Thesis for the Degree of Doctor of Philosophy

Exploring the Efficiency of Gliding Arc Discharge for the Decomposition of Persistent Organic Pollutants.

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Division of Earth and Environmental Systems

Pukyong National University

August, 2023

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(글라이딩 아크 방전을 활용한 잔류성 유기 오염 물질의 분해 연구)

Advisor: Dr. Il-Kyu Kim

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Amina Ouzar

A dissertation submitted in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy

in Department of Environmental engineering.
Division of Earth and Environmental Systems
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August 18, 2023

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초록

본 연구에서는 Gliding arc discharge (GAD) 방식 반응기의 난분해성물질 처리 성능을 평가하기 위해 모든 실험은 batch 형태로 진행하였으며, Eriochrome Black T (EBT)와 Tetracycline (TC) 를 대상물질로 선정하여 제거 특성을 확인하고자 하였다. 플라즈마를 공급하는 데 사용되는 주입 가스 유형과 상대습도을 달 리하여 활성종인 용존오존을 측정함으로써 반응기의 특성을 파악하고자 하였다. 또한, 대상 화합물 제거 특성을 파악하기 위해 pH 를 변수로 하여 연구를 수행하였다.

본 연구의 목적은 초기농도, pH, 처리기간, 무기물화율, 처리 후 잔류 부산물 등 다양한 요인을 고려하여 유기화합물을 효과적으로 분해할 수 있는 방법을 개발하는 것이다.

이 논문은 5 장 나눠지며:

- 플라즈마 상호 작용의 기술 상태를 보여주는 문헌 검토,
- 난분해성 물질 유기 화합물의 처리에 있어 NTP 적용의 주요 사항,
- 본 연구에 사용된 플라즈마 반응기,
- 글라이딩 아크 플라즈마에 의해 형성된 반응성 종의 생성을 정량적으로 측정하고 플라즈마 상호작용 분석,
- 반응성 종 의 생성과 대상물질의 분해에 대한 습도의 영향을 분석하기 위한 구체적이고 다양한 방전 조건,
- 플라즈마 촉매의 조합 방법을 제안하기 위한 노력으로 다른 촉매들을 도입함으로써 TC 의 플라즈마 열화를 향상시키는 기술.

최적의 상대 습도 조건에서 O_2 플라즈마는 30 분 처리 후 많은 양의 .OH 생성 값이 65.49 μmol/L 이며 공기 플라즈마 비하면 생성된 양의 약 3 배를 나타내었다. 최고의 EBT 탈색은 공기 플라즈마(96.51%)에 의해 달성된 반면 O_2 플라즈마는 TOC 제거로 무기물화율이 공기 플라즈마보다 약 20% 더 높은 것으로 나타났다.

EBT 제거에 대한 라디칼 소거능 효과는 ·OH 가 억제될 때 공기 플라즈마에서 유기 화합물의 분해에서 N 라디칼의 역할을 추가로 보여준다 (탈색율은 공기 플라즈마 경우에는 96.51%에서 83.33%로 감소한 반면, O_2 플라스마에서는 라디칼 소거능의 존재는 탈색의 더 큰 하락을 초래하여 52.57%에서 12.19%로 감소하였다.
TC 처리(초기 농도 5 mg/L)의 경우 처리 30 분 후 O_2 플라즈마에서 총 분해율 94.95%와 무기물화율 81.3%를 달성했으며 이는 일반적으로 오염 물질 처리에서 높은 무기물화율을 달성하기 어렵기 때문에 이런 결과를 얻는 것이 인상적이다. 반면에 공기 플라즈마는 각각 60.45% 및 57.34%의 분해율 및 무기물화율을 감소하였다. 이러한 결과는 GAD 반응기의 잠재력을 강조하며, 고항성 물질의 분해와 오염물질 처리에서 높은 광화율을 달성하는 효과적인 방법임을 보여준다.

키워드: 비열 플라즈마, 플라즈마-액체 상호작용, 폐수 처리, 플라즈마 촉매, 아조 염료, 테트라사이클린, 글라이딩 아크.

Abstract

In this study, the performance of the Gliding Arc Discharge (GAD) reactor in the treatment of refractory substances was evaluated through batch experiments. Eriochrome Black T (EBT) and Tetracycline (TC) were selected as target substances to investigate their removal characteristics. The reactor's properties were determined by varying the type of injected gas used to supply the plasma and the relative humidity by measuring the concentration of reactive species generated. Additionally, pH was used as a variable to assess the removal characteristics of the target compounds. The objective of this research is to develop an effective method for decomposing organic compounds by considering various factors such as initial concentration, pH, treatment period, mineralization rate, and residual byproducts after treatment. This paper is divided into five chapters, covering the following topics: Literature review showcasing the technological status of plasma interactions. Key considerations for applying Non-Thermal Plasma (NTP) in the treatment of refractory organic compounds. Plasma reactors used in this study. Quantitative measurement of reactive species generated by gliding arc plasma and analysis of plasma interactions. Specific and diverse discharge conditions analyzed to determine the influence of humidity on the generation of reactive species and the decomposition of target substances. Efforts to propose a combination method of plasma catalysts by introducing different catalysts to enhance the plasma degradation of TC. Under the optimal relative humidity conditions, O_2 plasma exhibited a significant improvement in the generation of $^{\cdot}$OH after 30 minutes of treatment, with a value of 65.49 μmol/L, approximately three times higher than that generated by air plasma. Air plasma achieved the highest EBT decolorization efficiency (96.51%), while O_2 plasma exhibited a TOC removal rate approximately 20% higher than that of air plasma. The radical scavenging effect on EBT removal demonstrated the additional role of N radicals in the decomposition of organic compounds by air plasma when $^{\cdot}OH$ was inhibited. The decolorization efficiency decreased from 96.51% to 83.33% in air plasma, while the presence of radical scavenging in O_2 plasma led to a greater decrease in decolorization, reducing it from 52.57% to 12.19%. For TC treatment (initial concentration of 5 mg/L), O_2 plasma achieved a total decomposition rate of 94.95% and a mineralization rate of 81.3% after 30 minutes of treatment. These results are impressive considering the challenge of achieving high mineralization rates in the treatment of pollutants. In contrast, air plasma showed a decrease in both decomposition rate and mineralization rate, reaching 60.45% and 57.34%, respectively. These results highlight the potential of the Gliding Arc Discharge reactor as an effective method for decomposing refractory substances and achieving high mineralization rates in pollutant treatment.

Key words: Nonthermal plasma, plasma-liquid interaction, wastewater treatment, plasma catalysis, azo dyes, tetracyclines, gliding arc discharge.

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General introduction

With a growing global population and increased demand for food, water is becoming an increasingly scarce resource and achieving security and sustainability in water resources is a major challenge. It is estimated that by 2050, the demand for water will increase by up to 55% due to population growth and changes in consumption of alimentary and material goods (n.d.Aquastat., 2022). To ensure that there is enough water to go around, we need to be more efficient in how we use water in agriculture, animal farming, textiles industries, cosmetic industries, as well as any other sector that requires the usage of water (Hassan and Carr 2018). In addition, a huge focus needs to be on protecting and managing our water resources. This includes better and more efficient water treatment technologies. Wastewater treatment is an essential process that ensures the safe discharge of wastewater into the environment and protects human health and the environment from harmful pollutants. Efficient wastewater treatment technologies are necessary to meet the growing demand for water and to protect the environment. The development and implementation of new and innovative technologies can improve the effectiveness of wastewater treatment and decrease the energy and resource requirements for the process (Dracea et al. 2018). Membrane filtration is one instance of a technology that can boost the effectiveness of wastewater treatment. Organic materials and pathogenic microbes can both be eliminated from wastewater by membrane filtering. This technology is thought to be more effective than certain established techniques for treating wastewater, such activated sludge. However, it has the disadvantage of high operation costs of the membrane and slow filtration speed. (Crini and Lichtfouse 2019). Another innovative technology that can be used for wastewater treatment is anaerobic digestion, which is a biological process that converts organic matter in wastewater into biogas by anaerobic microorganisms. The production of clean energy and the decrease in organic pollution are some of this process main advantages Unfortunately, it cannot be applied to effluents that are highly concentrated in persistent compounds that are toxic to the biomass responsible for the decontamination process (Moreau et al. 2008). Advanced oxidation processes (AOPs) are one such technology that can improve the efficiency of wastewater treatment. AOPs are a set of chemical processes that involve the in-situ production of highly reactive hydroxyl radicals (·OH) that can oxidize and break down organic and inorganic contaminants in wastewater (Capodaglio 2019). There are several types of AOPs, including photocatalysis, ozonation, and Fenton process. Although each form of AOP has advantages and disadvantages of its own, they all have the ability to increase the effectiveness of wastewater treatment.(Pham et al. 2020). For example, photocatalysis involves the use of a catalyst, such as titanium dioxide, and UV light to generate ·OH radicals. This process can remove a big range of contaminants from wastewater, including those known to be very recalcitrant such as antibiotics, pesticides, and certain dyes (Vecitis et al. 2009). Fenton's reagent involves the use of a mixture of hydrogen peroxide and iron to generate ·OH radicals. For the removal of refractory chemical substances like pesticides and herbicides, this technique is especially effective with a very short time of treatment. However, its main drawback is the high consumption of chemical reagents to sustain enough production of the radical, and its sensitivity to high solution pH (Wang and Xu 2012). Another category of emerging technologies belonging to AOPs is electric discharge in water, or more commonly non-thermal plasmas (NTPs).

NTPs are partly ionized gases with near-ambient temperature and several electron volts of average electron energy (Chen and Wirz 2021). They can be generated by electrical discharge applied in gases such as air, oxygen, argon etc. which are commonly named “feed gas”. NTPs typically contain radicals, ions, electrons, and neutral species. These elements contained in NTPs are classified as Reactive Nitrogen and Oxygen Species (RNOS), and depending on their applications, they can interact with a variety of substances, living things, body tissues, surfaces, etc. (Dobslaw and Glocker 2020). Quite recently, NTP studies have become a stimulating multidisciplinary topic of research used in various areas namely: material processing (Chang 2001), environmental applications (Capodaglio 2019), medical applications (Bekeschus et al. 2019), plasma assisted synthesis (Acayanka et al. 2013b) etc. in the field of environmental applications, NTPs were first used for the treatment of gases and the removal of Volatile Organic Compounds (VOCs) (Rubio et al. 2011; Schiavon et al. 2017), but currently, the research has been extended to tackle the problem of aqueous pollutants (Guo et al. 2018; Shang et al. 2019), disinfection (Laroussi 2002; Shen et al. 2016a), sludge treatment (Lim and Chun 2012), and even the synthesis of catalysts and adsorbing materials (Goujard et al. 2009; Hoeben et al. 2019). However, NTPs applications still present a high level of complexity, and many aspects of plasma treatment are still not thoroughly studied. This leaves adopting this type of technology for real life application not feasible. Particularly, the exact role of reactive species in the degradation mechanism, and the outcome of the plasma treatment are vague and need extensive analytical work to assess. The real-life application on effluent stays challenging due to its high complexity, especially in regards to the mechanisms involved in the degradation processes (Murugesan et al. 2020a).

The current literature has extensive research on the general topic of application of NTPs doe the degradation of persistent organic compounds. Studying various factors affecting the outcome and the mechanism. These research subjects are typically based on plasma sources from the reactor geometry to the gas used, plasma-liquid chemistry, and the final degradation potential. The results have shown in multiple articles that NTPs are very promising and are improving quickly towards the goal of application for real wastewater treatment. The main outlook of this PhD dissertation is based on both applied and fundamental studies on NTPs at atmospheric pressure and for aqueous solutions for the goal of decontamination. My four years of research work at Hazardous Pollutants Control Lab, division of earth and environment systems, department of environmental engineering, have been dedicated to: i) developing a plasma reactor that is efficient for the removal of the selected subject of treatment, ii) detecting and quantifying the amount of reactive species produced by NTP source, iii) evaluating the potential of these species for the treatment of organic compounds: namely an azo dye Eriochrom black T and an antibiotic Tetracycline by studying the degradation and mineralization achieved by the NTP treatment, iv) and exploring the possibility of enhancing the efficiency by combining plasma treatment with different catalysts such as persulfate, ferric and ferrous ions, and most remarkably the synergistic potential combining plasma process with potassium ferrate oxidation. This thesis has been divided into six chapters. The first chapter offers an overview of the literature review describing the topics of the present thesis, such as the general context of plasma, plasma classification, plasma-liquid interactions, different plasma reactors and current NTP applications. The second chapter contains the general experimental setups used in this work and related experimental measurement methods, techniques, and reagents. The third chapter consists of an investigation on the physical and chemical procedure for the plasma-liquid interaction using a gliding arc plasma reactor. RONS in liquid phase produced by the plasma setup are quantified under various relative humidity conditions. The discharge conditions of plasma setup are optimized based on the generation of RONS formed by the GAD reactor. The fourth chapter's main focus is on the effects of GAD treatment on azo dye, the removal efficiency was evaluated by the study of degradation and mineralization rates assessed by spectrophotometric and total organic carbon (TOC) analysis to achieve the best degradation and mineralization rates at the most optimum conditions. The role of reactive species was also investigated in this chapter by introducing scavenging species to the treated solutions and studying their effect on the removal rates. The fifth chapter is similar study to the previous chapter but with a different target compound, namely TC. The conditions of treatment were varied to identify the key parameters impacting the degradation mechanism. The sixth and the final chapter is an innovative and original study that investigates the effect of the combination of GAD plasm process with different catalysis on TC solutions. Different catalysts were used to assess the advantages and inconveniences while assessing the synergic effect. Four catalysis inducers were selected in this work, namely: Ferrous ions, Ferric ions, persulfates, and Ferrate. Finally, the overall conclusion of this study highlights the key findings and discusses the outlook for the future applications of plasma or plasma-catalysis in the elimination of persistent organic compounds.

Chapter I: Literature review.

This chapter includes a bibliography on the numerous subjects covered in this thesis, ranging from background information on plasma and plasma types to discussions of plasma-liquid interactions and nonthermal plasma applications in diverse sectors. The burgeoning topic of NTP applications for the treatment of wastewaters is given particular attention. namely the degradation of persistent organic compounds using different types of plasma reactors currently studied in the research world.

I-1: The general context of plasma.

Matter is defined as anything in this universe that holds weight and volume. The states of matter are often divided into three categories: liquid, solid, and gas. However, there is a fourth state of matter that is only spoken about in specific scientific areas, which is: Plasma, commonly referred to as the fourth state of matter. Irving Langmuir made the initial discovery when he observed that the electric and sound waves produced in the area between electrodes result in an ionized gas with evenly balanced ions and electron charges. He was also the first scientist to give the name “plasma” to a charged gas. (Langmuir 1928). Plasma is currently commonly defined as "a fully, or partially, ionized gas" that contains a large number of reactive species, such as excited atoms and electrons, molecules, and of course, free radicals.(Benstaali et al. 2002; Brisset and Pawlat 2016). Although the discovery of plasma is fairly recent, it has always been a natural phenomenon. It is believed that the universe is 99% consists of plasma matter (Locke et al. 2006): The sun is considered a huge ball of plasma. The polar lights or what is commonly called the aurora is also of plasma matter that occurs naturally when the earth’s magnetic field witnesses a disturbance caused by the solar wind and radiations about 100 kilometers above the earths close to the poles. This disturbance is due to the excitation and the ionization of atmospheric constituents leading to the emission of light of varying colors

Lightning is also another manifestation of plasma. It occurs when a big potential difference is created between the clouds and the earth at near atmospheric pressure. This event results from an electric discharge that forms when charged particles build up inside clouds during storms. This discharge stream consists of what are called accelerated electrons. These electrons, rich in energy, cause the ionization of the air, creating a highly conductive matter in form of a spark between the clouds and the earth (Kyere-Yeboah et al. 2023). This type of discharge (spark discharge) along with arc discharge, results in very high temperatures which is why this type of plasma is called thermal plasma.

I-2: Plasma classifications.

There are various factors taken into consideration when dividing plasmas into different categories. The most important one is temperature which classifies plasmas into hot and cold plasmas. However, the actual classification goes beyond that. Thermal (hot) plasma contains a high number density of electrons and ions which result in high collision frequency leading to a thermodynamic equilibrium. Therefore, thermal plasma occurs at a high temperature and pressure (Pradeep 2007), which requires higher power input and produces reactive species that are in thermodynamic equilibrium. Meaning that electrons, ions and neutral species temperature in thermal plasmas is approximately the same (Hoeben et al. 2019).

Hot and cold plasma are two different types of plasma that differ in their temperature and other properties (Locke and Thagard 2012). Hot plasma has a temperature that is high, usually between a few thousand and a few million degrees Celsius. This high temperature is necessary to create and sustain the ionization process that produces plasma. Examples of hot plasma include plasma in stars, fusion reactors, and lightning bolts. Cold plasma, on the other hand, refers to plasma that is at a much lower temperature than hot plasma, typically in the range of tens to hundreds of degrees Celsius. Despite the lower temperature, cold plasma still contains ionized particles and exhibits many of the properties of hot plasma. Cold plasma is used in a variety of applications, including sterilization, surface treatment, and plasma displays.

One key difference between hot and cold plasma is the amount of energy required to sustain them. Hot plasma requires a lot of energy to create and maintain, while cold plasma can be sustained with relatively low levels of energy. Additionally, the different temperatures of hot and cold plasma give them different physical and chemical properties, which makes them useful for different applications. When a pulse power of short duration or an electric field is applied to a gas passing through a gap at atmospheric pressure a special kind of plasma called "non-thermal" occurs. In this case the ionization degree is low enough to not cause heating up of the heavy particles like ions and molecules, which leads to maintaining the surrounding gas at ambient temperature despite the elevated electron temperature. Upon the application of an intense electric field, a self-propagating electron stream is formed in the discharge area. Applications of plasma technologies for many industrial uses have been researched. including metal reforming (Gangoli et al. 2008), coating and surface treatment (Clyne and Troughton 2019), agriculture for seed germination and quality control of fresh produce (Park et al. 2013; Randeniya and De Groot 2015), sterilization or disinfection (Křiž et al. 2012), in the medical fields for the treatment of wounds, cancer, etc. (Ursache et al. 2012; Wang et al. 2020) and of course in the field of decontamination and pollution removal (Massima Mouele et al. 2018; Sarangapani et al. 2019). The chemistry of plasma is driven by the ionization resulted from electrons possessing high energy, molecule excitation, and generation of oxidative species such as radicals. Consequently, there is considerable interest in the use of NTP for chemical reactions in environmental applications. Direct application of plasma on contaminated water does not only consists of the application of chemical oxidative moieties on the contaminants, but also combines the effect of UV radiation, heat, and the interaction of all active elements, therefore, NTPs can be an effective alternative to the conventional water treatment methods (Brisset and Pawlat 2016). Plasma method can destroy pollutants by generating highly reactive hydroxyl radicals with high non-selectivity, fast reaction, and with no major production of secondary pollution (Murugesan et al. 2020b). Plasmas range in temperature, size and density by several orders of magnitude, whether they are created in a lab or in the wild. Including both high and low temperatures, reactive species are produced, and the charged free entities in plasma make it electrically conductive. The collision of atoms, molecules, electrons, and reactive species is the basis for the promise of plasma technology in wastewater treatment and pollutant abatement. In addition to plasma that is generated naturally, artificial plasma can also be created using various plasma reactors.

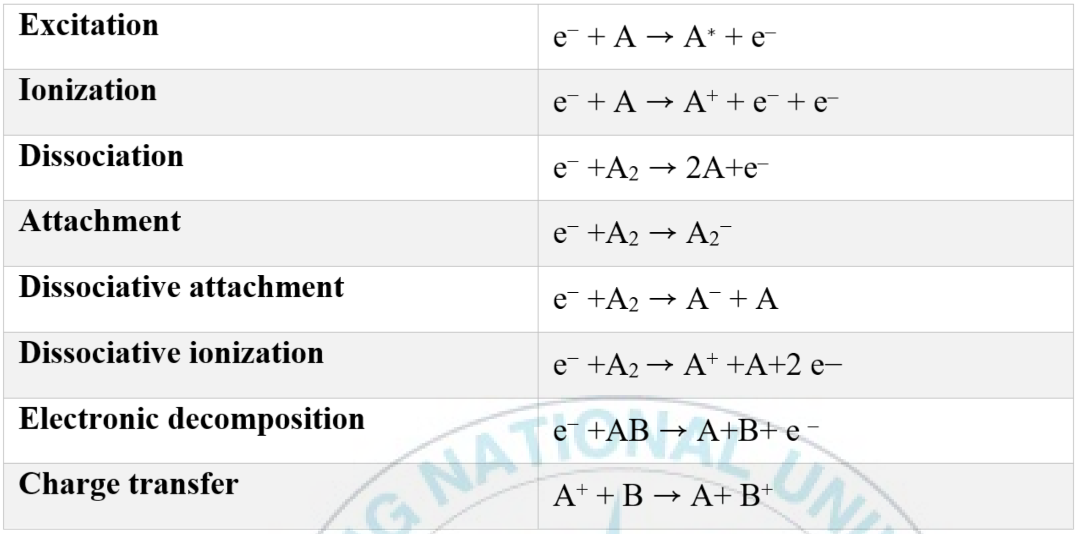
Highpower plasma generators are used in thermal plasmas to widely ionize the gas source and raise its temperature. In this case, the applied power is simultaneously transferred to all plasma particles, producing plasma in thermal equilibrium by giving electrons and heavy particles a uniform and high temperature (Te = T h.p 10 000 K) at the same moment.

The majority of thermal plasma production occurs at greater pressures and in the atmosphere. Due to their extremely high energy density and ability to produce a wide variety of active species, thermal plasmas are used in a wide range of industrial processes.

During and NTP discharge, instead of the kinetic energy of gas atoms and molecules, the energy delivered is mainly delivered to the electrons.(Mutaf-Yardimci et al. 2000). As a result, while the gas is still cold, the electrons acquire high energy and temperature (Te), which vary from 10,000 K to 100,000 K and are comparable to 1^{-10} eV. At the same time, the heavy particles existing in the gas discharge possess $T_{h.p}$ range from 300 to a maximum of 1000 K. ($T_e >> T_{h.p}$). The chemical reactions in plasma are started by energetic electrons. Generally, the following components are often needed to produce any type of NTP: a high voltage power source, electrodes, dielectric barriers, etc., a gap between the electrodes, and a flow of gas via this gap. Free electrons are produced when an electric field is applied between the reactor electrodes, giving these electrons a very high energy and causing them to accelerate. These atoms and molecules in the gas are ionized, excited, or dissociated when they come into contact with these incredibly energetic, rapidly moving electrons.as shown in the reactions illustrated in Table 1.

In plasma, these reactions are referred to as the primary reactions or primary processes, and they typically take 10^{-8} seconds approximately to be carried out and they result in the production of ions, excited atoms, electrons, and molecules (Moreau et al. 2005). The productions of the secondary plasma species will result from various recombination processes between the primary species, including those between ions, radicals, and neutral. The duration of this step, which are referred to as the secondary processes in plasma, is roughly 10^{-3} seconds.

Table 1: Primary reactions in non-thermal plasma discharge (Lukes et al. 2012; Whitehead 2016a).



Excitation	$e^- + A \rightarrow A^* + e^-$
Ionization	$e^- + A \rightarrow A^+ + e^- + e^-$
Dissociation	$e^- + A_2 \rightarrow 2A + e^-$
Attachment	$e^- + A_2 \rightarrow A_2^-$
Dissociative attachment	$e^- + A_2 \rightarrow A^- + A$
Dissociative ionization	$e^- + A_2 \rightarrow A^+ + A + 2\,e^-$
Electronic decomposition	$e^- + AB \rightarrow A + B + e^-$
Charge transfer	$A^+ + B \rightarrow A + B^+$

The literature has described various electrolysis technologies, such as dielectric barrier discharges, pulsed, contact glow discharge electrolysis, corona discharges, and gliding arc etc., that are based on high-voltage electrical discharges occurring either directly in the water (electrohydraulic discharge) or in the gas phase overhead the water (non-thermal plasma). Due to the complexity of these researched systems, the associated process factors, and the fact that such mechanisms are still poorly understood, there are some discrepancies in the conclusions drawn from the many studies that have been published in the literature. Due to these factors, it is not possible to compare the discharge reactors' configuration-based performance, which would have been intriguing considering their wide range. Although the experimental setups in numerous investigations differ, the findings might be discussed.

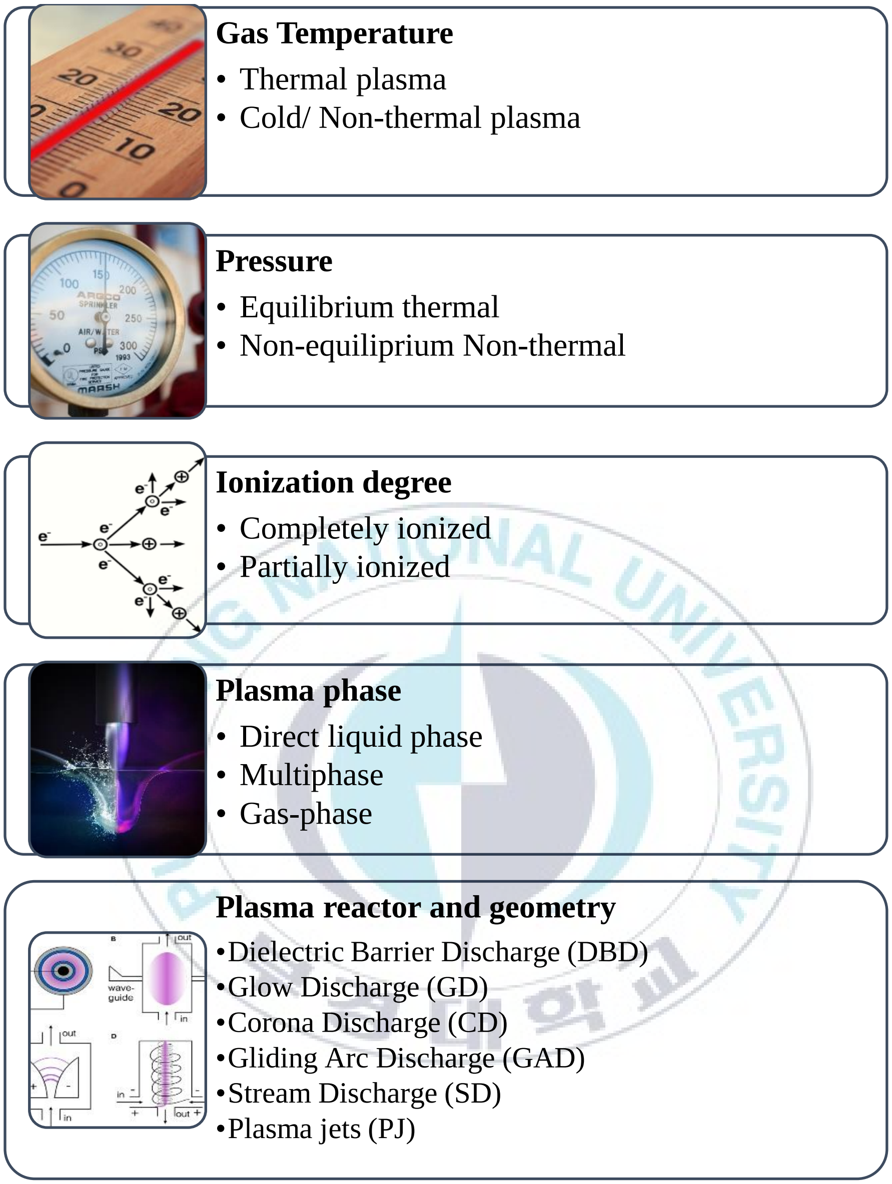


Figure 1: Different classification of plasma discharges (Mutaf-Yardimci et al. 2000; Palma et al. 2020; Zeghioud et al. 2020)

I-3: Plasma reactors.

I-3-1: Dielectric barrier discharge (DBD)

DBD is a plasma source initially developed for the production of ozone and later expanded to various applications like gas purification, surface treatment, disinfection, and decontamination

(Palma et al. 2020; Sang et al. 2021; Wardenier et al. 2019a). A dielectric material (like quartz, glass, ceramics, mica, or alumina) is either positioned in the discharge gap or at least one electrode in the DBD system is covered with a thin coating of a dielectric material (such as quartz, glass, ceramics, mica, or alumina). In some cases, an aqueous solution can act as the second electrode in the system. Due to its longer half-life than other oxidizing species, ozone production is seen as important in the breakdown of refractory compounds. This particular system falls under the category of a cold plasma created at atmospheric or low pressure, which offers the advantage of low operating costs due to limited power and gas consumption. In recent years, various DBD reactor geometries with different electrode configurations have been proposed for treating various wastewaters, highlighting the increased attention water treatment has garnered from researchers (Wardenier et al. 2019b).

I-3-2: Contact glow discharges (CGDE)

This is an unconventional approach to AOPs that involves electrochemical reactions occurring between an electric conductor (electrodes) and an ionic conductor surface (electrolyte) (Cui et al. 2018; Kong et al. 2018). This system facilitates charge transfer between the electrodes and the electrolyte when a sufficiently high voltage is applied. Aqueous electrolytes, solid electrolytes, and molten salts or ionic liquids are only a few of the different electrolyte types that have been mentioned in the literature. In CGDE, a porous glass separates the cathode, which is immersed in water, from the anode, connected to a thin wire that communicates with the water surface, and a continuous DC voltage is applied. This type of plasma produces far higher yields than traditional electrolysis, both in gas phase and aqueous solution, and significantly raises the temperature of all species in the discharge zone (anions, cations, and neutral species). As a result, hot plasma is the term used to describe the plasma produced in reactors. H_2O_2 is the main species generated in the liquid phase of this system, whereas H_2 is formed in the gas phase (Kong et al. 2017, 2018).

I-3-3: Corona discharges

The pulsed corona discharge typically occurs in a needle to plate electrode configuration, where the needle, such as tips, pinpoints, or thin wires, is connected to the high-voltage system, and the plate is grounded (Levko et al. 2016). The electrodes may be constructed from a variety of materials, such as copper, ceramic-coated stainless steel, titanium, and so on. In the corona system, the pulseless discharge produces a considerable number of oxidizing chemical species by generating a high flux of electrons through DC electrical discharge in either gas or liquid media. When discharge occurs in water with air or oxygen bubbling, H_2O_2 and O_3 are the primary chemically active molecules produced (Saud et al. 2021).

I-3-4: Gliding arc discharge (GAD)

Among different NTP types, GAD plasma has been extensively studied for the treatment of both gas and aqueous solutions, because it can be generated by simple electrode configurations, is very stable, easy and cheap to install, all while producing massive amounts of plasma reactive species (Pawłat et al. 2019). It is used for water treatment since it generates a high-temperature plasma by passing a gas through a high voltage (Lu et al. 2012). The arc is propelled along the electrodes by the gas flow, lengthening it until it bursts into a plasma plume. This process repeats itself from the initial break-down until the end of the discharge (Czernichowski 1994). At first, the generated plasma is considered thermal, then it cools down with the air flow until it becomes quenched plasma. Gliding arc discharge is known to be a good source for the generation of reactive oxidative species (Porter et al. 2009). When O_2 is used as a feed gas: Oxygen Reactive species (ROS) such as: “hydroxyl radical, and hydrogen peroxide” are formed. electric field.

One of the important applications of GAD in water treatment widely investigated by researchers is the degradation of organic pollutants. The high-energy plasma generated by GAD can break down organic compounds into smaller, less harmful molecules, leading to possible mineralization (Acayanka et al. 2013a; Merouani et al. 2013; Njoyim et al. 2016). GAD can be used for the treatment of wastewater from various sources, including industrial and municipal wastewater.

Another application of GAD in water treatment is the disinfection of water. The highly reactive species generated by GAD can kill bacteria, viruses, and other microorganisms in water. GAD can be used for the disinfection of drinking water, as well as for the treatment of wastewater before discharge into the environment (Njiki et al. 2020; Pawłat et al. 2019).

Overall, GAD is a promising technology for water treatment given its capability to generate highly reactive species that can degrade organic and inorganic pollutants and disinfect water. However, to maximize GAD performance and create scalable, affordable water treatment systems, more research is required.

Table 2 are presented to demonstrate the geometry and design of various plasma reactors and the main differences between their concepts and methods of generation.

Table 2: comparison of non-thermal plasmas applied for the removal of organic contaminants from aqueous solutions.

source	Generation	Advantages	Disadvantages	References
Corona discharge	○ The plasma discharge is generated in regions of strong electric field near sharp edges, points, or thin wires.	○ Operates at atmospheric pressure. ○ Low operational costs / simple configuration. ○ High electric field with high electron energy(10eV).	○ Small plasma area with inhomogeneous discharge. ○ Possibility of spark or arc formation	(Even-Ezra et al. 2009; Zhang et al. 2017)
Dielectric barrier discharge	○ The plasma discharge is formed between two electrodes separated by a dielectric barrier made of different materials such as quartz, ceramic or glass.	○ Operates at atmospheric pressure. ○ Flexible ○ Can be used for large volumes. ○ Steady plasma area. ○ Easily combined with other methods.	○ Low energy density. ○ Complicated reactor configuration.	(Dobslaw and Glocker 2020; Mahyar et al. 2019; Michielsen et al. 2017)
Contact glow discharge	○ The plasma discharge is formed between an electrode and an ionic surface called electrolyte under high voltage discharge directly into aquatic solution.	○ Operates at atmospheric pressure. ○ Higher yields of reactive species compared to conventional electrolysis.	○ Requires high power. ○ Can result in hot plasma.	(Cui et al. 2018; Sen Gupta 2015)

Gliding arc discharge	○ A non-thermal plasma generated when a gas flow passes through between two or more semi elliptic shaped electrodes.	○ Operates in atmospheric pressure. ○ Simple configuration with minimum investments and operational costs. ○ Powerful plasma density and high level of non-equilibrium. ○ High electron density (1011~1016 cm^{-3}). ○ Quick heat and mass transfer from the plasma plume to the aqueous solution thanks to the gas flow.	○ Limited range of feed gas flow in order to sustain the plasma volume. ○ Relatively low electron energy (1~1.5 eV).	(Burlica et al. 2013; Cui et al. 2018; Gharagozalian et al. 2017)

I-4: Plasma gas-liquid phase interactions:

I-4-1: Acid-base reactions:

Hydrogen ions in the reaction media are present in a significant amount of organic processes, that includes oxidation-reduction reactions.(Magureanu et al. 2015). Since the degradation potential of organic compounds frequently depends on pH, the acidity of the aqueous solution may be able to regulate reaction rates. For instance, due to electron liability of the bonds increases in the phenol aromatic ring, the basic form of phenol (i.e., phenolate ion) is highly reactive compared to the acidic form of the said compound (Lukes et al. 2014). Also, many organic dyes have a strong pH dependence that affects their reactivity and color stability; for instance, certain dyes' $OH^{\bullet}$ radical reactions are much faster at low pH (Benetoli et al. 2012; Li et al. 2016). Therefore, a key factor in the plasma-chemical breakdown of organic molecules in water as well as the plasma-induced inactivation of microbes in water is solution acidity. Since they can release hydrogen ions into aqueous solutions, the different RONS generated by discharges in gas-liquid and water environments have acid-base characteristics. Numerous research that exposed aqueous solutions to pulsed corona, DBD, or gliding arc discharges above water surfaces have documented the generation of acids and their impact on diverse processes. Some publications have even shown pH effects when the discharge was created directly in water (Brisset et al. 2011; Burlica et al. 2006). In this instance, the production of nitrous and nitric acids in the plasma-treated fluids was mostly responsible for the pH reduction.(Brisset and Hnatiuc 2012). However, solutions treated by the discharge generated in a nitrogen-free atmosphere and in the scenario where the discharge was generated directly in water were both observed to have a pH reduction.(Locke et al. 2006). Even in the instances when nitrous and nitric acids were produced, a thorough investigation has not been done to determine if the pH drop is entirely attributable to these acids. Numerous researchers have observed the production of nitrate and nitrite ions as well as an increase in the acidity of the liquid phase while using various plasma sources in an environment of air. (Bradu et al. 2020; Pan and Qiao 2019; Tsoukou et al. 2020). For gliding arc discharges, the acidic effect, and the generation of NO_2 and NO_3 ions in water were also demonstrated, along with an increase in solution conductivity. In the discussion that follows, a broad explanation for the changes in pH and conductivity brought on by air plasma in water is put forth. Liquid-phase reactions can be just as significant as some of the gas-phase reaction pathways described in Chapter I. When dissociated nitrogen and oxygen react in the gas phase to make NO in an air plasma discharge, they do so quickly with either O_2 (R 1) or ozone (R 2) to yield NO_2.

$$2NO + O_2 \rightarrow 2NO_2 \qquad \text{R 1}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{R 2}$$

After NO_2 dissolves in aqueous solution, nitrite NO^{-}_{2} and nitrate NO^{-}_{3} may be formed by an electron capture by NO_2 (R 3) or oxidation by NO (R 4) (Burlica et al. 2006)

$$NO_{2\,(aq)} + NO_{2\,(aq)} + H_2O \rightarrow NO^{-}_{2} + NO^{-}_{3} + 2H^{+} \qquad \text{R 3}$$

$$NO_{(aq)} + NO_{2\,(aq)} + H_2O \rightarrow 2NO^{-}_{2} + 2H^{+} \qquad \text{R 4}$$

The solution's acidity then rises, which, followed with a rise in solution's conductivity, and that favors and contributes to the disproportionation of NO^{-}_{2} into NO^{-}_{3} and NO as described in (R5). (Bradu et al. 2020)

$$3\ NO^{-}_{2} + 3\ H^{+} \rightarrow 2\ NO + NO^{-}_{3} + H_{3}O^{+} \qquad R\ 5$$

In a case of a neutral or alkaline medium, NO_2 may also be formed through the reaction of NO_2 with $OH^{\bullet}$ to yield peroxynitrous acid or its conjugate base peroxynitrite in liquid-phase (R 6). (Lukes et al. 2014). This unstable specie goes through isomerization to the produce NO^{-}_{3} as described in the reactions below.

$$OH^{\bullet} + NO_{2\ (aq)} \rightarrow [O{=}N{-}OOH] \rightarrow O{=}N{-}OO^{-} + H^{+} \qquad R\ 6$$

$$O{=}N{-}OO^{-} \rightarrow NO^{-} \qquad R\ 7$$

In all plasma discharges H_2O_2 is present, especially in the liquid phase. In these cases, peroxynitrite can be formed through the reaction of NO^{-}_{2} with H_2O_2. However, when O_3, NO^{-}_{2} are present in the solution, peroxynitrite are rapidly oxidized to generate NO^{-}_{3} and O_2, consequently reducing their concentration in the aqueous solution (R 8) (Tarabová et al. 2018).

$$NO^{-}_{2} + O_{3} \rightarrow NO^{-}_{3} + O_{2} \qquad R\ 8$$

I-4-2: Oxidation Reactions

The applicability of electric discharges to different areas of water treatment is thanks to the oxidizing characteristics of reactive species generated in aqueous or in gas–liquid interphase in some plasma reactor types. Understanding the nature of these species and the mechanism of their formations is very important. The most importantly relevant species formed in NTPs, such as ROS ($OH^{\bullet}$, $O^{\bullet}$ radicals, O_3, H_2O_2 and O_2) and RNS (NO^{-}_{2} and NO^{-}_{3}, and $NO_2^{\bullet}$, and peroxynitrite) are listed in table 2 along with their standard oxidation potentials E^0 ox.

Table 3: The rate constants for OH• radical and ozone through direct reactions with selected organic and inorganic compounds in water (Brisset et al. 2011; Lukes et al. 2014).

Ox + ne– = Red	E^{0}_{ox} [V]	Ox + ne– = Red	E^{0}_{ox} [V]
$OH^{\bullet} + H^{+} + e^{-} = H_2O$	2.85	$O_3 + 6H^{+} + 6e^{-} = 3H_2O$	1.51
$O^{\bullet} + 2H^{+} + 2e^{-} = H_2O$	2.42	$HO_2 + H^{+} + e^{-} = H_2O_2$	1.44
$ONOO^{-} + 2H^{+} + e^{-} = NO_2 + H_2O$	2.41	$O_2 + 4H^{+} + 4e^{-} = 2H_2O$	1.23
$O_3 + 2H^{+} + 2e^{-} = O_2 + H_2O$	2.07	$HONO + H^{+} + e^{-} = NO + H_2O$	1.00
$ONOOH + H^{+} + e^{-} = NO_2 + H_2O$	2.02	$NO^{-}_{3} + 4H^{+} + 3e^{-} = NO + 2H_2O$	0.96
$HO_2 + 3H^{+} + 3e^{-} = 2H_2O$	1.70	$NO^{-}_{3} + 3H^{+} + 2e^{-} = HONO + H_2O$	0.94
$H_2O_2 + 2H^{+} + 2e^{-} = 2H_2O$	1.68	$NO_2^{\bullet} + H^{+} + e^{-} = HNO_2$	0.9

Generally, organic compounds possess a low mean standard oxidation potential ($E^0 < 0.5$ V per NHE), while the oxidation potential of reactive species generated by plasmas is higher. Therefore, organic matter is susceptible to being attacked by these powerful oxidizers as the change occurring in the standard state Gibbs free energy G^0 of their reactions with RONS is negative. Consequently, with optimum concentrations of oxidants generated by the discharge, organic matter's oxidation by plasma is favorable thermodynamically. The main oxidant in play in the majority of decontamination processes brought on by NTPs, just like in the case of all AOPs, is an $OH^{\bullet}$ radical.

When plasma is created in air, both ROS and RNS are formed. They consist of peroxynitrite as a long-lived secondary species and nitrates/nitrates as primary species. Nitric oxide (NO), a crucial secondary species to all subsequent plasma processes occurring in the gas/liquid phase, is created in the gas phase as a result of the interaction of the parent species (N_2 and O_2) and/or the main species ($N^{\bullet}$, $O^{\bullet}$, $OH^{\bullet}$) under the discharge. The most likely reaction path when humid air is utilized as plasma gas over water involves the dissociation of either molecular oxygen or water molecules in the discharge zone, as demonstrated in reactions R 9 and R 10., $NO^{\cdot}$ is subsequently produced through the reaction of N_2 and $^{\cdot}N$ (R 11 and R 12) (Brisset and Pawlat 2016) (Bradu et al. 2020).

Table 4: Main reactions taking place in air and oxygen plasma discharge (Bradu et al. 2020; Brisset et al. 2008; Brisset and Pawlat 2016).

Air		**Oxygen**	
$O_2 + e^- \rightarrow 2O^{\cdot} + e^-$	R 9	$e^-_{aq} + O_2 \rightarrow O_2^{\cdot-}$	R 15
$H_2O + e^- \rightarrow H^{\cdot} + OH^{\cdot} + e^-$	R 10	$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot}$	R 16
$OH^{\cdot} + e^- \rightarrow H^{\cdot} + O^{\cdot} + e^-$	R 11	$HO_2^{\cdot} + O_2^{\cdot-} \rightarrow H_2O_2 + O_2$ (pH < 7)	R 17
$N_2 + O^{\cdot} \rightarrow NO^{\cdot} + N^{\cdot}$	R 12	$HO_2^{\cdot} \leftrightarrow H^+ + O_2^{\cdot-}$	R 18
$N^{\cdot} + O^{\cdot} + M \rightarrow NO^{\cdot} + M$	R 13	$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$	R 19
$N^{\cdot} + O_2 \rightarrow NO^{\cdot} + O^{\cdot}$	R 14	$O_2^{\cdot-} + O_2^{\cdot-} \rightarrow H_2O_2 + O_2$	R 20

Alternately, $NO^{\cdot}$ can be a formed when nitrogen radical reacts with O_2 to produce atomic oxygen as described in (R 14) (Zhao et al. 2005). In the of presence of O_2 , NO can fix oxygen atoms through an interaction with $O^{\cdot}$ or with O-donor species generated in the discharge area to form nitrogen dioxide ((R13)–(R15)) (Brisset and Pawlat 2016) (Brisset and Hnatiuc 2012)

I.5: Emerging organic contaminants studied in this dissertation:

Among the most widely prescribed medications in the world are antibacterial ones. Antibacterial drugs known as antibiotics have intricate molecular structures that can either kill or inhibit the growth of bacteria (Scaria et al. 2021). Antibiotics are categorized based on their chemical structure, mode of administration, range of activity, and mechanism of action. They are utilized in animal production as growth boosters and for medicinal purposes.(Daghrir and Drogui 2013; Liu et al. 2014). It should be mentioned that each year, antibiotic consumption substantially rises. For instance, between 2000 and 2015, there was a sharp rise in the global consumption of antibiotics, rising from 21 to nearly 35 billion daily doses, or almost a 65% increase according to (Scaria et al. 2021). Moreover, Klein et al. predicted that the utilization of antibacterial drugs will continue to grow to 200% by 2030 (Klein et al. 2018). Antibiotic resistance genes (ARGs), which have detrimental effects on human health, may emerge as a result of the misuse of antibiotics. ARGs are selected by antibiotics from microbial spontaneous mutations. This negates a drug's antibacterial properties and renders it incapable of destroying microorganisms (Gao et al. 2012; Li et al. 2020b). ARGs can thus spread to other bacteria through horizontal transmission, altering bacterial communities and causing them to become resistant to antibacterial drugs. The spread of strains including multidrug-resistant Mycobacterium tuberculosis, Clostridium difficile, and methicillin-resistant Staphylococcus aureus (MRSA) has already resulted in significant harm (Grossman 2016).

TC is one of the antibiotic classes that is currently most widely utilized. The first medications of the tetracycline family were isolated from Streptomyces species in the late 1940s. Since then, TC antibiotics have been commercialized owing to their clinical success. The more recent third generation of the tetracycline family demonstrates greater potency and efficacy. TC inhibits the ability of bacterial protein synthesis by attaching to the 30S ribosomal subunit of bacteria (Brodersen et al. 2000). According to (Fuoco 2012) this antibiotic's broad-spectrum activity enables it to inhibit the activity of the majority of Gram-positive and Gram-negative strains, protozoan parasites, as well as atypical organisms such chlamydia, rickettsia, and mycoplasma . TC is currently among the most widely used antibiotics because of its affordable cost and high level of effectiveness. Tetracycline overuse in livestock, human medicine, and other settings has significantly endangered the environment and public health (Bai et al. 2014). Recently, traces of TC have been found in a variety of places, including sediments, surface water, marine environments, soil, and even biota samples. TC harms ecosystems because it can build up along the food chain and be hazardous to the microbial population, which promotes the emergence and spread of antibiotic resistance (Nøhr-Meldgaard et al. 2021). In addition, TC creates threats to drinking and irrigation water and causes disruption of microbial flora in the human intestine. These detrimental effects raise serious concerns about TC contamination and present an emerging public health issue (Leng et al. 2020). TCe's slow rate of degradation, according to Monahan et al. (2022), may contribute to ecological imbalance. The study emphasizes the significance of TC-related environmental pollution because the effects have a negative impact on human health and lead to bacterial resistance. Additionally, it was noted that one of the primary factors contributing to antibiotic contamination of the food chain, which may have a negative impact on human health, is an inefficient wastewater treatment system (Monahan et al. 2022).

As previously mentioned, has broad-spectrum efficacy against many bacterial infections, making it useful in both human and veterinary medicine. TC is used to treat a variety of infectious conditions, including gastrointestinal infections, infections of the bones and joints, skin infections, and infections caused by bacteria that are sexually transmitted. TC is an effective treatment for infections caused by so-called biothreat pathogens such tularensis, Francisella, Bacillus anthracis, and Yersinia pestis, which can be fatal (Li et al. 2020a)

These antibiotics are reported to make up about 66% of all antibiotics used in Europe for the purpose of animal farming which counts for about 2300 tons. They rank third behind quinolones and penicillin as the most often used medications in Brazil (Lundström et al. 2016)

TC use for animal medication is thought to total more than 2500 tons per year in Europe. Additionally, given that antibiotics are utilized to promote animal growth, agriculture and aquaculture are some of the key industries where tetracyclines are used. In China, raw antibiotic usage for farming and human health care was 180 thousand tons, or 138 g per person annually. It was stated that 172 mg, 148 mg, and 45 mg of antibiotics per kilogram were administered to slaughtered pigs, chickens, and cows (Fiaz et al. 2021). As a result, TC contamination has become an emerging issue for the environment and human use.

TC consumption in South Korea and the UK is reported to be 732 tons and 240 tons every year respectively (Kim et al. 2011). The application of TC as a feed promoter in animal farms contributes to these considerably high TC levels. The next paragraphs go over the adverse effects of excessive TC use.

The Adverse Effects of excessive TC usage:

The inability of TC to be completely absorbed and digested by human and animal bodies due to its stability and low metabolism is the most frequent cause of TC contamination. As a result, the antibiotic's original form is excreted in around 75% of cases (Xu et al. 2021). The majority of TC contamination has been found in water sources, which leads to environmental pollution in the area and harms the ecological system. One of the main sources of TC pollution in the aquatic environment is its overuse in human and animal medicine as well as its usage as a growth stimulant in agriculture. TC is additionally used in aquaculture to feed fish. One can expect that in the aquatic environment, about 80% of the antibiotics used in aquaculture will be released (Amangelsin et al. 2023). TC’s high concentrations in rivers is believed to be an outcome of pharmaceutical production, hospital use, and veterinary operations in surrounding areas. Which results in bacterial resistance brought on by improper or excessive use of TC in fish farming. This situation is detrimental to aquaculture as fish diseases and aquatic bacteria may become resistant to antibiotics as well as affecting algal communities by inhibiting their growth (Xu et al. 2021)

Ineffective wastewater systems are one of the main reasons for the increased antibiotic concentrations in aquatic sources (Wang et al. 2018a) .Furthermore, it is said that TC's stable component makes environmental oxidation harder. Low pH can make TC unstable as well, but because of their low volatility, this results in them becoming less degradable. (Fiaz et al. 2021). Nevertheless, several techniques can degrade TC by dissolving it into smaller by-products with less harmful effects that can be nonhazardous the living beings and to the environment in general. There are several methods that have been developed to degrade pharmaceuticals and drugs in aquatic environments. Conventional treatment processes, which include biological, chemical, and physical removal techniques namely coagulation-flocculation, membrane filtration, and adsorption. These techniques offer many advantages but also some disadvantages, such as maintenance difficulties, economical costs, and production of secondary pollution (Amangelsin et al. 2023). In TC case, with its high toxicity and complex chemical structure, biological treatment is extremely complicated and ineffective (Fuoco 2012).

Plasma catalysis which is often referred to as plasma-assisted catalysis, plasma-driven catalysis, plasma-catalyst coupling, or plasma-enhanced catalysis is a hybrid process where a catalytic material is utilized in conjunction with a gas discharge resulting in a viable technique that yields an enhanced performance for a processing application like the elimination of contaminants in aqueous solutions (Korichi et al. 2020; Whitehead 2016b), treatment of volatile organic compounds (VOCs) (Van Durme et al. 2008; Nozaki and Okazaki 2013) and production of a range of chemicals such as ammonia, hydrogen and the conversion of CO2 (Chen and Wirz 2021).

Recent studies in the decontamination of persistent organic compounds by NTPs plasma are showing interest in the combination of plasmas with different catalysts to achieve higher efficiency, less toxic by-products generation and over all better technology control. Due to the creation of numerous different active species (such as vibrationally excited species, radicals, etc.) during plasma discharge, the chemistry in NTPs is highly complex, and as a result, the selectivity of the desired products in any particular reaction is often low. The selectivity and energy efficiency of a reaction can be improved by combining NTP with catalysts in a well-designed reactor system because it can combine the high selectivity of catalytic reactions with the low temperature performance of plasma reactions in a small reactor. Moreover, the energy consumption of a process, which can be high for particular processes when NTP is employed alone, can also be decreased by the addition of catalysts. NTP- catalysis can be categorized into three types: continuous operation in plasma catalyst system where the catalyst is added throughout the plasma treatment, sequential operation in plasma catalyst where the catalyst is added during the plasma operation system, and post plasma catalyst system where the catalyst is added post plasma discharge (Whitehead 2016b).

A catalyst may be introduced into the plasma discharge zone, which may change the electron distribution and affect the discharge type and the formation of transient reactive plasma species.(Marouf-Khelifa et al. 2008). The use of various kinds of catalysts in different types of plasma reactors has been reported in literature. For example, the combination of DBD reactor with the classic photocatalysts TiO2 and ZnO studied by (Farzinfar and Qaderi 2022) . DBD reactor was combined with ZnO nanoparticles for p-nitrophenol degdaration. In this combination the removal efficiency was impressively improved. This was credited to the activation of ZnO photocatalysts by the UV light emitted in the discharge. The results illustrated that the addition of an optimized quanityt of ZnO nanoparticles (250 mg/L) in the plasma reactor could increase the degradation of p-nitrophenol from 49 % to 91 %, whereas the UV/ZnO photocatalytic process alone only resulted in 12 % of removal. This indicatesa remarquable synergistic enhancement the degradation efficiency in the NTP- ZnO system process rather than a simple an additive effect . Moreover, the energy consumption analysis revealed that the NTP-ZnO system was 4 times more efficient than the plasma alone, which can be regarded as a significant step towards the application of plasma catalysis in an industrial scale (Farzinfar and Qaderi 2022)

Another study that combined DBD with ZnO/α-Fe_2O_3 catalyst for the treatment of amoxicillin (AMX). They studied the impact of different factors like contact time, initial concentration of both AMX and ZnO/α-Fe_2O_3, and solution pH on AMX degradation. In addition, the overall performance was evaluated by assessing the optimization results, kinetics model, degradation pathway, energy yield, and toxicity of the DBD-catalyst combined process. The key findings of this work is that AMX removal rate reached 99.3% after 18 min of treatment at the following conditions: peak voltage was at 15 kV, and ZnO/α-Fe_2O_3 concentration was at 400 mg/L, AMX initial concentration was at 16 mg/L , and initial pH started at 4.5 with a rate constant of 0.198

min−1, energy yield of 3 g kW−1 h−1, without any effluent toxicity. They concluded that the DBD-ZnO/α-Fe2O3 system exhibited a great potential for the removal of aqueous AMX degradation. (Ansari et al. 2020).

There are many other studies in the literature that tackled the plasma-catalysis hybrid process especially with DBD reactors and heterogenous type of catalyst. In this thesis, we opted to investigate the combination of GAD type of plasma with different homogeneous catalysts that are considered ecofriendly, affordable, and easy to analyze. The next chapters discuss all the results obtained throughout this research that is published in three different articles.

Chapter II: Materials and Experimental Methods.

II-1: Plasma Reactor:

In this present work, a lab-scale GAD reactor system (shown in figure 2) was used for all the plasma experiments. It was equipped with a 400 mL glass vessel of a cylindrical shape that makes up the reactor body. The reactor lid is connected to two 4 mm thick knives shaped stainless steel electrodes that are positioned divergently to the lid. An electric voltage of 15 kV was provided by an AC neo-transformer (DAEHANTRANS CO, LTD.) to power the plasma discharge.

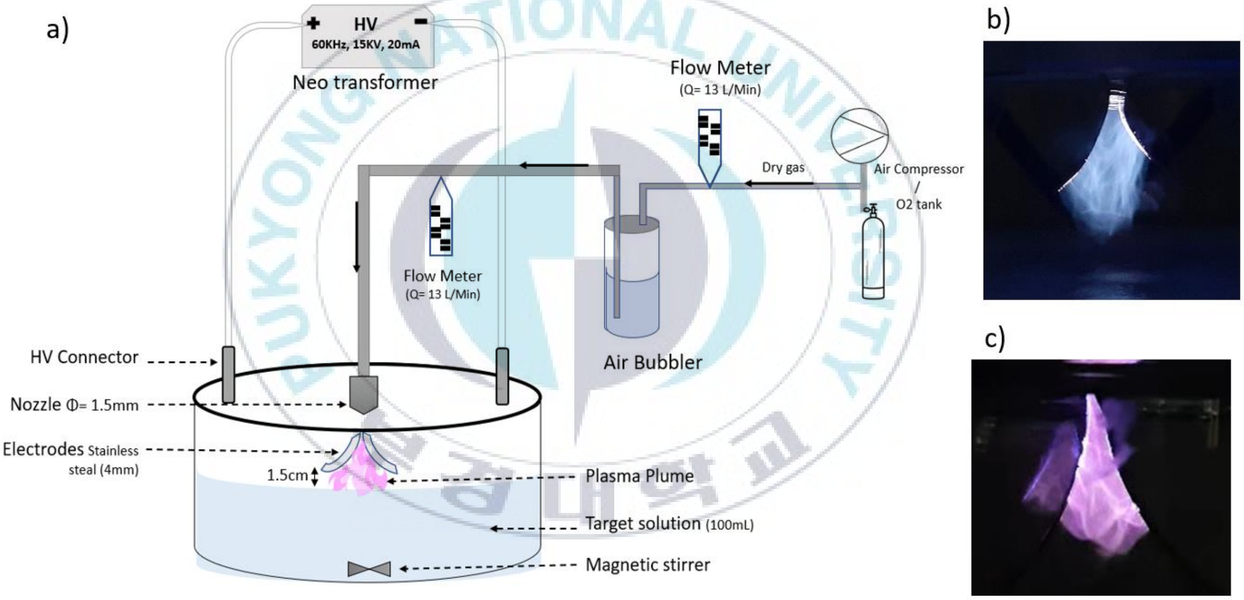


Figure 2 a) Experimental set up. b) photo of O2 plasma. c) photo of air plasma.
HT= 15 kV. Flow= 13 L/min.

Under atmospheric pressure and a continuous flow of the feed gas, an arc occurs during an electric discharge at the most narrow gap between the electrodes, which were spaced about 2 mm apart in this case. The plasma gas that passes through a nozzle of 1.5 mm diameter, drives the arc downward into the liquid interface (Ouzar and Kim 2022).

II-2: Chemicals and reagents:

Ultra-pure water was used in all experiments using a NEW HUMAN UP 900 (Korea, Human Co.) system purifier. All chemicals were of ACS reagent grade. Formaldehyde (37%), Eriochrome Black T (EBT), Phosphoric acid H_3PO_4, Sulfanilic acid and hydrogen peroxide were purchased from JUNSEI (Japan). Analytical grade 2,4-Dinitrophenylhydrazine (DNPH), Sulfanilamide, Sodium nitrite and potassium nitrate were from KANTO CHEMICAL CO., INC. Sodium azide was from DAEJUNG (Korea). Titanium oxysulfate- sulfuric acid solution was purchased from Sigma-Aldrich. Acetonitrile used for High-Performance Liquid Chromatography (HPLC) mobile phase and in the preparation of DNPH was from Burdick & Jackson (USA). TC was obtained from Alfa-Aesar (China). Hydrogen peroxide, phosphoric acid and sulfanilic acid were purchased from JUNSEI (Japan). ethanol (EtOH; 99.5%), tertbutyl alcohol (TBA; ≥99%), acetic acid (99.5%), salicylic acid (≥99.5%), Dimethyl sulfoxide (DMSO), Indigo Blue dye and Titanium oxysulfate-sulfuric acid solution were purchased from Sigma-Aldrich.

II-3: Chemical Analysis:

II-3-1: Hydroxyl radical ($^{\cdot}$OH):

A diode array detector equipped HPLC was used for radical quantification. Acetonitrile and ultra-pure water were employed as the mobile phase, which was maintained in isocratic mode at a flow rate of 1.0 mL/min. A 0.45 um PTFE filter was used to filter all samples and solvents before use. For UV-Visible analysis all samples were analyzed on a DR 5000 UV-spectrometer (HACH). EBT was detected at a wavelength of 530 nm.

II-3-2: Detection and quantification of H_2O_2:

H_2O_2 produced in both O_2 and air plasma, it was determined by a colorimetric technique using titanium sulfate. Titanyl ions react with H2O2 in a very acidic environment to produce a yellow-colored peroxotitanium (IV) complex that is visible at 407 nm and whose color intensity is inversely related to the H_2O_2 concentration. It is established that no other substances in solution interfere with the reaction of titanyl ions, which is unique to H_2O_2 .(Lukes et al. 2014).

$$\mathrm{NO_2^-} + \mathrm{H_2O_2} + \mathrm{H^+} \rightarrow \mathrm{NO_3^-} + \mathrm{H_2O} + \mathrm{H^+} \qquad \text{R 9}$$

$$3N_3^- + NO_2^- + 4H^+ \rightarrow 5N_2 + H_2O \qquad \text{R 10}$$

However, H_2O_2 can be decomposed by NO_2^- via reaction R21. That is why sodium azide (60mM) was added immediately after treatment in order to reduce NO_2^- into molecular nitrogen via reaction R22 and prevent their reaction with H_2O_2.

II-3-3: Detection and quantification of O_3:

Dissolved O_3 detection in samples was performed by a simple colorimetric standardized method (Method 4500-O_3) using Indigo Blue dye in acidic conditions (Bader and Hoigné 1981; Tarabová et al. 2018). The fast decolorization of indigo blue solutions by O_3 was assessed by the decrease in absorbance at 695 nm. The mixing ratio of plasma treated water with indigo reagent in our experiments was determined to be 1:1. We investigated whether H_2O_2 affects indigo blue decolorization by mixing a volume of indigo blue sample with H_2O_2 (1 mmole/L) but no remarkable decolorization was achieved. We however, still analyzed the samples within a few minutes after mixing with reagent to prevent any interference from possible long-lived species.

- ✓ Persulfate
- ✓ Fe^{2+}
- ✓ Fe^{3+}
- ✓ Ferrate

II-3-4: Detection and quantification of NO_2^- and NO_3^- :

The amount of NO_2^- and NO_3^- produced by air plasma of different RH% were measured by spectrophotometry (Shen et al. 2016b) (Shinn 1941). 10 mL of treated solution was added to 200 µl of 10 g/L diazotizing agent (sulphanilamide 10 g/L)at different treatment times, then incubated for 3 minutes at ambient temperature, another 200 µL of coupling reagent (N-(1-naphthy1)-ethylenediamine hydrochloride 1.0 g/L) and kept for 20min at room temperature. After incubation, NO_2^- levels were detected at 536 nm. For NO_3^- analysis, 10ml of the treated sample, 200 µl of 1mol/L hydrochloric acid and 20 µl of 0.8% sulfamic acid were mixed together, then NO_3^- concentrations were measured at 224nm.

II-4: Eriochrome Black T degradation experiments:

All experiments were performed at atmospheric pressure in presence of O_2 or air with flow rate equal to 13 L/min. The total duration of the treatment experiments ranged from 1 to 30 minutes. Aside from the effect of initial concentration experiments, initial concentration of EBT was set at 100 mg/L. The effect of pH and temperature was studied beforehand to decide whether this dye is a good candidate for this study or not. No odd results were found.

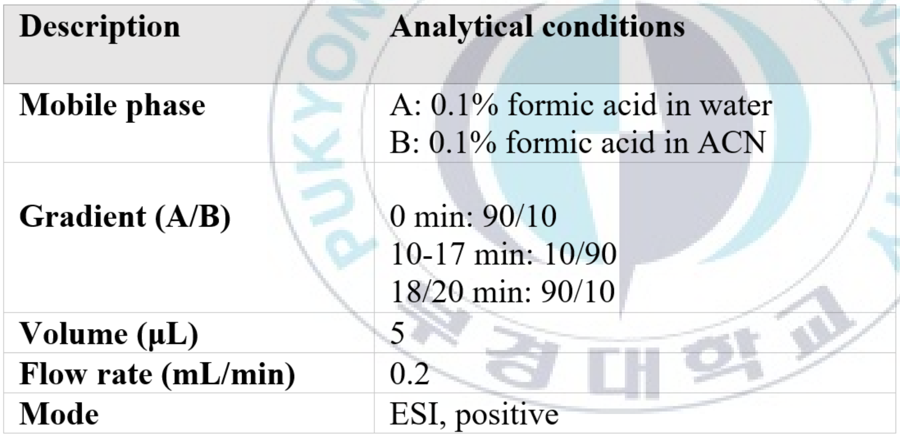
II-5: Tetracycline degradation experiments

Acetonitrile and 0.05 % phosphoric acid were combined in the mobile phase at a volume ratio of 90:10, with a flow rate of 1 mL/min. wavelength of 358 nm was chosen for TC peak detection.

The injection volume was 20 L, and the retention time was 10 minutes. Prior to the studies, fresh TC solutions were made at various concentrations and maintained in opaque container and away from direct sunlight to prevent the photodegradation of the TC molecule. Liquid chromatography with tandem mass spectrometry (LS/MS/MS) system UPLC/Xevo TQ-S mini (Waters, USA) equipped with column C18 Column (2.1100mm, 1.7 m) was used to investigate the degradation products of TC. LC/MS/MS scan chromatograms for the mass spectrum ranged from 100 to 600 m/z.

Table 5 lists all operational conditions.

Table 5: Analytical conditions of LC/MS/MS detection and analysis



Description	Analytical conditions
Mobile phase	A: 0.1% formic acid in water B: 0.1% formic acid in ACN
Gradient (A/B)	0 min: 90/10 10-17 min: 10/90 18/20 min: 90/10
Volume (μL)	5
Flow rate (mL/min)	0.2
Mode	ESI, positive

II-6: Analytical Measurements

During the experiments for the analysis of the selected compounds, different samples were collected from the reactor at different treatment periods. The samples were analyzed by a DR 5000 spectrophotometer for evolution of decolorization, or the measurement of reactive species like O_3, H_2O_2 or NO_2^-. The detected absorption was calculated to concentrations using Beer-Lambert law at the maximum wavelength assigned to each compound. The total organic carbon (TOC) was measured by the non-purgeable organic carbon method (NPOC)operated at 680 ^{o}C.

The decolorization, degradation and mineralization efficiency of the selected target compounds were evaluated according to these equations:

$$\text{Decolorization efficiency (\%)} = \left(1 - \frac{ABS}{ABS_0}\right) \times 100$$

$$\text{Degradation efficiency (\%)} = \left(1 - \frac{C}{C_0}\right) \times 100$$

$$\text{Mineralization efficiency (\%)} = \left(1 - \frac{TOC}{TOC_0}\right) \times 100$$

where:

ABS = EBT concentration at the treatment time (mg/L);

ABS_0 = initial EBT concentration (mg/L);

C = EBT concentration at the treatment time (mg/L);

C_0 = initial EBT concentration (mg/L);

TOC = total organic carbon at the generic treatment time (mg/L);

TOC_0 = initial total organic carbon (mg/L).

II-7: Potassium Ferrate Synthesis

Potassium Ferrate (VI) utilized in this work was prepared through wet oxidation method as described in (Hoang and Kim 2022; Park 2020). 30 g of KOH was added to 100 mL of NaOCl solution and stirred until completely dissolved. Then, the solution is cooled and filtered with GF/C filter to remove NaCl particles. The filtration process is repeated three to four times to ensure the complete removal of NaCl particles. Next, the filtered solution should be kept in the refrigerator to maintain cold temperature. Next step is to add 11.1 g of $Fe(NO_3)_3 \cdot 9H_2O$ to the solution and stirred for 40 minutes to synthesize FeO_4^{2-}. Up until this stage it is still in the liquid state. In order to transform it to solid 16.7 g of KOH is added while continuously stirring 40 minutes more, then stored for about 30 minutes. Then, after giving it some time to cool down, the solution is passed through a G4 glass filter, the filtrate is immediately administered to a saturated KOH solution (11M) and refrigerated again. A repeated step of filtration with GF/C filter paper is necessary before Ferrate (VI) crystals are obtained. The associated chemical reactions are listed here. (Hoang and Kim 2022):

$$Fe^{3+} + 3OH^{-} \rightarrow Fe\,(OH)_3$$

$$2Fe\,(OH)_3 + 3NaClO + 4NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + 5H_2O$$

$$Na_2FeO_4 + 2KOH \rightarrow K_2FeO_4 + 2NaOH$$

The Ferrate (VI) particles that remain on the filter paper are washed with a mix of different solvents namely 25ml n-hexane, 10ml methanol, and 10 ml diethyl ether four times. The particles then are collected and put in a vacuum dryer chamber. The purity of the final Ferrate obtained was measured with a DR 5000 UV-spectrometer (HACH) using spectrophotometric analysis (Li et al., 2005). We carried out the experiments when the purity achieved was above 93%.

Chapter III: Measurement of reactive species and effect of relative humidity.

III-1: Generation of reactive species under different relative humidity conditions.

Although plasma methods offer a promising method for degradation of persistent toxic compounds, their application in wastewater treatment facilities currently is rather difficult. Typically, reactor setups that demand a high electric energy consumption for extended treatment times are needed to operate most NTPs. Also, the use of noble gases such as helium and argon for a plasma source is economically challenging. Researchers are urged to work on developing plasma techniques that would reduce treatment time and gas flow rates while employing less expensive feed gases. When executing plasma for the treatment of aqueous solutions, air is the best substitute as it is the most available, least expensive, and the safest to use. However, air is only composed of twenty-one percent oxygen which results in a low ROS content. According to certain studies, increasing the gas feed's humidity will boost the plasma solution's hydroxyl radical concentration. In contrast to when an oxygen or air plasma source is used, we chose to evaluate the effect of relative humidity on ROS production in air in this study. Humidity was introduced to the reactor discharge area by simply passing the feed gas through a water bubbler. RH was set to four conditions: 0~5% considered as dry gas conditions; 30% low humidity; 50% medium humidity and >80% for high relative humidity conditions. The efficiency of our GAD reactor is demonstrated by measuring the amounts of $\cdot OH$, H_2O_2, NO_2^- and NO_3^- formed under different feed gas and relative humidity conditions. EBT removal efficiency was also evaluated by spectrometric analysis and by studying the total organic carbon removal rate. All experiments were repeated three times, the mean and standard deviation were calculated.

III-1-1: Effect of relative humidity on RONS production:

·OH role in plasma chemistry is essential due to its powerful oxidizing potential of 2.8 V. This oxidizing power makes its lifetime extremely short has a short 2 ns (Hoeben et al. 2000)) making it a difficult task to measure quantitavely in water, sometimes even impossible. Some techniques have been suggested for ·OH analysis namely Optical Emission Spectroscopy OES, electron paramagnetic resonance (EPR), electron spin resonance (ESR), and laser-induced fluorescence spectroscopy (LIF),As for the quantification, chemical probes are mostly chosen to quantify the concentration of ·OH radicals (Kanazawa et al. 2013).

We opted to use dimethyl sulfoxide (DMSO), which presents several advantages as a chemical probe. DMSO is highly soluble in water and can trap most ·OH generated in solution. Also, it is less likely to react with other plasma species thereby influencing the detection of ·OH In addition, it is nontoxic even at relatively high concentrations (Sahni and Locke 2006). Moreover, it is highly reactive with ·OH (Soman et al. 2008) (k = 4.5~7.1× 10^9 mol/L/s) forming methane sulfinic acid, methyl radicals and formaldehyde (HCHO) according to the following reactions:

$$\mathrm{HO^{\cdot} + (CH_3)2SO \rightarrow CH_3SO_2H + CH_3} \qquad \mathrm{R23}$$

$$\mathrm{CH_2 + HR \rightarrow CH_4 + R^{\cdot}} \qquad \mathrm{R24}$$

$$\mathrm{CH_3 + O_2 \rightarrow CH_3OO^{\cdot}} \qquad \mathrm{R25}$$

$$\mathrm{2\,CH_3OO^{\cdot} \rightarrow HCHO + CH_3OH + O_2} \qquad \mathrm{R26}$$

Studies have found that the methan (CH_4) generated in reaction R24 was only 0.3~0.5% of the reaction of DMSO with ·OH (Chen et al. 2016), HCHO produced by the reactions R25 and R26 is the major product, and the quantification of HCHO formed is an indirect way for the quantification of ·OH consumed in the system. HCHO concentrations in treated samples is determined by a deravitization reaction with 2,4-dinitrophenylhydrazine (DNPH) to form hydrazone (HCHO -DNPH). An example of the chromatogram is presented in figure 3.

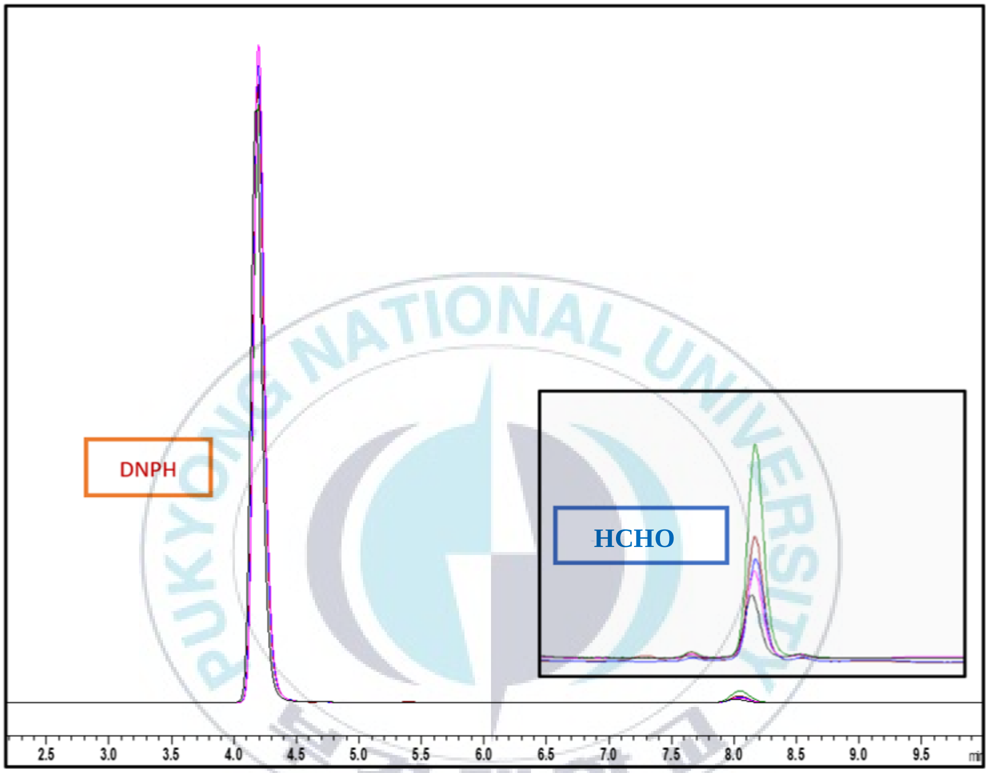


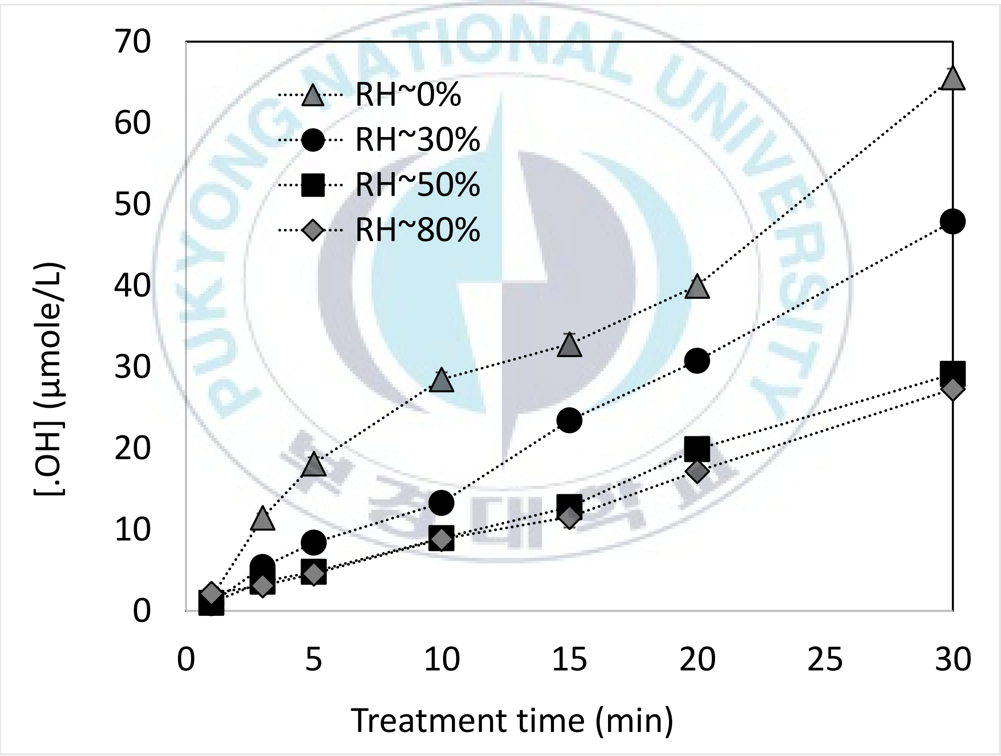
Figure 3: Chromatogram of HCHO samples detected during plasma treatment.

Radical Concentration is calculated based on reaction stoichiometry and experimental data which indicates that each one mole of HCHO generated in the plasma is equal to 2 moles of ·OH formed and reacted with DMSO (Tai et al. 2004).

III-2-1: Generation of ·OH :

Concentration of ·OH generated under different relative humidity conditions is shown in figure 4. In O_2 plasma case: the amount of ·OH increased along discharge time throughout all humidity conditions, the highest yield was achieved under the dry gas condition (RH~0%) which resulted in maximum ·OH amount of 65.49 µmole/L after 30 minutes. We can see that RH has a negative effect on ·OH formation, especially when RH was at 50% and above, approximate only 28 µmole/L was generated after same period of treatment.

a)



b)

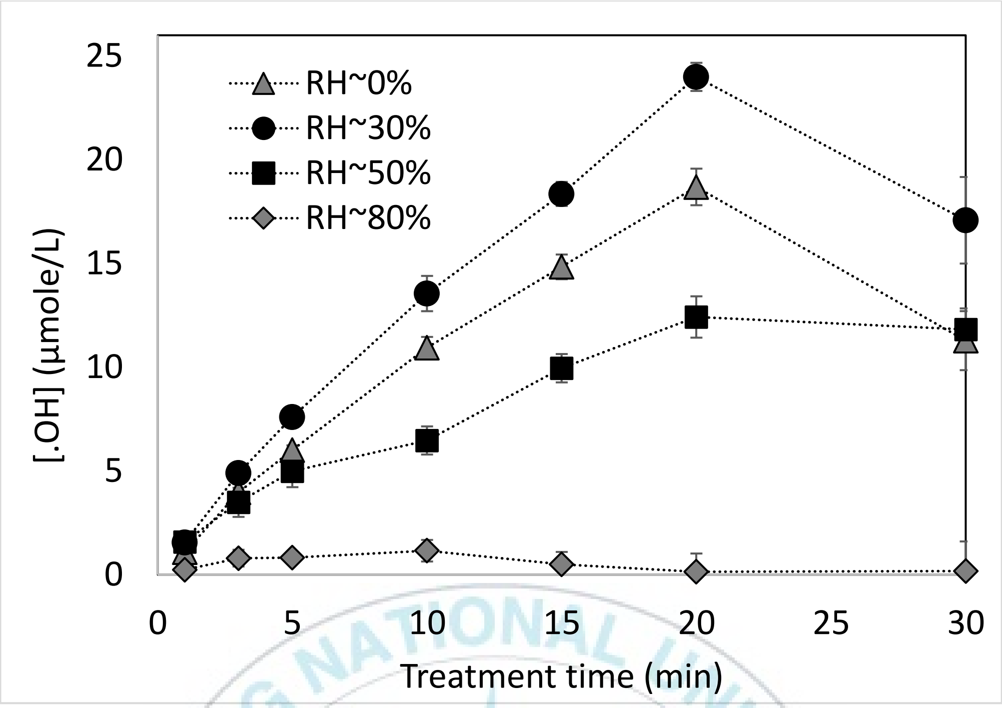


Figure 4: Amount of hydroxyl radical (·OH) generated in DMSO under plasma discharge a) in Oxygen b) in air with different Relative Humidity rates.

In contrast, feed gas with a 30% RH showed enhanced ·OH production in air plasma, reaching a level of 23 mole/L. However, in the case of RH=80%, higher RH percent resulted in a smaller ·OH concentration. At all instances, ·OH concentrations were less than 1 mol/L. The generation of electrons is prevented as a result of a number of circumstances, including temperature drop in high humidity gas feeds. Plasma's chemical characteristics were also impacted by the rise in humidity.

Nitrogen and oxygen molecules mostly react to form nitrogen oxide when plasma is generated in air conditions without humidity, as demonstrated in reaction (R27) and (R28). Equation describes how, when humidity rises, electrons interact with gaseous water molecules to ionize or atomize them (R31). consequently, ·OH radicals, H_3O^+ and $H_2O_2$are generated (Bradu et al. 2020).

$$\mathrm{N + O \rightarrow NO} \qquad \text{R27}$$

$$\mathrm{NO + O \rightarrow NO_2} \qquad \text{R28}$$

$$O_2 + O + M \rightarrow O_3 + M \qquad R29$$

$$N_2^{*} + H_2O \rightarrow OH + H + N_2 \qquad R30$$

$$H_2O + e^- \rightarrow H_2O^+ + 2e^- \qquad R31$$

$$2H_2O^+ \rightarrow HO^{\cdot} + H_3O^+ \qquad R32$$

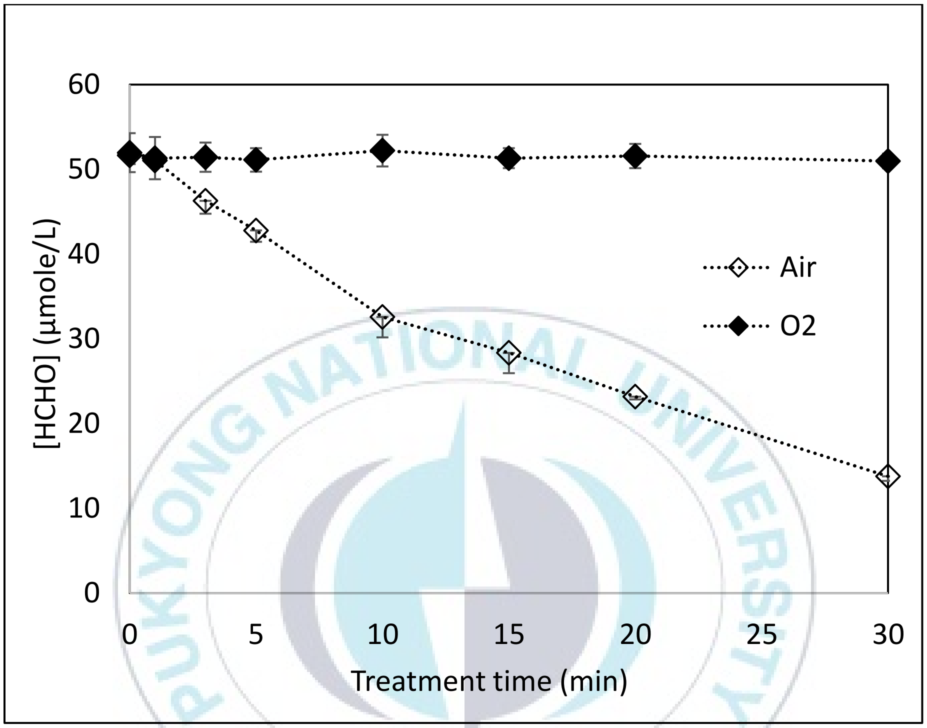


Figure 5: Evolution of formaldehyde (HCHO) concentration under different feed gas. initial concentration 50 µmole/L

The HCHO-DNPH derivative combines with long-lived plasma species in a post discharge reaction, which is likely the cause of the $\cdot$OH drop 20 minutes after discharge. We treated a solution of DMSO spiked with a known concentration of formaldehyde prior to plasma treatment in order to evaluate the stability of formaldehyde, and we then compared the results to those of untreated 230 mmole/L DMSO. We determined optimum relative humidity conditions to carry of the rest of studies (0 percent for O_2 plasma and 30 percent for air plasma). Figure 5 displays the outcomes of plasma treatment in O_2 and air discharges of a 50 mole/L formaldehyde solution. Even in the absence of DMSO, HCHO is not oxidized in O_2 plasma. Figure 6 a) demonstrates that the concentration of HCHO remains constant throughout the whole treatment period, proving that HCHO is a stable product in an O_2 environment. On the other hand, the HCHO starting concentration under air dropped over the course of the treatment and reached 13.78 µmole/L by the time the sample was discharged, resulting in an approximately 74% degradation of the HCHO. However, (Kovačević et al. 2017) have found that HCHO is stable under air plasma generated by DBD. For comparison with the findings of (Kovačević et al. 2017), we treated a solution of DMSO (230 mmole/L) spiked with 45 µmole/L of HCHO then compared it with when DMSO and HCHO were treated separately. The results are presented in figure 6 b)**.** For O_2, the results are exactly similar to the findings of (Kovačević et al. 2017), adding DMSO to DMSO solution increases HCHO concentration in the same pattern as when HCHO is generated by DMSO alone, if 45 µmole is subtracted from the spiked system the results will overlap as is shown in the graph, confirming the idea that HCHO is not oxidized in these circumstances. So, in this instance, the measurement of ·OH is accurate. In air plasma however, after 20 minutes of treatment, HCHO concentrations reduced more noticeably in all systems. Given that HCHO is purportedly stable in plasma, this drop is most likely the result of the post reaction that occurs during the derivatization period. Gliding Arc plasma is known particularly for the generation of long-lived post discharge species inducing a post reaction effect on the derivatization agent (Bradu et al. 2020; Lukes et al. 2014).

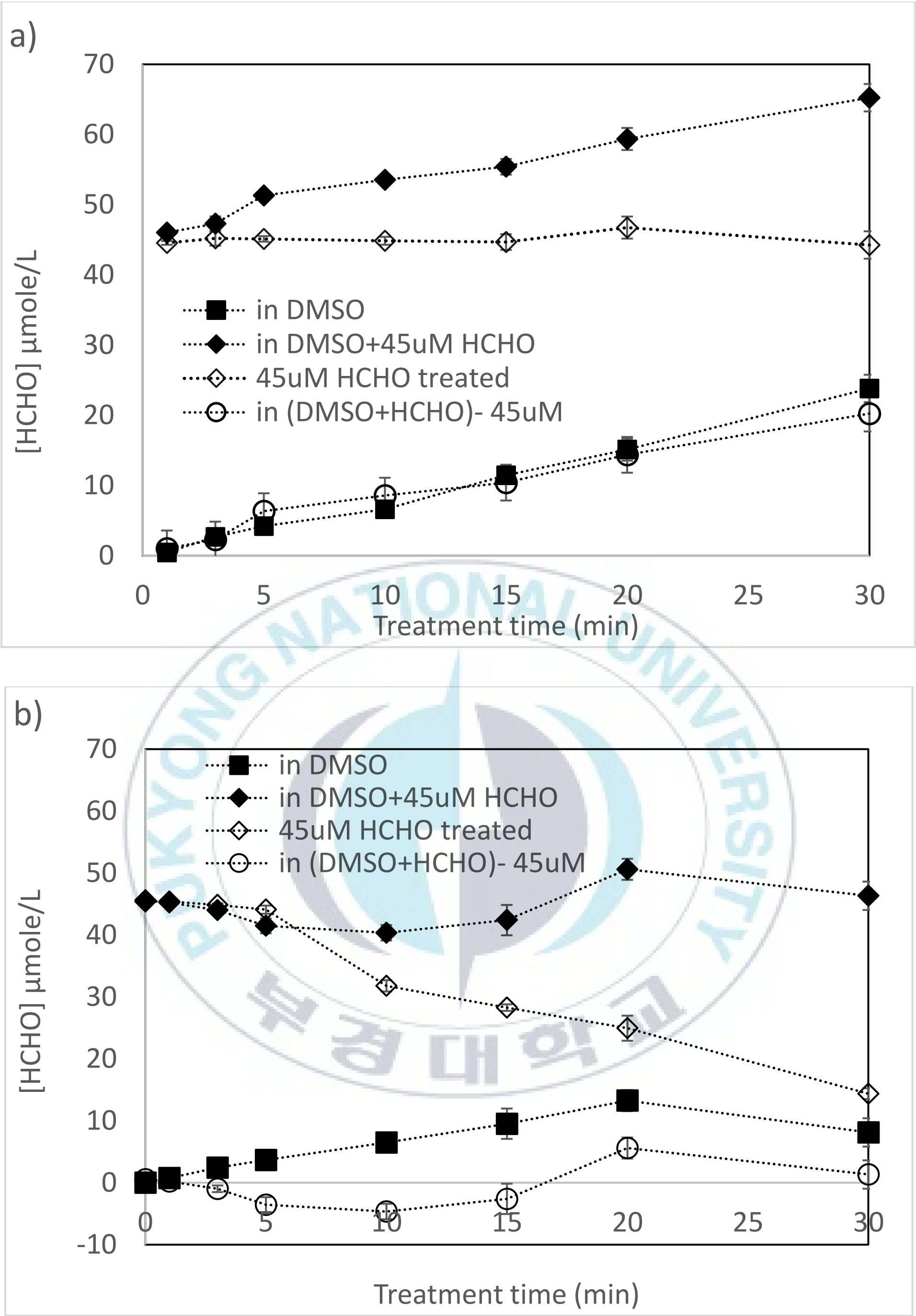


Figure 6: HCHO measured in treated samples with and without DMSO in Gliding Arc discharge in a) O2; b) Air. Initial concentrations: HCHO, 45 µmol/L; DMSO, 230 umol /L.

Tampieri et al. (2021) measured the concentrations of ·OH produced in an atmospheric pressure plasma jet (APPJ) with helium as the working gas while terephthalic acid (TA) was selected as the chemical probe. They reported that ·OH concentration reached 1.8x 10^{-12} mole/L at an optimum pH of 3 (Canal et al. 2021). Another study that used TA to quantify ·OH in an aqueous phase pulsed electrical discharge plasma was reported by Sahni et al. The production rate of ·OH was 1.67×10^{-8} mole/s for a direct discharge into water at an applied voltage of 45 kV.

III-2-2: Generation of H_2O_2:

H_2O_2 amounts generated in GAD are illustrated in figure 10. Just as it was constated for ·OH: a 30% of humidity in air feed gas enhanced the generation of H_2O_2 compared to other humidity rates, achieving the highest concentration of 177.25 µmole/L. O_2 plasma also gave the best results at dry condition, the highest H_2O_2 rate was 575.95 µmole/L. We notice that, in optimum humidity conditions of both feed gases, O_2 plasma generated approximately 3 times more of ·OH and H_2O_2.

III-2-3: Generation of O_3:

The different concentrations of O_3 produced in GAD plasma are shown in figure 8. In contrast to what was constated for ·OH and H_2O_2.The relative humidity did not contribute to a huge enhancement in O_3 generation when it increased from 0% to 30%. In the other hand, and similarly to the other reactive species, higher humidity rates caused a major decrease in ozone generation.

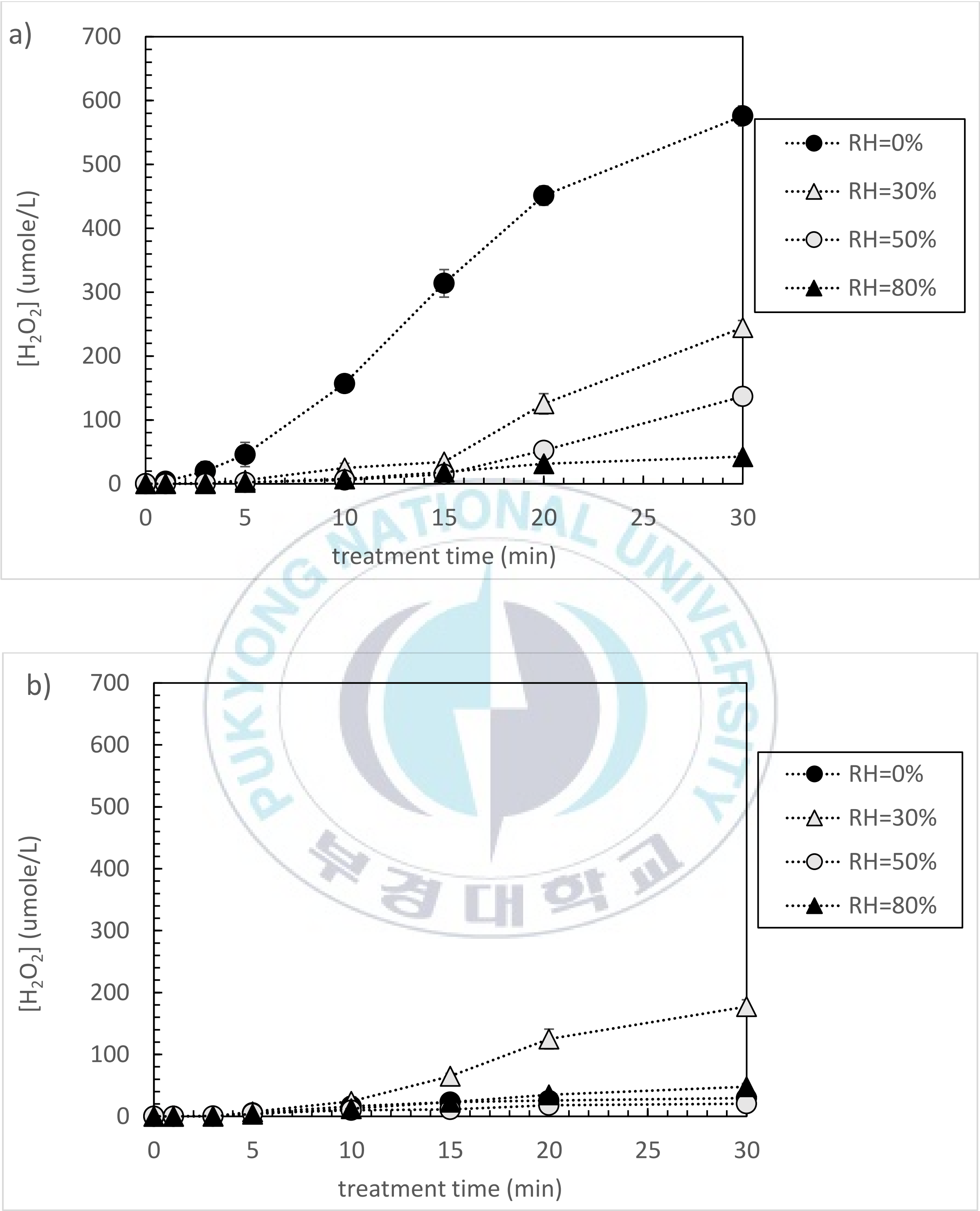


Figure 7: Concentration of hydrogen peroxide H_2O_2 as function of the gas relative humidity: a) in O2; b) in air.

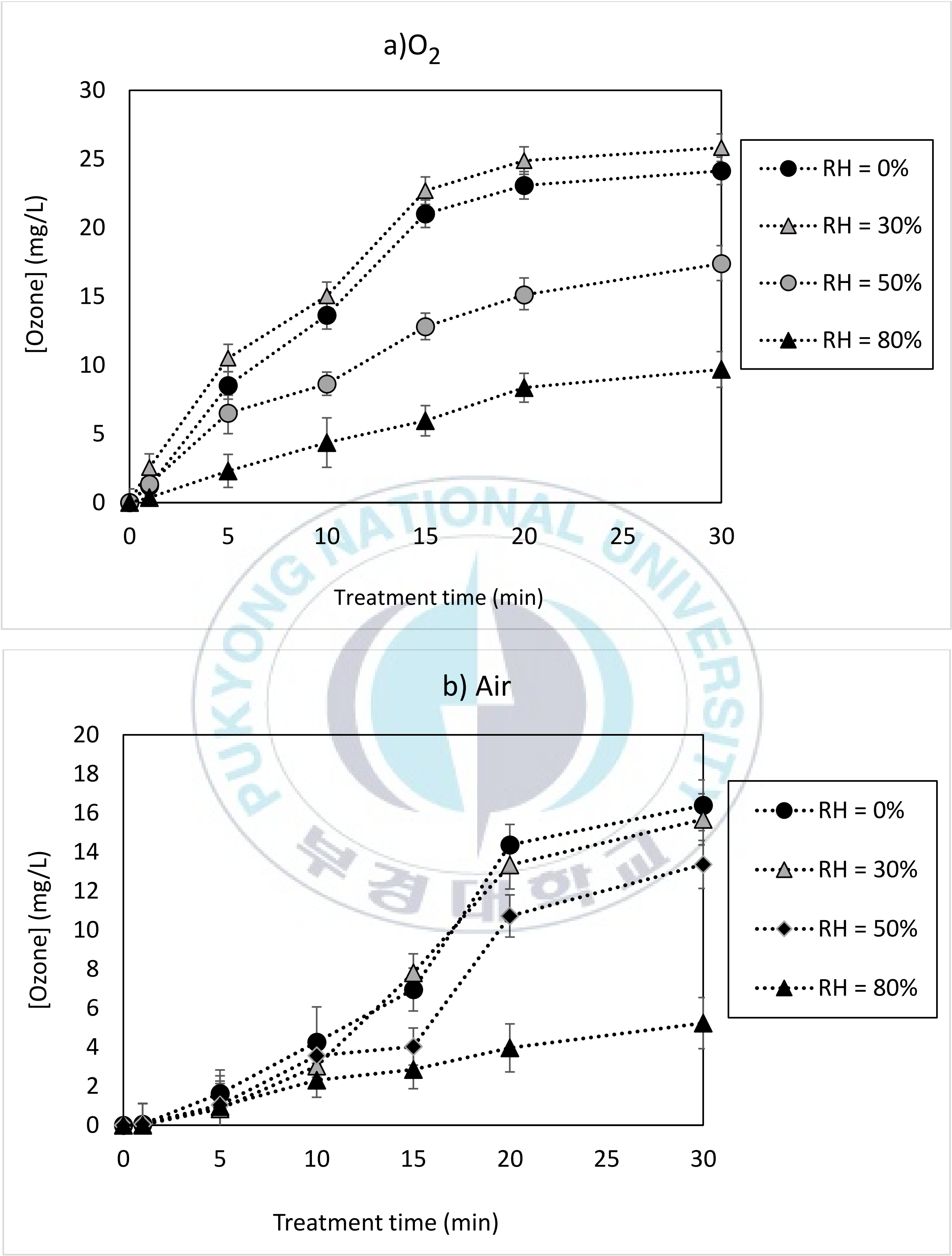


Figure 8: Concentration of hydrogen peroxide O_3 as function of the gas relative humidity: a) in O_2; b) in air.

III-2-4: Generation of Nitrogen species:

The presence of nitrites and nitrate ions serves as the primary indicator of nitrogen species formation in aqueous solutions. The results are illustrated in figure 9. NO_2^- and NO_3^- concentrations varied depending on relative humidity rates. For NO_2^-, in the cases of RH= 0; 30; and 50%: NO_2^- concentrations increased in the first half period of discharge, after that, the values witnessed a drastic decrease. The following reacting can be explains how the oxidation of NO_2^- into NO_3^- takes place when the amount of $2OH^{\cdot}$ Is at excess in the aqueous solution. (Marouf-Khelifa et al. 2006)

$$HNO_2 + 2OH^{\cdot} \rightarrow HNO_3 + H_2O \qquad R35$$

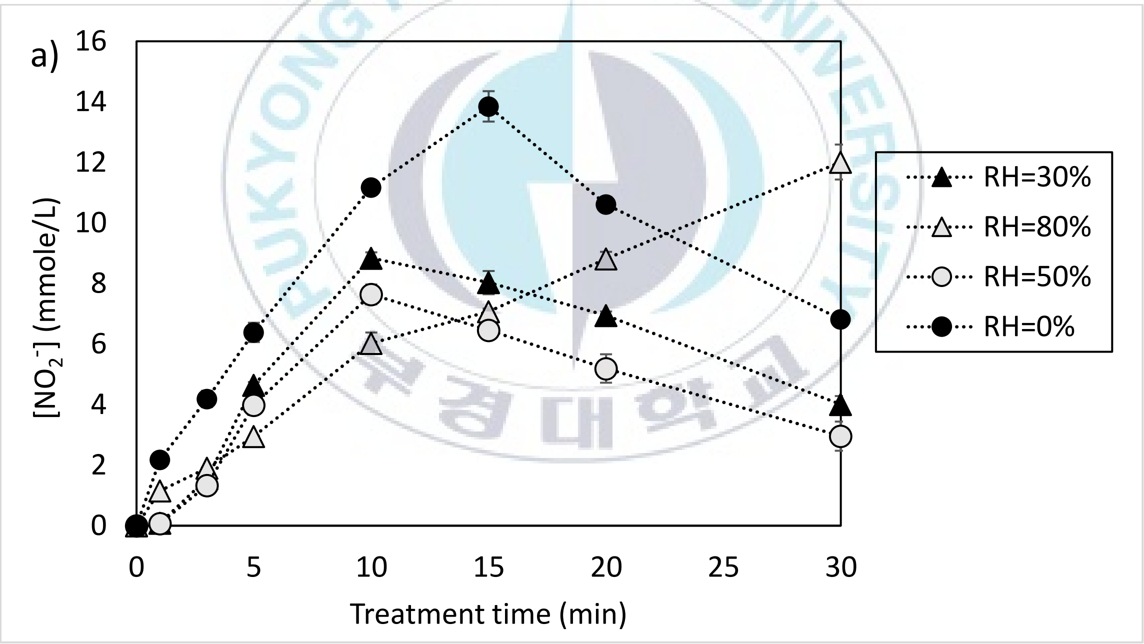


Figure 9: Concentration of a) nitrite (NO_2^-) and b) nitrate (NO_3^-) as function of air relative humidity.

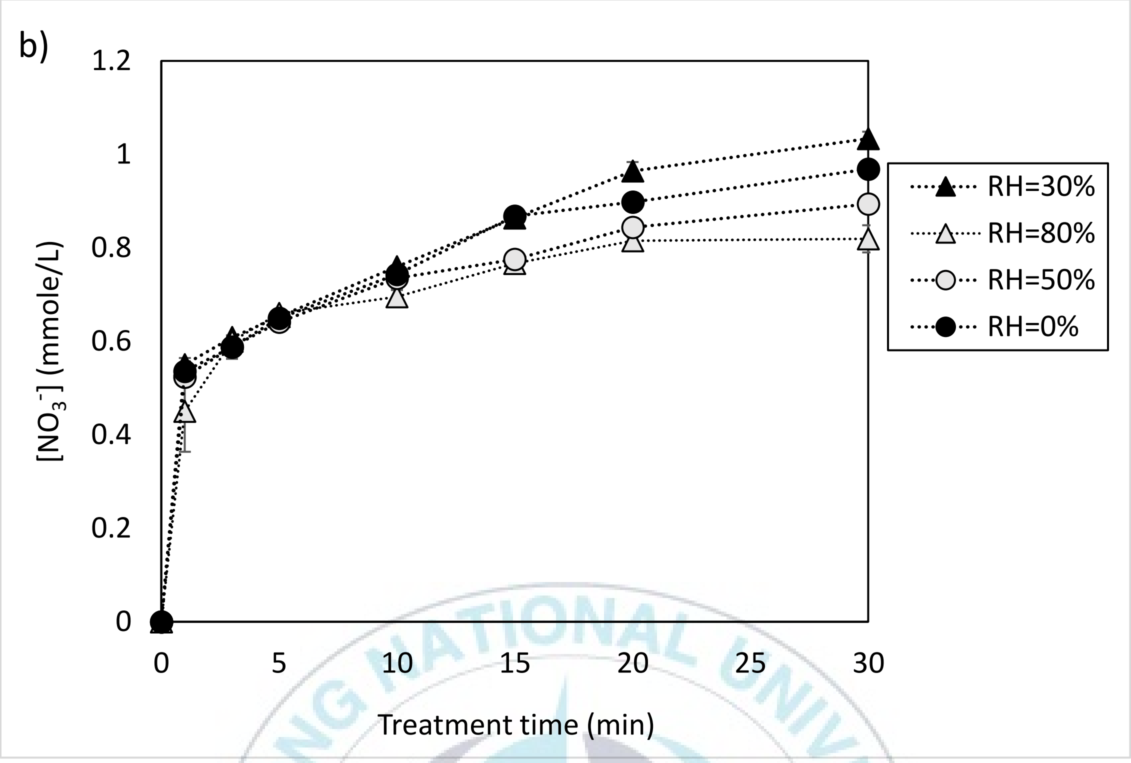


Figure 9: Concentrations of a) nitrite (NO_2^-) and b) nitrate (NO_3^-) as function of air relative humidity.

The presence of nitrous/nitric acids is reflected by NO_2^- and NO_3^-. Also, nitrous acid is not stable at pH~2.6, it slowly disproportionates into NO_3^- as plasma treatment carries on. (Brisset et al. 2008) explained this behavior as nitrite concentration results from synthesis step and degradation step, at the same time the nitrate concentration continuously increases especially that low pH favors disproportionation of nitrite into nitrate. This is evident in the results obtained for NO_3^- as the concentration increased for all treatment times regardless of RH%.

III-2-5: Reactive species generated by GAD under optimum conditions:

Figure 10 a) shows the concentration of $^{\bullet}OH$ produced during air and O_2 plasma treatment. The amount of $^{\bullet}OH$ created in the aqueous solution increased along the discharge time, as indicated in the graphs, with the highest concentration of 59.72 µmole/L being attained under O_2 plasma after

30 minutes of treatment. In air plasma case, after 15 minutes a maximum amount of $^{\bullet}$OH of 17.96 µmole/L was detected; however, prolonged treatment durations resulted in a large drop in $^{\bullet}$OH concentration. This can be explained by the fact that after 15 minutes of discharge, the HCHO-DNPH product will likely combines with long-lived plasma species .(Brisset et al. 2008).

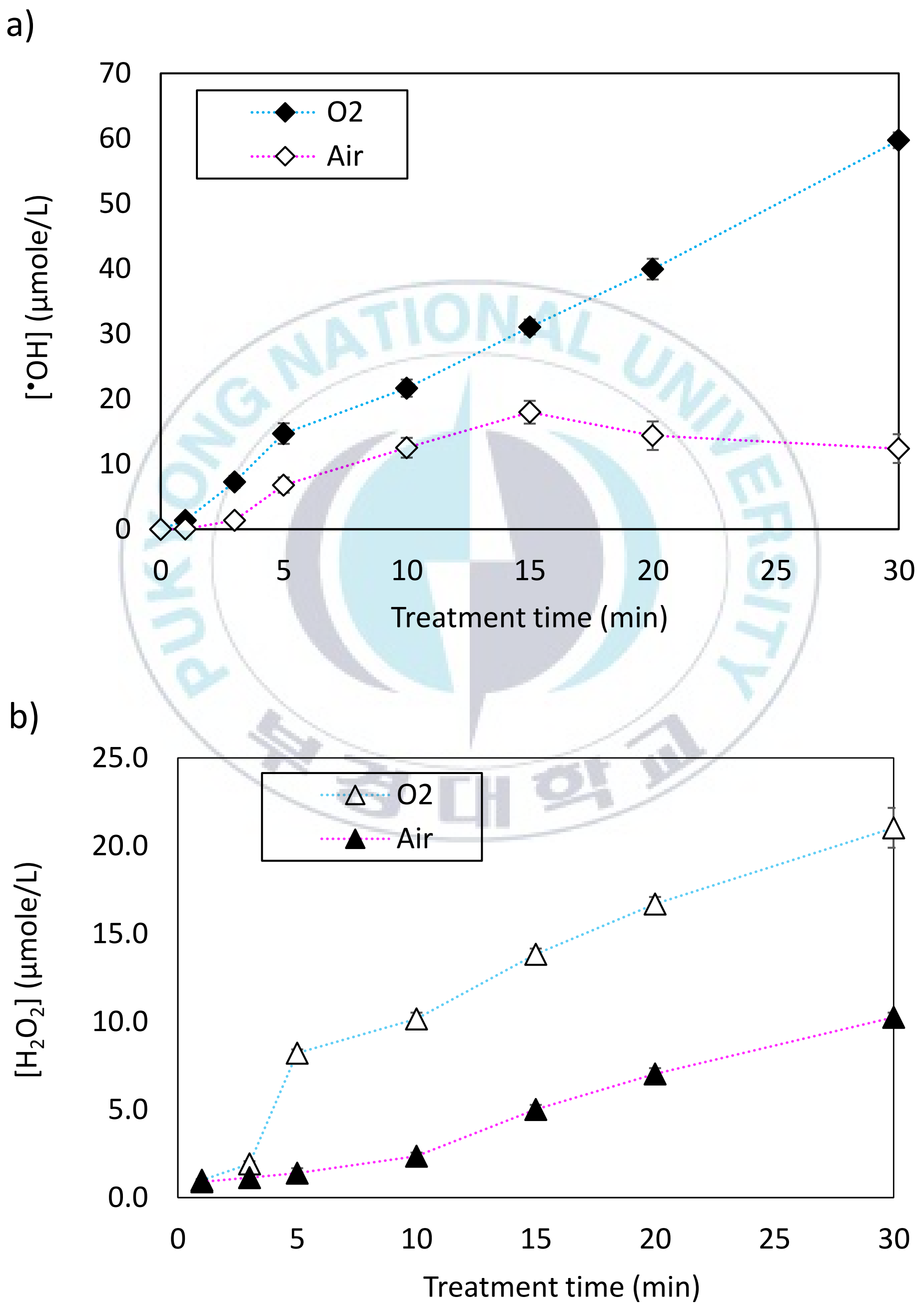


Figure10: Concentrations of reactive species generated in plasma: a) •OH; b) H_2O_2 ; c) NO_2^-; d) NO_3^-.

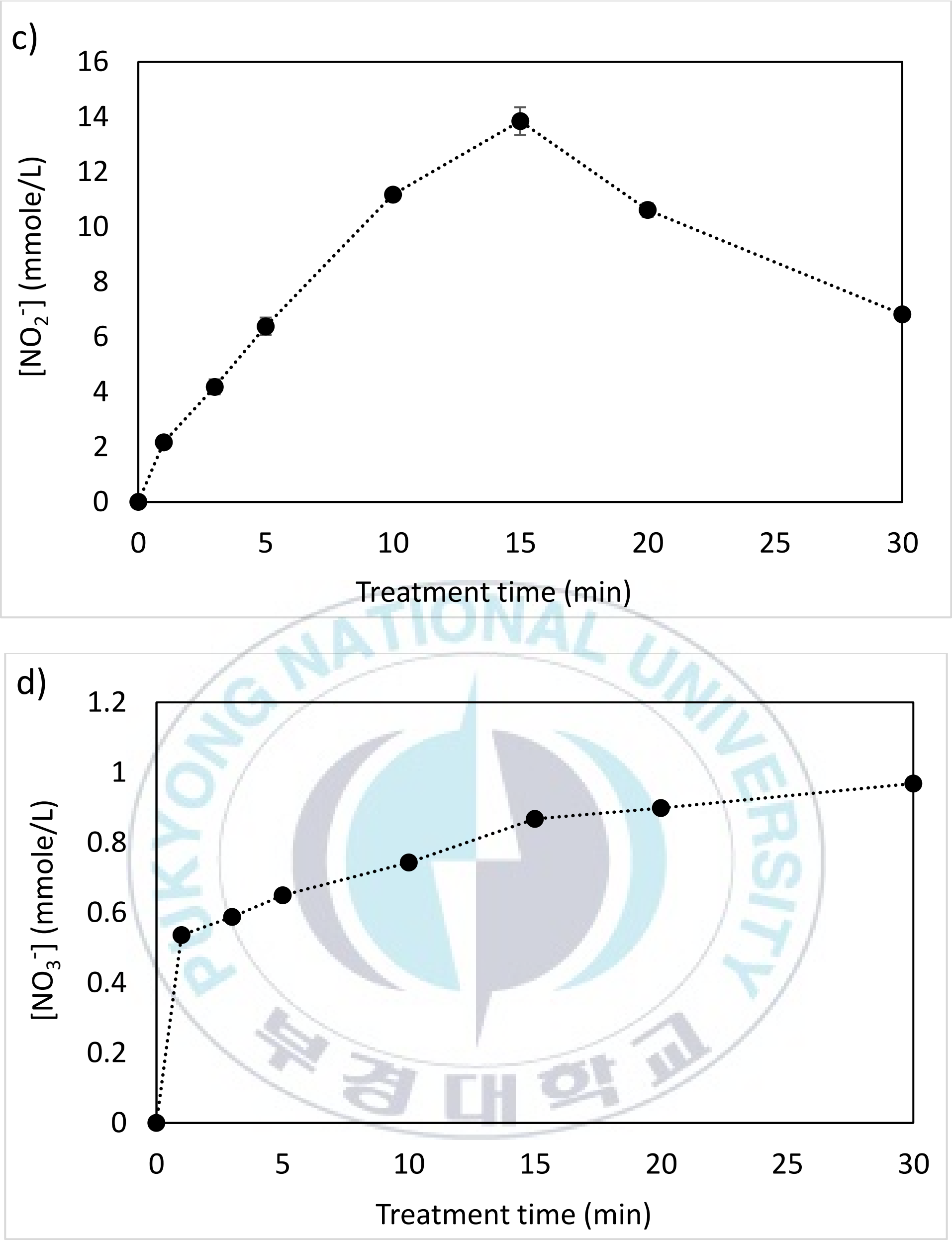


Figure 10: Concentrations of reactive species generated in plasma: a) $^{\bullet}OH$; b) H_2O_2 ; c) NO_2^-; d) NO_3^-.

Figure 10 b) illustrates the H_2O_2 concentrations achieved by GAD plasma. Likewise, to $^{\bullet}OH$, O_2 plasma generated approximately double the amount of H_2O_2 in comparison to air source. At the end of the discharge H_2O_2 reached 21.03 and 10.75 µmole/L for O_2 and air plasma respectively.

The results NO_2^-; NO_3^- amounts generated in GAD reactor under air plasma are shown in figure 10.c) and figure 14.d). 5 minutes of treatment reaching 14.78 mmole/L at 5 minutes. After that, the concentration continuously decreased until the end of treatment achieving 11.47 mmole/L. This decrease is explained by oxidation of NO_2^- into NO_3^- according to the reaction R6. (Marouf-Khelifa et al. 2006)

$$\mathrm{HNO_2} + 2\mathrm{OH}^{\cdot} \rightarrow \mathrm{HNO_3} + \mathrm{H_2O}$$

The presence of NO_2^- and NO_3^- in aqueous solutions treated by plasma indicates the presence of nitrous and nitric acids. Nitrous acid is also said to be unstable at pH values close to 2.6, steadily disproportionating into NO_3^- while plasma processes continue. According to Brisset et al explanation .'s of this pattern, NO_2^- results from a synthesis process followed by a degradation step, whereas the concentration of NO_3^- constantly rises. In particular, the low pH brought on by the discharge encourages the disproportionation of NO_2^- into NO_3^-. It is clear from figure 13 d) that NO_3^- concentrations rise steadily over the course of treatment.

O_3 normally forms over the water-air interface in the gas phase, but it is readily dissolved and eventually dissociates in the liquid phase. Figures 11.a and 11.b show the residual O_3 concentrations determined using the colorimetric approach for O_2 plasma and air plasma, respectively. With longer treatment times, the concentration of dissolved ozone rises. O_3 plasma showed a tiny and negligible change in ozone concentration during mixing and 30 minutes of post-reaction. On the other hand, air plasma caused an ongoing staining of indigo blue, which isn't necessarily caused by a larger O_3 concentration but is instead attributed to the reaction of NO_2^- and NO_3^-, which are both present in air plasma (Pawłat et al. 2019).

III-3: pH variations of treated solution under GAD plasma:

The fluctuation of pH in DMSO solutions treated with air and O_2 plasma at various humidity levels were studied and illustrated in figure 11. Since the same approach was used in ultra-pure water and similar results were obtained, it should be highlighted that the presence of DMSO had no effect on the acidification of treated samples. The results weren't very different overall.

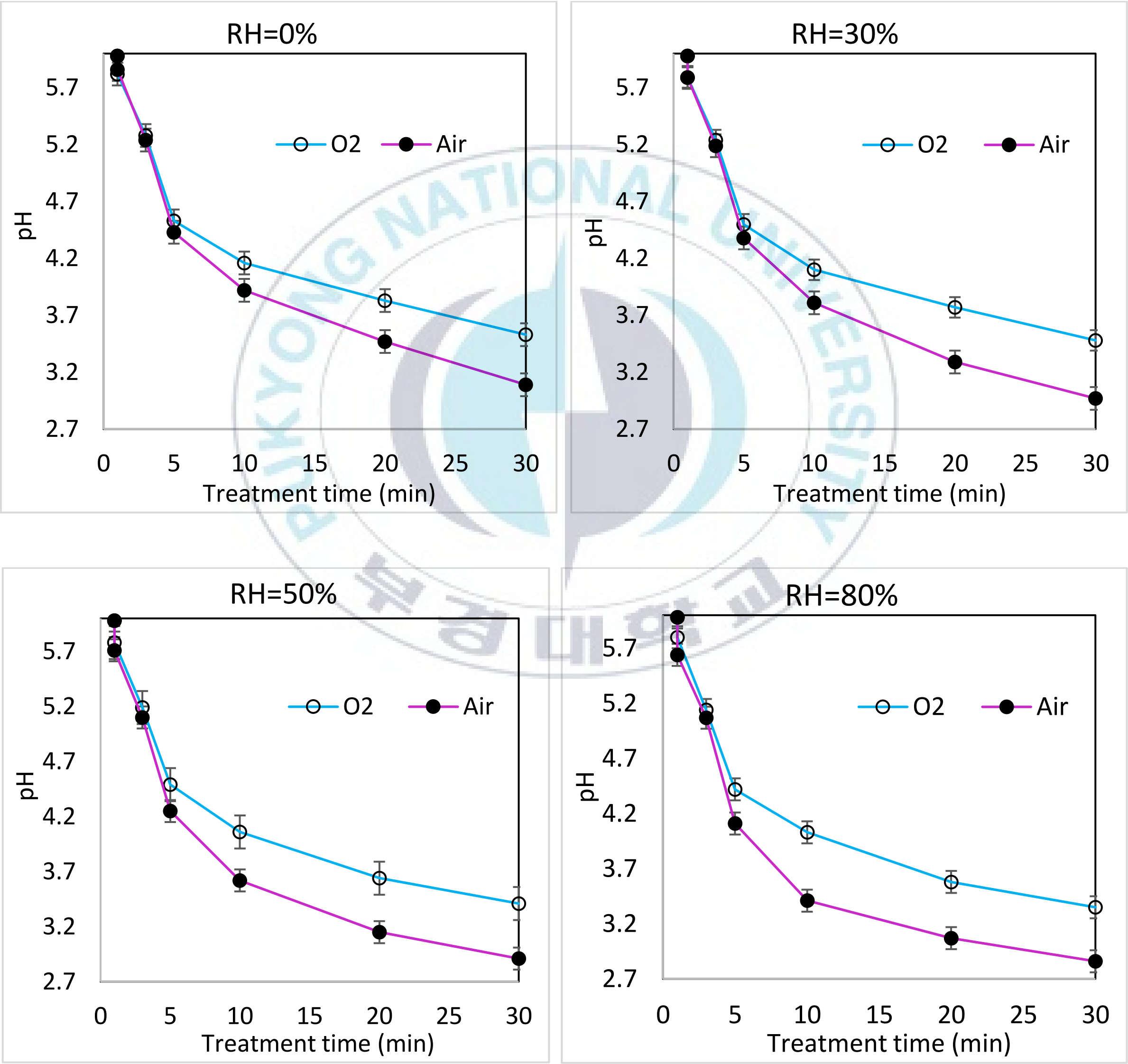


Figure 11: pH evolution during plasma discharge on DMSO. (Initial pH~6.0.8)

In all cases, the pH dropped during the course of the discharge duration, with somewhat lower values being achieved under air plasma , and it eventually reached a pH of 2.75 after 30 minutes.

Air plasma, regardless of RH, generates more acid species. (Protons and nitric acids produced from the water molecules infused into the treated solution.

Chapter IV: Plasma treatment of Organic Pollutants

IV-1: Chapter Introduction:

To test the effectiveness of GAD and optimum humidity condition, experiments were conducted on a model wastewater. Organic azo dye Eriochrome Black T (EBT) and antibiotic Tetracycline (TC) were chosen as a model target contaminant due to its large usage indifferent industries. Textile industry is a significant source of water pollution responsible for about 50% of wastewater discharge with an alarming amounts of organic pollutants (Tehrani-Bagha et al. 2010) (Meerbergen et al. 2017). Based on the attachment of an azo group (-N=N-) between the aromatic rings, the selected dye is categorized as belonging to the azo family of dyes. The primary issue with azo dyes is that they are carcinogenic. Additionally, they cause major environmental problems since they affect ecosystems in addition to endangering human lives.(Li et al. 2016). These dyes build up in soil and sediment after discharge due to their propensity to persist in the face of standard treatment. They are easily moved to various bodies of water that are habitats for varied aquatic life. (Lellis et al. 2019). Additionally, dyes have the capacity to add color to a variety of materials, harming the aesthetics of water bodies.(Imran et al. 2015). Moreover, they reduce light's ability to pass through water, which slows photosynthesis and lowers dissolved oxygen levels, which impacts the entire aquatic biota.(Hassan and Carr 2018). Some chemical structures that are considered as a source of toxic, mutagenic, and carcinogenic aromatic amines which are linked to liver cancer and bladder tumors, are also found in textile dyes. Therefore, these toxins must be processed or mineralized before being released into the environment.

Antibiotics, particularly those belonging to the Tetracycline family, are one of the chemical compounds categorized as pharmaceuticals and personal care products (PPCPs) in the environment. This is because of the potential threats they cause to both the aquatic environment and human health. Due to misuse and poor disposal, their discharge into surface and ground waterways needs to be limited and removed.(Chen et al. 2021; Li et al. 2020a). Many antibiotic residues would interfere with human physiology and would be difficult to remove using traditional biological and chemical methods. In this chapter, the removal of TC by plasma GAD under different conditions is investigated.

IV-2-1: Eriochrome Black T removal:

The removal of EBT by GAD plasma was evaluated by the measurement of its decolorization and mineralization by spectrophotometric and total organic carbon TOC analysis. Evidently, great decolorization results were obtained under air plasma as shown in figure 12.

The EBT solution's initially dark hue progressively lightened. The reactive species attack on the chromogenic component of the dye molecule is what causes the EBT solution to change color. We used DMSO, a radical scavenger, and water to EBT samples made in order to examine the involvement of ·OH in this decolorization. The results are presented in figure 16 a). The decolorization rates are the highest when air was used as plasma atmosphere reaching 96.51% at 30 minutes of discharge. O_2 plasma despite producing more ·OH could only achieve 52.57% of decolorization. This might be the result of reactions with RNS generated in air discharge. The high amount of ·OH generated in O_2 plasma is most probably engaged in oxidative reactions with EBT intermediates in the solution. This is more apparent when EBT is dissolved in DMSO. The decolorization rate decreased to 83.33% under air plasma, however only 12.19% was achieved in O_2 plasma. The kinetic study of EBT decolorization is illustrated in figure 17. The decolorization of EBT under plasma follows a pseudo-first order reaction. The reaction rate has the highest value (k = 0.1339 s-1) in air plasma when EBT was prepared in water.

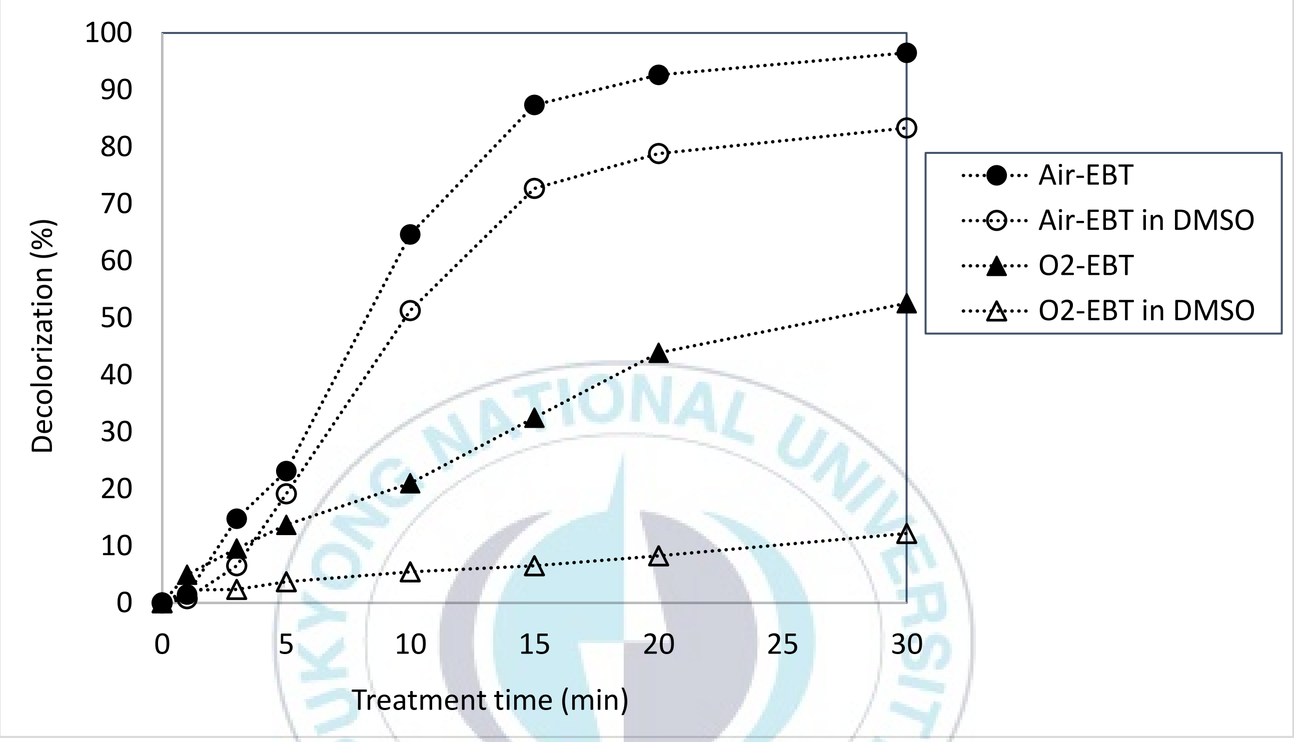


Figure 12: decolorization rate of EBT under different treatment conditions Initial concentration 100 mg/L. RH~30%.

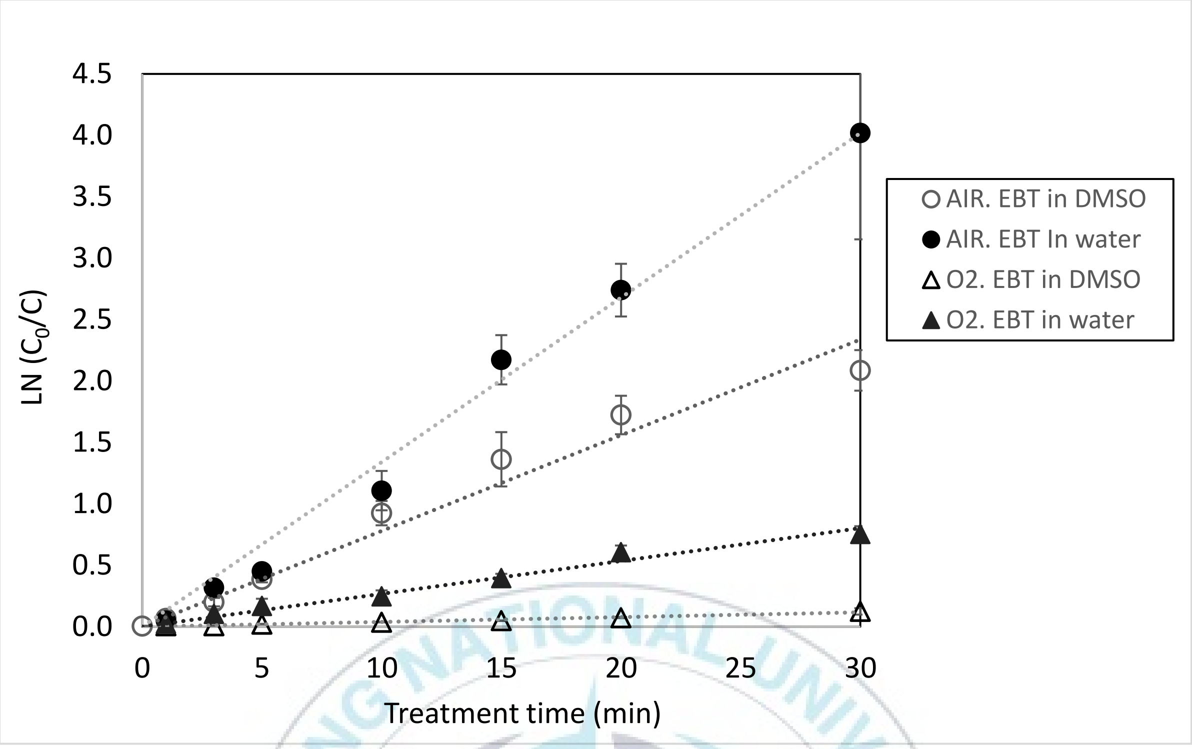


Figure 13: EBT decolorization kinetics Initial concentration 100 mg/L. RH~30%.

Figure 14: treated samples of EBT after plasma treatment. Initial concentration 100 mg/L. RH~30%. Air plasma, flow rate = 13 L/min.

The lowest rate of decolorization for EBT prepared in DMSO is observed in O_2 plasma (k = 0.0039 s-1). If we compare the outcomes of one treatment time, the impact of humid air plasma is more apparent. Even when the target molecule is produced in a radical scavenger solution, air plasma demonstrates better decolorization potential after plasma discharge, as illustrated in figure 15. These findings support the theory that plasma in humid air is able to achieve interesting results of removal using a variety of oxidative species rather than just relying on ROS, which can interact with intermediate products.

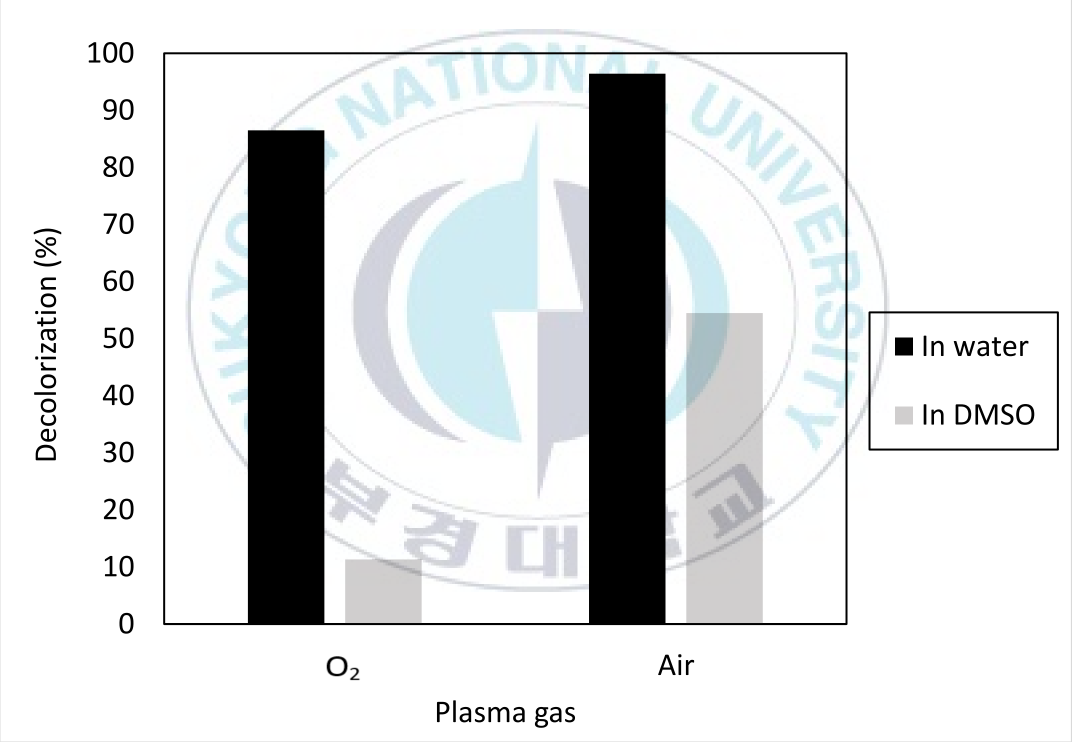


Figure 15: comparison of EBT decolorization rates under various plasma discharge parameters after 30 minutes of plasma discharge. RH 30%, initial concentration 100 mg/L

IV-2-2: EBT mineralization:

The results of the TOC removal trials are shown in figure 16. Compared to air plasma, which had a TOC abatement rate of 57.47% at the end of the treatment, O_2 plasma had a superior degradation rate of 79.91% . Due to the greater creation of OH and H_2O_2, which are more potent at targeting intermediates from initial EBT molecule disintegration, higher degradation rates of EBT are anticipated when O_2 is applied. We should be aware of ·OH is more reactive towards aromatic rings due to the presence of multiple reactive sites. The decolorization of EBT by plasma reactor type Helium Atmospheric Pressure Plasma Jet (APPJ) was studied by (Li et al. 2019a). They reported that after 6 minutes of treatment, there was approximately a decolorization of 80% achieved. Which is very impressive given the short time of discharge. However, the treated volume in this case was only 1mL. which is very small compared to our system where 100mL of the dye solution was treated.

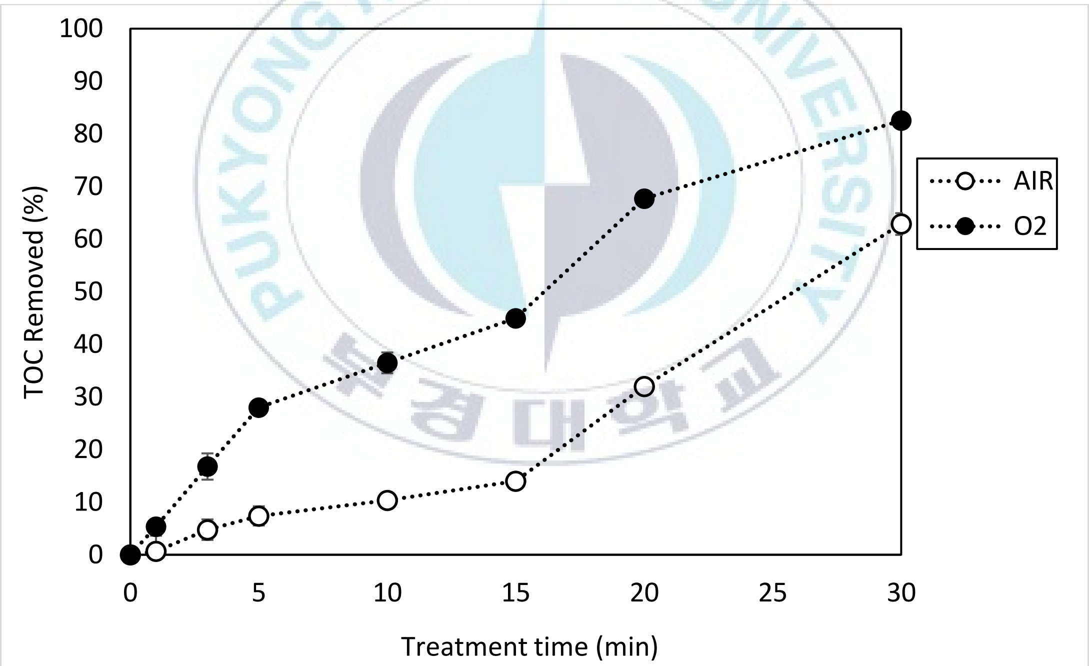


Figure 16: Total Organic Carbon (TOC) of EBT treated in O_2 and air plasma.

Based on UV-Vis spectra and FTIR analysis, they established that the azo group is an easily destroyed part in the EBT molecule, followed by the aromatic rings which are oxidized by ·OH to yield smaller molecular weight byproducts. (Gogoi et al. 2019) findings indicate that: at the beginning of the degradation process, the degradation reactions mainly contain the breaking of the azo bond. The oxidation of EBT has possibly produced an intermediate compound as 4-(naphthalen-2-yldiazenyl)naphthalene-1-sulfonateSmall molecules were created through further oxidation of this intermediate, the oxidation of residual EBT molecules, and ring cleavage. This is demonstrated by the drop in TOC during plasma treatment, especially under O_2 gas. Since the solution contains a variety of reactant species, including EBT molecules, numerous intermediates, and plasma reactive species in the liquid phase, determining the precise oxidation process is challenging. Nevertheless, Three steps are typically involved in the degradation process: bond-breaking oxidation, ring-opening, and full oxidation. (Huang et al. 2012).

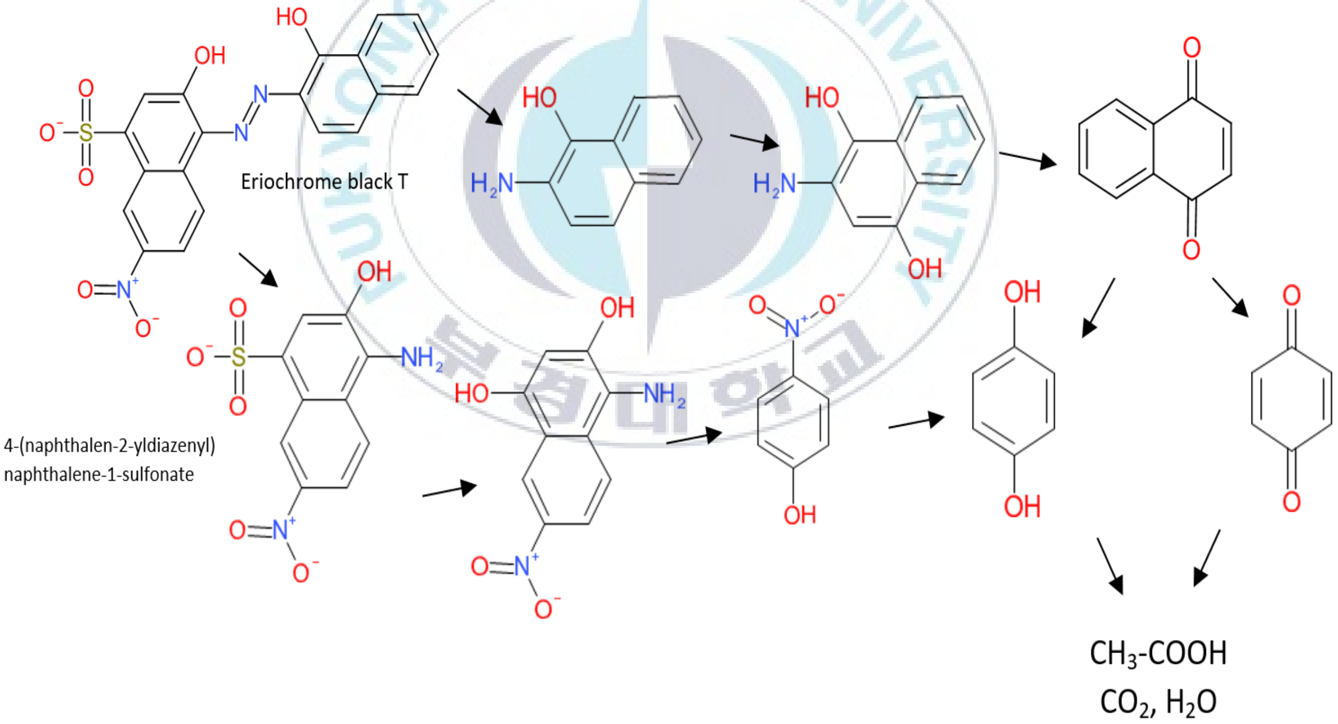


Figure 17: Proposed degradation pathway for the mineralization of Eriochrome black T by plasma process.

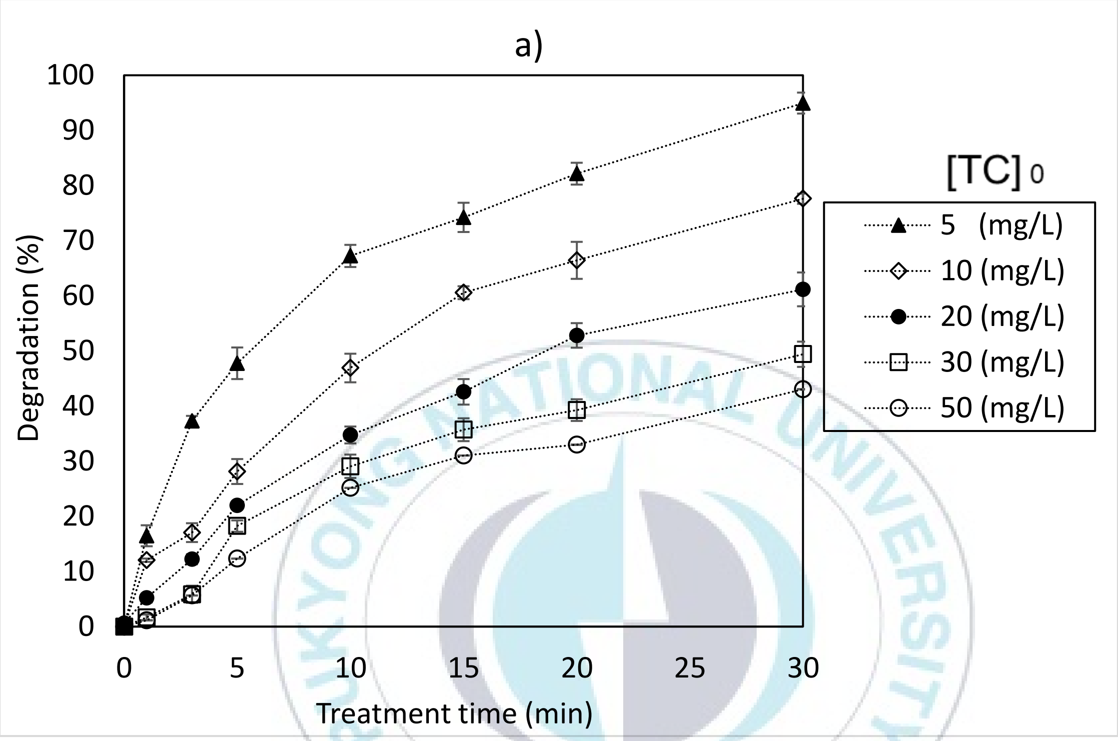
We can suggest a general reaction mechanism for the mineralization of treated EBT by plasma, which is shown in figure 17, based on the observed decrease in decolorization and mineralization on treated EBT and the findings of (Gogoi et al. 2019; Huang et al. 2012; Li et al. 2019a)

IV-3-1: Tetracycline removal:

Antibiotics, particularly those belonging to the Tetracycline family, are one of the chemical compounds categorized as pharmaceuticals and personal care products (PPCPs) in the environment. This is because of the potential threats they cause to both the aquatic environment and human health. Due to misuse and poor disposal, their discharge into surface and ground waterways needs to be limited and removed.(Chen et al. 2021; Li et al. 2020a). Many antibiotic residues would interfere with human physiology and would be difficult to remove using traditional biological and chemical methods. In this chapter, the removal of TC by plasma GAD under different conditions is investigated.

IV-3-2: Effect of TC initial concentration:

The impact of TC initial concentration on the degradation efficiency is shown in Figure 18. The findings demonstrate that the degrading efficiency decreased with the starting concentration under both air and O_2 plasmas. Due to the same discharge power and voltage circumstances used in these studies, roughly an equal amount of RONS would be produced, which is only enough to degrade a small quantity of TC. As a result, the oxidation process of RONS on TC molecules was slowed down as the initial concentration was increased. By the end of the treatment, the removal rates had reached a value of 94.95% for the smallest TC initial concentration of 5 mg/L, but the degradation rates had dropped to 43.05% for the highest beginning concentration of 50 mg/L. Notably, the degradation increased and occurred more quickly when O_2 was the working gas. Although the degradation rates for TC solutions treated with air were not as striking as they were when O_2 was used, it was still clear that a lower initial concentration led to greater efficiency. The type and quantity of reactive species present in aqueous solution (ROS in O_2 plasma and ROSNS in air plasma) directly affect the rate of TC degradation. The speedier removal of the TC with O_2 plasma is due to the much higher concentration of ROS generated under O_2 gas feed circumstances compared to that with air.



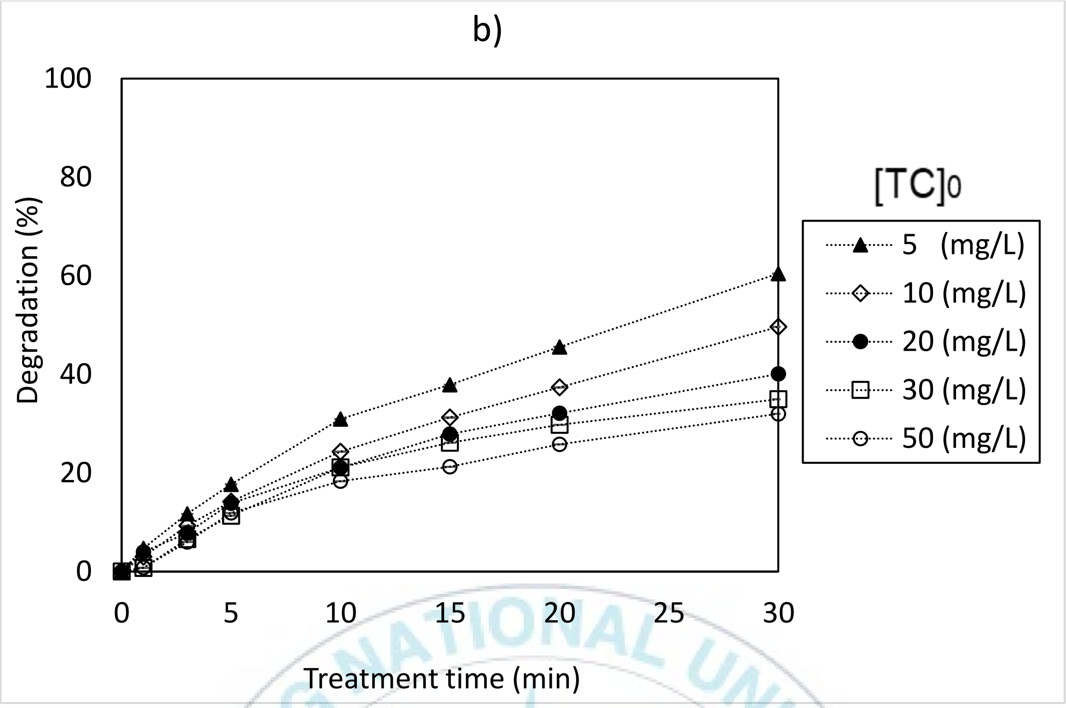
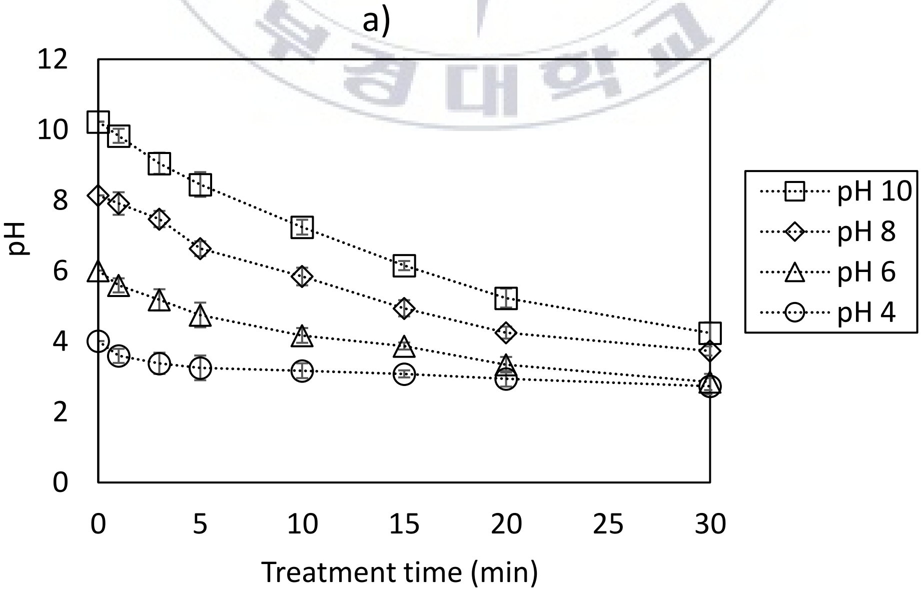


Figure 18 Effect of TC initial concentration on degradation rate depending on plasma gas. a) O_2; b) air. (V= 70 mL. Flow= 13 L/min.).

Fang et al. investigated the use of DBD plasma to treat TC. The degradation rates attained using air and oxygen as working gases follow a pattern that is comparable to what we described in this work. Reactive species may compete with intermediates in processes at increasing concentrations, slowing the pace at which TC degrades. Organic substance that resembles humic acids and enolic and acylamino groups of various aromatic rings are said to be the main by-products.(Wang et al. 2011). When treating TC with DBD plasma, Fang et al. looked into the topic. Similar patterns to those we described in this work can be seen in the reported results on the degradation rates attained with air and oxygen working gases. In competitive interactions with intermediates at greater concentrations, reactive species may slow the breakdown of TC. Enolic and acylamino groups of various aromatic rings, as well as organic debris that resembles humic acids, are said to constitute the main by-products.(Wang et al. 2011).

IV-3-3: pH effect:

Same as with most wastewater treatment processes, pH is a crucial parameter In plasma discharge procedures that influences the type and amount of reactive species produced as well as the method by which oxidants interact with the organic compounds present in aqueous solution.(Ursache et al. 2012; Wang et al. 2016). TC solutions of various initial pH values (10; 8; 4; and 6 being TC natural pH) were prepared and treated under both working gases for the same treatment times applied previously in order to evaluate the evolution of pH under plasma discharge. The findings are shown in figure 19. The pH values of all samples exposed to plasma discharge significantly decreased. This is attributable to GAD plasma's capacity to produce species that are acidifying, particularly air plasma, which caused the greatest pH drop, dropping to a value of 2.35 by the end of the discharge. Even the solutions that started with strong basic had eventually a very acidic pH by the end of the treatment but compared to the TC solution at its natural pH, they had reached slightly higher pH levels (from 10 to 4.24 and 3.54 under O_2 and air plasma respectively).



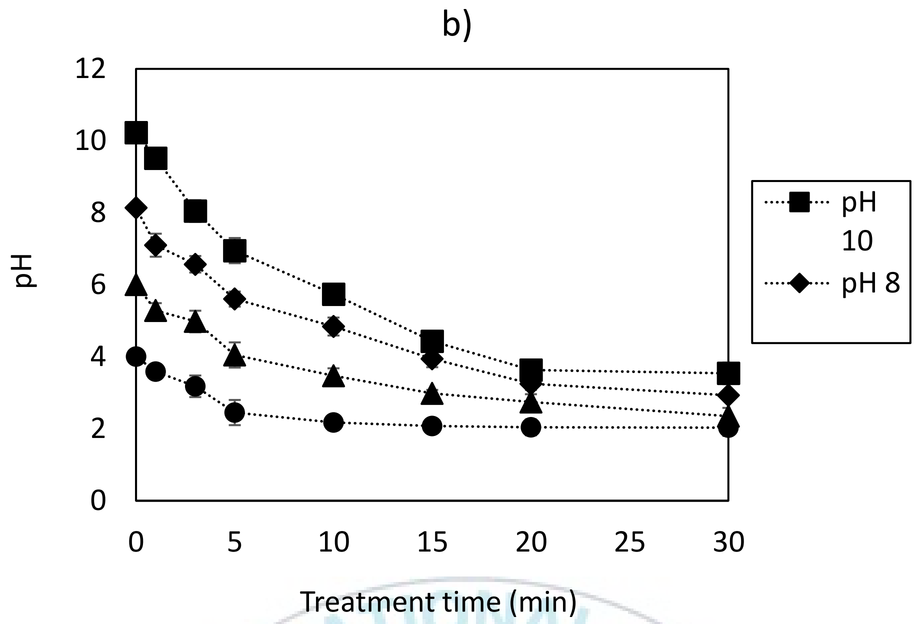


Figure 19 evolution of pH during plasma treatment of TC solutions prepared at different initial pH value: a) O_2; b) air. ([TC]= 10 mg/L. V= 70 mL. Flow= 13 L/min.).

The removal effectiveness of organic compounds treated with NTP is significantly influenced by pH. As a result, we chose to investigate the development of TC degradation efficiencies in air and O_2 plasma at different initial pH values. Findings are displayed in figure 20 a). GAD is less effective under alkaline settings; at the highest initial pH value of 10, the rates of TC degradation for O2 and air plasma fell to 17.1% and 7.58%, respectively, demonstrating that treated solution pH variations have less of an impact on air plasma. demonstrating that treated solution pH variations have less of an impact on air plasma. According to other investigations, the degrading efficiency of TC was noticeably reduced in an alkaline environment.(Fang et al. 2021; Li et al. 2020a). The chemical structure of the TC molecule and its various pKa values can be used to explain how pH affects the rate of TC breakdown. As shown in figure 22 b): The TC molecule has two carbonyl groups and two enolic groups in conjugated double-bond configurations. This enables the TC molecule to take on several shapes in an aqueous solution by allowing for varied pKa values at various functional groups. (Babić et al. 2007).

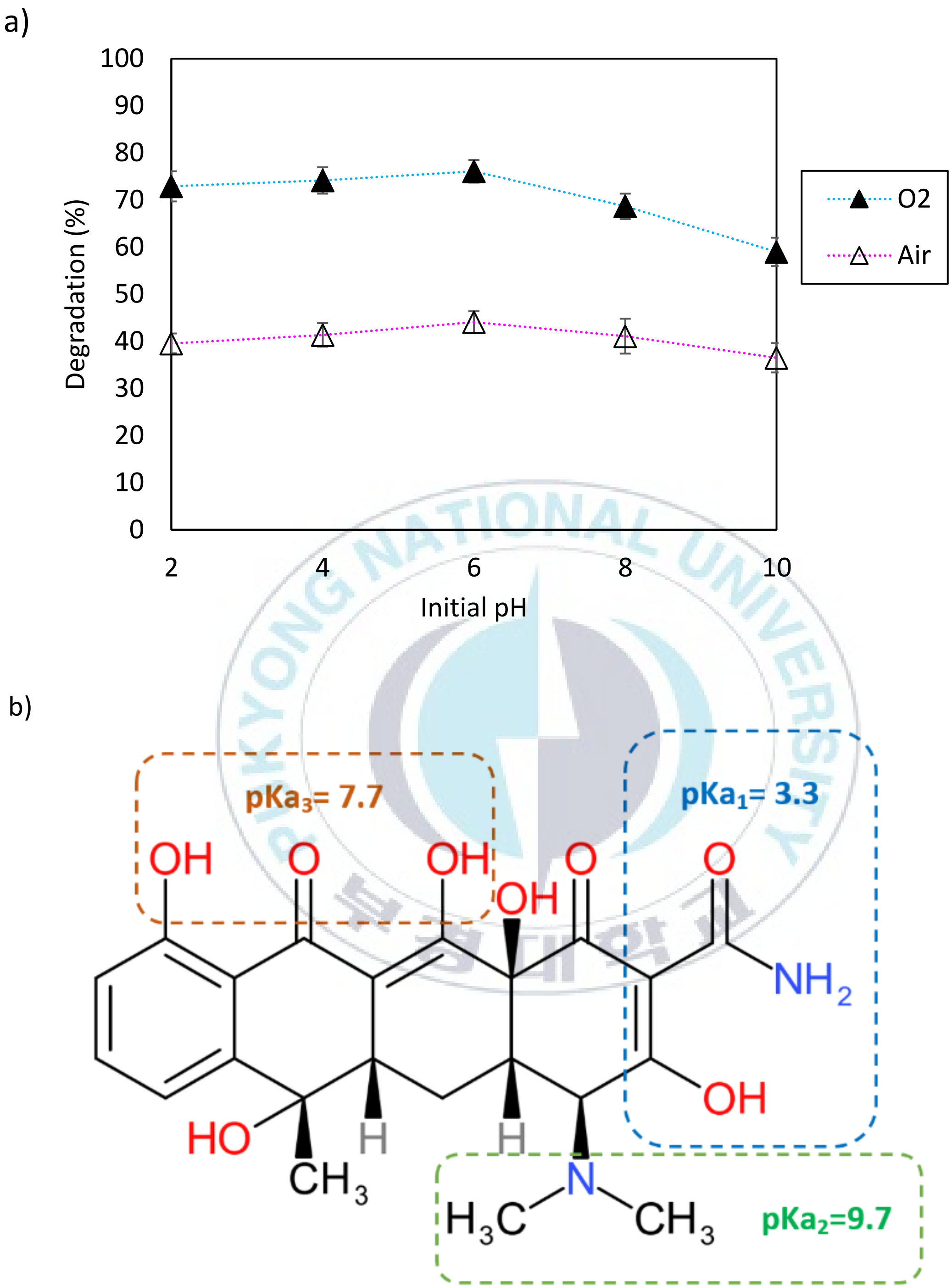


Figure 20 a) Removal of TC after during plasma treatment in function of initial pH value of TC solutions. b) TC chemical structure and pKa of each active site in the molecule. ($[TC]_0$ = 10 mg/L. V= 70 mL. Flow= 13 L/min).

At alkaline pH conditions, pKa values of (-CONH2), (N-CH_3), and (C-OH) (3.3, 9.7, and 7.7, respectively) can cause the deprotonation of TC, which will result in contraction of the bond length while also increasing the stability of the molecular structure. Reactive organisms' ability to operate will therefore be constrained in the solution. Additionally, it has been found that high pH environments restrict the production of •OH, which results in low removal efficiency.(Dong et al. 2019). The following reactions describe how the reaction of ions and protons present in aqueous solutions to create hydrogen radical might produce additional •OH in an acidic solution. The latter boosts the plasma's therapeutic potential by converting hydrogen peroxide into more •OH.

$$e_{aq}^{-} + H^{+} \rightarrow H^{\cdot}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$$

$$H^{\cdot} + H_2O_2 \rightarrow H_2O + OH^{\cdot}$$

IV-3-4: Effect of radical scavengers

By preparing TC (an initial concentration of 10 mg/L) dissolved in DMSO solutions of various doses, we conducted radical scavenging tests to determine the role of ROS generated in the GAD system generally and $^{\bullet}$OH specifically. For $^{\bullet}$OH, DMSO works as a potent radical scavenger.(Kovačević et al. 2017; Sahni and Locke 2006; Tai et al. 2004). As illustrated in Figure 21, The remarkable inhibition of TC degradation by DMSO suggests the significance of •OH in the oxidation process of TC. More significantly in O_2 plasma treatment, and with DMSO dose of µ230 mole/L, TC elimination removal decreased from 52.21% (without DMSO) to 4.34 % in the presence of DMSO. On the other hand, TC degradation decreased from 35.7% to 7.38% at the same DMSO dose in air plasma, although having a lower initial removal efficiency.

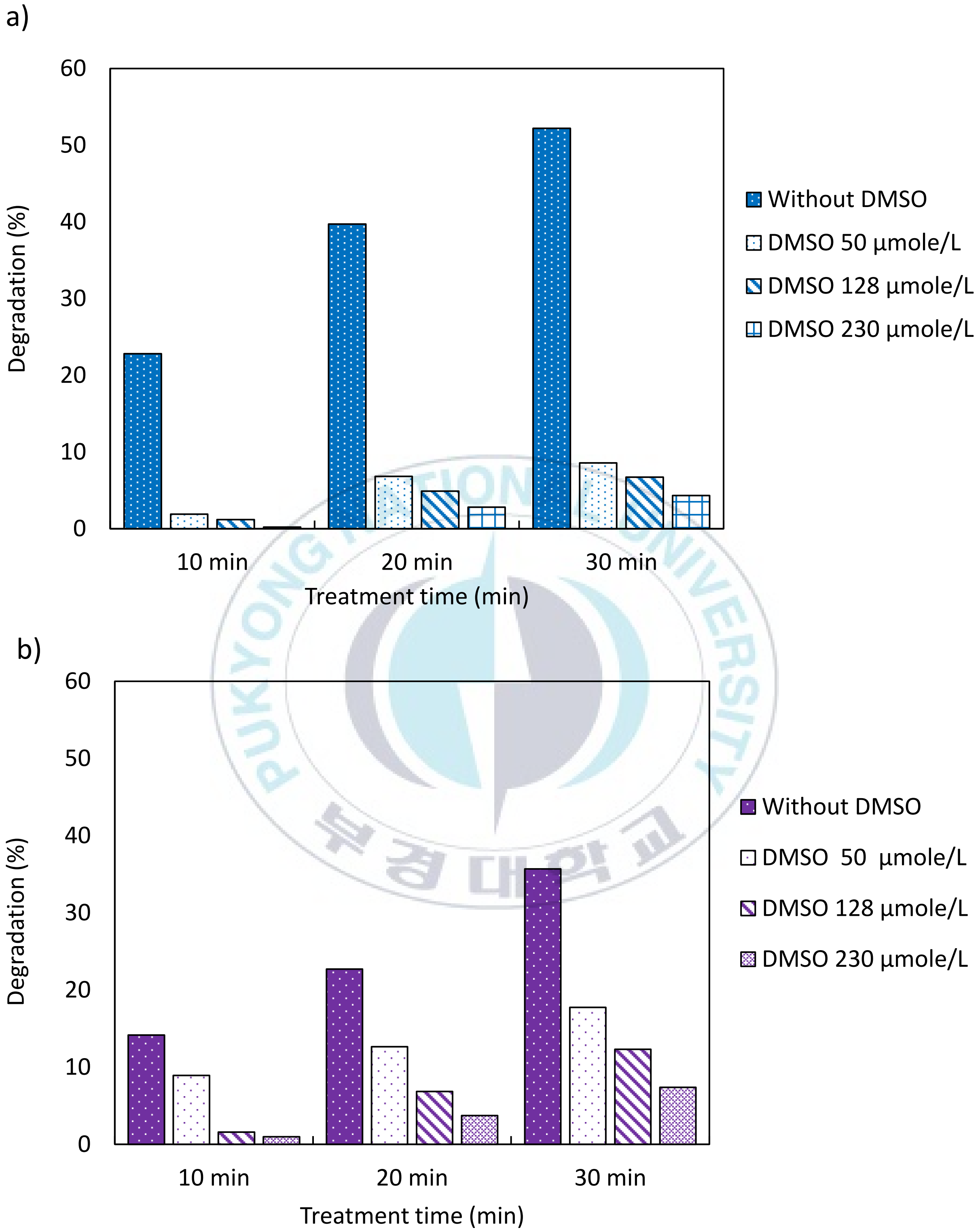


Figure 21: Influence of radical scavenger presence on TC removal . a) O_2; b) air. ([TC]= 20 mg/L. V= 70 mL. Flow= 13 L/min).

The ability of RNS in the air plasma system to boost degradation potential when •OH oxidizing powers are inhibited in the aqueous solution further reveals the difference between the decline of removal efficiency under O_2 and air plasma. Due to its low cost and generally acceptable degradation efficiency in the presence of radical inhibitors, air plasma may still be recommended and supported for water treatment in WWTPs despite O_2 plasma's great performance.

A further indication of the differences between the drop in removal efficiency under O_2 and air plasma is the capacity of RNS in the air plasma system to enhance degradation potential when •OH scavengers are present in solution. Despite O_2 plasma's superior performance, air plasma may still be suggested and encouraged for water treatment in WWTPs due to its inexpensive cost and generally acceptable degradation rated when radical scavengers are present in the effluent.

IV-3-5: Tetracycline Mineralization efficiency :

One important factor in assessing the effectiveness of a water treatment process is mineralization efficiency which is based on the TOC removal rate. The change in TOC obtained in the present work of TC treatment under plasma is represented in figure 22. TOC removal increased through the treatment time, more remarkable for smaller TC initial concentrations. When initial TC concentration was 5 mg/L TOC removal reached 81.3% and 57.34% for O_2 and air plasma respectively. With the increase in TC initial concentrations, the removal efficiency decreased, indicating that the organic charge and by-products formed during the treatment affects negatively the mineralization of organic matter present in treated solutions.

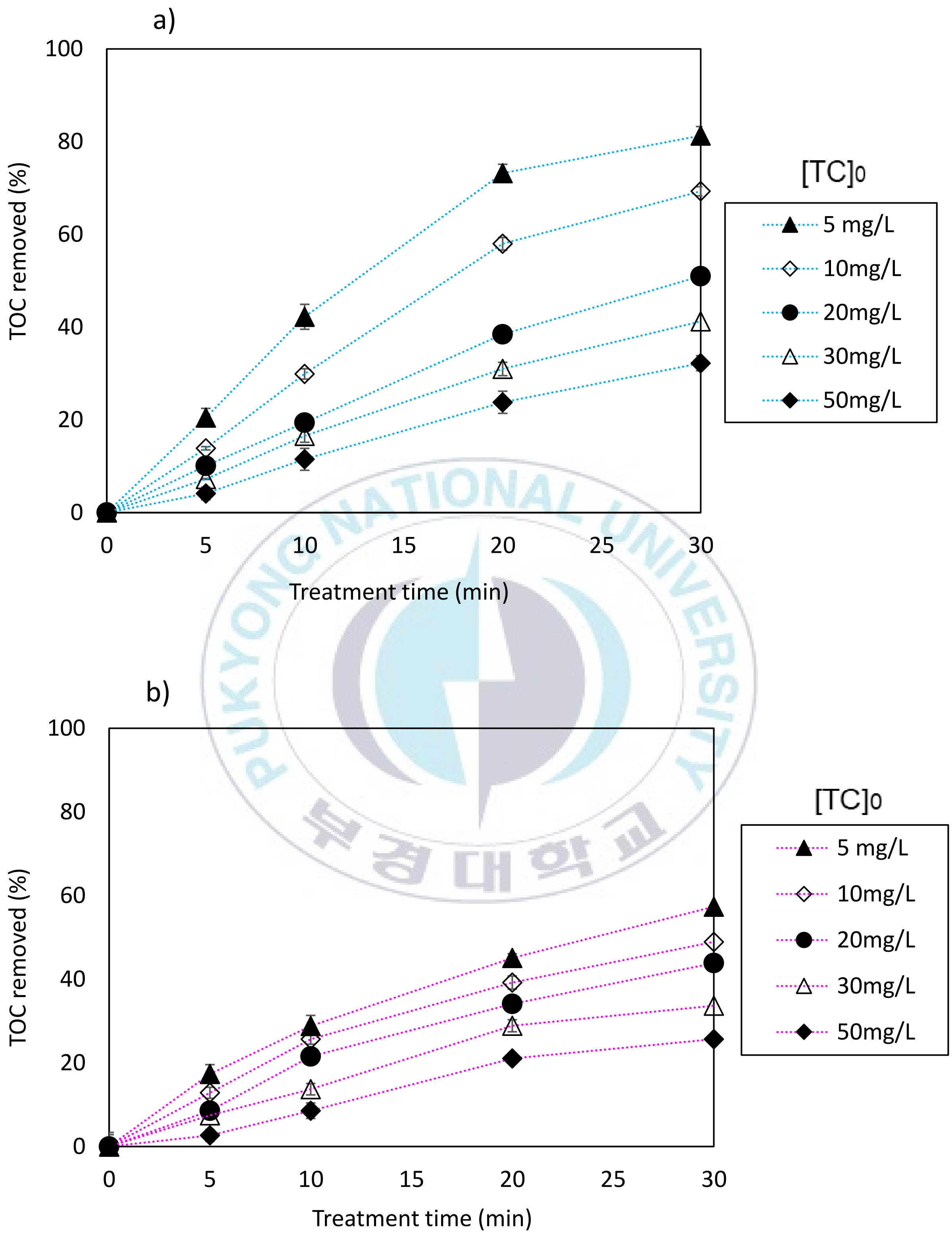


Figure 22: Removal of Total Organic Carbon (TOC) in TC solutions under plasma treatment a) O_2; b) air. (V= 70 mL. Flow= 13 L/min.).

IV-3-6: Intermediates of Tetracycline and suggestion of a degradation pathway:

The identification of intermediates formed after the degradation of any hazardous chemical compound is very important for the purpose of determining the pathway of decompositions, the mechanism, and the toxicity of the final treated solutions. In this work TC intermediates were analyzed by Ultra High-Resolution Q-TOF LC MS/MS (Q-TOF MS) and identified by the LC/MSMS spectrum. All samples were treated for 20 minutes under plasma discharge. The suggested pathway is illustrated in figure 27. TC molecule contains three kinds of functional groups of rich electron density making it vulnerable to radicals attack (Wu et al. 2020). These functional groups are namely: double bond, phenolic group, and amine group as shown in figure 23 b). Among these functional groups, the phenolic group is the main electrophilic attack site on TC as confirmed by the work of Chen et al., 2021. The double bond in this region is considered more likely to be subjected to •OH (Chen et al. 2017).

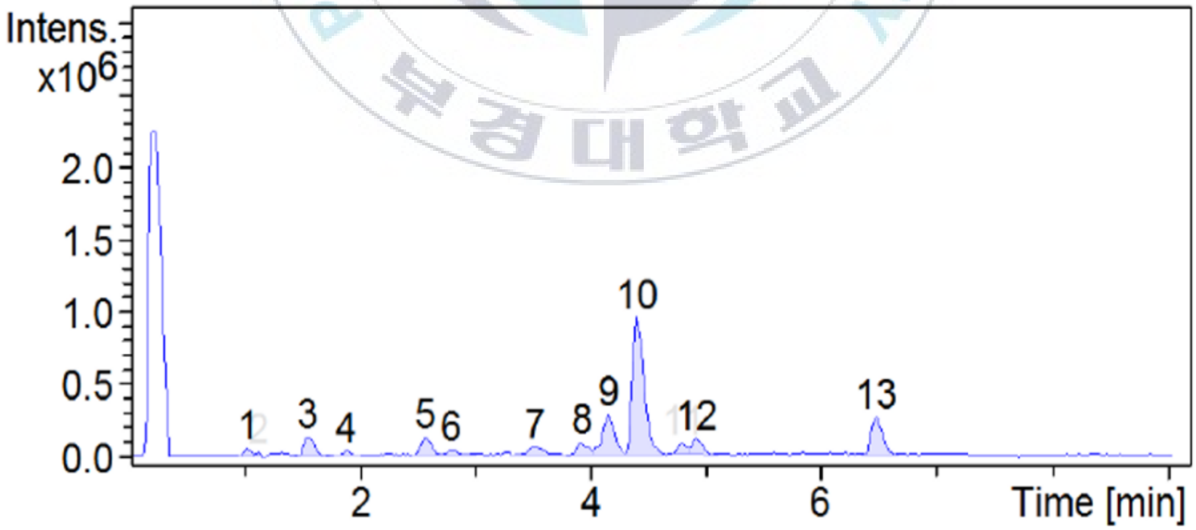


Figure 23 : a) Q-TOF LC/MS/MS peak area-time profile of degradation product

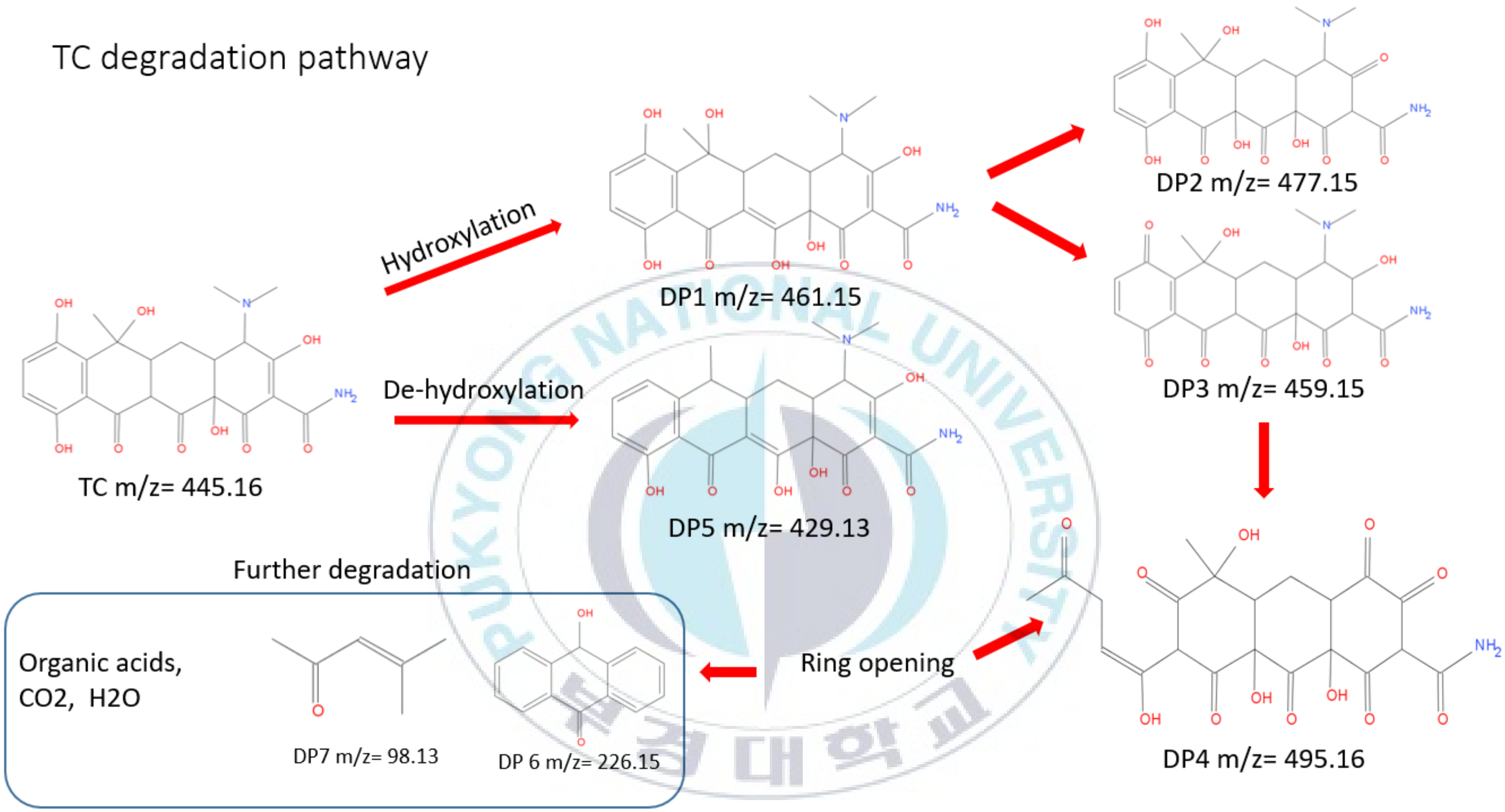


Figure 23: b) Proposed degradation pathway for TC treated by GAD plasma.

Hence, the primary intermediates of DP1 and DP2 (m/z 461.15 and 429.13, respectively) were formed by •OH radicals attacking through hydroxylation and de-hydroxylation processes.

IV-3-7: Toxicity evaluation:

TC and its degradation products toxicity was evaluated by Toxicity Estimation Software (T.E.S.T.) according to quantitative structure-activity relationship (QSAR) prediction represented by mutagenicity of TC is shown in Figure 24. Our proposed TC oxidation pathway via NTP is similar to that in Wang’s electrochemical oxidation pathway (Wang et al. 2018b). In Wang’s work, the toxicity of TC intermediates was evaluated by luminescent bacteria (Vibrio fischeri). From Wang’s work, we know that the primary intermediate in our experiment of m/z 461 and 432, and secondary intermediates m/z 461 and 477 are as toxic as TC m/z 445. Further degradation intermediates such as m/z, 495 are 226 are harmful to aquatic organisms and with continuous degradation of these by-products, the m/z 459, 429, 98 and 89 by-products possess low mutagenicity potential, thus, no toxic. We validated that by evaluating estimation program results which showed that half of TC degradation products showed higher toxicity indicating “mutagenicity positive”. However, the other half of degradation products have exceptionally low mutagenicity values suggesting the toxicity reduction in the TC degradation process. Nevertheless, since some TC degradation products display larger mutagenicity than TC, environmental concerns regarding TC post-treated solutions are valid.

TC and its byproducts of degradation According to the quantitative structure-activity relationship (QSAR) prediction provided by the TC's mutagenicity, toxicity was assessed using the Toxicity Estimation Software (T.E.S.T.). Wang's electrochemical oxidation mechanism and the TC oxidation pathway we have presented share similarities (Wang et al. 2018). In Wang's research, luminous bacteria were used to gauge the toxicity of TC intermediates. they principal intermediate in our experiment, with m/z 461 and 432, and secondary intermediates with m/z 461 and 477, are equally hazardous to TC with m/z 445. Aquatic species are harmed by further degradation intermediates such m/z 495 and 226; as a result, the m/z 459, 429, 98, and 89 byproducts are continuously degraded.

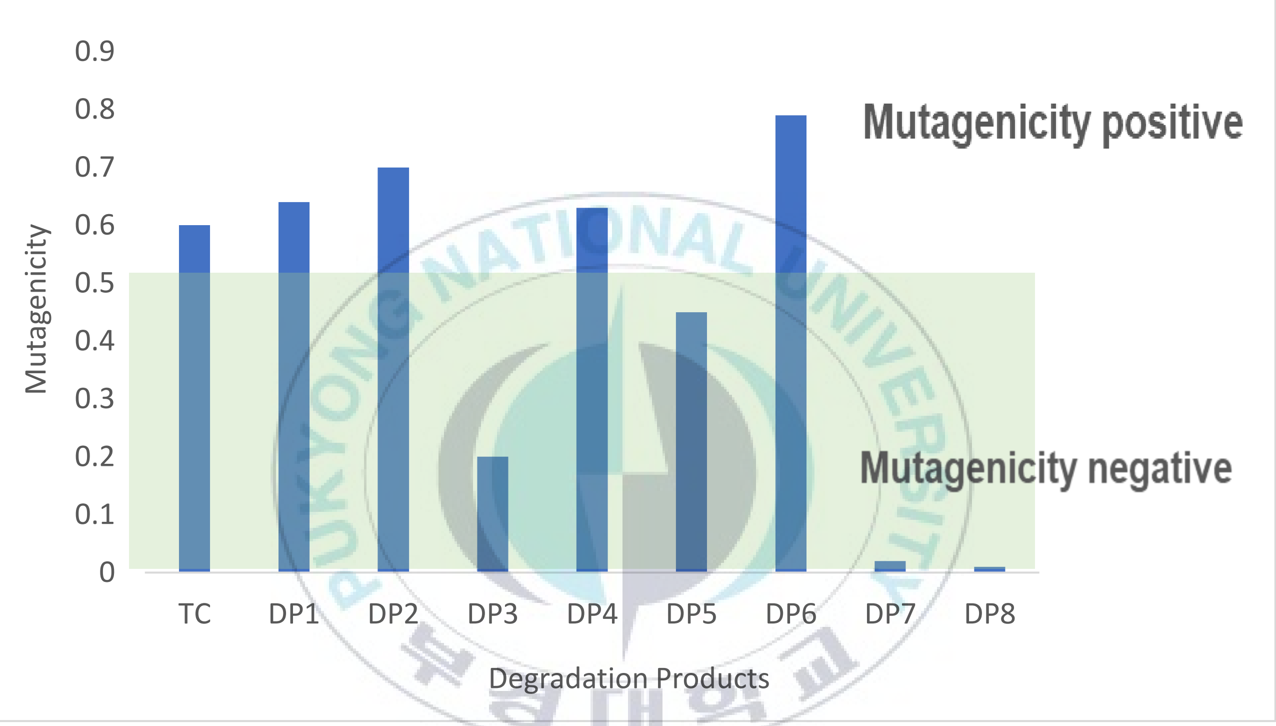


Figure 24: Toxicity evaluation of TC and its degradation intermediates by T.E.S.T program.

Overall, the degradation potential of GAD plasma over TC is very promising. However, ways of improvement should be studied. In the next chapter, a combination of GAD plasma with homogeneous catalysis is investigated.

Chapter V: Combination of plasma and homogenous catalysis for TC degradation:

V-1: Chapter introduction:

In this chapter, the optimization of the performance of the NTP technology coupled with a homogenous catalysis for the degradation and mineralization of TC was studied. For this purpose, four different catalysts namely Persulfate (PS) Ferrous ions (Fe^{2+}), Ferric ions (Fe^{3+}) and Ferrate (Fe VI) were added to TC solutions treated with GAD plasma in air atmosphere. Investigations were done into the effects of the catalyst dosage, plasma treatment period, TC starting concentration, pH, and radical scavenger presence. Additionally, a thorough analysis of the four systems' plasma and catalyst synergistic effects on TC removal was conducted.

V-2: Influence of catalysts and combination process on GAD performance:

As reported in the literature (Shukrullah et al. 2020; Whitehead 2016b), catalysts can improve the performance of NTPs including GAD. Experimental testing was carried out with and without catalysts for this reason. The experiments, in particular, were conducted by using the same voltage (15 kV), same gas feed which is air, and equal value of flow and relative humidity. Results in terms of TC degradation (%) and mineralization (% TOC removed) are reported in Figure 25. The effect of catalysts presence was remarkable, the results of the hybrid process increased for all the added catalysts. In fact, in catalysts absence, the degradation and mineralization of TC only reached 30.75% and 25.67% respectively. With the combination processes, those values were all improved. Especially in the case of combination with Ferrate and Fe^{2+} ions. The degradation percentage reached 99.18% for plasma-ferrate and 97.28% for plasma-Fe^{2+} systems after 30 minutes of treatment, which results in almost 70% of improvement. In plasma-Fe3$^+$ system, there was roughly 10% and 3% improvement in degradation and mineralization respectively.

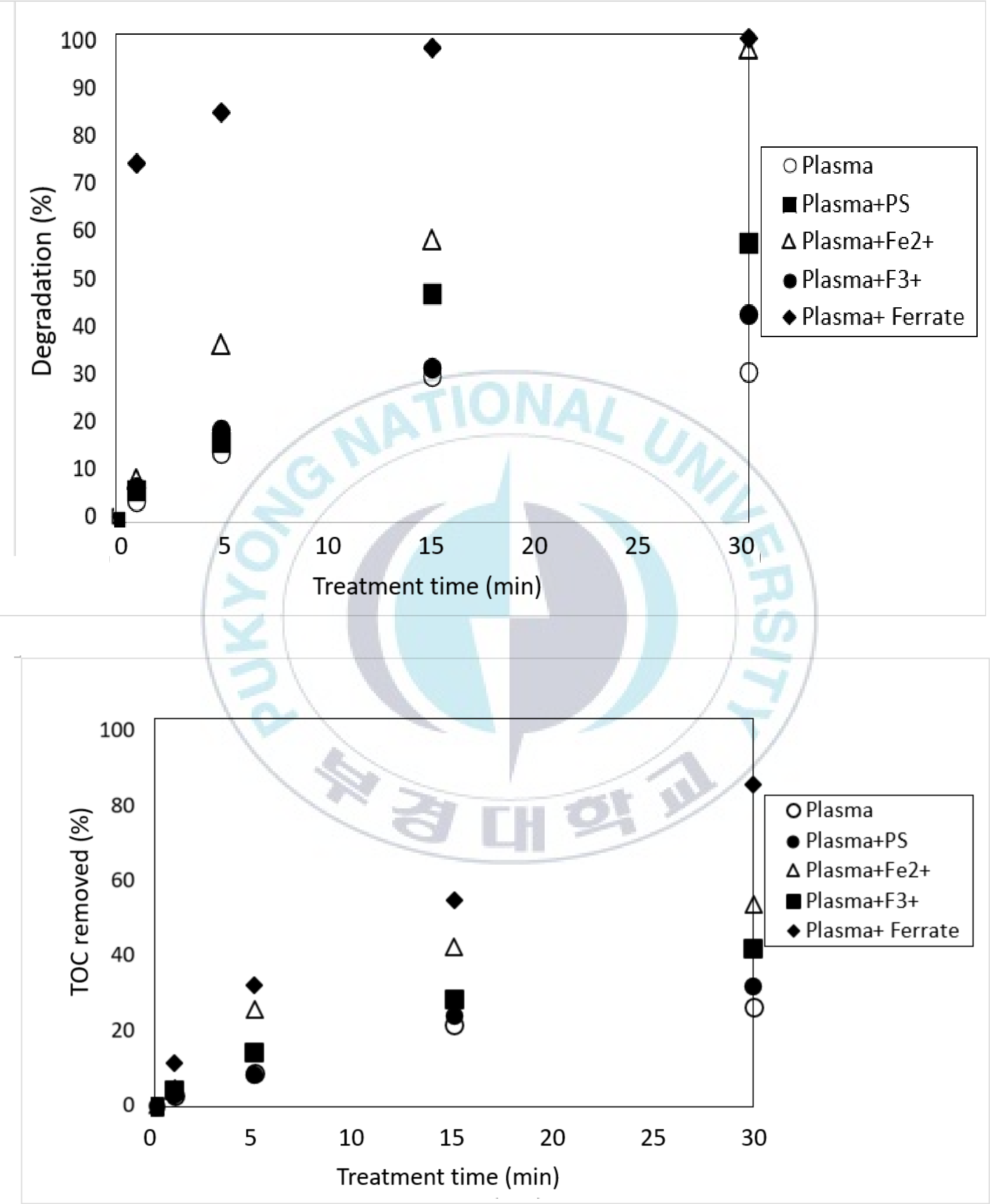


Figure 25: Influence of catalysts on the efficiency of GAD plasma reactor for TC removal: degradation (**a**) and mineralization (**b**) TC initial concentration: 50 mg/L. catalyst: 50 g. Applied voltage: 15 kV. Air flow rate: 13 L/min.

The main reactions of the homogenous Fenton-like method above taking place in GAD/Fe^{2+} and GAD/Fe^{3+} systems and which are responsible for the enhancement of degradation and mineralization of TC are stated below. It starts with the in-situ generation of extra $^{\bullet}OH$ from Fe ions oxidation by H_2O_2 produced by GAD plasma which will only add more oxidation power in the aqueous solutions. The $^{\bullet}OH$ will then react directly not only with TC in water during plasma/catalysis coupling but also with the generated by-products (increase of mineralization). Thus, a decrease in the content of organic carbon is expected in the presence of catalyst (Korichi et al. 2020; Slamani et al. 2018).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$$

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\bullet} + HO^- + Fe^{3+}$$

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$$

$$HO^{\bullet} + H2O2 \rightarrow H_2O + HO_2^{\bullet}$$

$$HO^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + HO^-$$

Similar results were reported by (Hirami et al. 2023) where a combination of plasma DBD system with Fe ions on Ibuprofen solutions improved the degradation significantly. They constated an enhancement in degradation from 75.9% in plasma alone to 88.3% when combined with an iron-based catalyst. As for mineralization, TOC decreased from 32.5 mg/L to reach 15.7 mg/L after 6 hours of reaction in the plasma-Fe based system.

In the GAD-PS system, TC degradation and mineralization were also improved by treatment time. Apparently, PS particles are activated under the plasma reactor which will result in persulfate radical responsible for promoting more oxidation of TC molecules. The enhancement of PS on TC degradation was more obvious at degradation rates compared to mineralization rates which came off rather humble, the results can be explained with the ability of electric discharge to produce all types of RONS of high reactivity which can oxidize TC into small organic molecules, etc. longer discharge time leads to more production of RONS, and with the presence of PS catalyst, an additional radical is introduced to the overall oxidizing potential of the process, therefore enhancing the degradation efficiency of TC. Furthermore, besides RONS, plasma can also produce shockwaves and UV–visible light irradiation. These physical factors effects may contribute to the activation of PS to yield $^{\cdot}$OH and $SO^{\cdot -}{}_{4}$ leading to achieving better higher TC degradation efficiency compared to GAD treatment alone. The activation of sulfate particles is explained in the following reactions:

$$S_2O_8^{2-} \overset{\text{Plasma}}{\rightarrow} 2SO_4^{\cdot -}$$

$$HSO_5^{-} \overset{\text{Plasma}}{\rightarrow} SO_4^{\cdot -} + \cdot OH$$

$$SO_4^{\cdot -} + OH^{-} \rightarrow SO_4^{2-} + \cdot OH$$

$$SO_4^{\cdot -} + H_2O \rightarrow HSO_4^{-} + \cdot OH$$

$$SO_4^{\cdot -} + SO_4^{\cdot -} \rightarrow S_2O_8^{2-}$$

$$S_2O_8^{2-} + SO_4^{\cdot -} \rightarrow S_2O_8^{\cdot -} + SO_4^{2-}$$

$$S_2O_8^{2-} + \cdot OH \rightarrow S_2O_8^{\cdot -} + OH^{-}$$

$$HSO_5^{-} + SO_4^{\cdot -} \rightarrow H^{+} + SO_5^{\cdot -} + SO_4^{2-}$$

$$HSO_5^{-} + \cdot OH \rightarrow H^{+} + SO_5^{\cdot -} + OH^{-}$$

The activation of sulfate radicals by plasma was reported by the literature.(Li et al. 2019b; Shang et al. 2022a). The treatment of sulfamethoxazole (SMX) in a water falling film DBD combined with peroxymonosulfate (PMS) and peroxydisulfate (PDS) catalysts was studied. A significant improvement in the degradation and mineralization of SMX was achieved. It was also stated that, but PMS resulted in higher SMX degradation compared to PDS.

The GAD-Ferrate process seems to be the most effective hybrid system according to the results obtained in this study. However, it should be considered that Ferrate has a strong oxidative power on its own and that in plasma-ferrate system it is more of a hybrid of two AOPs than just a plasma catalysis process. The effect of catalysts alone on TC removal is investigated in the next section.

V-3: Effect of catalyst on TC without plasma discharge

Figure 26 illustrates the effect of Fe $^{2+}$, Fe^{3+} , PS, and Ferrate on the removal of TC with no interference of plasma. TC solutions in these experiments were introduced in the same plasma reactor without turning the power on nor the feed gas just stirring. Catalysts concentrations were added to TC solutions and samples were taken for HPLC analysis after each time of treatment. The results show that only Ferrate has the ability to oxidize TC solutions. It has a quick oxidizing potential after 2 to 3 minutes the degradation rate reached 60% and never increased again. This is due to ferrate dissociating in aqueous solution and losing its oxidizing power.

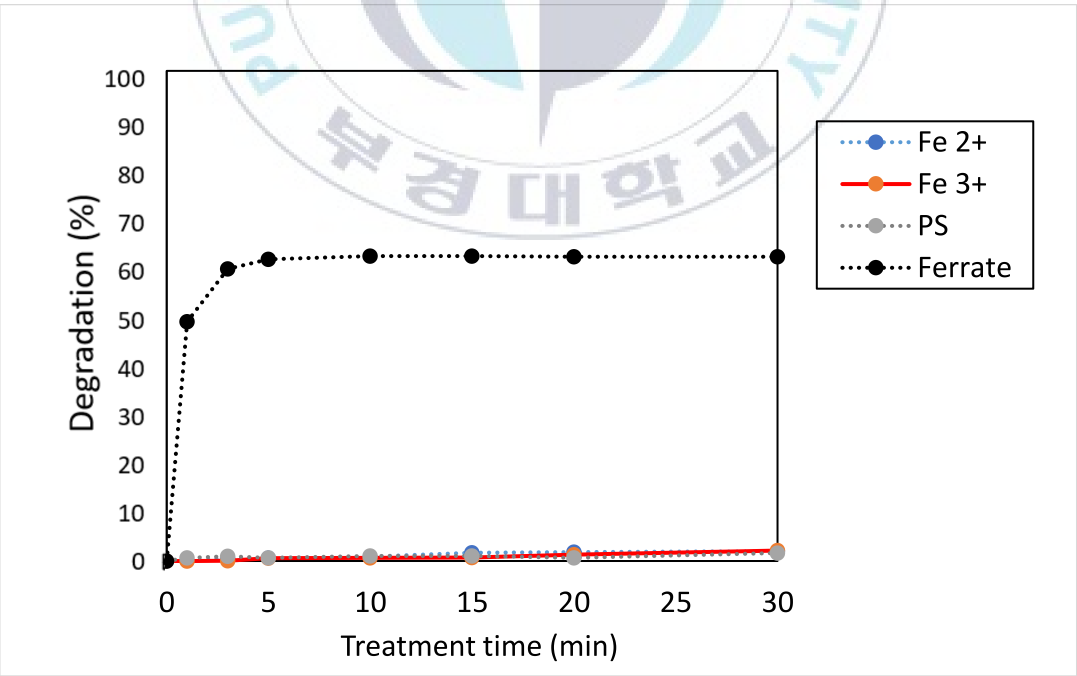


Figure 26: Effect of catalysts on TC removal without plasma discharge.

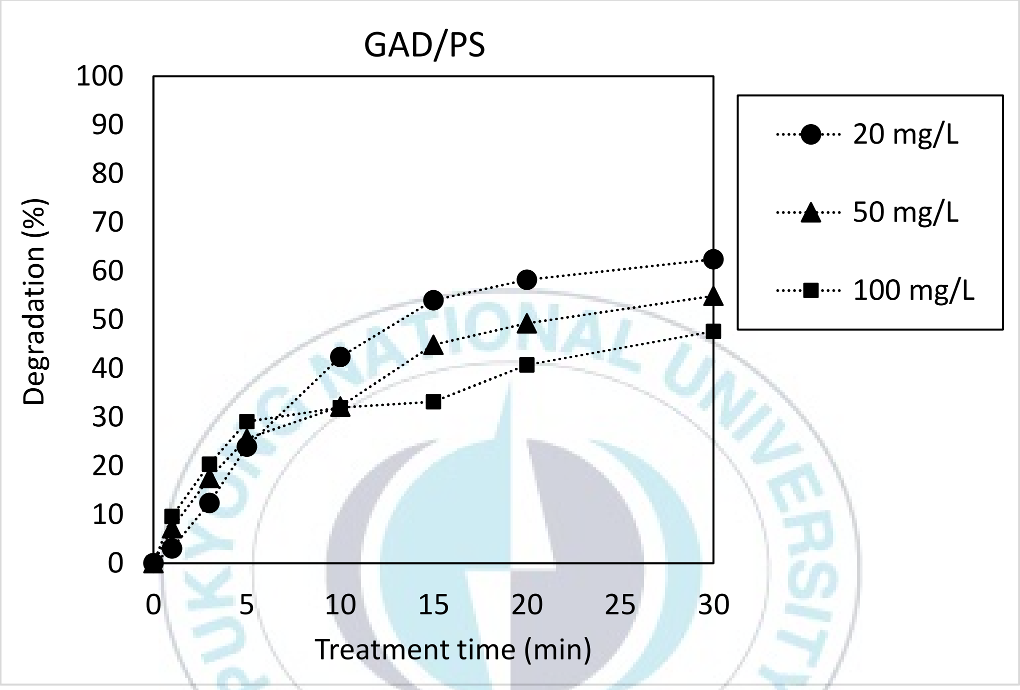
TC initial concentration: 50 mg/L. catalyst: 50 g. Applied voltage: 15 kV. Air flow rate: 13 L/min.

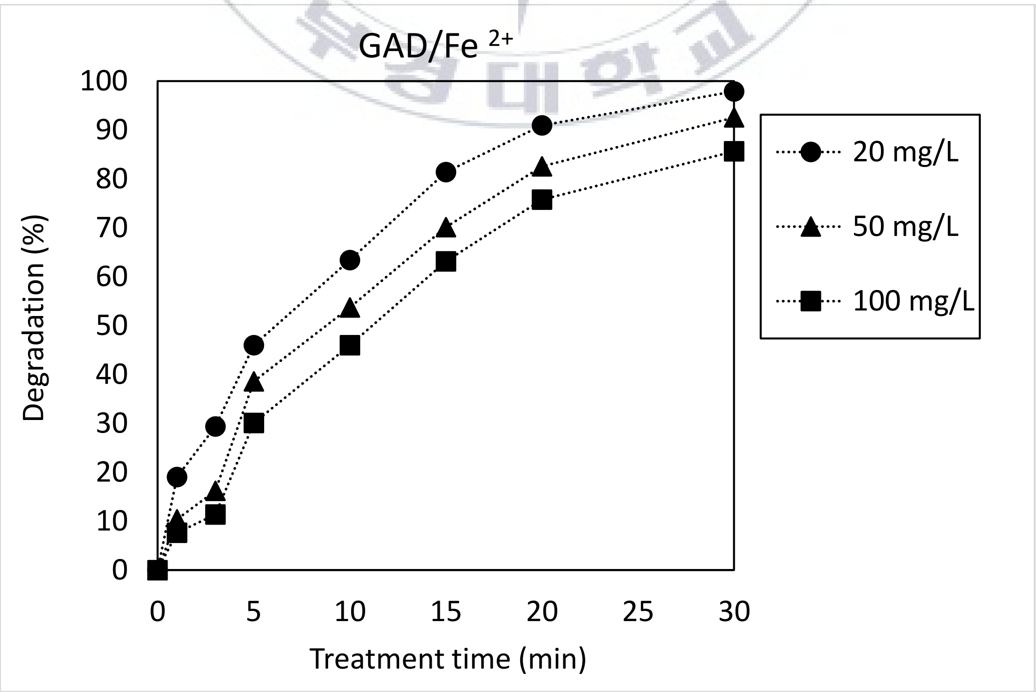
This finding is in line with data from the literature: adding a packing material to the DBD plasma reactor improved the performance of the device used for CO_2 conversion (Michielsen et al. 2017), Due to the packing material's high dielectric constant, which enables the formation of more micro discharges additional to DBD discharge, a powerful electric field is produced at the packed material's edges. They reported on the effect of multiple packed materials on the efficiency of NTP. It was found that a crucial factor in the DBD plasma's performance is the nature of the packed material. Due to their high dielectric constant, quartz, alumina, and silica glasses are among the most popular materials utilized for this purpose. Furthermore, adding dielectric materials in the form of spheres or pellets to the NTP reactor causes the electric field to grow, increasing the electron energy. In general, it is possible to confirm that the surface activation may be the cause of the packing material's better effect.

.In the literature, there are a few works about the use of combination process between plasma and other AOPs. Actually, the combination of ferrate process with NTP of gliding arc type is an original work that has not been done before. The findings, however, can be compared those applying plasma with classic Fenton or Fenton-like processes.

V-4: Effect of TC initial concentration.

As shown in figure 27, the degradation efficiency of TC decreased with bigger initial concentrations, whether in presence of catalysts or not. It seems that higher concentration especially affects the plasma-Fe^{3+} system. The following is an explanation of the results: Numerous types of RONS are created when an electric discharge occurs in water or in the gas/liquid interface just above the water surface. These species that have entered water and the secondary radical species that they have produced (such as $^{\bullet}OH$ and $OONO^{\bullet}$) are susceptible of oxidizing TC to produce lighter organic entities and carbon dioxide., etc. Smaller TC initial concentrations lead to more chances for RONS to attack the organic structure, hence increasing the removal percentage.





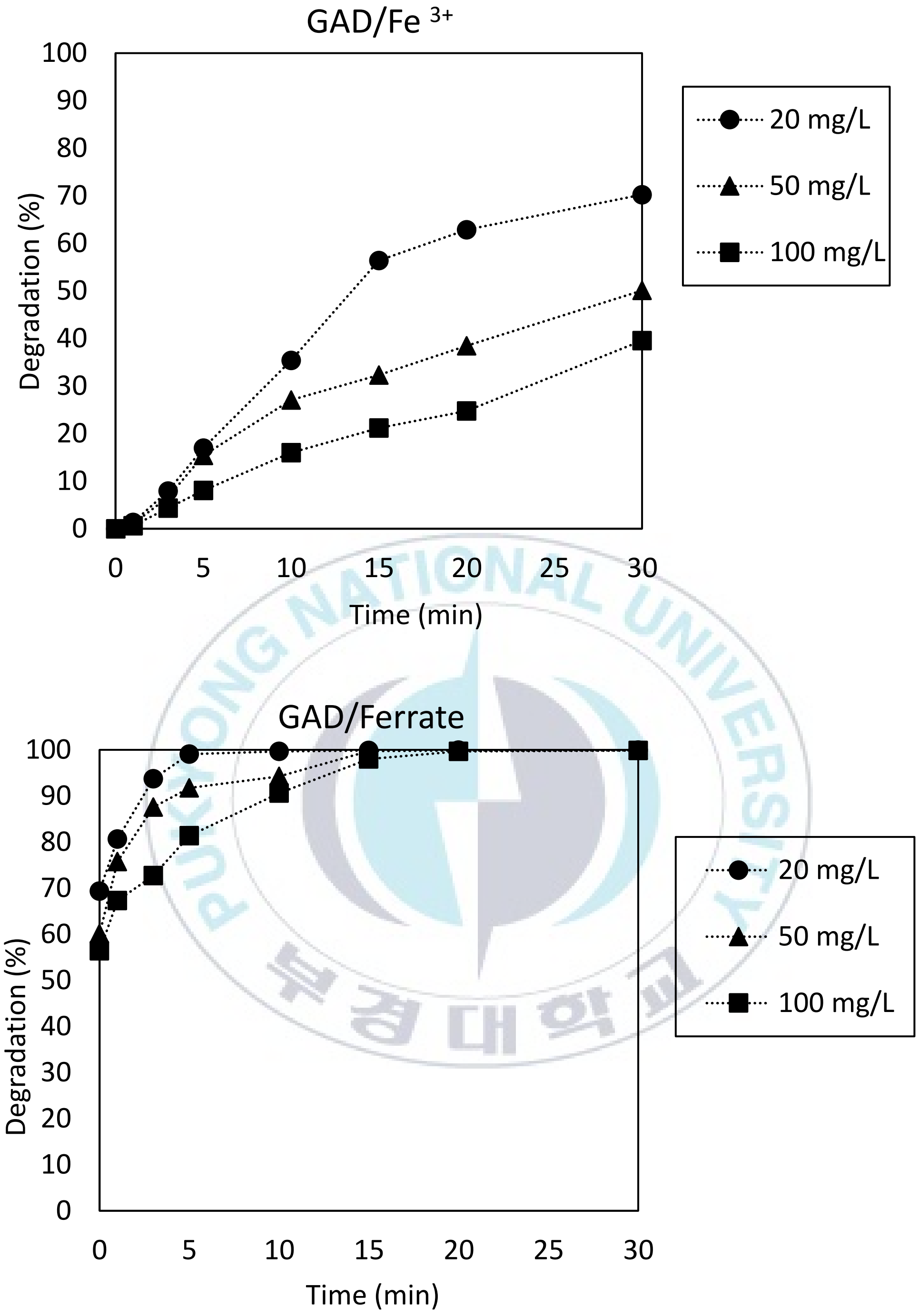
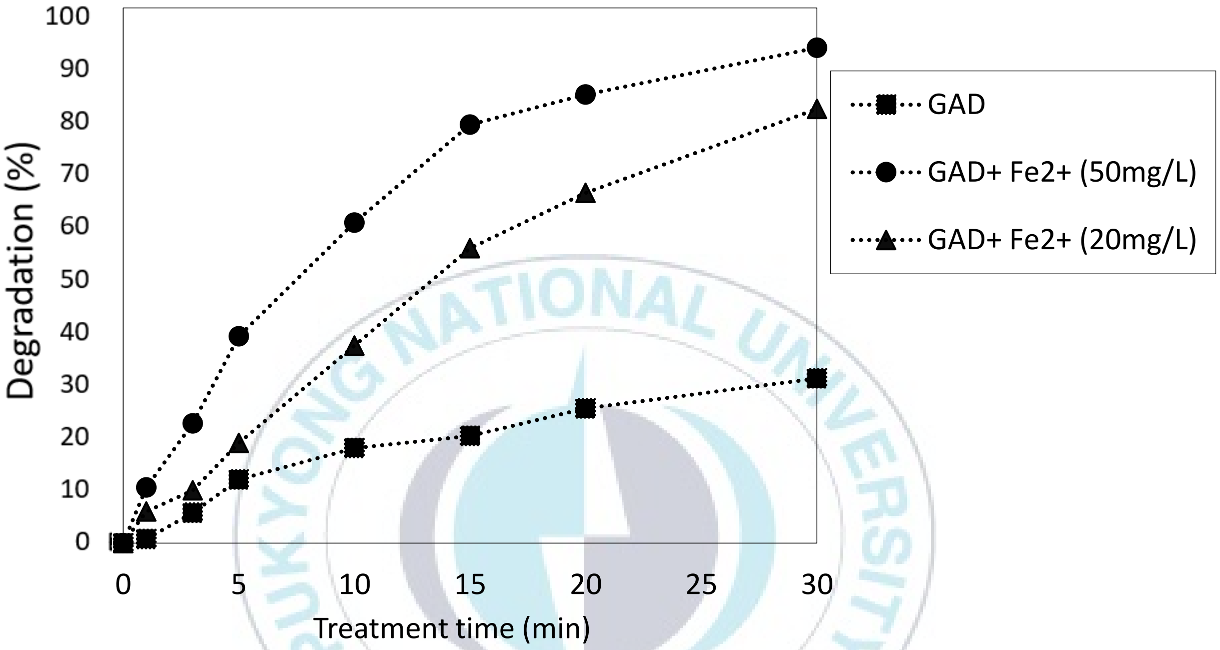


Figure 27: Effect of TC initial concentration. catalyst: 50 g. Applied voltage: 15 kV. Air flow rate: 13 L/min.

It is crucial to explore the two methods that were combined to create this hybrid process separately in order to set the stage for talking about the mechanism and effects of plasma catalysis. A catalytic material is placed into a reactor exposed to stream of RONS generated by GAD can provide alternative reaction pathways with lowered energy consumption and shortened treatment time. These can increase the yield of the physico-chemical reactions involved in the generation of plasma species and engaged in the attack on organic matter, increasing the overall yield of the process and thereby improving the efficiency of the process. At first, we investigated the effect of the selected catalysts on TC solutions without the effect of plasma discharge. Results are presented in figure 31. As shown in the figure, and contrary to Ferrate, PS, Fe $^{2+}$, Fe $^{3+}$ alone cannot oxidize TC which translated to absence of removal rate percentage even after 30 minutes of reaction. Ferrate being a strong oxidant could contribute up to 60% of TC removal after 2 minutes of reaction, after that no change has been observed due to the fact that ferrate loses its oxidation power after all molecules engage in reaction with the organic matter.

V-5: Optimization of catalyst dosage: and treatment time: Ferrate, Fe $^{2+}$, Fe $^{3+}$ and PS

The effect of catalysts doses on the removal efficiency is presented in figure 28. The degradation efficiency indeed improves at a higher concentration of Fe^{2+} with 10% difference between a dose 20 mg/L and 50 mg/L. However, in the field of wastewater treatment, it is more encouraged to use lower dosages of catalysts to cut costs. Ferrate had shown a gap between removal rate only in the first minutes of treatment. After around 10 minutes, both 20 mg/L and 50 mg/L of ferrate doses combined with GAD resulted in the total degradation of TC. GAD-Fe^{3+} showed an enhancement of degradation rate despite being minimum. The most interesting results were constated in the GAD-PS system. In the first 50 minutes of treatment, a higher dose of PS achieved relatively higher degradation. However, as the plasma discharge carried on, there was a shift in the results. Smaller concentration of PS (20 mg/L) achieved higher degradation. This can be explained by the reaction of sulfate radicals with the abundant amount of ROS present in the solution after prolonged treatment time (Sang et al. 2021; Shang et al. 2022b). From this point of view, it is better to apply lower dosages of this catalyst to avoid its engagement in any reactions that do not benefit the pollution abatement process.



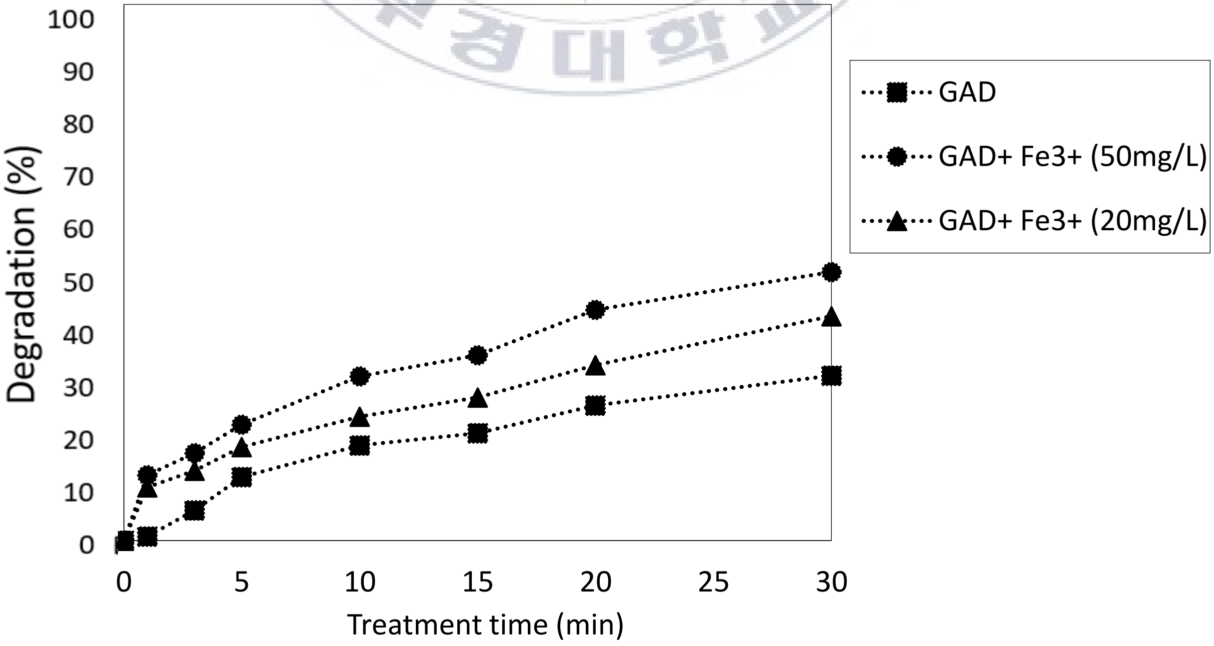


Figure 28: Effect of catalyst dose in function of plasma treatment time.

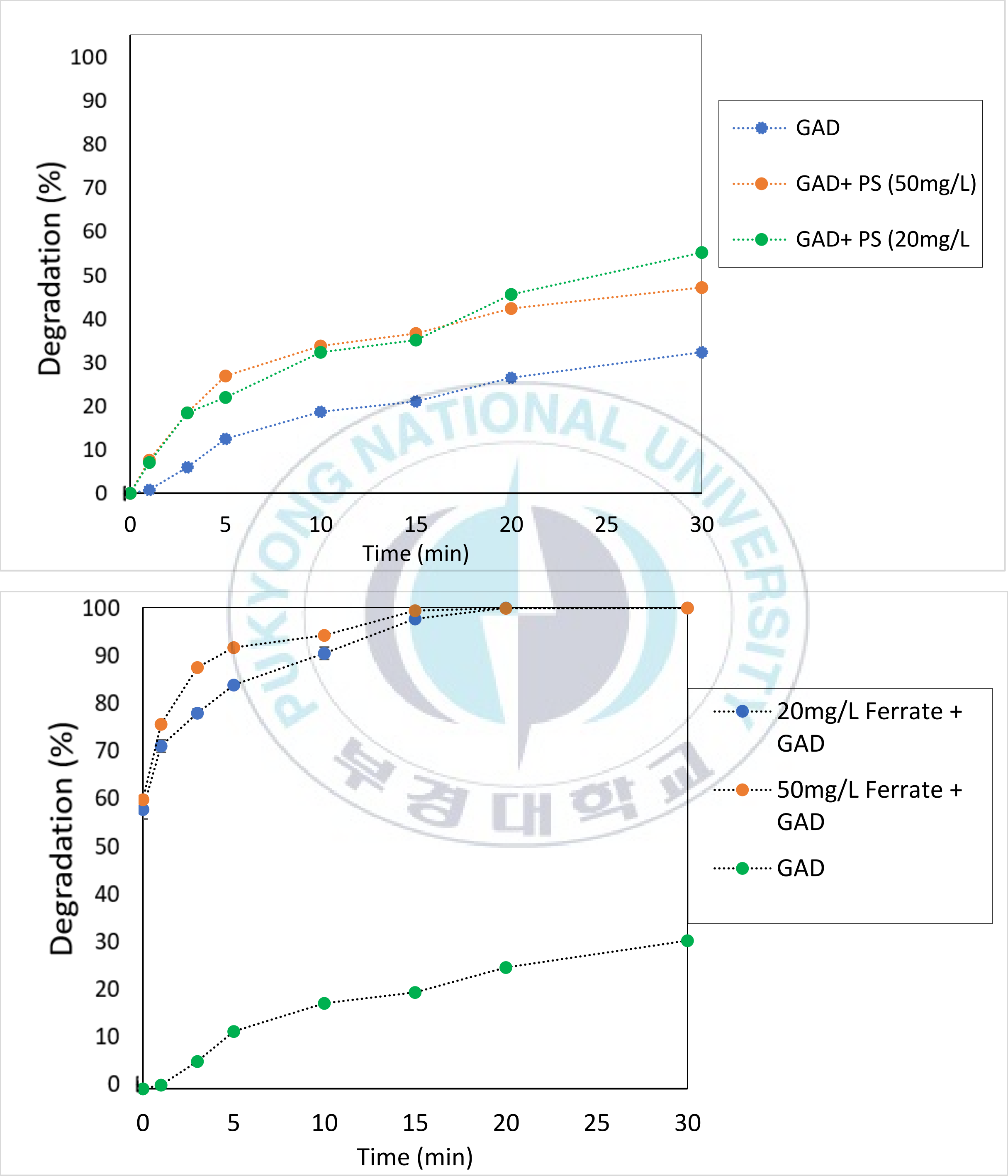


Figure 28: Effect of catalyst dose in function of plasma treatment time. TC initial concentration: 50 mg/L. Applied voltage: 15 kV. Air flow rate: 13 L/min.

The main reactions of the homogenous Fenton-like method above taking place in GAD/Fe^{2+} and GAD/Fe^{3+} systems and which are responsible for the enhancement of degradation and mineralization of TC are stated below. It starts with the in-situ generation of extra $^{\bullet}OH$ from iron oxidation by H_2O_2. Produced by GAD plasma. The $^{\bullet}OH$ will then react directly not only with TC in water during plasma/catalysis coupling but also with the generated by-products (increase of mineralization). Thus, a decrease in the content of organic carbon is expected in the presence of catalyst.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$$

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\bullet} + HO^- + Fe^{3+}$$

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$$

$$HO^{\bullet} + H2O2 \rightarrow H_2O + HO_2^{\bullet}$$

$$HO^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + HO^-$$

V-6: Removal efficiency of plasma catalysis in presence of Dimethyl Sulfoxide

As mentioned in the previous chapter, DMSO is extremely reactive with $^{\bullet}OH$ resulting in a strong inhibition effect when TC solution is prepared in DMSO. The results are shown in figure 29. A decrease in TC removal efficiency was observed in the presence of DMSO for all systems. The degradation rates decreased from 20.69% to 9.84% in plasma which means a 10% of degradation potential was inhibited by radical scavenger. However, when plasma catalysis is applied, it is observed that the gap in this decrease is reduced to 4%, 20%, 10% , GAD-Fe^{2+}, GAD-Fe^{3+} and in GAD-PS systems respectively. Which indicates that despite the presence of radical inhibitors, the combination process with achieve higher degradation rates compared to plasma alone. GAD-ferrate system in the other hand, have exhibited an opposite outcome in the presence of DMSO compared to other systems. The degradation efficiency in presence of DMSO was actually higher than its absence. This can be contributed to the complex nature of the treated solution. DMSO

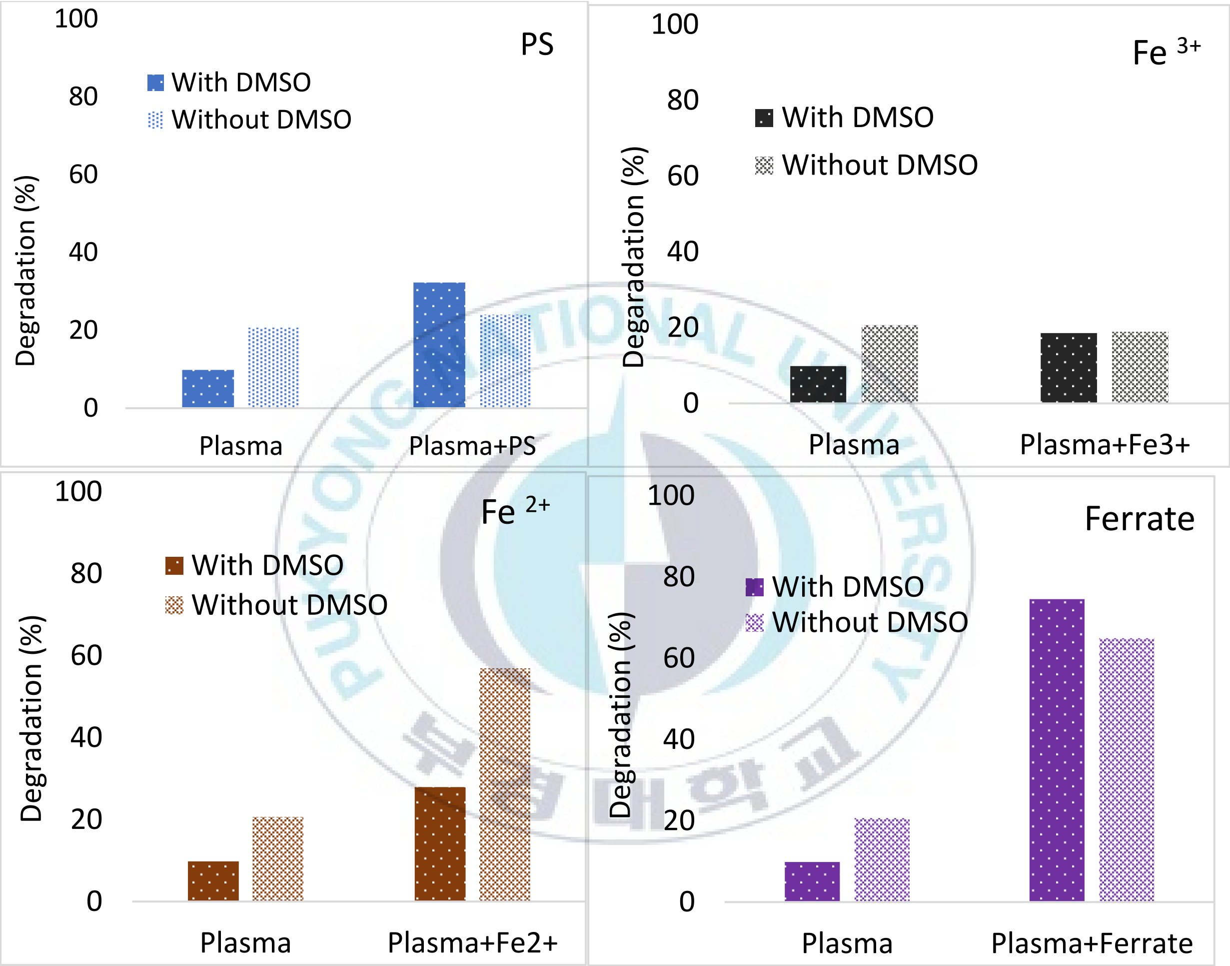


Figure 29: Removal efficiency of plasma catalysis in presence of DMSO treatment time: 15 minutes. TC initial concentration: 50 mg/L. Catalyst: 30 mg/L

Consuming initial $^{\bullet}$OH species generated by the plasma discharge. But in presence of ferrate and Fe^{3+} which is the decomposition product of ferrate will produce more $^{\bullet}$OH through the treatment time. The accumulated concentration of these radicals can be quickly consumed by all the different species present in the aqueous solution. (Brisset and Pawlat 2016) described how the chemical reactions within GAD plasma are too complex to be predicted.

V-7: Effect of scavengers on TC removal by plasma catalysis:

The effect of ethanol (EtOH), p-benzoquinone (p-BQ), tert-butyl (TBA) on TC removal was studied and shown in figure 36. Although we used DMSO as $^{\cdot}$OH scavenger in the previous sections. We opted for another type of scavenger here which is TBA. TBA is also considered as a popular $^{\cdot}$OH scavenger (Wang et al. 2011). EtOH and p-BQ were selected as scavengers for oxidative $SO^{\cdot-}_4$ and superoxide anion radical ($O^{\cdot-}_2$) k = 0.9–1.0 × 109 M^{-1} s^{-1}). Due to the importance of free electrons in the solution on the major plasma interactions, we added salicylic acid as a scavenger for electrons.(Shang et al. 2022b). Figure 30 presents the degradation efficiency of TC by GAD treatment alone in the presence of different scavengers.

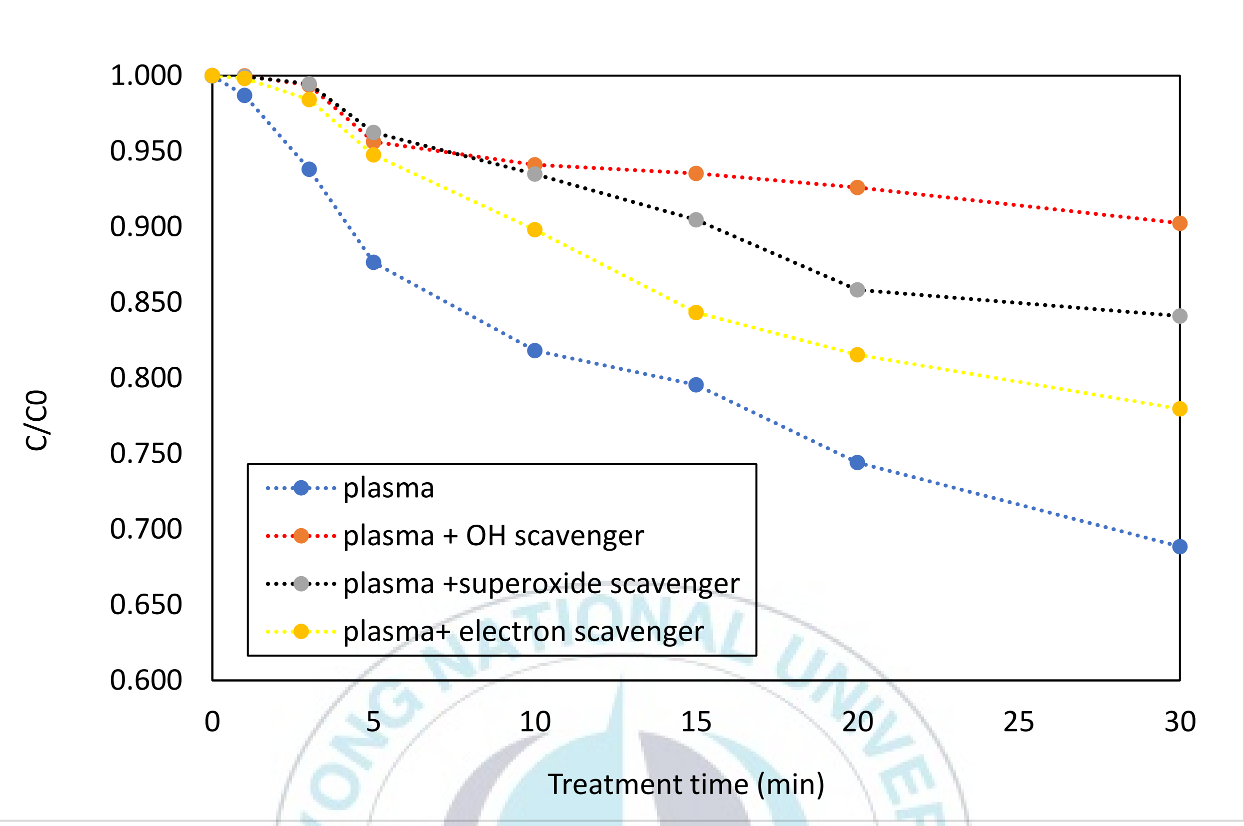


Figure 30: Effect of reactive oxygen species on TC degradation in GAD plasma reactor in the presence of salicylic acid as electrons scavenger; Tert-Butyl TBA as OH scavenger; and p-Benzoquinone p-BQ as Superoxide scavenger. TC initial concentration: 50 mg/L. radical scavengers' concentration: 100 mM

The results indicate that TBA effect was the most noticeable as the removal rate dropped from 30% to 10% in presence of TBA, further solidifying the role of $^{\cdot}OH$ in the plasma degradation. Superoxide radicals also managed to decrease the removal efficiency in their presence indicating that indeed it engages with TC oxidizing reactions. The figure also shows that electrons are involved in this oxidation since the removal rate dropped to 20% after 30 minutes of treatment.

Figures 31 and 32 show the effect of different radical scavengers on the degradation of TC in plasma and GAD-PS systems. EtOH as a scavenger of $SO_4^{\bullet -}$ had showcased the role of this radical in the hybrid process. $SO_4^{\bullet -}$ is a short-lived radical specie generated in situ by cleaving the peroxide bond in the persulfate molecule via energy and electron transfer reactions (Sang et al.

2021). Although it is reported that PS can attack some organics directly, without the need to be activated to a radical species, in plasma based technologies the activation is the most probable scenario (Zhang et al. 2019). Over the past years, PS based AOPs have received a lot of interest as a practical substitute to traditional $^{\bullet}$OH based AOPs. It is necessary to research more about plasma-based PS since PS radicals possess a relatively powerful redox potential.

Organic compounds react with $SO_4^{\bullet-}$ and $^{\bullet}$OH via similar pathways; (i) hydrogen abstraction, (ii) electron transfer, and (iii) addition−elimination. The difference lies in a preferred reaction pathway and the reaction kinetics. For example, the oxidation of saturated hydrocarbons such as alkanes and aliphatic alcohols by $SO_4^{\bullet-}$ is known to proceed through hydrogen abstraction similar to $^{\bullet}$OH (Dong et al. 2019)

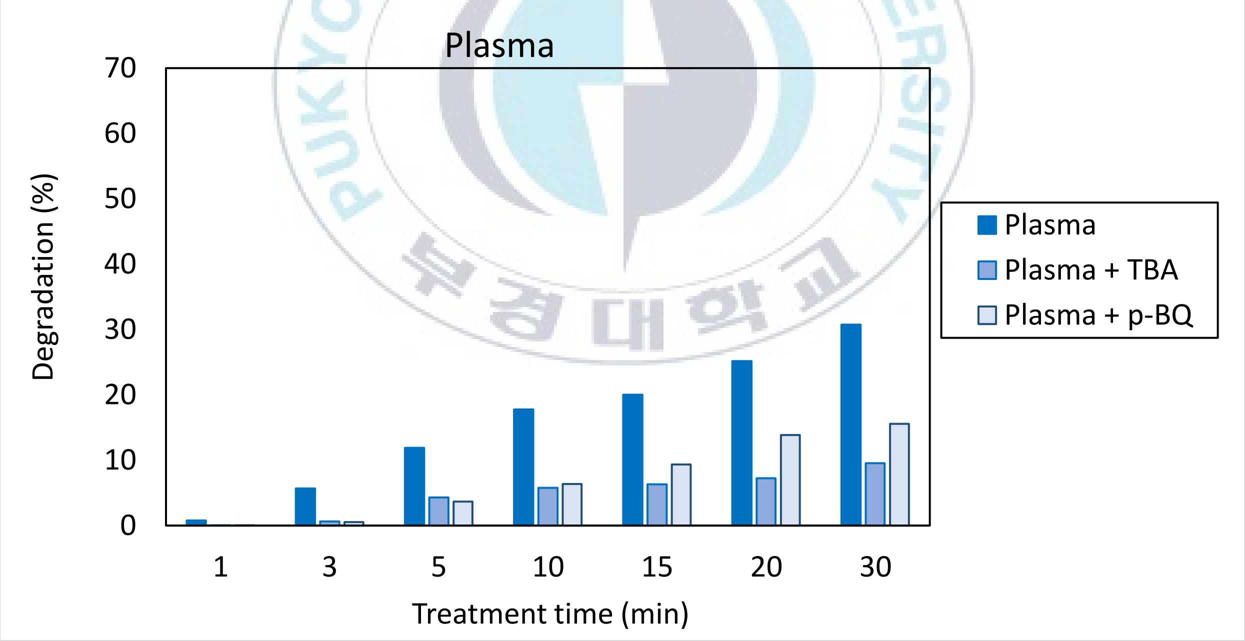


Figure 31: Influence of reactive oxygen species (ROS) on TC degradation in GAD plasma reactor in the presence of scavengers. TC initial concentration: 50 mg/L. Applied voltage: 15 kV. Air flow rate: 13 L/min.

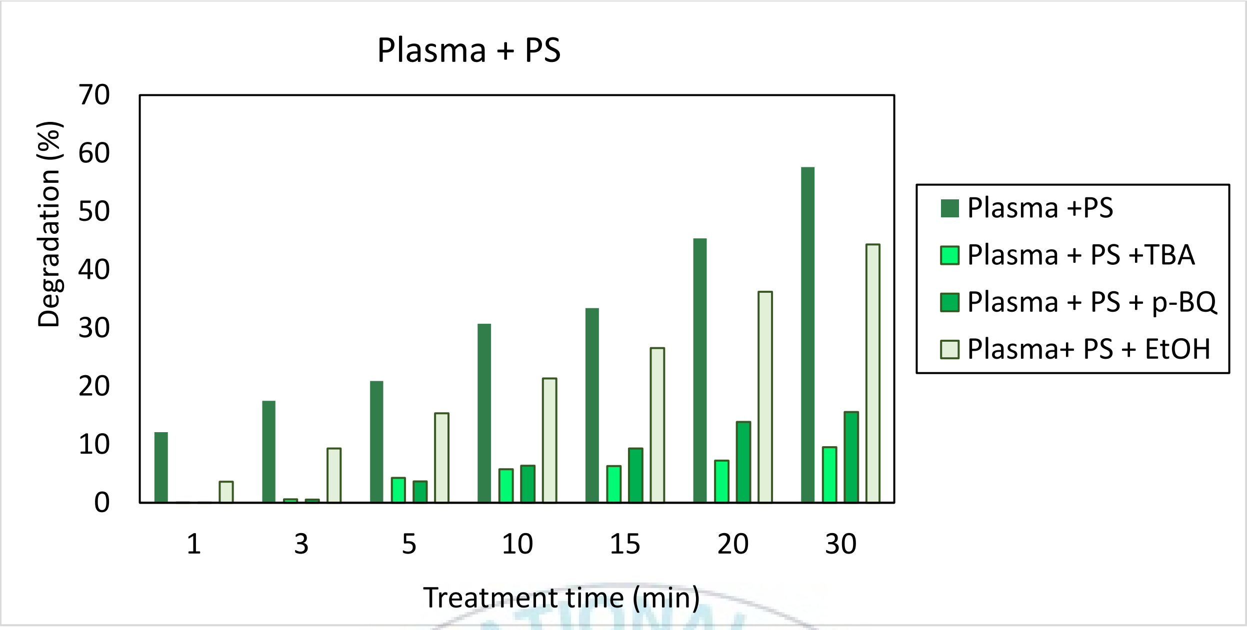


Figure 32: Influence of reactive oxygen species on TC degradation in GAD plasma reactor in the presence of EtOH as persulfate scavenger; Tert-Butyl TBA as OH scavenger; and p-Benzoquinone p-BQ as Superoxide scavenger. TC initial concentration: 50 mg/L. Applied voltage: 15 kV. Air flow rate: 13 L/min.

Although the hybrid process of GAD with different homogenous catalysts has not been extensively studied, the use of various kinds of heterogenous catalysts in different types of plasma reactors has been reported in literature. For example, the combination of DBD reactor with the classic photocatalysts TiO_2 and ZnO studied by (Farzinfar and Qaderi 2022) . DBD reactor was combined with ZnO nanoparticles for p-nitrophenol degdaration. In this combination the removal efficiency was impressively improved. This was credited to the activation of ZnO photocatalysts by the UV light emitted in the discharge. The results illustrated that the addition of an optimized quanityt of ZnO nanoparticles (250 mg/L) in the plasma reactor could increase the degradation of p-nitrophenol from 49 % to 91 %, whereas the UV/ZnO photocatalytic process alone only resulted in 12 % of removal. This indicatesa remarquable synergistic enhancement the degradation efficiency in the NTP- ZnO system process rather than a simple an additive effect . Moreover, the energy consumption analysis revealed that the NTP-ZnO system was 4 times more efficient than the plasma alone, which can be regarded as a significant step towards the application of plasma catalysis in an industrial scale (Farzinfar and Qaderi 2022)

Another study that combined DBD with ZnO/α-Fe_2O_3 catalyst for the treatment of amoxicillin (AMX). They studied the impact of different factors like contact time, initial concentration of both AMX and ZnO/α-Fe_2O_3, and solution pH on AMX degradation. In addition, the overall performance was evaluated by assessing the optimization results, kinetics model, degradation pathway, energy yield, and toxicity of the DBD-catalyst combined process. The key findings of this work is that AMX removal rate reached 99.3% after 18 min of treatment at the following conditions: peak voltage was at 15 kV, and ZnO/α-Fe_2O_3 concentration was at 400 mg/L, AMX initial concentration was at 16 mg/L , and initial pH started at 4.5 with a rate constant of 0.198 min−1, energy yield of 3 g kW−1 h−1, without any effluent toxicity. They concluded that the DBD-ZnO/α-Fe2O3 system exhibited a great potential for the removal of aqueous AMX degradation. (Ansari et al. 2020).

photocatalysis, plasma reactor and integrated plasma photocatalysis reactor which gave 1.2%, 50.8%, and 98% removal in 2 min respectively. The solution pH, dosage, and loading of AgFeO2 in photocatalyst was investigated. The integrated plasma photocatalysis gave 95% degradation of 250 ml solution of 30 ppm methyl orange at pH 3 with 0.5 g/l of 2.5% AgFeO2/CNTs/TiO2 photocatalysis in 2 min. The integrated plasma photocatalysis reactor increased the number density of active species, particularly OH. in wastewater which makes it a good choice for azo dyes degradation (Hafeez et al. 2021).

Overall, plasma type GAD combined with homogenous catalysis with Fe^{2+}, Fe^{3+}, and PS, or hybrid process of plasma with ferrate oxidation shows a promising potential for the treatment of recalcitrant pollutant such as TC. Especially, the combination with ferrate oxidation has displayed a significant prospect as it is already a very effective oxidant that managed to induce a remarkable degradation rate in short time. Its downside is its inability to promote higher mineralization rate. In GAD-ferrate system, this drawback seems to be solved as the hybrid process managed to totally remove TC from the aqueous solution as well as achieving high levels of mineralization. Another advantage of the hybrid process is the shortened time of the treatment. Which is undoubtedly considered an important factor in future applications of these processes in the field of water decontamination since it promotes less energy consumption and consequently cost-effectiveness.

Conclusion:

The main objective of this study was to establish an efficient method for the treatment of persistent organic contaminants using one of the most promising technologies among advanced oxidation processes which non-thermal plasma. For this purpose, a non-thermal plasma of gliding arc type was used. Two model pollutants were selected in this study. For a starter, as the plasma reactor was being developed and optimized, an azo dye namely EBT was chosen to test the efficiency of the plasma produced through a variation of conditions. Significantly, the effect of feed gas, relative humidity, pH, and treatment time on the generation of plasma reactive species ($^{\cdot}OH$, H_2O_2, O_3, NO_2^-, and NO_3^-) was investigated. Followed by an experimental study about the treatment of the selected dye under optimized conditions of humidity and feed gas nature. Both decolorization and mineralization rates were tested in this case. The main results about this section of the thesis are in the following:

- The most optimum relative humidity level for air plasma was achieved at 30% by producing the highest concentrations of RONS. Which was the case for dry O_2 plasma as any introduction of humidity decreased the production levels of ROS.
- In their significant optimum conditions of humidity, O_2 plasma showed an excellent performance through the production of large amount $^{\bullet}OH$ (65.49 μmol/L) after 30 min of treatment. Which was nearly 3 times the amount produced by air plasma.
- The best EBT decolorization was achieved by air plasma (96.51 %) while O_2 plasma resulted in better mineralization rate with TOC removal (approximately 20% higher than air plasma). This was explained by ROS in O_2 plasma engaging in subsequent reactions

with aromatic compounds formed as byproducts of EBT initial decolorization since •OH is more attracted to aromatic functional groups than to azo bonds.

- The effect of radical scavenger DMSO on the removal of EBT further showcases the role of RNS in the decomposition of organic compounds in air plasma when ·OH is inhibited (decolorization rate decreased from 96.51% to 83.33% in air plasma, while, in O_2 plasma, DMSO's presence caused in a bigger drop in decolorization, moving from 52.57% to 12.19% by the end of treatment.
- A degradation pathway was suggested taking into consideration the results of this study and the available literature knowledge about the action of plasma species on EBT specifically and azo dyes generally.

The second section of this work focuses on investigating the potential of plasma gliding arc for the treatment of TC antibiotics. TC has been subjected to plasma remediation by various research before but as far as we know, this is the first time it is being treated by a gliding arc type of plasma. Different parameters were tested to establish the best conditions for TC removal efficiency namely, initial concentration, pH, plasma gas, radical inhibitions etc. The key findings are:

- A total degradation rate of 94.95% was achieved in O_2 plasma by the end of the treatment for TC initial concentration of 5 mg/L. Accompanied by mineralization rate of 81.3%. which is impressive since generally in contaminants treatment it is difficult to achieve high mineralization rates. Air plasma on the other hand resulted in 60.45% and 57.34% rates of degradation and mineralization respectively.
- TC degradation products were identified by mass spectroscopy analysis and a degradation pathway was proposed based on its structure, the plasma chemistry and mass spectrometry

data. It was established that the double bonds, aromatic rings, and amino groups are attacked by reactive species.

- The estimation of degradation products toxicity was performed by T.E.S.T software. It was found that some of the resulting products had higher toxicity than TC while the others had exceptionally low toxicity, suggesting that if applied in industrial scale. Further treatment should be carried out.

Overall, the results may offer useful information for the practical use of GAD plasma in the removal of antibiotics from environmental matrices and environmental remediation in general.

The last section of this work consists of an innovative approach to the world of plasma catalysis. This type of hybrid technology is receiving attention for the advantages and potential it possesses. 4 types of species namely Fe^{2+}, Fe^{3+} , PS, and Ferrate, were introduced into the plasma reactor to perform a homogeneous type of plasma catalysis. Experimental results showed that:

- All systems showed improved degradation rates. Especially GAD-Ferrate and GAD-Fe^{2+} systems where total degradation was achieved at a shorter treatment time compared to plasma alone (from 30% by plasma alone to 99.18% and 97.28% for GAD-Ferrate and GAD-Fe^{2+} systems respectively).
- The effect of catalysts alone on TC was studied, only TC has an oxidizing effect on TC peaking at 60% removal after 2 minutes of reaction. Since ferrate is a powerful oxidant on its own the plasma-ferrate system can be considered as a hybrid combination system more than just a plasma catalyst process.

- The results of the combined systems definitely showed a potential synergic effect was formed after the addition of different catalysts.
- Different values of initial pH were tested to see their effect on TC treatment. It was found that pH values do not result in big differences in removal. Plasma by default generates large amounts of acidifying species. As a result, no matter what the initial pH value is set at, the solution pH will always become acid after some period of plasma discharge.
- The catalysts doses influence on the performance were tested. It shows that even small dosages of ferrate and Fe^{2+} (20 mg/L) can achieve total degradation of TC.
- Different radical scavengers (such as DMSO and TBA, p-BQ, EtOH, salicylic acid for the inhibition of $\cdot OH$, superoxide, $SO_4^{\bullet-}$, and electrons respectively) were used to establish the role of reactive species in the degradation process.

Overall, this research contributes to a better knowledge of how organic compounds can be treated in nonthermal plasma in general gliding arc type and in combination with ferrate process or other catalysts. The results can be applicable not just to TC and EBT, but they can serve as a guide for other similar hazardous contaminants. We believe that further research and experimental examination can lead to better understanding of the complex nature of advanced oxidation and of the even more complex application of plasma catalysis hybrid methods. New strategies should tackle on:

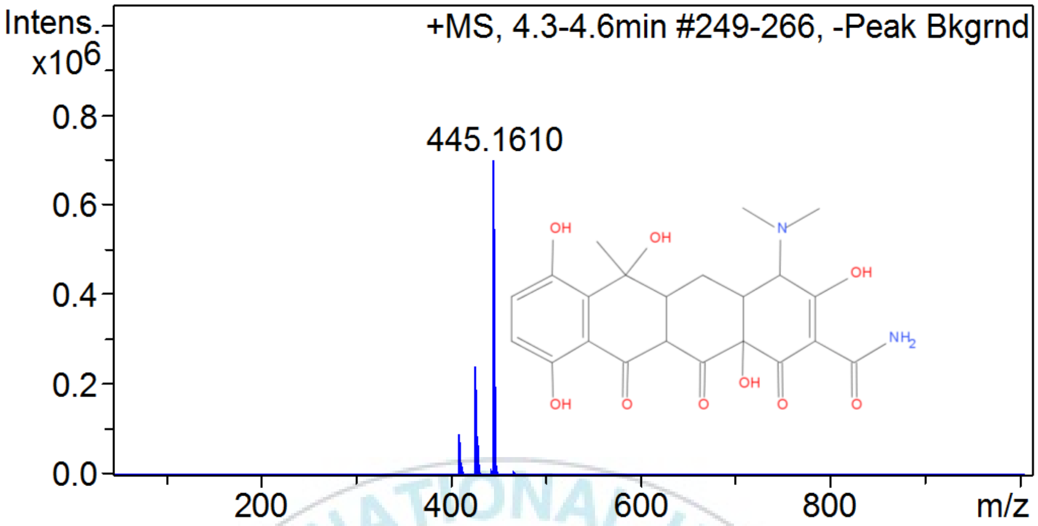
i. The development of standards for comparative evaluation among plasma- catalysts or between other AOPs combined with plasma or with catalysts or all together as the hybrid process has more potential to improve performance and cut down on the expenses.

ii. Establishment of standard experimental procedures to control the occurrence of unwanted intermediates and boost degradation mechanisms that result in less harmful by-products.

iii. Improvement of plasma reactor’ design and geometry. More focused should be on the potential of continuous reactor design and the possibility of integrating reactive species analysis outlets to facilitate monitoring of the plasma process.

Annex

TC spectra:



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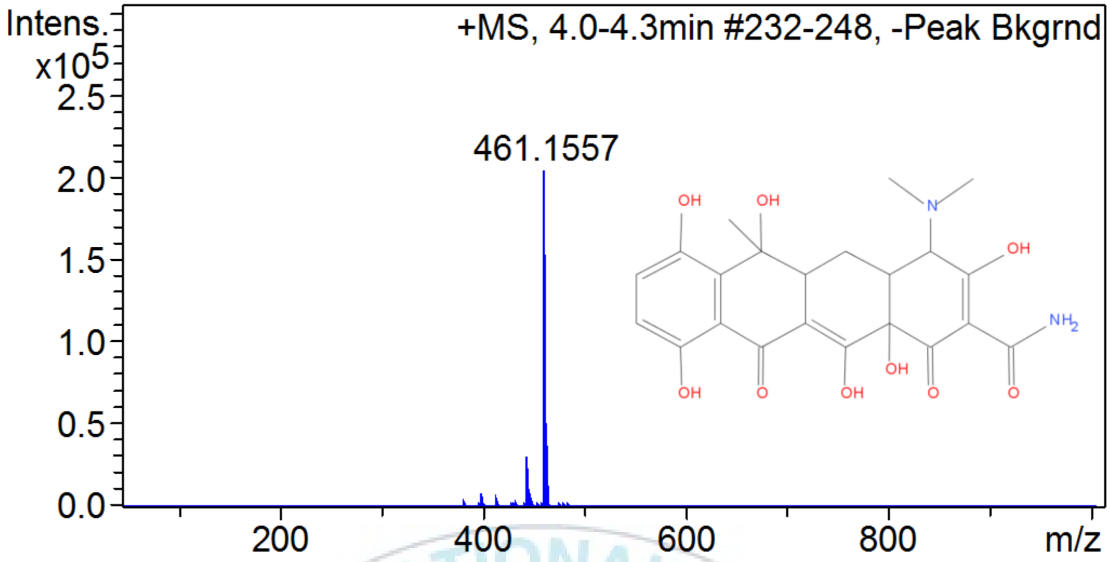
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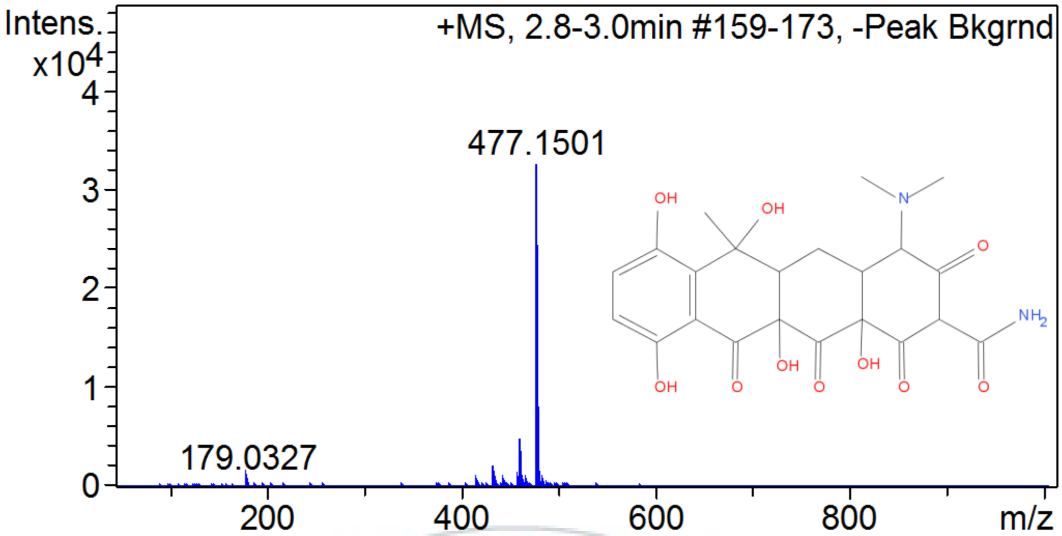
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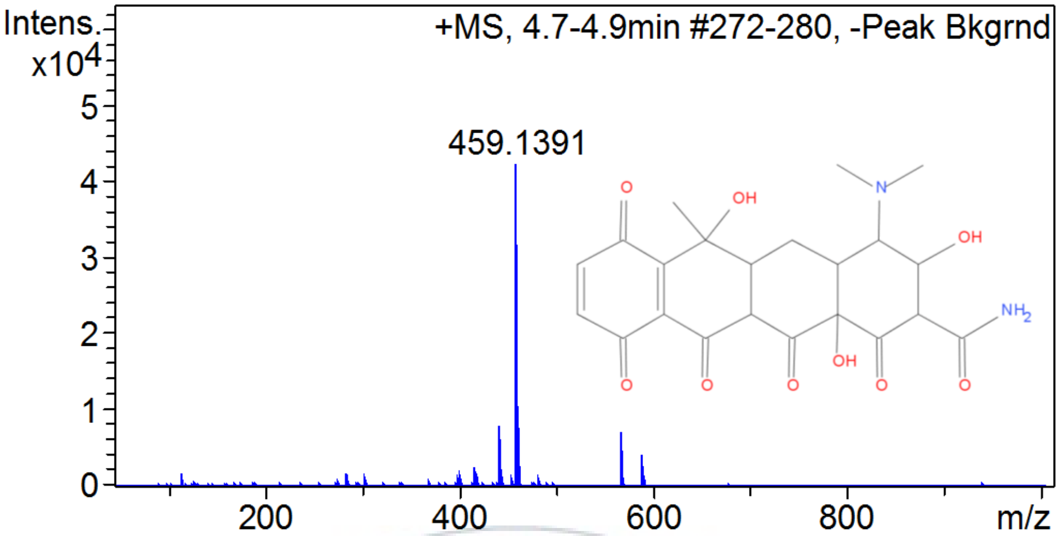
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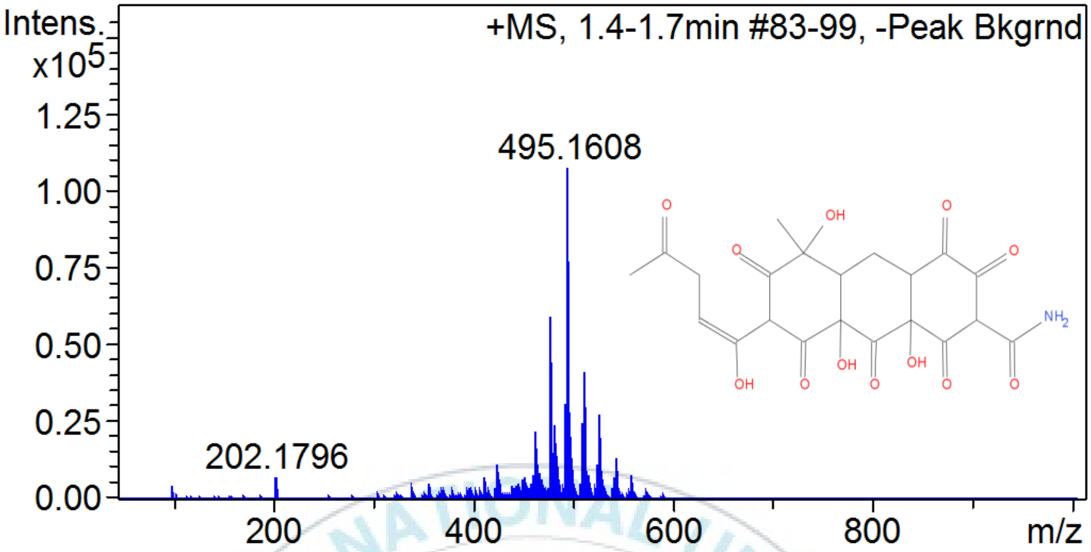
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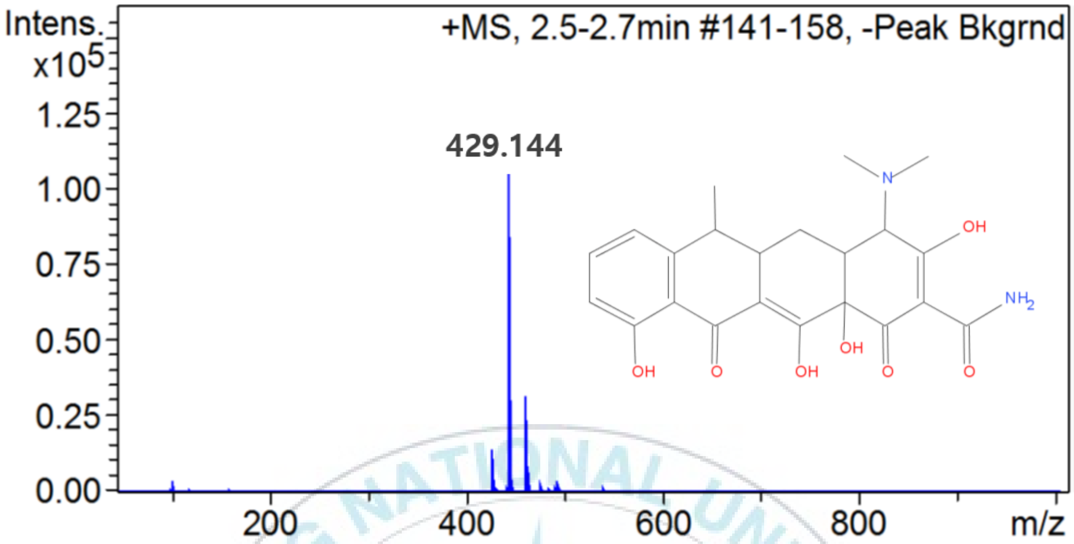
DP5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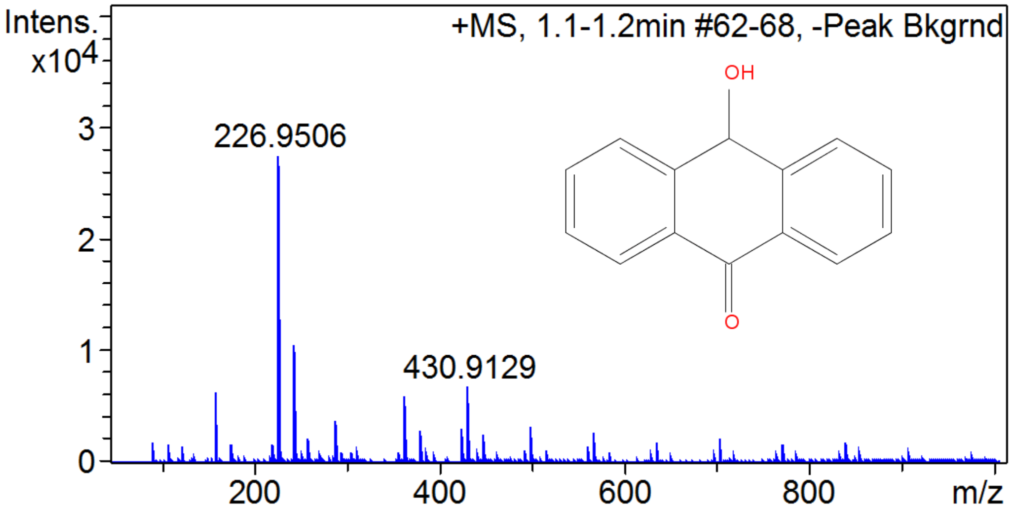
DP06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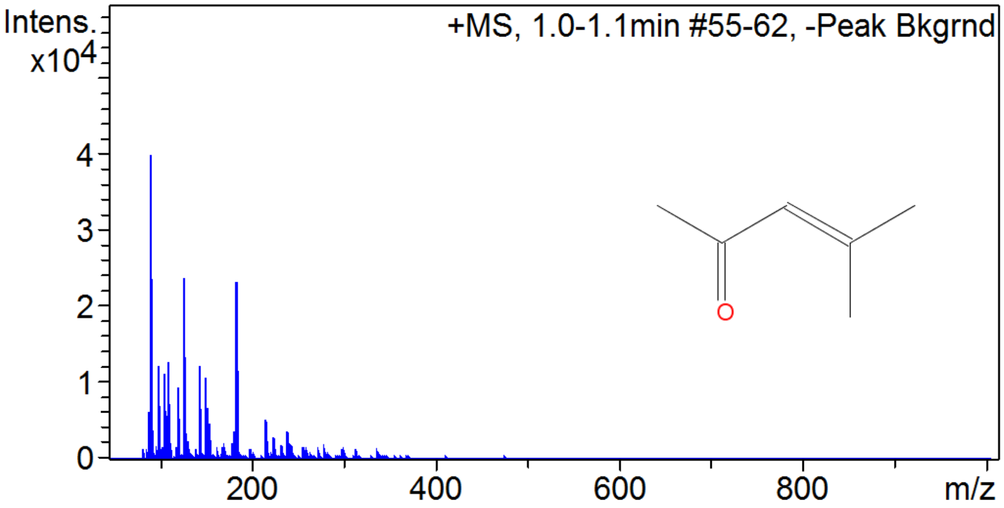

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600
800
m/z
O

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