that solution pH has a significant effect on the efficacy of CBZ removal in the system investigated here. Figure 3.3 shows that for the conditions employed in these experiments, those conducted at pH 3.5 achieved the highest CBZ removal in comparison to those conducted at pH values of 7 and 10.5. This can be attributed to a number of consequences of the equilibrium reaction between $^{\bullet}OH$, OH^-, $O^{\bullet -}$ as follows (equation 3.1):

$$^{\bullet}OH + OH^- \Leftrightarrow O^{\bullet -} + H_2O \quad pK_a = 11.9 \qquad (3.1)$$

These consequences include: 1) $^{\bullet}OH$ is scavenged by OH^-, which increases in concentration with increasing pH [38, 48]; 2) at pH 10.5, the concentration of OH^- may be even higher than that of the compound, resulting in a higher tendency for the OH^- to react with $^{\bullet}OH$ [38]; 3) $^{\bullet}OH$ reacts with organic molecules as an electrophile, however $O^{\bullet -}$ behaves as a nucleophile and thus in the reaction with CBZ, $^{\bullet}OH$ attacks the molecule through electrophilic addition, but $O^{\bullet -}$ does not undergo this reaction; 4) $^{\bullet}OH$ is more oxidative under acidic conditions [48] (the reaction rate constant of $^{\bullet}OH$ with organic molecules is higher under acidic conditions) [49].

The equilibrium reaction between H_2O_2 and HO_2^- may also contribute to the higher CBZ degradation rate and better overall CBZ removal at lower solution pH values. This equilibrium reaction is as follows:

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ ,\ \ pk_a = 11.6 \qquad (3.2)$$

Equation 3.2 shows that higher pH values lead to the formation of HO_2^-, which is nearly 300 times more effective as a scavenger for $^{\bullet}OH$ (rate constant=$7.5 \times 10^9\ M^{-1}\ s^{-1}$) than H_2O_2 is for $^{\bullet}OH$ (rate constant = $2.7\times 10^7\ M^{-1}s^{-1}$) [38, 49]. Thus, with higher levels of HO_2^- at high pH, one would expect decreased concentrations of $^{\bullet}OH$, due to increased scavenging and lower degradation rates. The difference between averaged energy depositions of the experiments in three pH levels is less than 9%.

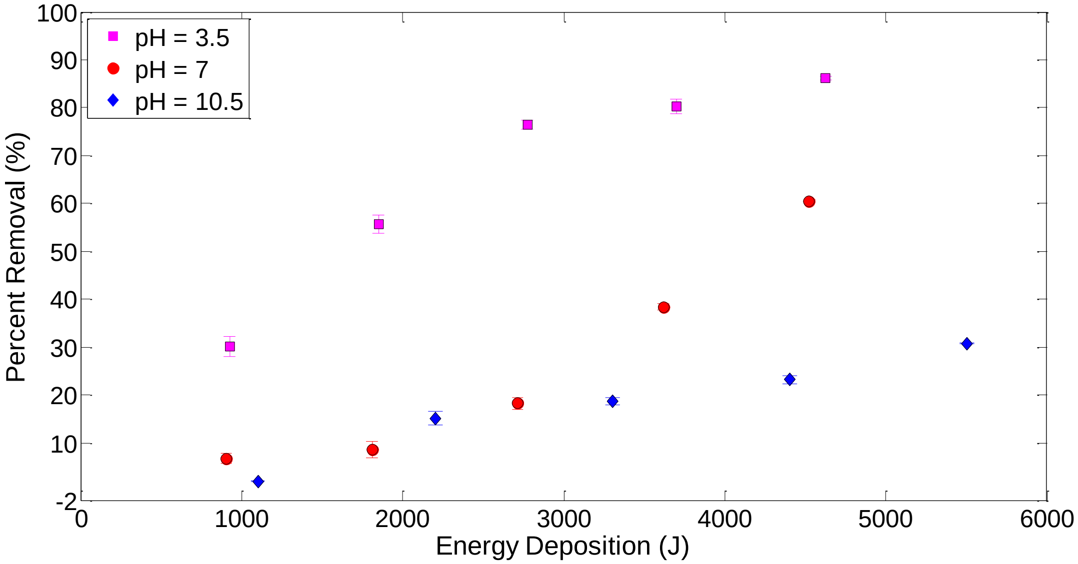

Figure 3. 3. Effect of pH on the efficacy of CBZ removal by pulsed corona discharges. Initial CBZ concentration = 0.5 mg.L^{-1}, gas phase = Ar; gas flow rate = 50 mL.min^{-1}. Error bars represent one standard deviation of the average of two sets of data.

Solution Conductivity

Figure 3.4 shows the percent CBZ removal versus input energy for experiments conducted at conductivities of 150 and 500 μS.cm^{-1}, and indicate that solutions with lower conductivities provide better CBZ removal. This result is consistent with the results obtained by others [44, 45], and there are several possible reasons for this observation. First, lower solution conductivities may result in better oxidation of CBZ as to achieve a higher conductivity, the Cl$^-$ concentration was increased. The Cl$^-$ anion has a scavenging effect on $^{\bullet}$OH, which would lead to a lower concentration of this strong oxidant [52]. Second, the solution conductivity changes the physiochemical characteristics of the plasma generated. Higher conductivities will shorten and widen the plasma channel (less opportunities to contact the water molecules), which will also become brighter due to enhanced UV formation [50]. Furthermore, the inverse proportionality of dielectric relaxation time (τ) (the time required for ions in solution to rearrange) and conductivity relationship (equation. 3.3) indicates that higher solution conductivities result in smaller relaxation times [53].

$$\tau = \frac{\epsilon_0 \, \epsilon_r}{\delta} \tag{3.3}$$

where ϵ_0 represents the electric permittivity of free space (F/m), ϵ_r represents the relative permittivity of solution and δ represents the electrical conductivity of the solution. Channel dimensions and relaxation times will affect the discharge, plasma chemistry, and therefore the reactive species generated, which are responsible for the degradation of CBZ [38, 53]. Shih and Locke (2011) studied the effect of solution conductivity on the generation of oxidative species such as $^{\bullet}OH$ [50], and demonstrated the decreasing intensity of $^{\bullet}OH$ and H_2O_2 (less number of radical species in excited state) generated with increasing solution conductivity. They also observed a maximum intensity of other oxidants including $^{\bullet}O$ and also O_2 gas at 150 µS.cm^{-1}, which decreased with increasing the solution conductivity. They found that the intensity of all radical species ($^{\bullet}OH$, $^{\bullet}O$, $^{\bullet}H$) decreases when the solution conductivity exceeds 500 µS.cm^{-1}, which could be due to the shorter length of plasma channel and also shorter duration of electrical pulse in higher conductive solutions. The results of the study conducted by Dors et al. showed a decrease in phenol degradation when solution conductivity increased from 1 to 600 µS.cm^{-1}. They ascribed this result to a reduced concentration of $^{\bullet}OH$ [51]. The difference in energy depositions of the two sets of experiments shown in Figure 3.4 is about 11%.

It should be noted that while treatment efficacy of CBZ is improved with lower solution conductivities, the conductivity of drinking water is in the range of 500 µS.cm-1. Therefore, the majority of experiments were conducted in higher conductivity solutions (i.e., 500 µS.cm-1 range).

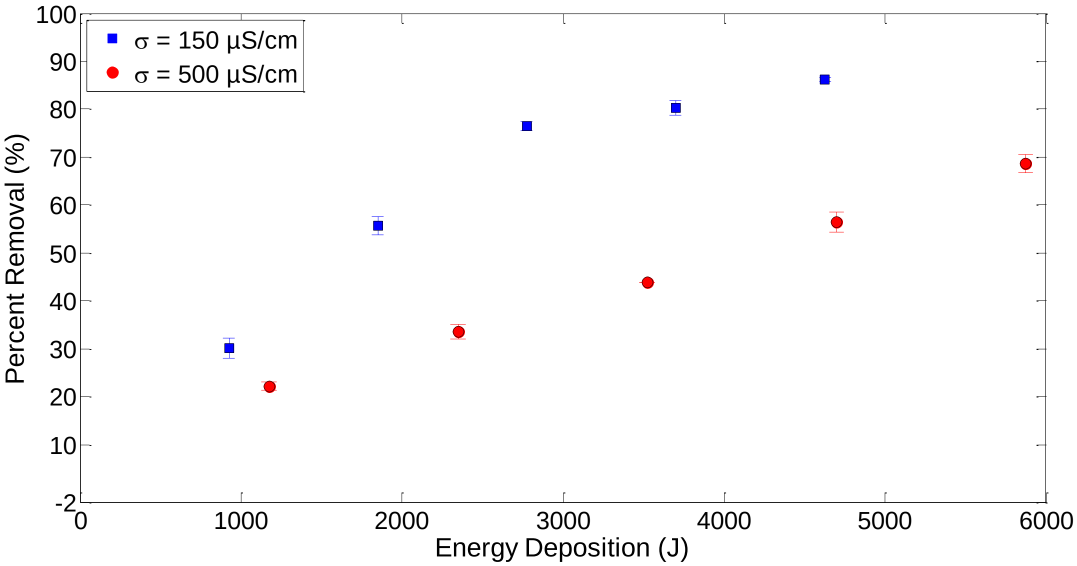

Figure 3. 4. Effect of solution conductivity on the efficacy of CBZ removal. Initial CBZ concentration = 0.5 mg.L^{-1}, gas phase = Ar; gas flow rate = 50 mL.min^{-1}, solution pH = 3.5. Errors bars represent one standard deviation of the average of two sets of data.

Electrical Characteristics

The averaged voltage waveforms are shown in Figure 3.5 for different solution conductivities (150 and 500 µS.cm^{-1}) at deposited energy input. As displayed in voltage waveform, while the peak applied voltage is constant in both cases at approximately 30KV, the voltage decay is different after the peak discharge. As the solution conductivity increases, current dissipation is faster, resulting in decreasing in the length of discharge channel [50]. This also causes more rapid voltage decay and shortening the voltage pulse width. This is confirmed with the higher discharge current in higher conductivity. Voltage rise time is independent of the solution conductivity and it is about 15 ns for both conductivities.

The effect of solution conductivity on current waveforms (Figure 3.6) shows a decrease in breakdown pulse duration with the increase in solution conductivity. Unlike the voltage rise time, the current rise time is dependent on the solution conductivity. It is estimated to be of approximately 7 ns for higher conductive solution which is shorter than that of in solution with lower conductivity with rise time of about 9 ns. This is associated to more ions and thus more charged species present, which could enhance the Joule heating when the strong electric filed is applied. This will subsequently result in facilitated bubble formation and also faster electrical discharge inception (according to the bubble theory of discharge breakdown). On the other hand, in solution with lower conductivity, the discharge channels are thinner and longer than in the higher conductive solution [50]. Additionally, they are not branched and they straightly spread towards the counter electrode; however, more filamentary branches exist in solution with higher conductivity, which could propagate in different directions. The latter will lead to faster dissipation of discharge, faster occurrence of breakdown, and thus shorter current rise time.

Although more rapid voltage decay and higher discharge current during the pulse is representative of higher volume of plasma and radicals generated with the increase in solution conductivity, it does not necessarily lead to higher removal efficiency of CBZ as it can cause an opposite effect on chemical and physical activity of electrical discharge as discussed in the solution conductivity section in this chapter.

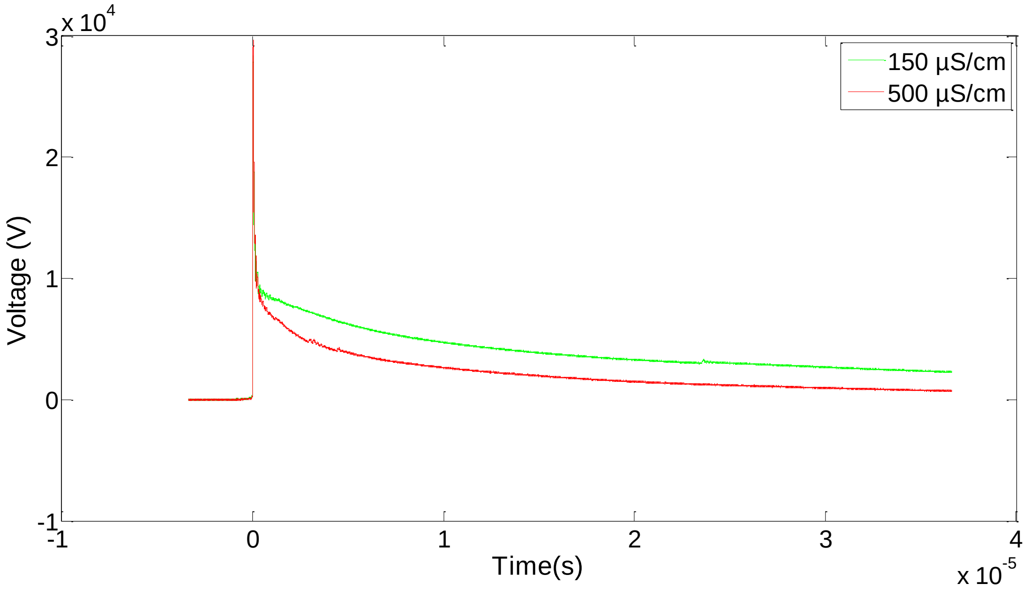

Figure 3. 5. Discharge Voltage Waveforms at Solution Conductivity of 150 and 500 µS.cm^{-1}

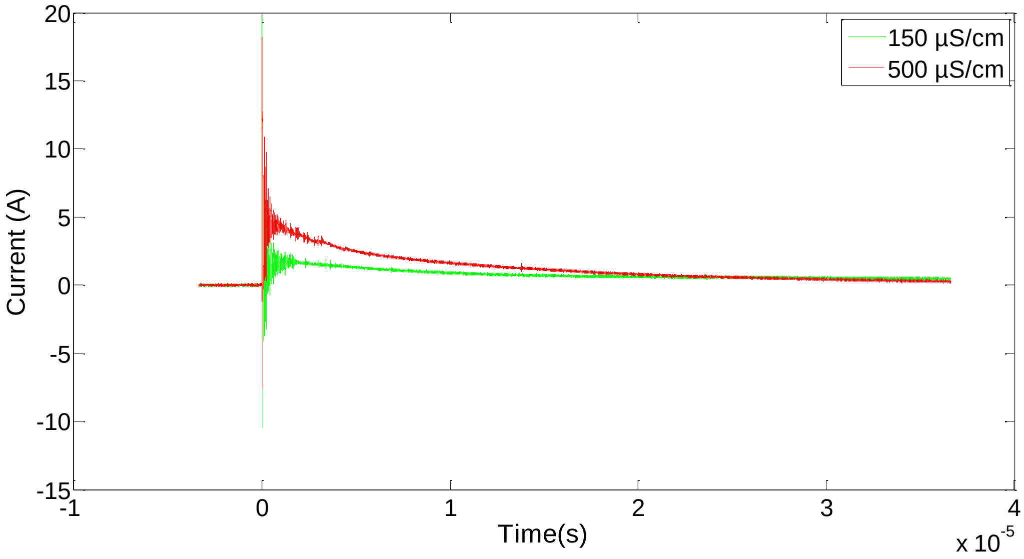

Figure 3. 6. Discharge Current Waveforms in Solution Conductivity of 150 and 500 µS.cm^{-1}

Gas Bubbling and Gas Type

The results from these experiments show the efficacy of CBZ treatment by corona discharge improves when a gas is bubbled into the plasma region, and that O_2 has the best effect on removal while Ar and N_2 demonstrate relatively similar removal trend (Figure 3.7). CBZ removal reached 94%, 69%, and 55% after 25 minutes of treatment in the presence of O_2, Ar and N_2, respectively. The difference between averaged energy deposited in these experiments is less than 8%. Where no gas phase was discharged into the plasma region, the CBZ removal was less than 27%. The higher CBZ removal achieved in the presence of O_2 was likely due to the generation of O^{-}_2, $^{1}O_2$, and O_3 [47], in addition to $^{\bullet}OH$, $^{\bullet}H$, $^{\bullet}O$ radicals produced in the presence of argon and nitrogen. There are two potential reaction pathways for the degradation of CBZ in the presence of O_3. CBZ may either be oxidized by O_3 directly or the O_3 may cause water molecules to dissociate thereby generating $^{\bullet}OH$.

According to the bubble theory of electrical breakdown in liquid [37], discharge propagation is facilitated in the presence of bubbles through gas saturation. Therefore, in direct underwater discharge (no gas bubbling) a significant amount of input power is consumed to form the water bubbles resulted from vaporization of water molecules, which requires more input power [54].

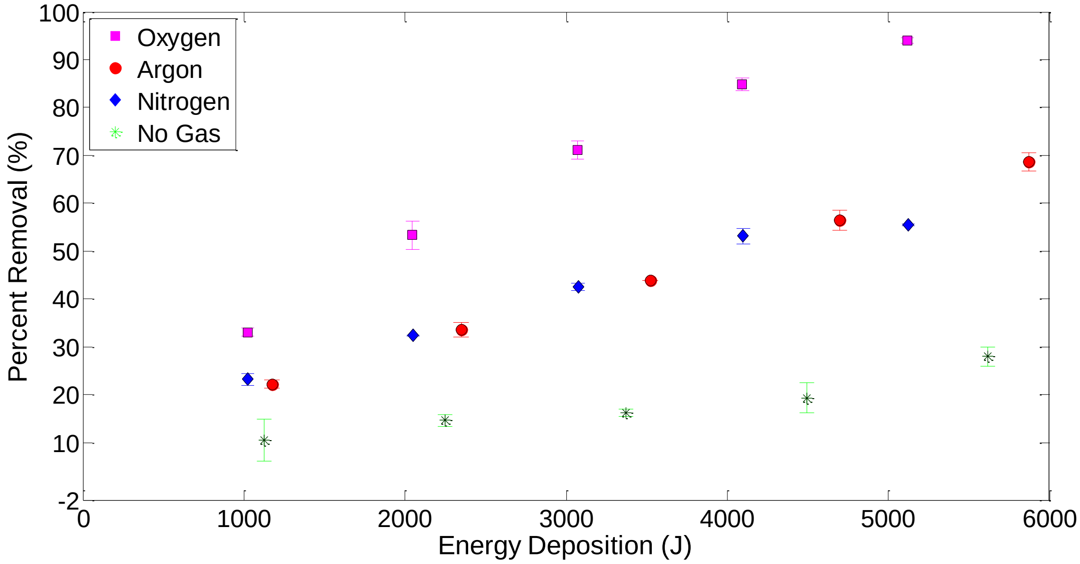

Figure 3. 7. Effect of gas bubbling on the efficacy of CBZ removal. Initial CBZ concentration = 0.5 mg.L^{-1}, solution conductivity = 500 µS.cm^{-1}, gas flow rate = 50 mL.min^{-1}, pH = 3.5. Errors bars represent one standard deviation of the average of two sets of data

Gas Flow Rate

CBZ removal increased with increasing the Ar flow rate from 20 to 50 mL.min^{-1} as shown in Figure 3.8. This increase in CBZ treatment efficacy was likely due to the fact that higher Ar flow rates facilitate a larger electron avalanche formation yielding a larger plasma streamer in the liquid phase. This would result in the generation of more reactive species. The energy deposition difference for these two sets of experiments is approximately 6%. Sun et al. (1999) studied the effect of O_2 and Ar gas flow rates ranging from 0 to 60 mL.min^{-1} on the emission intensity of the $^{\bullet}$OH and $^{\bullet}$O radicals. They found an increase in these radicals density with an increase in gas flow rate until leveling off at flow rate of about 50 mL.min^{-1} [47]. They also achieved higher phenol removal in higher gas flow rates.

In another study conducted by Clements et al. (1987), the effect of gas flow rate on the radical density also showed the same result [37]. The intensity of $^\bullet$O and $^\bullet$OH increased when O_2 and Ar gases were bubbled through the plasma region at higher rates until a leveling off point at about 50 mL.min^{-1} gas flow rate.

Ar gas also was bubbled through the reaction region at 100 mL.min^{-1}, using a second power supply. The result demonstrate lower CBZ removal efficiency as the Ar flow rate was increased to 100 mL.min^{-1}. However, for this case, the energy deposition calculations showed lower energy input supplied; it is unsure of whether the achieved lower removal efficiency is due to the lower energy deposition or the oversaturation of aqueous phase with Ar at some point. The lower energy deposition could cause the weaker electric field which would result in lower concentration of reactive species generated in the aqueous phase, ultimately lowering the degradation level of CBZ. On the other hand, oversaturation of aqueous phase with Ar would generate larger concentration of bubbles, and therefore a narrower layer of water being exposed to the electrical discharge. This would lead to a decrease in the concentration of reactive species generated resulting in lower removal efficiency.

Therefore, the results of the experiment with the flow rate of 100 mL.min^{-1} are not comparable with two other gas flow rates (i.e. 20 and 50 mL.min^{-1}) and thus a complementary experiment will be required. The estimated energy deposition in this experiment is approximately two times lower than the rest experiments (see Table 3.1).

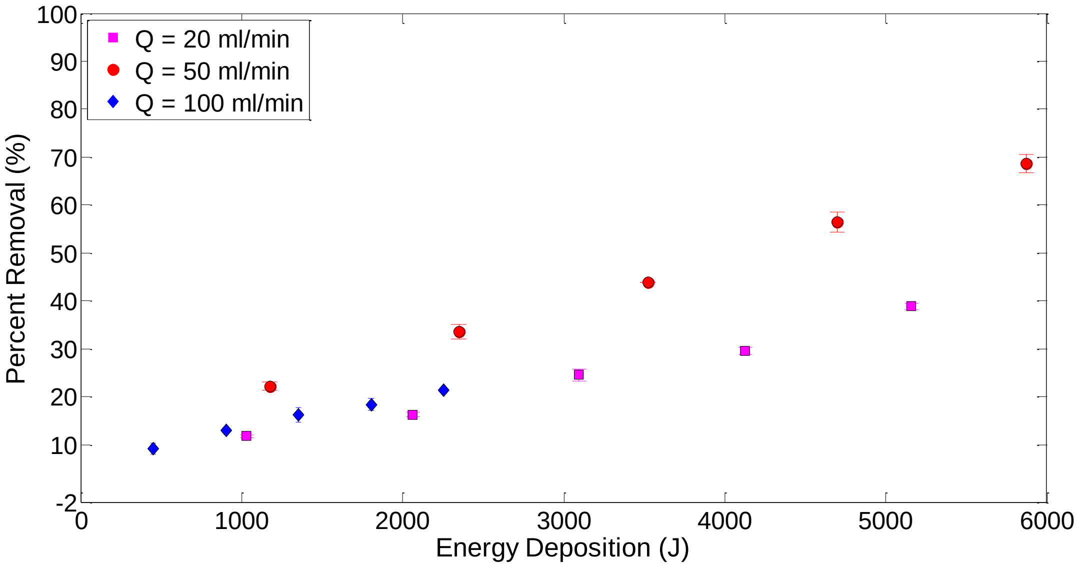

Figure 3. 8. Effect of gas flow rate on the efficacy of CBZ removal. Initial CBZ concentration = 0.5 mg.L^{-1}, solution conductivity = 500 µS.cm^{-1}, gas phase = Ar, pH = 3.5. Errors bars represent one standard deviation of the average of two sets of data.

Electrical Characteristics

Analysis of electrical characteristics of voltage and current waveforms for different gas flow rates could also explain the Ar flow rate effect in more detail. As shown in Figure 3.9, the decay rate of voltage waveforms is different for different Ar flow rates. The voltage decays more rapidly when argon is bubbled through the HV electrode in higher flow rate (50 mL.min^{-1}), which is confirmed by a higher discharge current obtained (Figure 3.10). This also leads to shortening the voltage pulse width and a decrease in current pulse duration. This phenomenon indicates more plasma and ion production in the low density regions which could result from faster discharge inception and current dissipation when gas is bubbled in higher flow rates. The next rapid voltage decay, which shows a lower discharge current, occurs when Ar is bubbled through the HV electrode at 20 mL.min^{-1} flow rate.

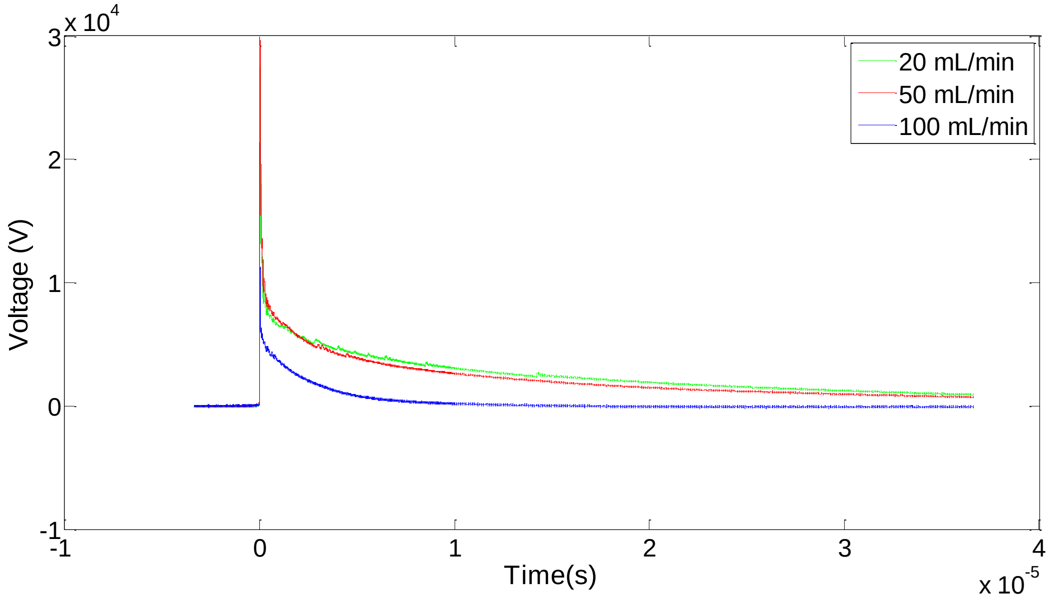

Figure 3. 9. Discharges Voltage Waveforms in Different Argon Flow Rates

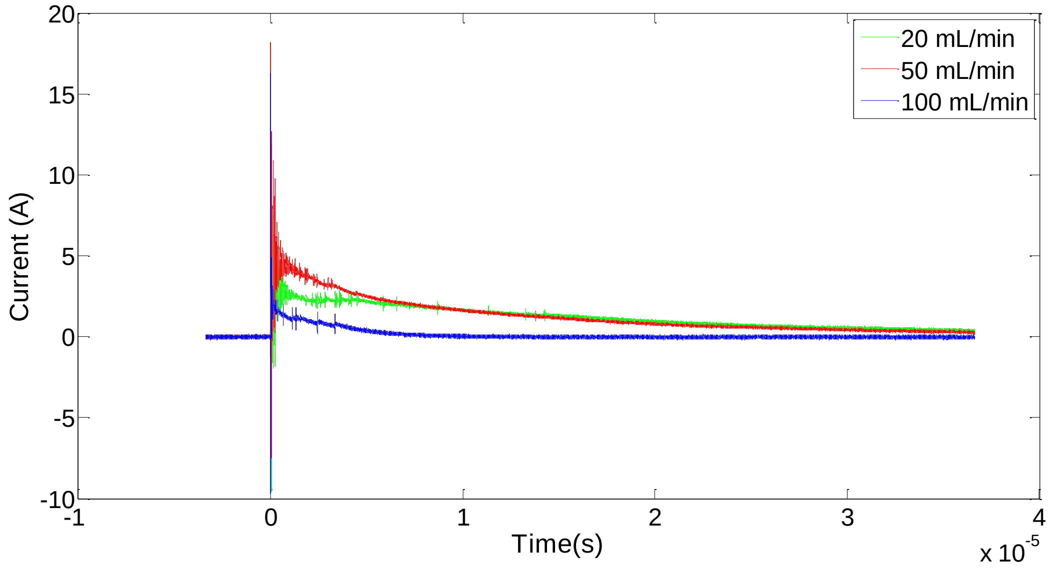

Figure 3. 10. Discharges Current Waveforms in Different Argon Flow Rates

To detect the possible by-products, HPLC/MS/MS in total ion current (TIC) has been employed. Although the results have shown the degradation of CBZ under different conditions, decomposition by-products were not detected. This implies that by-products are generated at concentrations lower than the method detection limit (MDL). More work is required to determine the potential for byproduct formation using this technology.

3.4 Conclusion

Submerged electrical discharge is characterized by the in-situ generation of reactive radicals that have the potential to initiate chemical reactions with organic molecules. The results demonstrate that this technique has the ability to remove highly persistent CBZ from aqueous solutions. The results show higher CBZ removal efficiency in solutions with acidic pH (3.5) and lower conductivity (150 µS.cm^{-1}). The degradation level is also substantially enhanced by gas bubbling, O_2 in particular, through the HV electrode into the reaction region. CBZ removal is further improved when the Ar flow rate is increased to 50 mL.min^{-1}. In the present work, CBZ has been removed up to 94% from the simulated polluted drinking water samples, taking these influential variables into account to enhance the removal efficiency.

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Chapter 4: Conclusion

Recalcitrant micro-organic pollutants and particularly pharmaceuticals are considered to be of great concern for aquatic environment and human health. Regarding this issue, various methods have been investigated to eliminate the pharmaceutical residuals from the water bodies and lower the risk of their potential impacts on exposed consumers. Submerged electrical discharges have been introduced as the most effective approach whose application is increasing rapidly by many researchers to eliminate trace, but toxic, concentration of pharmaceuticals.

In the present work, the generation of electrical discharges directly in water and its capability on removal of one of the most persistent pharmaceuticals, CBZ, has been investigated and the general knowledge of applicability of electrical discharges has been expanded. The achieved results are listed below.

- The results demonstrate that this technique has the ability to remove highly persistent CBZ from aqueous solutions.
- To facilitate the discharge generation and propagation, to enhance the reactive species formation and to improve the organics degradation efficiency, strong electric fields are required. In order to

- meet this requirement, high values of applied voltage (it needs to be high enough so that the thermal plasma is not generated) and lower values of internal electrode distance (not too short) are necessary, which have been followed in this work.
- HV and ground electrodes gap should be adjusted small enough to prevent spark generation and achieve higher average electric field strength (AEFS). This could result in more concentrated plasma and larger amount of subsequent reactive species. In the present investigation, a reactor was chosen in which the HV and ground electrodes had 2 cm distance.
- The efficacy of CBZ removal was greatly influenced by solution pH. The results show that acidic pH is desired for achieving higher CBZ removal as compared to neutral and basic conditions. This result could be ascribed to the higher oxidation ability of $^{\bullet}OH$ in acidic conditions due to its higher reaction rate. The result could be also attributed to the scavenging effect of OH^- for $^{\bullet}OH$ which exist in high concentration in basic solutions, resulting in decreasing the concentration of $^{\bullet}OH$ which is mainly responsible for CBZ degradation. Additionally, under basic conditions, HO_2^- anion is produced as the product of H_2O_2 ionization, which acts as a very strong scavenger for $^{\bullet}OH$ (large reaction rate constant) and decreases its concentration.
- The effect of solution conductivity on CBZ removal efficiency indicates that solutions with lower conductivities provide better removal. High concentration of Cl^- anion in highly conductive solutions will decrease the $^{\bullet}OH$ concentration

due to its scavenging effect. Furthermore, faster dissipation of current into the surrounding medium in higher conductivities will decreases the plasma channel length, which ultimately lowers the generation of reactive species. Shorter dielectric relaxation time in higher conductive solutions also affects the discharge and leads to decreased concentration of radicals generated in plasma.

- Gas bubbling through the HV electrode significantly facilitated the discharge initiation and also improved the degradation efficiency of CBZ compared to the conditions where no gas was bubbled through the electrode. The efficiency of CBZ removal was highly improved when O_2 was bubbled into the plasma region, following by Ar and N_2 at relatively the same level.
- Higher removal efficiency in the presence of O_2 was likely due to the generation of O_3, O^-_2, $^1O_2$ in addition to $^\bullet OH$, $^\bullet H$, $^\bullet O$ radicals which are also formed when Ar and N_2 gases are present.
- CBZ treatment efficacy was higher when the gas (Ar) flow rate was raised to 50 $mL.min^{-1}$. This is likely due to larger volume of excited electrons, resulting in more concentrated plasma and more reactive species.

Aqueous electrical discharge is characterized by chemical-free (no external chemical requirement) technique owing to in-situ generation of reactive species initiating the chemical reactions with organic molecules. Moreover, it is capable of successful degradation of highly recalcitrant organic compounds such as pharmaceuticals.

In the present work, CBZ has been removed up to 94% from simulated polluted drinking water samples, taking the influential variables into account to enhance the removal efficiency.

Recommendations for Future Study

Underwater electrical discharges are capable of treatment of the recalcitrant pharmaceuticals in water and wastewater treatment facilities. To improve the destruction efficiency and to expand the knowledge in this filed, following remedies are suggested.

1. The initial concentration for treatment should be at lowest level. This is because of lower concentration of CBZ in the environment than the tested concentration in this study. CBZ concentration in the present study was 0.5 mg.L^{-1}. Therefore, to simulate the real situation and to gain more reliable results for future investigation, lower concentration of CBZ needs to be tested.
2. Degradation of pharmaceuticals, CBZ in our study, should be investigated in higher solution volume. The reactor volume of this work was 100 ml. Less concentration in higher volume increases the destruction efficiency of the technique.
3. Due to the strong electric fields applied, deterioration of electrode tip is inevitable in the course of treatment process, which could affect the

reproducibility of degradation results. Therefore, pinhole reactor geometry might be a better alternative for plasma technique.

4. More investigation is required to fully understand the nature of organics tendency towards reactive radicals, the physical effects in the treatment processes, and to detect the potential transformation by-products.
5. Considering the transformation of organic compounds to other by-products, the toxicity study is recommended to determine as to whether the by-products are more or less toxic than parent compound.
6. If this technique is intended to be applied as a tertiary part of wastewater treatment processes, the tested samples should be prepared from the wastewater facilities so that a better simulation can be achieved and the effect of other substances on the removal efficiency can be taken into account. In the present study, CBZ was added to the DI water and the salt (NaCl) was added to simulate the conductivity of the tap water.

Appendix

In the electronic file submitted to Dr. Sarah Dickson, electrical characteristics raw data, LC/MS/MS chromatograms, and sample calculations are provided.