

Far UV-C Light Mediated Degradation of CBZ and SMX: Role of DBD Plasma-Produced Nitrates and Hydrogen Peroxide

6.1 Introduction

Organic micro-pollutants (OMPs) are increasingly found in freshwater environments, posing risks to aquatic life and human health [Hughes et al., 2013] [Gavrilescu et al., 2015]. These pollutants often enter waterways through bodily waste and the improper disposal of medications, making untreated or poorly treated wastewater a key source of OMPs in the environment [Ahmed et al., 2022; Burzio et al., 2022; Kumar et al., 2021; Luo et al., 2014; Yacouba et al., 2021]. To address this issue, new wastewater treatment methods, including membrane technology and AOPs, are being developed to efficiently eliminate these contaminants.

In the last decade, there has been a growing interest in using KrCl* excilamp generating far UV-C (222 nm) as a potential alternative for conventional O₃ and UV-based AOPs for the degradation of OMPs [Li et al., 2023b; Tsenter et al., 2022; Xu et al., 2023b]. The underlying principle relies upon the capability of this source to degrade pollutants under direct photolysis and in AOP [Xu et al., 2023b]. However, the time for the direct degradation of the micro-pollutants is relatively higher than that of KrCl*/AOP. DBD based NTP techniques are being merged with KrCl* excilamp in order to make the degrading process more chemical-free and environmentally benign. DBD based NTP can produce reactive oxygen and nitrogen species (RONS) such as O₃, H₂O₂, •OH, HO₂•, O₂•, ¹O₂, NO₂⁻, and NO₃⁻ during the electrical discharges [Jangra et al., 2023b] [Rathore et al., 2024]. DBD has emerged as a promising method for degrading hard-to-break organic materials, such as phenolic chemicals, insecticides, medications, and antibiotics. However, the low oxidation potentials of particular RONS are the main technical constraints related to DBD applications. Also, because there is little transfer of species created by plasma into the liquid phase, the established NTP techniques are inefficient and have a comparatively high energy cost. Also, the leftover concentration of NO₃⁻ after the degradation process, if it exceeds 50 ppm, it is classified as a pollutant.

In this chapter, we have performed a comparative study of the degradation of Carbamazepine (CBZ) and Sulfamethoxazole (SMX) through a system of DBD Plasma, KrCl* excilamp (far UV-C; 222 nm), LPUV (UV-C; 254 nm), and in the different combinations of these. The selection of CBZ and SMX as model pollutants is based on their distinct molar absorption coefficients and reaction rates at wavelengths of 222 nm and 254 nm. The concentration of the •OH, H₂O₂, NO₃⁻, and NO₂⁻ have been measured and correlated with the degradation profile. The kinetics of the degradation have been analyzed, and it is found that the faster degradation has occurred in the case of the DBD Plasma + KrCl* excilamp in TW. The E_{EO} for each method has been calculated and compared to the known most electrically effective method. Analysis has been done on experimental data pertaining to the energy costs and removal efficiency of these different approaches. The outcomes are also compared with information found in literature to give a general picture of the effectiveness of AOPs in converting micro-pollutants. Using HR-MS analysis, a possible mechanism underpinning the degradation of SMX and CBZ as well as their individual degradation processes have been discussed.

6.2 Selection of Micro-pollutants

Two environmentally significant micro-pollutants, CBZ and SMX, were selected for this study based on their frequent detection in wastewater treatment plant effluents and possible harmful impacts on the aquatic ecosystem [Feijoo et al., 2023] [Peixoto et al., 2022]. In addition, CBZ and SMX were selected because of their unique photochemical and physicochemical properties at 222 nm and 254 nm. These pollutants exhibit significant variations in their molar absorption coefficients (ϵ) at 222 nm and 254 nm, as depicted in Figure 6.1. The molar absorption coefficient of CBZ at 222 nm is 22182 $\text{M}^{-1} \text{cm}^{-1}$, whereas it decreases to 5327 $\text{M}^{-1} \text{cm}^{-1}$ at 254 nm. That means CBZ will degrade four times faster under 222 nm direct photolysis compared to 254 nm. In the case of SMX, the molar absorption coefficient at 222 nm is 8200 $\text{M}^{-1} \text{cm}^{-1}$, and at 254 nm it is found as 14468 $\text{M}^{-1} \text{cm}^{-1}$. That means SMX will degrade 1.8 times faster under 254 nm compared to 222 nm. So, the differences in absorbance and reactivity towards KrCl^* excilamp (222 nm), LPUV (254 nm), $\bullet\text{OH}$, NO_3^- and H_2O_2 are particularly important for identifying and explaining the potential role in decomposition efficiency among the selected micro-pollutants.

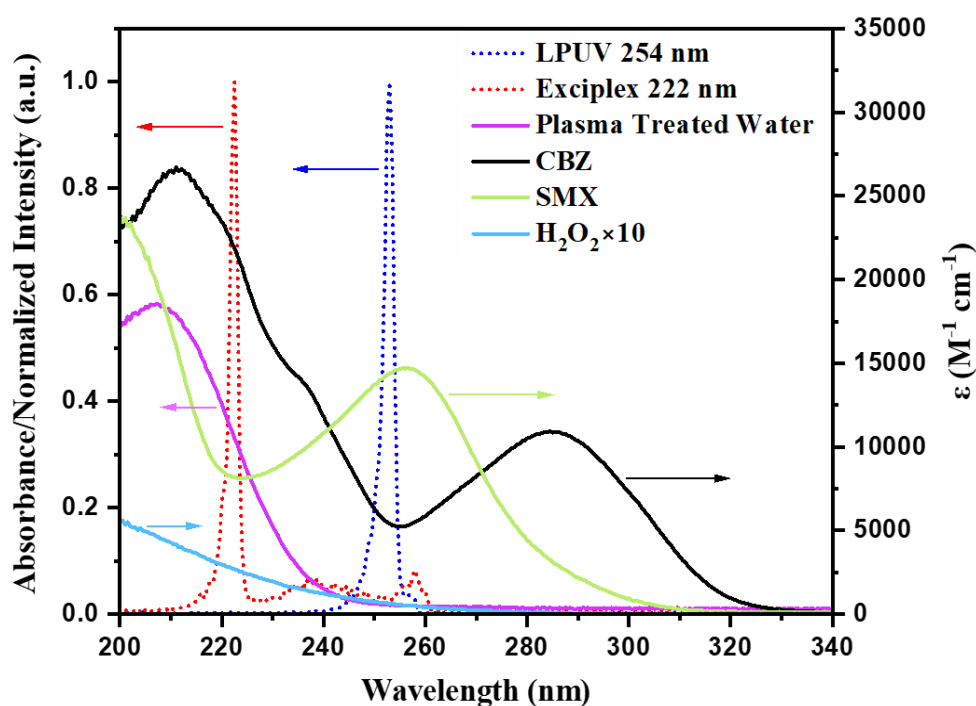


Figure 6.1: Molar absorption spectra of CBZ, SMX, and $\text{H}_2\text{O}_2 \times 10$ and UV-vis absorption spectra of plasma treated water (PTW) along with emission spectra of far UV-C 222 nm excilamp and LPUV source.

6.3 Reagents and Test Waters

Analytical grade SMX and CBZ were purchased from Sigma-Aldrich and used without further purification. All stock solutions for SMX, CBZ, H_2O_2 , and plasma-treated water (PTW) were prepared in lab-grade DIW and TW. The characteristics of the water matrix are listed in Table 6.1. Different-sized quartz plates were purchased from Kedar Scientific (Mumbai, India). H_2O_2 (30% w/v) was purchased from Sigma Aldrich. Research grade Krypton balanced with 1% Chlorine (99.99%) was procured from Alchemie Gases and Chemicals Pvt Ltd, India. Argon gas (99.999%) was procured from Scientific and General Agencies, India. SMX ($\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3\text{S}$), Carbamazepine ($\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$), and Isopropanol (IPA, $\text{C}_3\text{H}_8\text{O}$) were purchased from Sigma Aldrich. All of the stock solutions were prepared with DIW and TW. A conventional LPUV lamp was purchased from Phillips, India. Mercury-free planner far UV-C KrCl^* (222 nm) excilamp was developed using standard laboratory practices.

Table 6.1: Characteristics of DIW and TW were used in this study.

Water matrix	Temperature (°C)	pH	Conductivity (μS/cm)	TDS (ppm)	H ₂ O ₂ (mg/L)	NO ₃ ⁻ (mg/L)
TW	25	5.63	304	114	0	5.7
DIW	25	6.91	3	1	0	0

6.4 Plasma and UV Exposure Experiments

A DDBD based NTP device has been developed and used for the degradation of CBZ and SMX in different water matrices. As a source of far UV-C at 222 nm a DBD-based planar KrCl* excilamp has been developed and used for the degradation process. A 40 W (Philips) low-pressure conventional mercury lamp (LPUV) emitting 254 nm has also been used to compare the results. The schematic and original view for the DBD-based KrCl* excilamp and DDBD plasma source is shown in Figure 6.2 (a) and (b), respectively. The details about the development of both the sources is already discussed in Chapter 2.

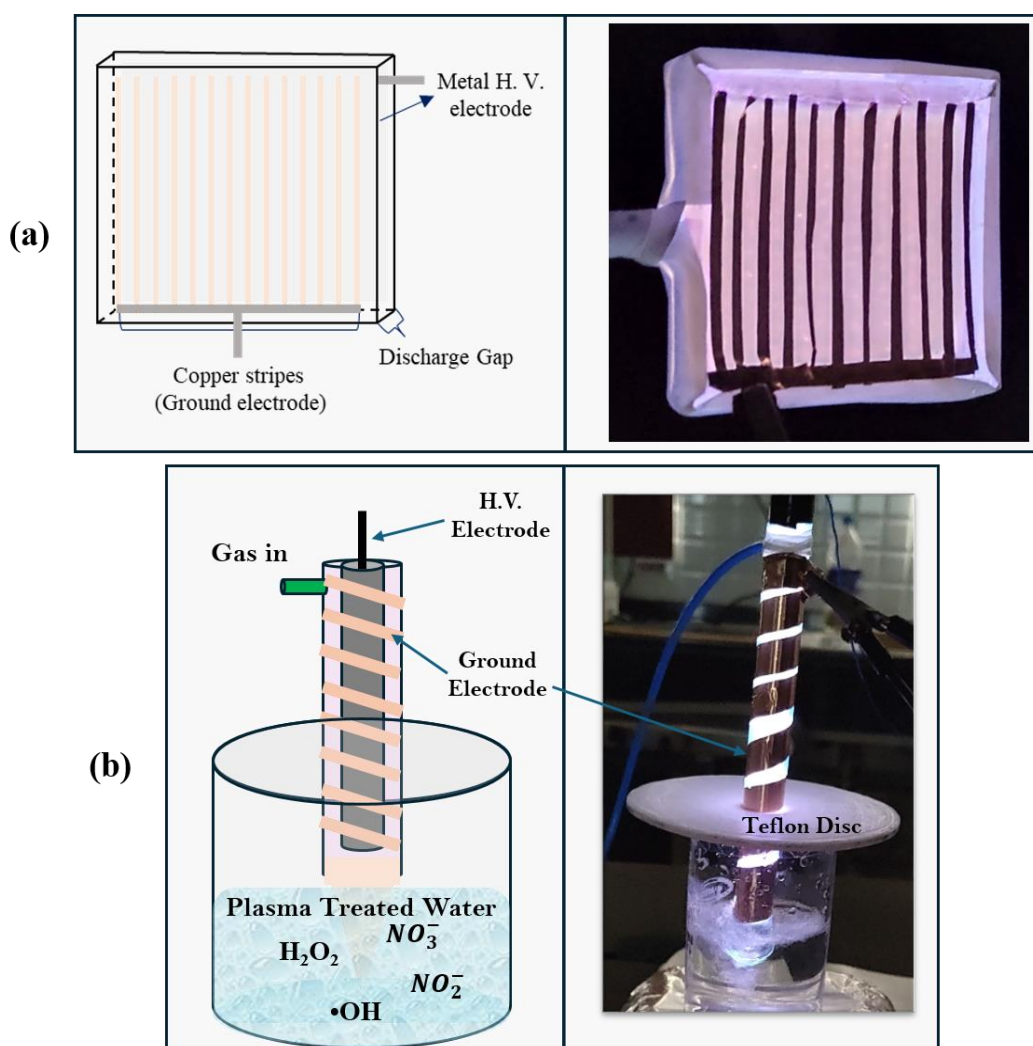


Figure 6.2: Schematic and original view of (a) Planar KrCl* excilamp (b) DDBD Plasma reactor.

Experimental Setup for the OMPs Degradation under DDBD Plasma and Planar KrCl* excilamp is discussed in section 2.8.2. The degradation studies are carried out using a single-step process for plasma, LPUV and KrCl* excilamp and a two-step process for coupling plasma with LPUV and KrCl* excilamp. The results are divided into four distinct categories for wastewater treatment as,

1. Using DDBD plasma to generate reactive species in DIW and TW, as well as characterizing them and their effects on the breakdown of various micro-pollutants.
2. Using UV light in DIW and TW at wavelengths of 222 nm and 254 nm to observe how various micro-pollutants degrade under direct photolysis.
3. Employing DDBD plasma pretreatment followed by LPUV or KrCl* excilamp treatment in DIW and TW.
4. Quantification of the amount of •OH produced by combining the two procedures and its effect on the various micro-pollutants' degradation.

6.5 Electrical Characteristics of DDBD Reactor and KrCl* Excilamp

The developed DDBD plasma source and KrCl* excilamp were powered using a bipolar pulsed power source. The V-I characteristics has been used to calculate the energy consumed and power consumed during plasma discharge using the following equations:

$$\text{Energy Dissipated, } E = \int_0^T v(t) \cdot i(t) dt \quad (6.1)$$

$$\text{Power Dissipated, } P = E \cdot f \quad (6.2)$$

Where $v(t)$ is the applied voltage, $i(t)$ is the discharge current, T is the time period, and f is the frequency (25 kHz for the DDBD reactor and 20 kHz for KrCl* excilamp). The power dissipated into the electrical discharge is obtained at nearly 15.44 W (at an optimized parameter of 5 kV/25 kHz) and 17.16 W (at an optimized parameter of 8 kV/20 kHz) for DDBD reactor and KrCl* excilamp, respectively.

6.6 Optical Emission Spectroscopy and Absolute Intensity Measurements

6.6.1 Optical Emission Spectra (OES) of DDBD Plasma

A strong electric field is produced in the space between the dielectric and the electrode due to space charge building over the dielectric surface as the applied voltage increases. N₂ emission band peaks dominate the air spectra during DDBD plasma creation because stray electrons accelerate and accumulate enough energy to disintegrate or ionise the molecules or atoms in the air, as illustrated in Figure 6.3. To understand the excitation behaviour of different molecules and for the characterization of the plasma, the emission spectra of the DDBD plasma source has been recorded. The air DDBD plasma process will produce excited state atoms, crucial intermediates for producing reactive species in an aqueous solution. Figure 6.3 displays the OES of argon plasma in the range of 200 – 900 nm. In the ultraviolet or visible region, the different excited states of the nitrogen [N₂(C-B)] can be visualised from the spectrum. The obtained spectra mainly display prominent emission band peaks for the electronic transition of the nitrogen second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) system from a high-energy vibrational band to a low-energy vibrational band along with weak intensity emission bands of the N₂⁺ first negative system ($C^3\Sigma_u^+ \rightarrow B^3\Sigma_g^+$). The prominent peak at 309 nm illustrates the OH (A-X) generated during

plasma formation [Laux et al., 2003]. Different excited argon atomic lines are observable in the visible and infrared between 670 and 850 nm.

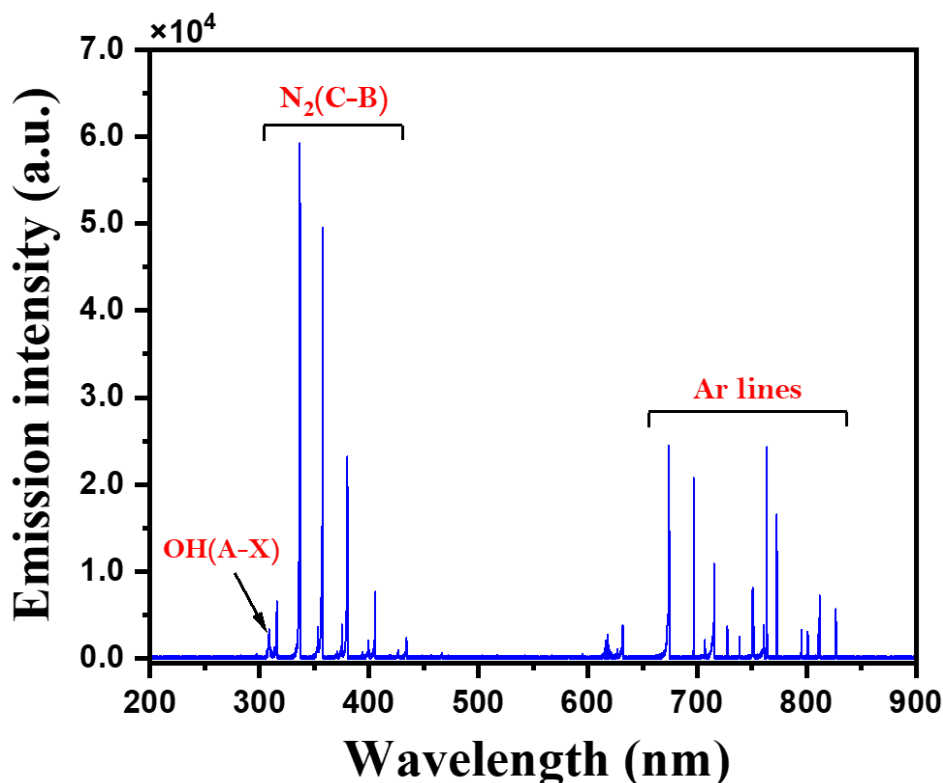


Figure 6.3: Emission spectrum of the argon DDBD plasma.

6.6.2 OES Spectra of KrCl* Excilamp and Absolute Irradiation Intensity:

The OES of developed KrCl* 222 nm excilamp is shown in Figure 6.4 (a). Figure 6.4 (a) shows several weak transition bands at 235 nm (B-A transition for KrCl*) and 240 nm (C-A transition for KrCl*), in addition to a strong 222 nm spectral band corresponding to the B-X transition for KrCl*. These weak bands contribute to the breakdown of contaminants by increasing the production of active radicals in addition to the 222 nm spectral band. Because of its narrow and intense band at 222 nm, which is considered highly advantageous, we observed a narrow band with FWHM of 1.95 nm at reduced gas pressure (150 mbar) with minimal lamp heating. The absolute intensity of the excimer 222 nm has also been measured, and a maximum of 1.15 mJ/cm² has been reported. The intensity increases linearly with increasing input voltage up to a certain value (1.05 mJ/cm²). Still, at higher voltages, it becomes saturated due to the power dissipated in heating other than the discharge, as shown in Figure 6.4 (b). Therefore, for further experimentation, Far UV-C excilamp has been operated at 8 kV and 20 kHz of the frequency throughout the experiments and the value of the intensity used is 1050 μ W/cm².

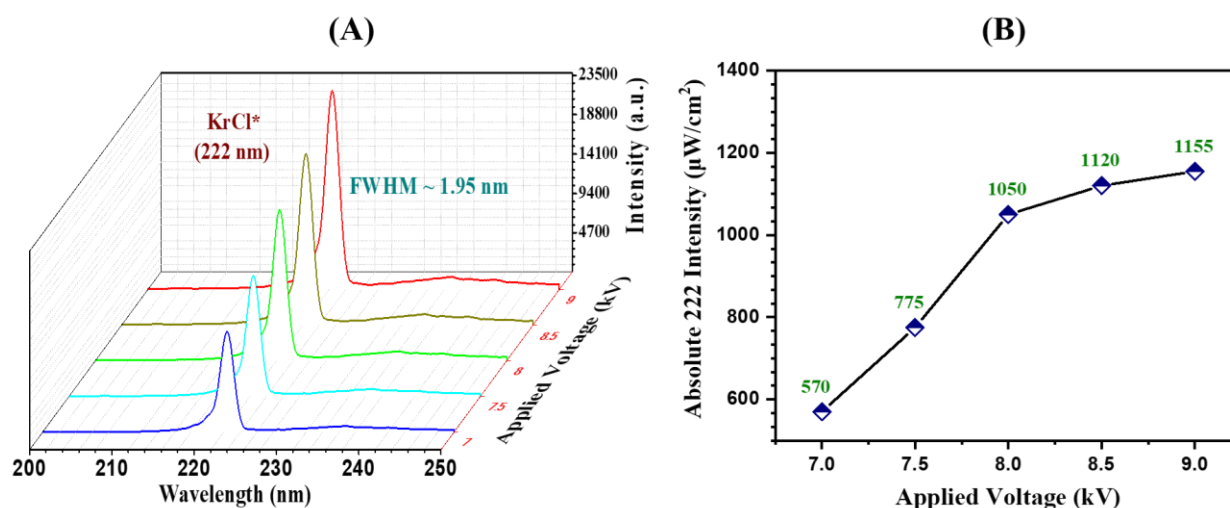


Figure 6.4: (a) Emission spectra of the KrCl* 222 nm excilamp at a gas pressure of 150 mbar and different applied voltages and (b) absolute intensity of the KrCl* 222 nm excilamp at different applied parameters.

6.7 Measurement of Reactive Species in DIW and TW and their Roles in Degradation Process

6.7.1 Hydroxyl Radical via Terephthalate Probe

$\bullet\text{OH}$ is a strong oxidizing reactive species that plays a vital role in the degradation of various micro-pollutants. According to earlier research, $\bullet\text{OH}$ could also efficiently break down SMX and CBZ in an aqueous solution [Amina et al., 2018; Xiao et al., 2020; Zhang et al., 2022a]. To quantify the concentration of $\bullet\text{OH}$ captured in the different aqueous solutions, fluorescence spectra for various treatment durations have been recorded as shown in Figure 6.5 and then compared with the standard fluorescence curve of HTA.

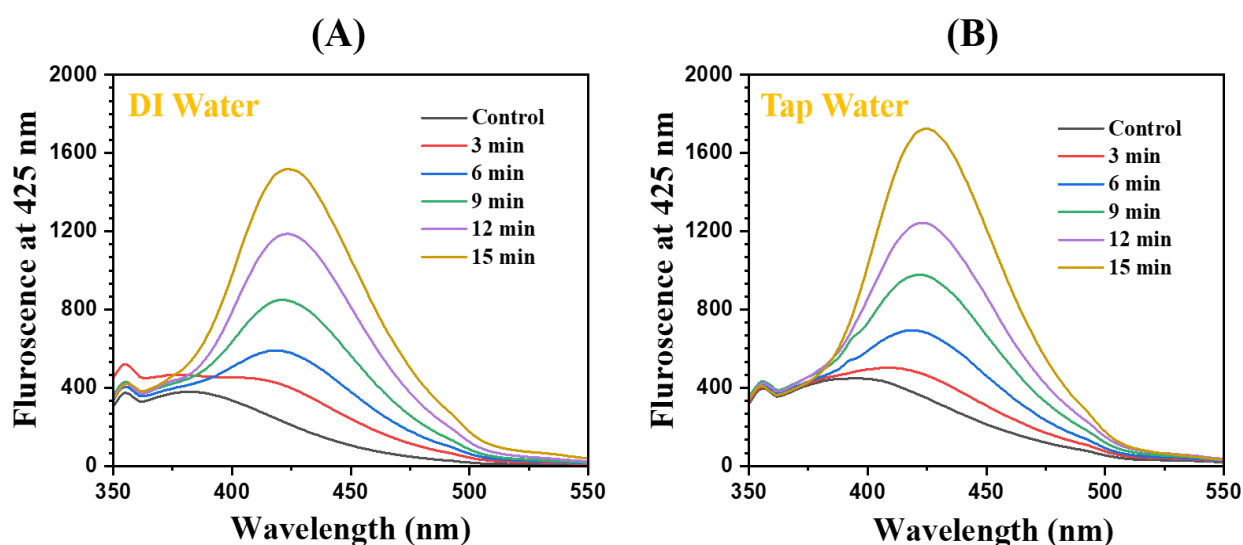


Figure 6.5: Fluorescence spectra of TA in (a) DI water and (b) after treatment with DDBD plasma source.

As illustrated in Figure 6.6 (a), the concentration of $\bullet\text{OH}$ in aqueous solution reaches $20 \mu\text{M}$ after 3 min of DDBD plasma treatment in DIW and TW and increases continuously as the treatment time progresses. In addition to directly producing $\bullet\text{OH}$ by electron dissociation (equation 6.3), water molecules can also be triggered and ionised to produce H_2O^+ , which is then

reacted with other molecules to produce H_3O^+ and $\bullet OH$ (equations 6.4 and 6.5) [Zhang et al., 2017].



The concentration of $\bullet OH$ increases with increasing plasma exposure time in both types of water matrix, but the rate of production of the $\bullet OH$ is higher in TW ($8.24 \times 10^{-8} \text{ M s}^{-1}$) as compared to DIW ($7.91 \times 10^{-8} \text{ M s}^{-1}$). This is due to the fact that the presence of dissolved minerals, such as salts and metal ions, in TW can serve as catalysts for the production of $\bullet OH$ during plasma treatment [Canal et al., 2021]. The above-mentioned concentration of $\bullet OH$ were measured in the DIW or TW, while it dropped to almost zero when measured in the presence of SMX or CBZ. This is because SMX and CBZ have a distinct advantage over TA in the competition for $\bullet OH$ in spiked water. As a result, there is minimal interaction between TA and $\bullet OH$, which is why we did not find any HTA when SMX and CBZ were present.

6.7.2 Hydrogen Peroxide

Figure 6.6 (b) shows that the concentration of H_2O_2 in the DIW and TW is gradually increased with increasing the plasma exposure time and reaches 1.2 mg/L after 15 min of the plasma exposure. Aqueous H_2O_2 is generated by the combination reaction of the aqueous phase $\bullet OH$ (equation 6.6) [Zhang et al., 2017], as well as the penetration of gaseous H_2O_2 has the potential to be the source of aqueous H_2O_2 (equation 6.9). However, no $\bullet OH$ were detected in the treated solution in the presence of SMX and CBZ. At that point, no H_2O_2 should be correspondingly present in the aqueous solution, according to equation 10. The concentration of H_2O_2 in the SMX and CBZ solution gradually increased with the discharge time and reached ~ 1 g/L after 15 min of plasma exposure. Therefore, the combination of aqueous $\bullet OH$ is not only a major source of aqueous H_2O_2 ; rather, the dissolution of gaseous H_2O_2 (equation 6.9) may play a regnant role in the production of aqueous H_2O_2 , as supported by Chen et al. [Chen et al., 2019]. The main reactions involved in the generation of H_2O_2 in the gas and aqueous phase are as follows [Zhang et al., 2017] [Van Gils et al., 2013]:



In contrast to $\bullet OH$, the concentration of H_2O_2 reduces relatively little when SMX and CBZ are present in the aqueous solution, suggesting that the aqueous H_2O_2 has no discernible impact on the degradation of SMX and CBZ. But the above results demonstrate the crucial role of $\bullet OH$ in the degradation of SMX and CBZ. The role of H_2O_2 in aqueous solution generated by the DDBD plasma is not significant. However, the photolysis of aqueous H_2O_2 (via 222 nm KrCl* excilamp) can generate $\bullet OH$ in the aqueous solution. Hu et al. [Hu et al., 2023] perform the degradation of SMX using oxygen plasma and reported that the aqueous phase $\bullet OH$ is the main cause of the degradation. However, H_2O_2 in the aqueous phase plays a negligible role in the degradation of

SMX. To sum up, the leftover concentration of H_2O_2 can be used for the faster degradation of SMX and CBZ via photolysis of H_2O_2 using 222 nm UV-C light to generate $\bullet OH$.

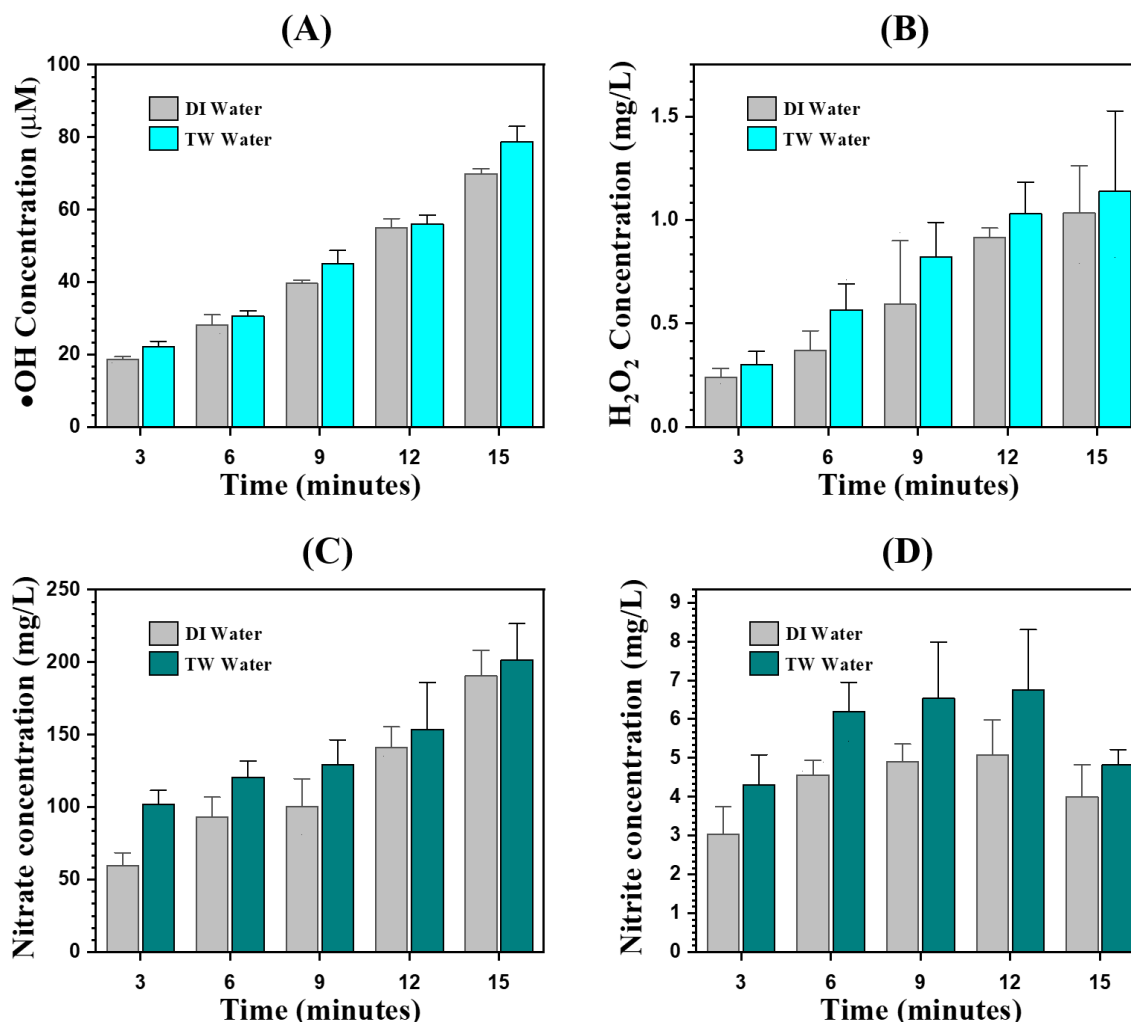
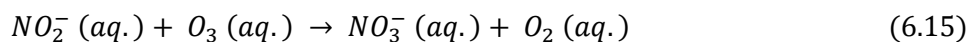
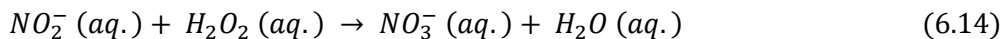
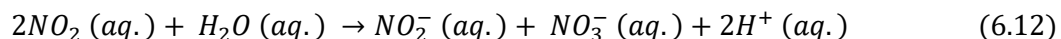


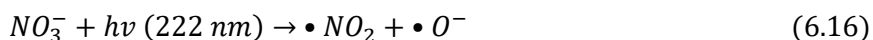
Figure 6.6: Reactive species generated by DDBD plasma reactor. (a) Concentration of $\bullet OH$ in DIW and TW, (b) Concentration of H_2O_2 in DIW and TW, (c) Concentration of NO_3^- in DIW and TW, and (d) Concentration of NO_2^- in DIW and TW after DDBD plasma treatment over different exposure times.

6.7.3 Nitrites and Nitrates

Along with reactive oxygen species (ROS), the DDBD plasma also generates reactive nitrogen species (RNS), especially NO_2^- and NO_3^- , in the aqueous medium. The concentration of NO_2^- and NO_3^- has been detected using spectrophotometry, and their concentration increased with respect to plasma exposure time. Equation 6.11 states that NO is created when N_2 in the gaseous medium reacts with primary oxygen species. The electron produced by the plasma process has the ability to dissociate N_2 to form atomic nitrogen in addition to atomic oxygen. The detailed reaction mechanism involved in the formation of NOx is also explained by Rayaroth et al. [P Rayaroth et al., 2024]. The formation of RNS during the DDBD plasma process is evidenced by the NO_2^- and NO_3^- generated and shown in Figure 6.6 (c) and (d). The concentration of NO_2^- and NO_3^- increased with time in both types of water matrix, and SMX and CBZ spiked solutions. The maximum concentration of NO_3^- (201 mg/L) has been recorded after 15 min of treatment, whereas the NO_2^- (5.9 mg/L) concentration reached maximum after 9 min and started decreasing at further treatment. This is because, after a certain time interval, NO_2^- starts converting into NO_3^- after reacting with H_2O_2 and O_3 (equation 6.14 and 6.15).



Rayaroth et al. [P Rayaroth et al., 2024] performed the degradation of CBZ in ultrapure water. They reported that the concentration of NO_2^- decreased when the solution was spiked with CBZ and treated with the plasma, whereas the concentration of NO_3^- increased in the presence of the CBZ. A similar pattern is observed in this study, and we found that the concentration of NO_2^- is almost identical when SMX and CBZ are spiked in DIW and TW. However, the concentration of NO_3^- increases up to twofold, indicating that the nitrogen in the SMX/CBZ and their intermediate products are oxidized to release NO_2^- ions. On the other hand, NO_3^- is not involved in the product formation or in the degradation process. Therefore, this residual concentration of NO_3^- can be utilized to produce $\bullet OH$ under photolysis ($\lambda < 240$ nm) via equation 6.16 and 6.17, which can improve the overall efficiency of the process.



It is to be emphasized that the Photolysis of H_2O_2 and NO_3^- takes place in the presence of far UV-C light, which is why the wavelength 222 nm was chosen. Due to the prolonged degradation time of CBZ and SMX when exposed to plasma, we have employed DBD plasma to generate a pool of reactive species, specifically H_2O_2 and NO_3^- . These reactive species are then used as a radical promoter under 222 nm KrCl* excilamp.

6.7.4 Hydroxyl Radicals from PTW and Far UV-C Light

An in-house developed planar 222 nm KrCl* excilamp is utilized for the photolysis of H_2O_2 and NO_3^- in an aqueous solution. Because of higher molar absorption coefficients of H_2O_2 at 222 nm ($274.19\text{ M}^{-1}\text{ cm}^{-1}$) compared to 254 nm ($67.51\text{ M}^{-1}\text{ cm}^{-1}$), the rate of production of $\bullet OH$ is found higher in the case of far UV-C light (see Figure 6.1). Enhanced generation of $\bullet OH$ from the DDBD plasma produced H_2O_2 ($\sim 1 - 1.5\text{ mg/L}$) is observed in the KrCl* system compared to LPUV in both water matrices, i.e., DIW and TW. This is one of the benefits of employing a DDBD plasma reactor in conjunction with far UV-C radiation. On the other hand, the presence of NO_3^- in the PTW provides an additional advantage because in a recent study by Wu et al. [Wu et al., 2020], it was reported that NO_3^- can be used as a source of $\bullet OH$ and RNS in photochemical AOPs, adding to the radicals generated by the UV-AOPs for OMPs oxidation. When a similar concentration of H_2O_2 and NO_3^- were added to the DIW and TW separately, it was found that the rate of production of $\bullet OH$ in the presence of H_2O_2 and NO_3^- (DDBD produced) was significantly higher. As can be seen from Figure 6.7, the concentration and rate of production of $\bullet OH$ measured in DIW for plasma + KrCl* excilamp ($46.7 \times 10^{-8}\text{ M s}^{-1}$) is higher as compared to plasma + LPUV ($32.2 \times 10^{-8}\text{ M s}^{-1}$) and plasma alone ($8.24 \times 10^{-8}\text{ M s}^{-1}$). The main reason for the lower production of $\bullet OH$ in the case of LPUV is that NO_3^- does not absorb appreciably at 254 nm. However, NO_2^- and NO_3^- are absorbed very strongly at shorter wavelengths, i.e., below 240 nm [Payne et al., 2022] [Vinge et al., 2020]. Therefore, an in-house developed KrCl* 222 nm excilamp is used for the OMP degradation in the present investigation instead of an LPUV lamp.

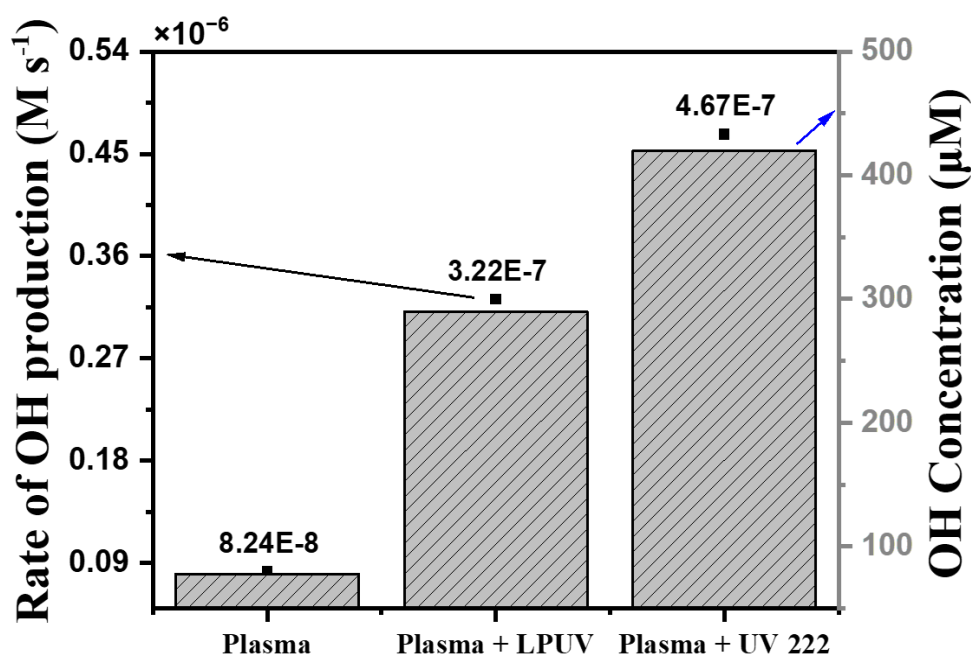


Figure 6.7: $\bullet\text{OH}$ concentration and their rate of production under Plasma, Plasma + LPUV, and Plasma + UV 222.

6.8 Role of RONS on the Degradation of CBZ and SMX

It can be visualized from Figure 6.1 that the water treated using DDBD plasma absorbs more photons of 222 nm light than 254 nm light. Payne et al. [Payne et al., 2022] conducted a comparative analysis of $\bullet\text{OH}$ generation in various AOPs such as 222 nm/ NO_3^- , 222 nm/ H_2O_2 and 254 nm/ H_2O_2 . They observed that the 222nm/ NO_3^- system generated the highest amount of $\bullet\text{OH}$ in the water matrix, surpassing the 222 nm/ H_2O_2 and 254 nm/ H_2O_2 systems. The present study investigates the degradation of SMX and CBZ using five distinct treatment methods i.e., Plasma, LPUV, KrCl* excilamp, Plasma + LPUV, and Plasma + KrCl* excilamp. To gain insight into the practicability, the degradation process is conducted by utilizing two different water matrices, namely DIW and TW. Firstly, the aqueous solution of SMX and CBZ in DIW is treated using DDBD plasma, and only ~ 11.2 % degradation of CBZ takes place after 15 min of plasma treatment. In contrast, the degradation of CBZ in TW (real water matrix) decreases further up ~ 6.5 % due to the presence of different ions in the TW and their competition with the plasma-generated reactive species. But in the case of SMX, 15 min of plasma treatment shows ~ 30 % degradation in DIW, which decreases to ~ 23 % when the treatment is performed in TW, as shown in Figure 6.8. Rayaroath et al. [P Rayaroath et al., 2024] also reported comparable findings, as they observed a degradation rate of more than 90 % for CBZ in pure water, whereas the degradation rate decreased to 83 % when subjected to TW during a treatment time of 40 min.

In the case of only LPUV treatment for 15 min, the degradation performance for CBZ was much poorer and only 4.75 % degraded in TW, whereas in DIW, it decreased further to ~ 3.4 %. The main reason behind this degradation behaviour would be the lowest molar absorption coefficient of CBZ at 254 nm (see Figure 6.1). In contrast, due to the higher molar absorption coefficients of SMX at 254 nm, LPUV shows exceptional performance in the degradation of SMX, and ~ 57 % of SMX degradation takes place in the case of DIW in just 15 min of treatment (see Figure 6.8). Further, the degradation of SMX accelerates in the TW under LPUV due to the presence of NO_3^- and other ions and reaches up to ~ 63.7 %. In contrast, CBZ shows a higher molar absorption coefficient at 222 nm, therefore; it degrades faster under direct photolysis of 222 nm KrCl* excilamp (~ 34.7 %) in DIW and also due to higher absorption of NO_3^- at 222 nm, the degradation of CBZ becomes higher (~ 42.7 %) in the case of the TW matrix. Liu et al. [Liu et al., 2023b] also found that CBZ degraded faster in the secondary effluents than ultrapure water. In

the case of SMX, the 222 nm light is less effective as compared to LPUV and degraded only ~ 25 % pollutant in 15 min of the treatment, i.e., the degradation is approximately two-fold slower in DIW under 222 nm as compared to LPUV. However, due to the tendency of 222 nm to form more $\bullet\text{OH}$ in the presence of NO_3^- , the degradation in TW is higher and reaches ~ 60%, approximately equal to the LPUV treatment under TW. The LPUV or KrCl^* excilamp (222 nm) has been integrated with the DDBD plasma to improve degrading efficiency and shorten treatment time. The degradation of CBZ and SMX by the combination of plasma and KrCl^* excilamp is remarkable; in the case of DIW, the full degradation of CBZ and SMX required just 15 min and 10 min, respectively. Additionally, the rate of degradation accelerated in the case of TW, and it only took 12 min and 8 min for CBZ and SMX to completely degrade, which is perhaps due to the presence of more NO_3^- and reactive species (see Figure 6.8).

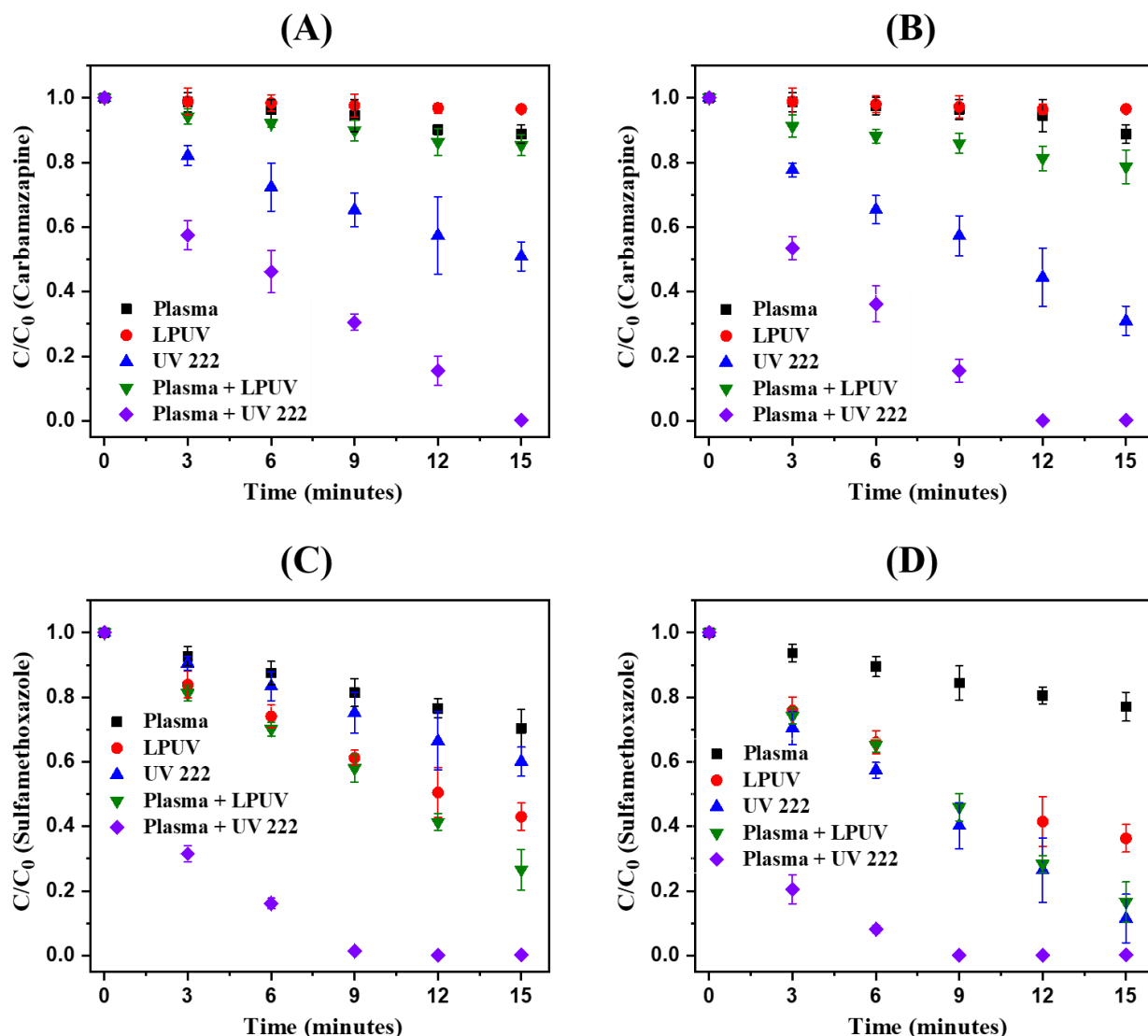


Figure 6.8: Degradation profiles of CBZ in (a) DIW; (b) TW and degradation profiles of SMX in (c) DIW; (d) TW in the case of Plasma, LPUV, UV 222, Plasma + LPUV, and Plasma + UV 222 ($C_0 = 10$ mg/L, UV Intensity = $1050 \mu\text{W}/\text{cm}^2$ and pH 6-7).

UV/ H_2O_2 based AOPs are currently being used for the treatment of wastewater. Still, the problem lies in adding H_2O_2 externally and then the extraction/removal of residual H_2O_2 after wastewater treatment, which is the biggest problem [Deng et al., 2015] [Bokhari et al., 2020]. This study addressed the first problem by integrating the DDBD plasma with KrCl^* excilamp. The H_2O_2 produced by the DDBD plasma in this hybrid system is within the bounds established by global regulatory bodies. Thus, the external addition of H_2O_2 to the reactor is eliminated by this

method. Furthermore, because H_2O_2 has a low molar absorption coefficient at 254 nm, LPUV can only photolyzed a small fraction of H_2O_2 into $\bullet\text{OH}$. We have utilized a far UV-C source (222 nm) to target this issue because H_2O_2 have high molar absorption coefficient at 222 nm, which has allowed to convert H_2O_2 into $\bullet\text{OH}$. Thus, the use of a 222 nm source also solves the second issue of residual H_2O_2 . This combination also offers an added benefit, as long-lived plasma species like NO_3^- have a greater ability to absorb 222 nm photons compared to 254 nm photons. This enhances the feasibility and chemical-free nature of the aforementioned process, which can also be referred to as green AOP. Figure 6.9 displays the decomposition rate at which CBZ and SMX degrade when subjected to various treatment processes for a duration of 15 min.

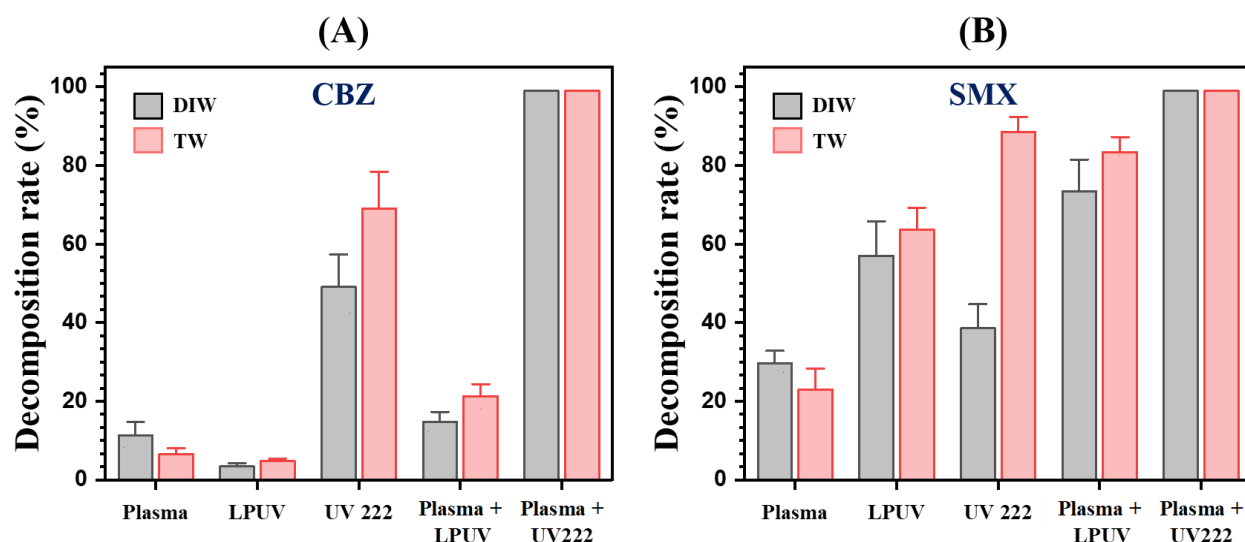


Figure 6.9: Degradation rate of (a) CBZ and (b) SMX using different methods for 15 min of treatment.

Figure 6.10 shows that the k values of SMX and CBZ have supported their respective degradation trends. All treatment methods follow pseudo-first-order kinetics model, with the Plasma + KrCl^* excilamp method exhibiting the greatest k value (0.341). When utilizing plasma + KrCl^* excilamp in DIW, the rate of CBZ degradation is thirty times faster than using plasma alone. Moreover, it is a remarkably 114 times faster than using LPUV alone and ten times faster when utilizing KrCl^* excilamp alone. In the case of SMX in DIW, the degradation rate is 15 times faster under Plasma + KrCl^* excilamp than using only plasma. Comparing the degradation to LPUV, however, it is just six times quicker. It is clear that the rate of SMX degradation is 1.3 times higher than the rate of CBZ degradation in the DIW by comparing the k values of the pollutants in the Plasma + KrCl^* excilamp. On the other hand, both micro-pollutants exhibit the same degrading behaviour in the TW.

The degradation process is significantly aided by the use of plasma with far UV-C radiation. This is primarily because nearly all the plasma-produced species have a higher absorption of 222 nm light, as illustrated in Figure 6.1. The generation of NO_3^- and H_2O_2 by plasma is of significant importance in the breakdown process of both micro-pollutants. The results demonstrate that the complete degradation time varies significantly across different methods, owing to the distinct properties of the micro-pollutants. But the complete degradation time for the Plasma + KrCl^* excilamp exhibits a substantial disparity compared to other treatment methods for both pollutants. The approach employed in this study has the advantage of keeping the plasma/Far UV-C devices out of contact with the wastewater, which prevents it from soiling unwanted microorganisms and prolongs their lifespan. This procedure is also environmentally friendly because no additional external chemicals are being used as a catalyst or radical promoter. Further research is required, to test the system's effectiveness with other pollutants as well as on the mixture of the contaminants. Additionally, in order to determine whether the suggested

technology can be applied in industrial wastewater treatment plants, testing on actual industrial wastewater is required.

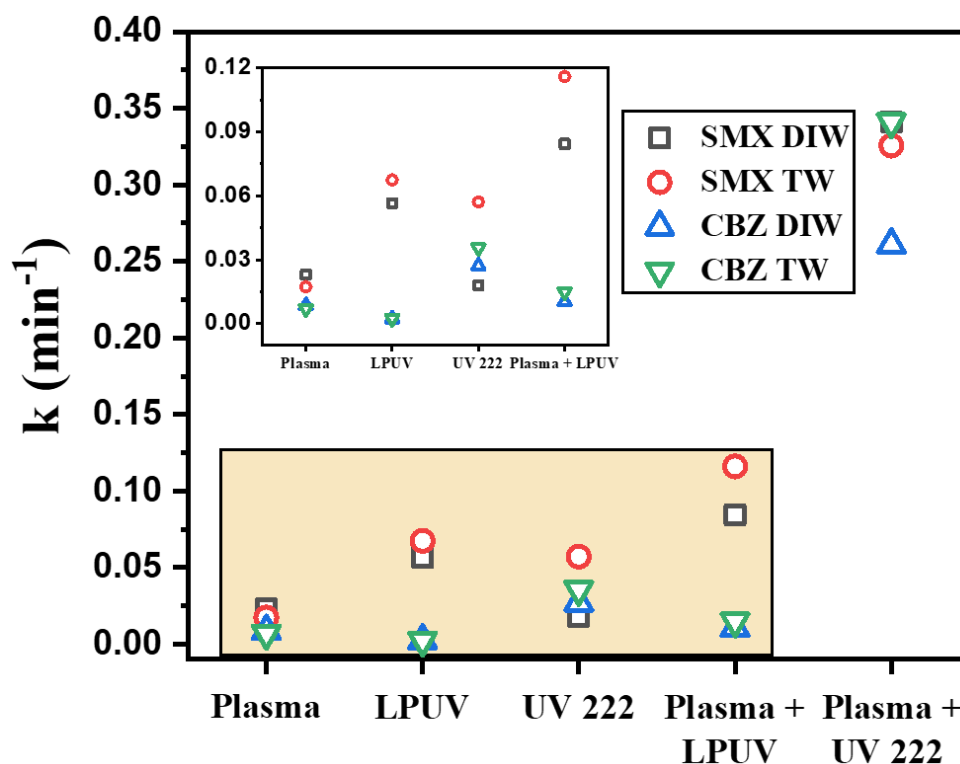


Figure 6.10: Respective k values for the different methods in the DIW and TW for the degradation of SMX and CBZ ($C_0 = 10$ mg/L, UV Intensity = $1050 \mu\text{W}/\text{cm}^2$ and pH 6-7).

A comparison of different reactors/processes for the degradation of SMX and CBZ is shown in Table 6.2. It demonstrates that, in comparison to other reactors and processes previously documented in the literature, the OMPs degradation time in plasma + KrCl* excilamp is significantly shorter.

Table 6.2: Comparison of different methods/reactors for the degradation of SMX and CBZ.

Sr. No.	Micro-pollutant	Conc.	Lamp/Light Intensity	pH	Deg. (%)	Time (min)	Catalyst	Ref.
1	SMX	1-10 mg/L (250 mL)	LED; low-pressure; 5W; $44\text{W}/\text{cm}^2$ at 1 cm; 550 nm	6	100	70	Mn-WO ₃	[Yazdanbakhsh et al., 2020]
2	SMX	10 mg/L (100 mL)	Visible light; 4W	5	98	480	AgNbO ₃	[Lu et al., 2022]
3	SMX	20 mg/L	DBD Plasma; 38.12W	5.4	98.48	4/20	-	[Hu et al., 2023]
4	SMX	50 mg/L (50 mL)	222 nm; 1.2 mW/cm ²	-	99	60	TiO ₂ /BDD	[Suzuki et al., 2022]

5	CBZ	100 µg/L	254 nm; 30W	-	99	55	TiO ₂	[Franz et al., 2020]
6	CBZ	1 ppm in 50 mL electrolytes	Electro-Fenton	-	99	40/180	Fe ₃ O ₄	[Liu et al., 2018]
7	CBZ	20 mg/L (40 mL)	DBD Plasma; 35.7 W	6.40	97.9	48/48	H ₂ O ₂ 0.1 mM	[Yu et al., 2022]
8	CBZ	5 mg/L (50 mL)	Visible light; 5.86 mW/cm ²	5-7	100	30	Ag ₃ PO ₄ /GO	[Chen et al., 2022a]
9	CBZ	10 mg/L (100 mL)	DDBD + Far UV-C (222 nm) 1.05 mW/cm ² ; 32.6 W	6-7	99.9	12	-	This Work
	SMX				99.9	8	-	

6.9 Electrical Energy per Order (E_{EO}) Comparison and Degradation Mechanism

Energy cost is often viewed as the most important parameter, along with degradation rate, when choosing the most efficient wastewater treatment method. The E_{EO} concept has been applied to assess the energy needs for eliminating each OMP through different procedures. The initial concentration of pollutants and the power consumed in each treatment method have been used to compute the E_{EO} values (equation 5.5) for SMX and CBZ degradation. Figure 6.11 shows the electrical energy required in the process of degrading SMX and CBZ by various treatment processes. The most electrically efficient approach for degrading SMX in DIW is LPUV, but in TW, it is KrCl* excilamp due to the increased production of •OH in the system. Plasma + KrCl* excilamp is the most electrically efficient approach for degrading CBZ in DIW, while KrCl* is the most energy-efficient approach in TW. Since the plasma process requires more power than some other processes, the E_{EO} of the Plasma + KrCl* excilamp process is slightly higher than only KrCl* excilamp. But, when considering the degradation of various micro-pollutants, the Plasma + KrCl* excilamp approach is the most stable and suitable due to its distinctive ability to produce higher quantities of •OH.

In general, plasma systems consume a significant amount of power. However, if it is possible to generate a large quantity of RONS in the treated water using plasma, even at a low power threshold, then the system could become more energy efficient. Therefore, more investigation is needed to create an NTP source that is more energy efficient. This research underscores the potential for making plasma systems more energy-efficient, offering hope for sustainable water treatment solutions.

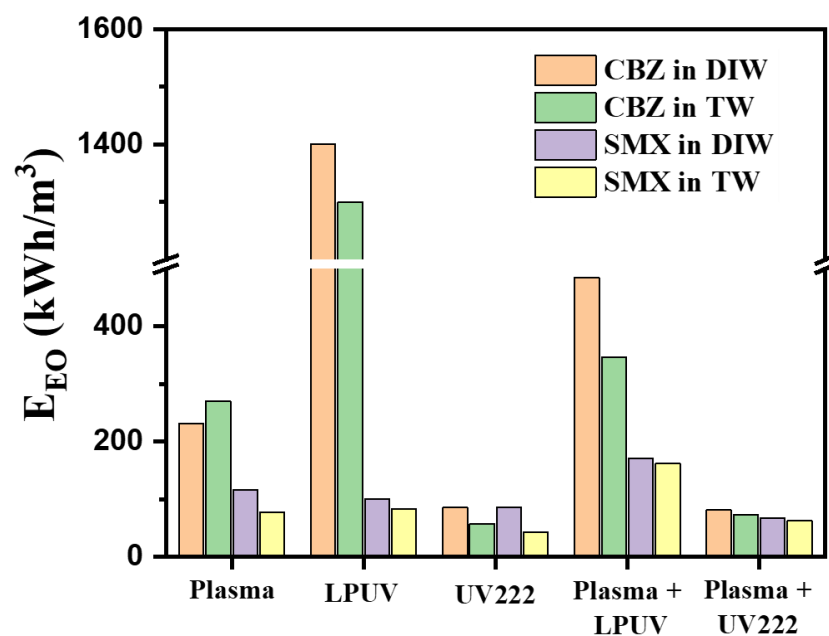


Figure 6.11: Electrical energy per order required in the process of degrading SMX and CBZ by various treatment processes.

The Plasma + KrCl* excilamp approach-based degradation studies of the SMX and CBZ in DI and TW are also confirmed by scavenging studies, as seen in Figure 6.12 (a). These studies examine the role of the reactive species, especially $\bullet\text{OH}$, in the Plasma + KrCl* excilamp-based degradation mechanism. This study uses Isopropanol (IPA) as a scavenger for $\bullet\text{OH}$. The experiments are carried out using the Plasma + KrCl* excilamp approach with and without a scavenger. It is found that adding IPA considerably reduces the rate of SMX and CBZ degradation. Without adding any scavengers, the degradation rate of SMX in a treatment time of 9 min is found to be 98.58% and 99.99% in DI and TW, respectively. However, with IPA as a scavenger, SMX exhibits only 11.51% and 29.51% degradation in DI and TW, respectively. A similar trend has been obtained in the case of CBZ, which degrades 69.52% and 84.52% in DI and TW, respectively, without a scavenger. In contrast, it degrades only 17.19% and 22.29% in DI and TW, respectively, when a scavenger is introduced. Therefore, this experiment shows that $\bullet\text{OH}$ are highly involved in the degradation mechanism of SMX and CBZ. Figure 6.12 (b) depicts the suggested reaction process for OMPs degradation under the plasma + KrCl* excilamp. We have investigated several ways to generate $\bullet\text{OH}$, such as the breakdown of plasma-produced NO_3^- and H_2O_2 when exposed to excimer 222 and the interaction of O_3 and/or KrCl* excilamp 222 nm light with the water molecules. This research underscores the need for further investigation into the potential of plasma coupling with far UV-C (222 nm) to develop a more efficient wastewater treatment process. We can aid in the development of more effective and long-lasting water treatment technologies by investigating and improving these approaches further.

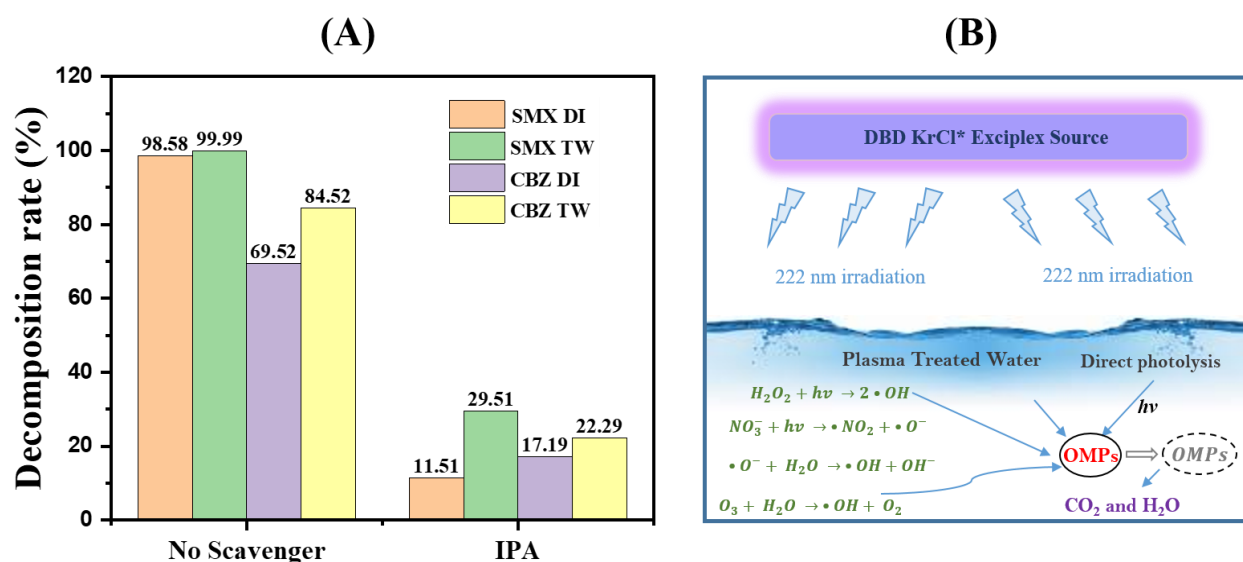


Figure 6.12: (a) Quenching studies of hydroxyl radicals during Plasma + UV 222 approach based degradation of CBZ and SMX in DI and TW, and (b) Proposed Plasma-UV₂₂₂ mediated degradation mechanism of OMPs.

6.10 Conclusion

This work shows the development and uses of a DBD-based KrCl* excilamp and a DDBD plasma reactor to degrade SMX and CBZ in an aqueous solution. The UV/H₂O₂ based AOPs are generally recommended for OMP degradation, however, these processes necessitate the addition of H₂O₂ to the water matrix. In our case, the plasma-produced long-lived species (NO_3^- and H₂O₂) are utilized under 222 nm KrCl* excilamp for the enhanced generation of $\cdot OH$, and consequently, faster degradation of the OMPs. This hybrid technique eliminates the burden of removal of residual H₂O₂ and hence can be termed as greener technique. The degradation of CBZ under DDBD plasma alone requires 210 min for 99.9% degradation, whereas KrCl* excilamp alone requires 40 min of treatment for the same level of degradation. Interestingly by coupling DDBD plasma with KrCl* excilamp, for the 99.9 % degradation of CBZ requires only 12 min of treatment.

In comparison to previous methods, the required E_{EO} for the OMP deterioration from this hybrid strategy is quite low (73.38 kWh/m³). When comparing the CBZ and SMX deterioration over time using this hybrid technique, we find that SMX requires 8 min of treatment to reach full degradation while CBZ requires 12 min. It's interesting to see that all other approaches take significantly longer to degrade two selected OMPs with differing physical properties. But this hybrid strategy is quite successful because it takes almost the same amount of time for both OMPs to degrade. Using HR-MS, the intermediate and byproducts are identified, and a degradation pathway has been suggested. Additional research is needed before this method can be used for treating actual wastewater that contains different types of OMPs.