Degradation of Carbamazepine and Sulfamethoxazole in Water by Dielectric Barrier Discharge Plasma Coupled with Far UV-C (222 nm) System

Kiran Ahlawat[1], Ramavtar Jangra[1], and Ram Prakash[1,*]

Department of Physics, Indian Institute of Technology Jodhpur, Rajasthan, India, 342037

*Author to whom correspondence should be addressed: ramprakash@iitj.ac.in

1.1 Materials

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. Sulfamethoxazole ($C_{10}H_{11}N_3O_3S$), Carbamazepine ($C_{15}H_{12}N_2O$), and Isopropanol (IPA, C_3H_8O) were purchased from Sigma Aldrich. All of the stock solutions were prepared deionized water and tap water. A conventional LPUV lamp was purchased from Phillips, India. Mercury-free planer far UV-C KrCl* (222 nm) excilamp was developed using standard laboratory practices.

Table S1. Physical properties of Sulfamethoxazole and Carbamazepine.

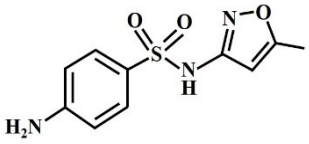
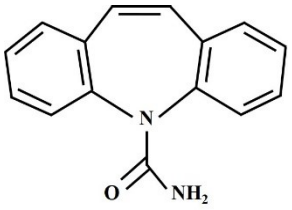
Compound name	Chemical structure	Formula	Molar mass (g mol-1)	Solubility (mg/L)
Sulfamethoxazole (SMX)		$C_{10}H_{11}N_3O_3S$	254.022	610
Carbamazepine (CBZ)		$C_{15}H_{12}N_2O$	236.27	112

Table S2. Characteristics of DIW and TW used in this study.

Water matrix	Temperature (° C)	pH	Conductivity (µS/cm)	TDS (ppm)	H_2O_2 (mg/l)	NO_3^- (mg/l)
TW	25	5.63	304	114	0	5.7
DIW	25	6.91	3	1	0	0

1.2 Development and Process of KrCl* excimer source

The fabrication of DBD based KrCl* excilamp consisted of multiple parts. Firstly, the gas gap was evacuated up to 1×10^{-5} mbar of base pressure by using a roughing vacuum pump and the turbo molecular pump. After evacuating, the vacuum system was flushed with Argon ten times in a controlled manner to decrease the impurities up to a relatively low level. The gas gap was again evacuated up to 2×10^{-6} mbar pressure and filled with a mixture of research-grade KrCl gas (99.99%) by using the needle valves. The Kr/Cl_2 gas pressure of 150 mbar was optimized in the experiment and finally, the excilamp was pinched for further experimentations. The complete experimental setup used for the fabrication of KrCl* excilamp is shown in **Fig. S1**.

The developed excimer source was operated by a bipolar pulsed power supply [1-10 kV, 5-40 kHz, 1 A, 2 μsec pulse width] at different power settings. For the visualization of voltage and current waveforms, a high voltage probe (Tektronix P6015A, 1000:1) and a Rogowski coil (Pearson 110, 0.1 V/A, 20 ns rise time) were connected to a four-channel mixed domain oscilloscope (Tektronix MDO3014, bandwidth 100 MHz, 2.5 GS/s). A calibrated thermocouple and IR camera were used to measure the temperature of the excimer source during experimentation.

The KrCl* excimer can be formed by two mechanisms:

1. Three-body ion-ion recombination reaction,

When the electric field is applied between the electrodes of DBD excilamp, the discharge of gases takes place below atmospheric pressure, triggering the generation of highly energetic electrons, which cause the ionization and excitation of krypton and chlorine molecules. The cations of krypton and anions of chlorine get involved in a three-body recombination reaction with an atom/molecule of active species or buffer gas (M) and form the excimer (KrCl*) as,

$$Kr^{+} + Cl^{-} + M \rightarrow KrCl^{*} + M \quad (R1)$$

2. A harpoon reaction, i.e., a two-body reaction.

An excimer can also be formed by a harpooning reaction in which the excited krypton transfer its loosely bound electron to the chlorine molecule to form an electronically excited state of KrCl*.

$$Kr^{*} + Cl_2 \rightarrow KrCl^{*} + Cl \quad (R2)$$

Generally, the KrCl* excimer have a short lifetime and decomposes rapidly in the nanosecond timescale and emits photons having a wavelength of 222 nm as

$$KrCl^{*} \rightarrow Kr + Cl + hv\,(222\,nm) \quad (R3)$$

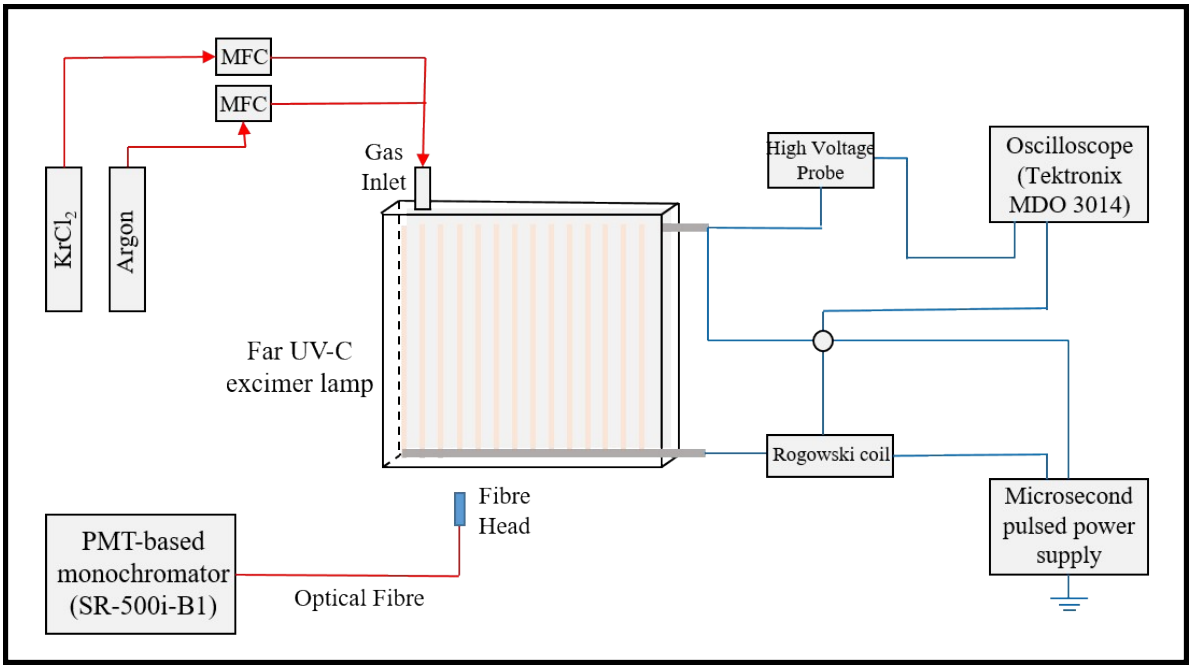


Fig. S1. Complete experimental setup for the development of far UV-C planer excimer source.

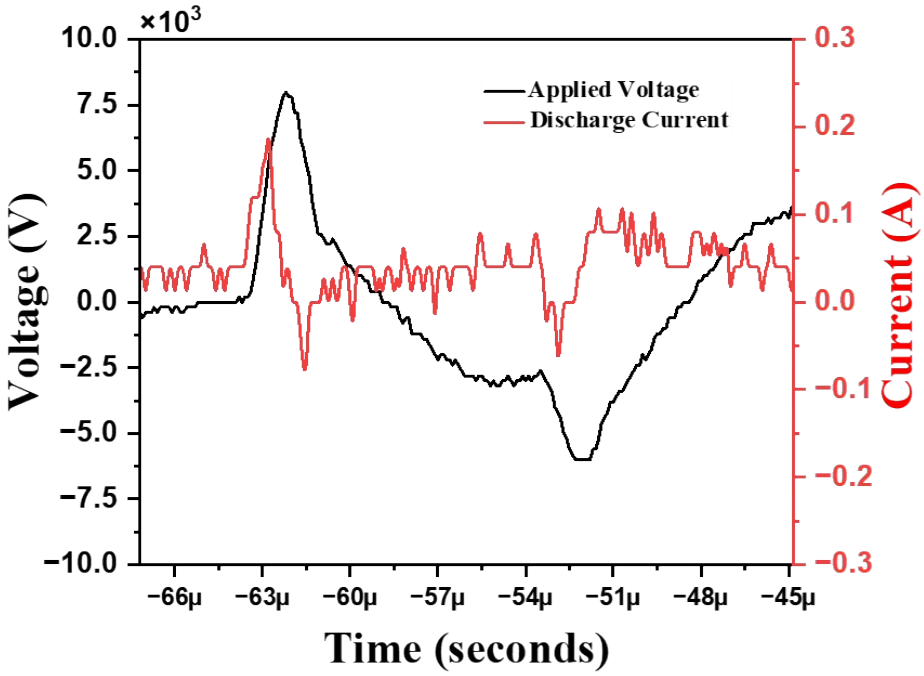


Fig. S2. Typical V-I characteristics of the used power source

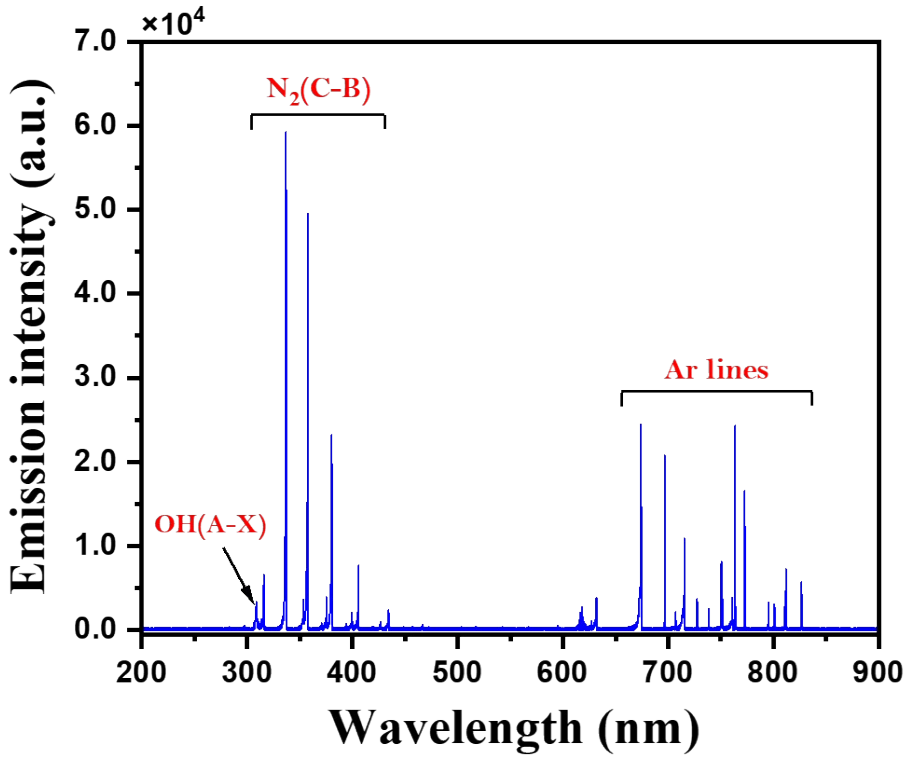
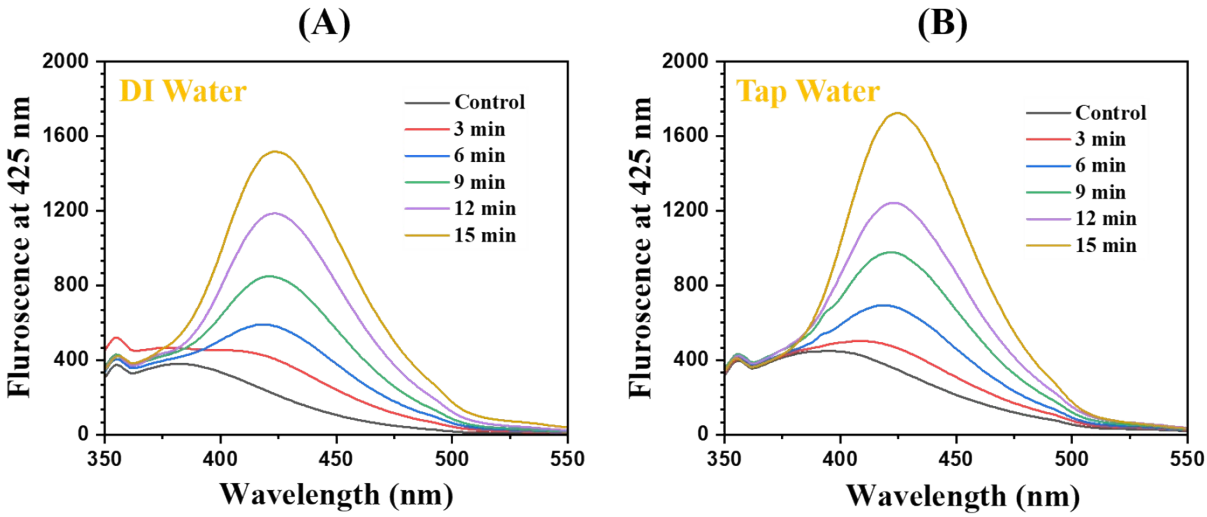


Fig. S3. Emission spectra of the atmospheric DDBD plasma.



72

73 **Fig. S4.** Fluorescence spectra of TA in **(a)** DI water and **(b)** Tap water after treatment with

74 DDBD plasma source.

75

76 ***Table S3.*** *Concentration of H_2O_2, NO_3^- and NO_2^- in the aqueous solution in the presence of*

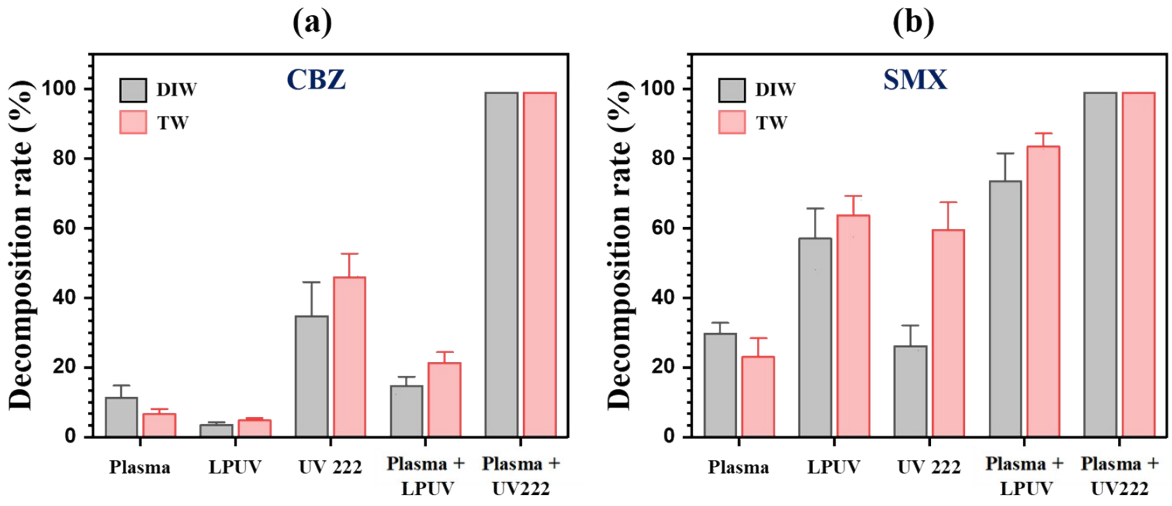
77 *SMX and CBZ.*

Time (minutes)	NO_2^- **(mg/L)**				NO_3^- **(mg/L)**				**H_2O_2 (mg/L)**			
	CBZ		**SMX**		**CBZ**		**SMX**		**CBZ**		**SMX**	
	DIW	**TW**	**DIW**	**TW**	**DIW**	**TW**	**DIW**	**TW**	**DIW**	**TW**	**DIW**	**TW**
3	5.74	6.52	6.12	7.72	61.2	106	59.3	96.1	0.17	0.26	0.19	0.23
6	6.96	8.12	7.66	8.92	91.8	115	92.6	103	0.31	0.51	0.34	0.44
9	7.15	8.74	7.58	7.43	105	133	100	140	0.46	0.74	0.51	0.78

12	7.27	8.93	8.02	10.1	147	157	153	163	0.76	1.03	0.83	0.98
15	6.17	7.02	7.27	8.22	188	208	191	213	0.93	1.09	1.02	1.12

78

79



80

81 **Fig. S5.** Degradation rate of **(a)** CBZ and **(b)** SMX using different methods for 15 minutes of

82 treatment (C_0 = 10 mg/L, UV Intensity = 1050 µW/cm^2 and pH 6-7).

83

84 **Table S4.** Time required for the complete degradation of SMX and CBZ under various

85 treatment processes.

Complete Degradation (min)	**CBZ**		**SMX**	
	DIW	TW	DIW	TW
Plasma	180	210	90	120
LPUV	420	390	30	25

UV 222	60	40	60	30
Plasma + LPUV	90	60	22	20
Plasma + UV 222	15	12	10	8

86