



**“Degradation of organic compounds using low temperature plasma”
+
previous studies**

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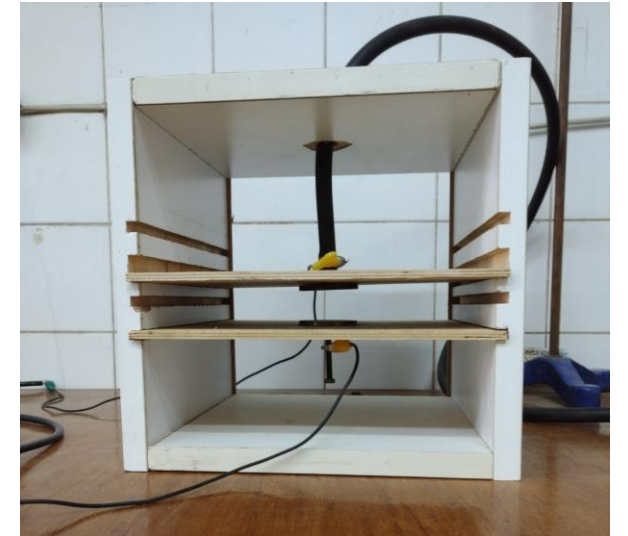
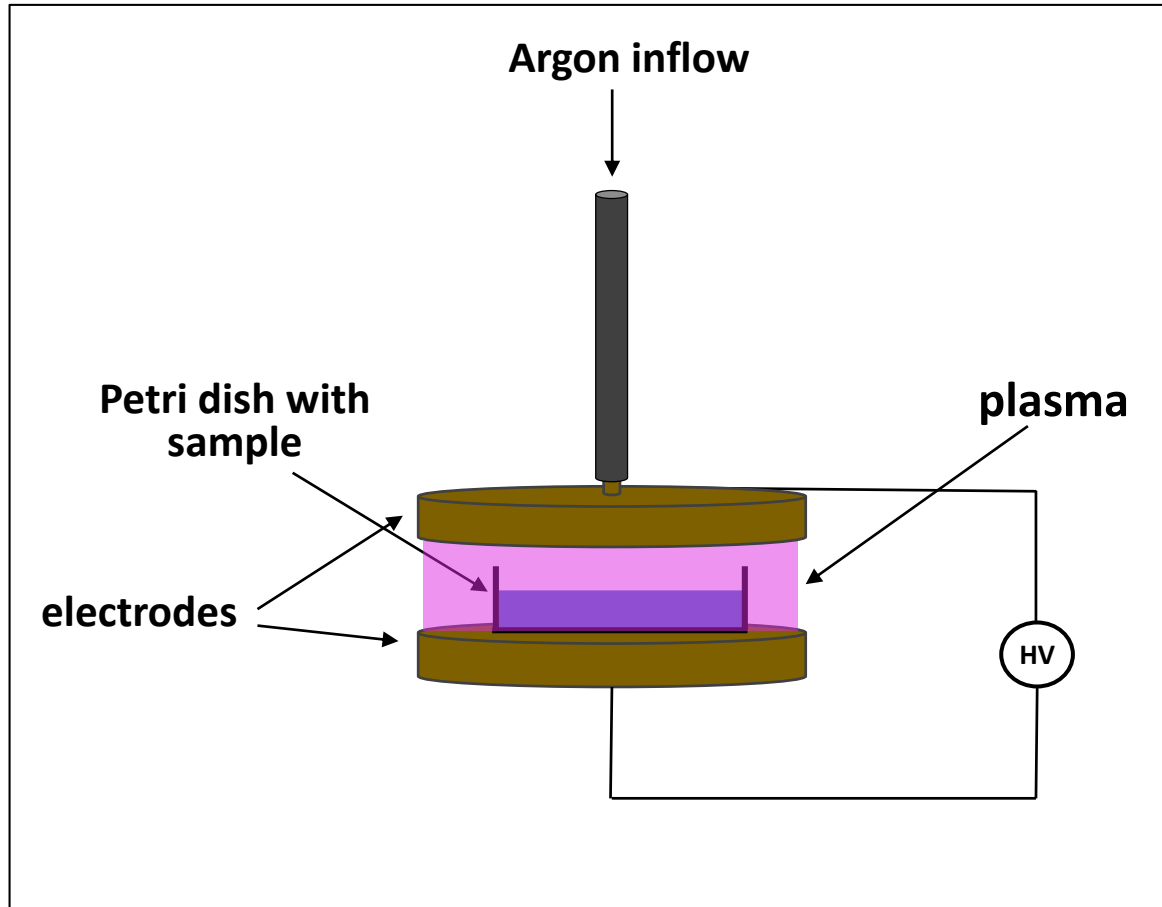
Tanta University

“Degradation of organic compounds using low temperature plasma”

The aim of the work:

- Degradation of organic compounds by using Dielectric Barrier Discharge (DBD) and Atmospheric Pressure Plasma Jet (APPJ).
- Studying the formed species through the process.
- Investigating the degradation rates and the removal efficiencies of the organic compounds after the exposure to the low temperature plasma.

Dielectric Barrier Discharge (DBD) and Atmospheric Pressure Plasma Jet (APPJ)



The setup of Dielectric Barrier Discharge (DBD) and Atmospheric Pressure Plasma Jet (APPJ)

it consists of two electrodes, the upper one has a hole where the gas inflows, connected to the power supply.

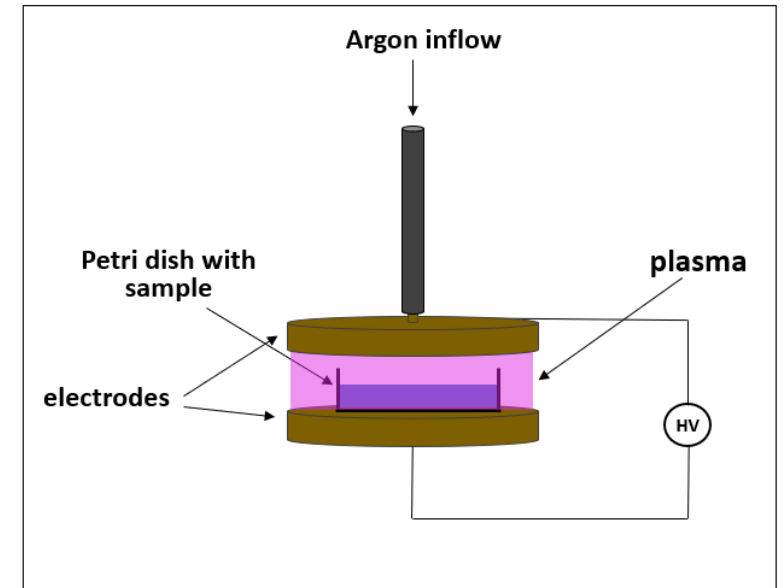
The sample in the petri dish is exposed to the plasma between the two electrodes.

- the advantages of this setup are

it doesn't require a vacuum i.e it works in the atmospheric pressure.

it uses the air as working gas in addition to the used gas (argon) which means diverse of species.

it can be used as just a dielectric barrier discharge or just as a plasma jet or both of them together.



Previous studies

Removal of cyanide from water by means of plasma discharge technology ⁽¹⁾

The motivation is to remove cyanide, whose anion $\text{-C}\equiv\text{N}$ is poisonous, from water.
by using two type of Dielectric Barrier Discharge plasma reactors.

-- **The process:** The sample is treated in a distilled water once and in a waste water once .

-- The sample gets treated by plasma reactors.

Using spectrometer, the concentrations of cyanide as function of time are measured to get **the degradation rates K.**

$$C/C_o = e^{-kt}$$

The removal efficiency is also calculated for each reactor.

$$\text{Removal (\%)} = \frac{C_o - C \times d}{C_o} \times 100$$

The DBD plasma reactors:

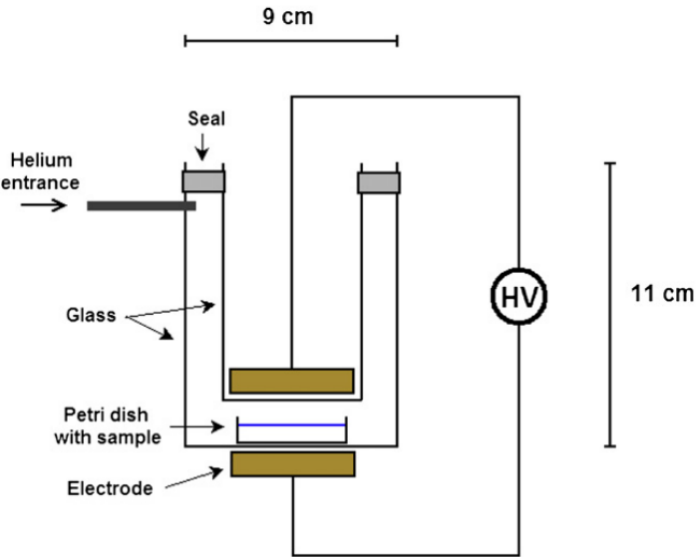


Fig. 1 – Scheme of the plasma reactor R1.

R1: conventional batch reactor

It consists of two electrodes, connected to high voltage, between them a petri dish with sample.

The system is sealed and has a helium entrance.

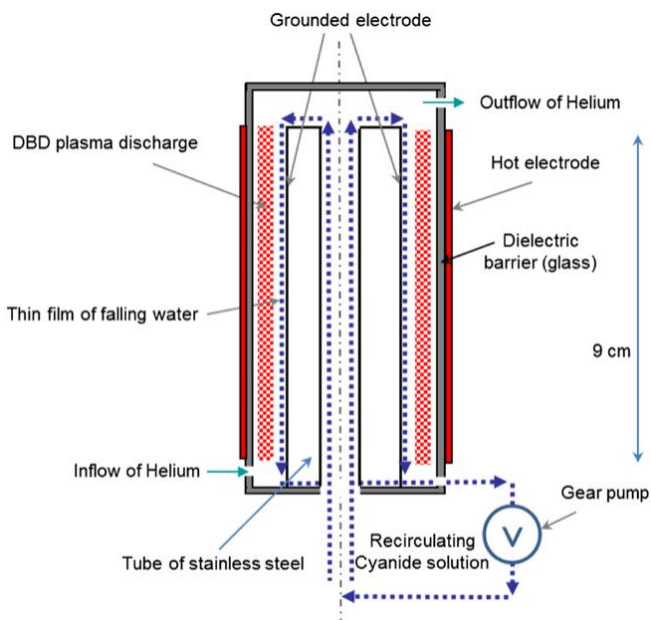


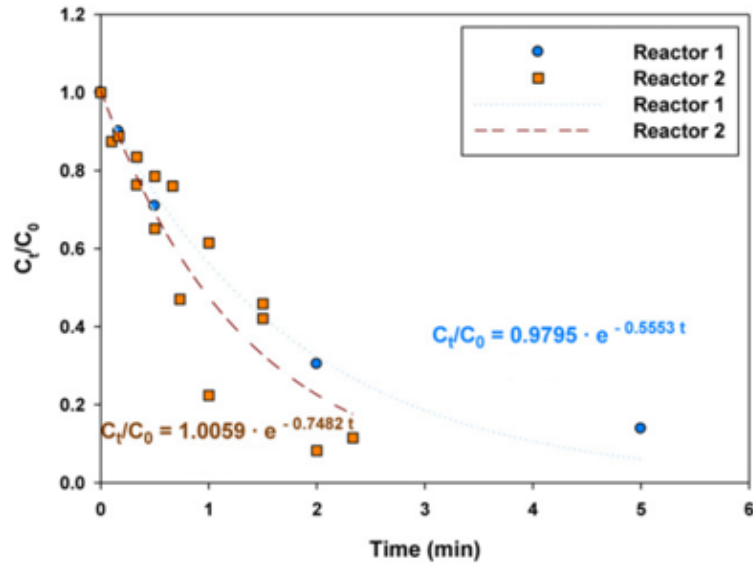
Fig. 2 – Scheme of the plasma reactor R2.

R2: coaxial thin falling water film reactor

It consists of two parts, each has two electrodes between them a layer of glass with inflow of helium.

The water (sample) gets pumped from the bottom to the top then falling beside the plasma.

The results:

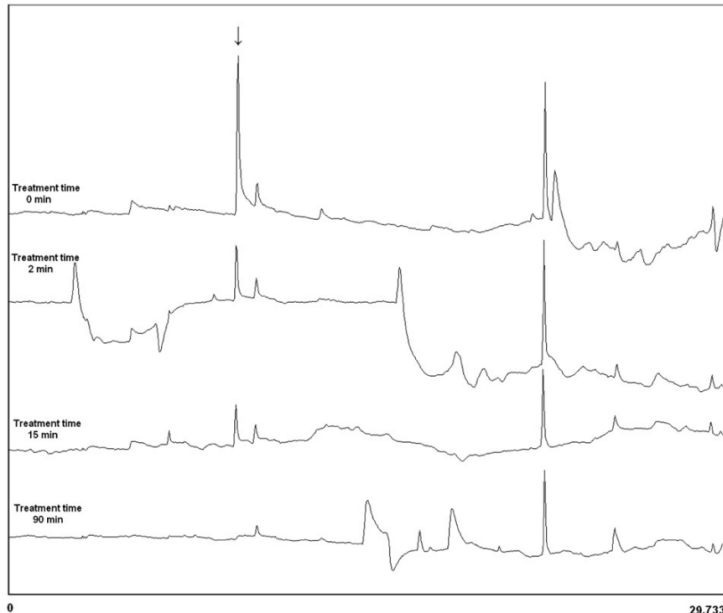


- The diagram of **Removal of cyanide from distilled water**, C/C_0 vs time (min).

The **degradation rates** are $K_{R1}=0.5553\text{min}^{-1}$ and $K_{R2}=0.7482\text{min}^{-1}$

The **removal efficiency** is 99% in 15min for R1 and in 3min for R2

-- R2 has a slightly better performance than R1 which could be related to the greater surface of water exposed to the plasma irradiation in R2.



- The diagram of **Removal of cyanide from wastewater**, where Hydrogen cyanide peak is marked with an arrow, by **Gas Chromatography with Nitrogen-Phosphorus Detector (GC-NPD)**.

The **degradation rate** is $K_{R2}=0.2462\text{min}^{-1}$

the **removal efficiency** is 92% in 90min for R2

-- the efficiency of the reactor declines due to the great concentration of dissolved organic matter in the wastewater.

Direct and Indirect Treatment of Organic Dye (Acid Blue 25) Solutions by Using Cold Atmospheric Plasma Jet ⁽²⁾

The motivation is to remove Acid Blue 25 (AB25), a dye material, from water using cold atmospheric pressure plasma jet (APPJ) by direct and indirect treatment.



-- for the **direct treatment**, the AB25 in water is exposed directly to the plasma jet.

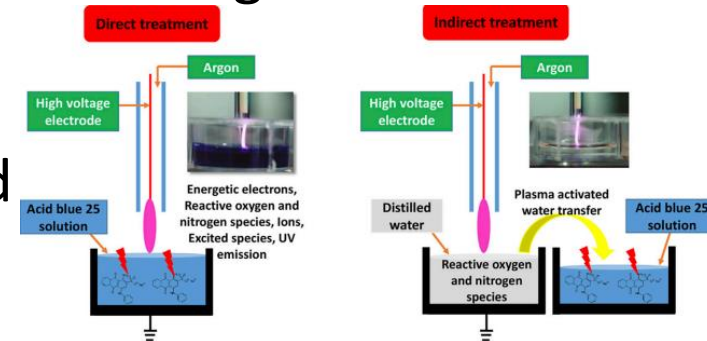
for the **indirect treatment**, a distilled water is exposed to plasma jet forming PAW then the AB25 solution is mixed with the PAW.

-- the plasma get characterized by Optical Emission Spectrometer and the concentrations of AB25 get determined to obtain the **degradation rate K**.

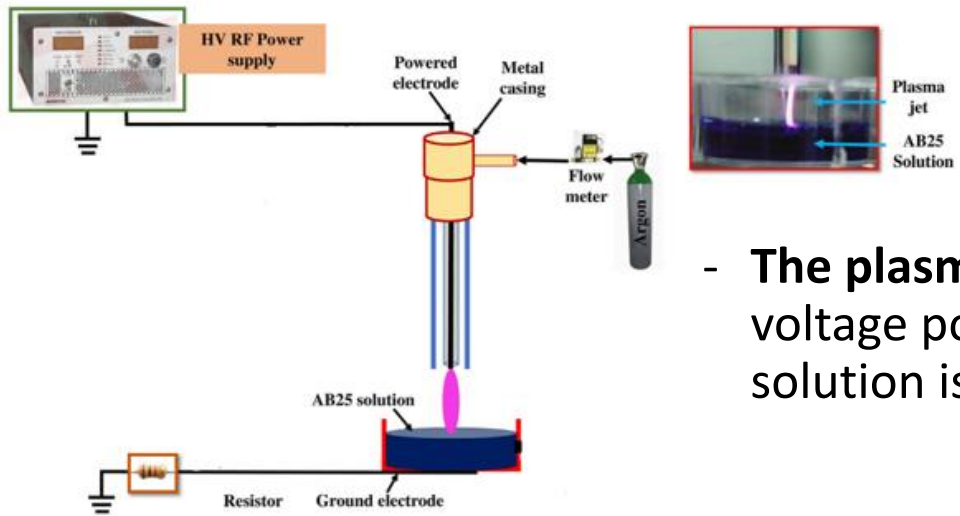
$$C/C_0 = e^{-kt}$$

The **removal efficiency** is also calculated

$$Removal (\%) = \frac{C_0 - C \times d}{C_0} \times 100$$

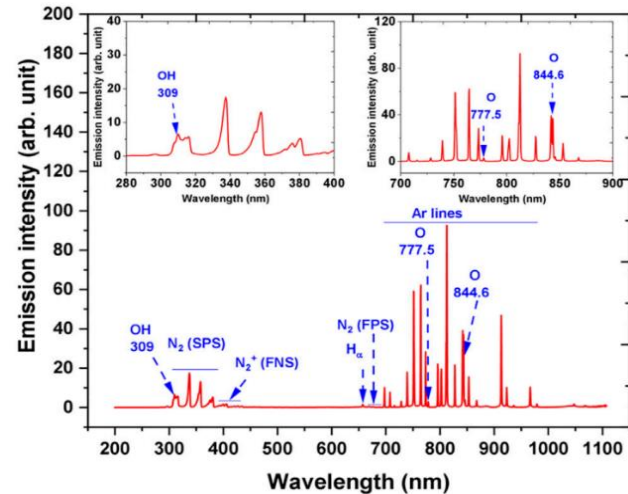


The cold atmospheric pressure plasma jet (APPJ)



- **The plasma jet** consists of a **powered electrode** connected to the high voltage power supply and the **ground electrode** where the petri with the solution is placed, with a **gas flow of argon**.

Optical Emission Spectroscopy (OES)



- Optical Emission Spectrometer was used for the **detection of excited species** in argon plasma in the air interacting with the liquid.
- Excited species such as **hydroxyl radical (HO)**, **atomic hydrogen (H)**, **atomic oxygen (O)**, **atomic argon**, **nitrogen second positive system (SPS)**, **nitrogen first positive system (FPS)** and **nitrogen first negative system (FNS)** were observed.
- Many authors have reported that **HO and O radicals** are considered as one of the **main short-lived ROS** in the plasma discharge, and they **can directly react with organic pollutants** which lead to degradation.

The results of direct treatment

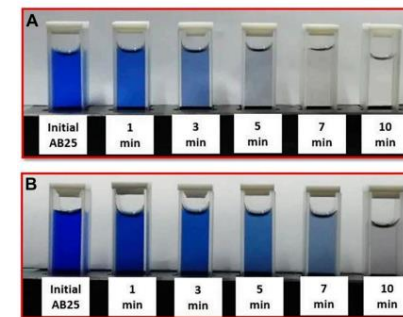
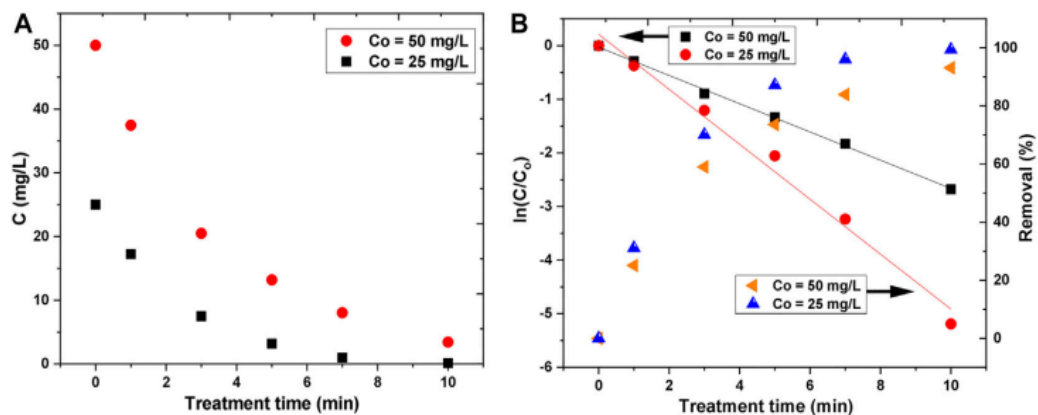
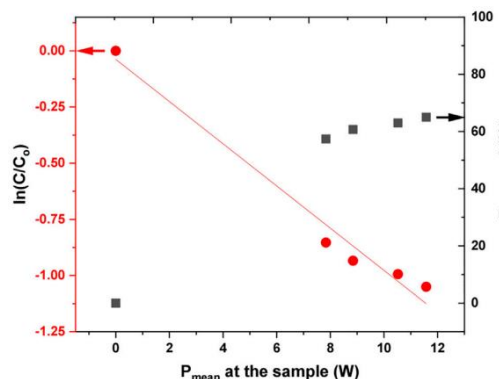


FIGURE 9 | Colour change of AB25 samples during the direct treatment by APPJ (A) $C_0 = 25$ mg/L (B) $C_0 = 50$ mg/L at $V_0 = 5$ ml, Ar flow 1 slm, and P_{mean} power at the sample 11 W.

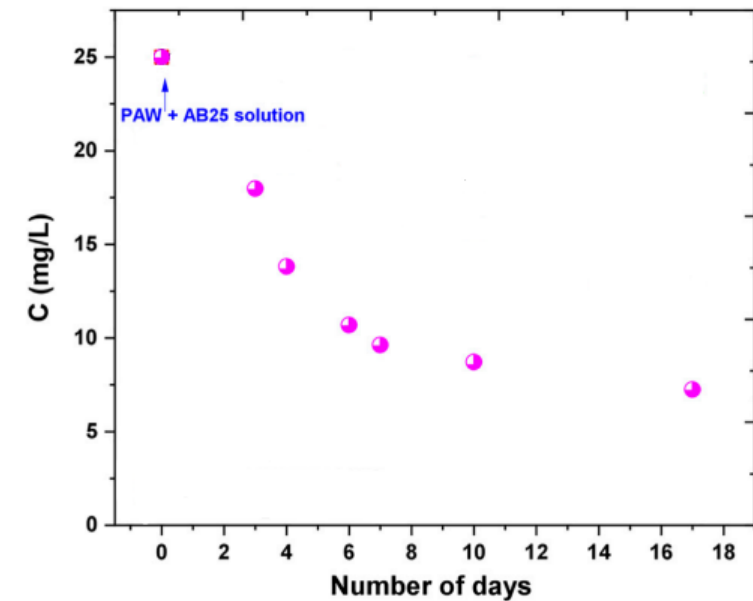
- With the **increase of treatment time**, the **concentration of AB25 was decreased exponentially**.
- The **removal efficiency** values were about **87% for 25 mg/L** and **73% for 50 mg/L** within **5 min** and was about **100% for 25 mg/L** and **93% for 50 mg/L** within **10 min**.
- The **degradation rates** are $K_{c25} = 0.512 \text{ min}^{-1}$ with $t_{1/2} = 1.35 \text{ min}$ and $K_{c50} = 0.263 \text{ min}^{-1}$ with $t_{1/2} = 2.63 \text{ min}$

The influence of deposited power

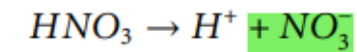
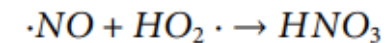
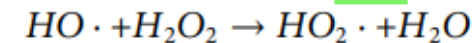
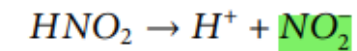
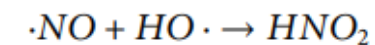
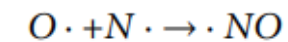
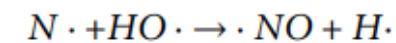
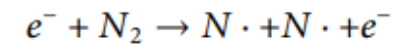
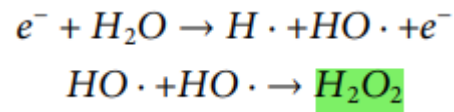


- the higher degradation of AB25 was accomplished when there was more power transferred to the sample.
- **Increasing the input power** shows **slower degradation** compared to **increasing the treatment time**.
- **It is more effective to use lower power and longer treatment times.**

The results of indirect treatment



- The maximal **removal percentage** of about **71% within 17 days**.
- **The long-lived species** such as H_2O_2 , NO_3^- , and NO_2^- in PAW are the responsible for the AB25 degradation here due to the indirect treatment.
- H_2O_2 , NO_3^- , and NO_2^- in PAW can be produced from $HO\cdot$, $O\cdot$, $H\cdot$ and N species as following:



- it was observed that H_2O_2 was the important **long-lived ROS** in the **PAW** in the **indirect treatment process**.

Performance of non-thermal plasma reactor for removal of organic and inorganic chemical residues in aqueous media ⁽³⁾

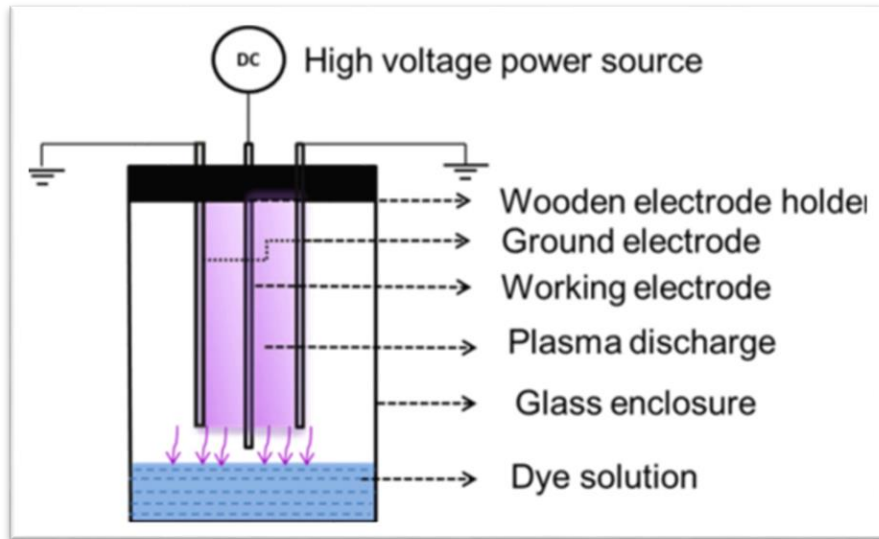
The motivation is degradation of azo (**orange G** and **congo red**) and non-azo (**crystal violet** and **coomassie brilliant blue**) textile **dyes** and removal of hardness in an aqueous medium.

The process: Dye **degradation efficiency** was evaluated at different **applied voltages** (2–6 kV), and **initial dye concentrations** (5–25 ppm).

- At every **10 min interval** for **30min**, **dye concentration** were measured.
- The samples were collected at every **15 min interval for 60 min** and **water hardness** is measured using the standard ethylenediaminetetraacetic acid (EDTA) titration method.
- The **degradation efficiency** was calculated using

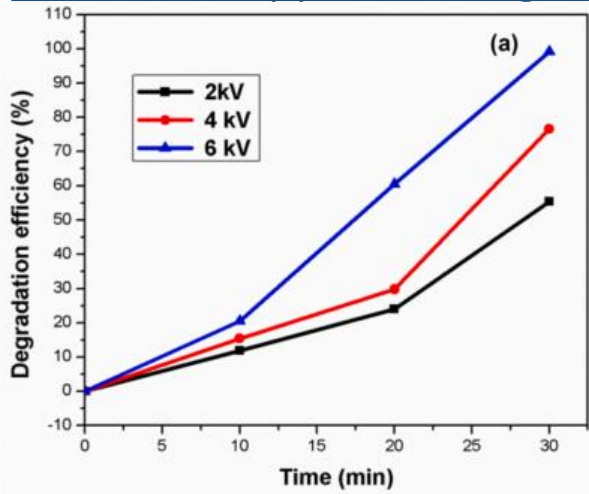
$$Efficiency (\%) = \left[\frac{C_o - C}{C_o} \right] \times 100$$

the plasma discharge reactor:



- It consists of **two ground electrodes** and **working electrode** which connected to the high voltage power supply, where **the plasma** is formed between each ground electrode and the working one at the middle.
- This arrangement was enclosed in a glass chamber and **placed just above the dye liquid surface.**
- The **atmospheric air** is used as the plasma gas

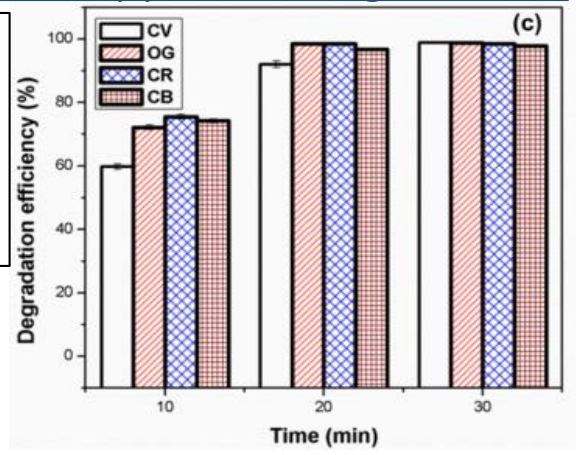
the role of applied voltage on the degradation of CV:



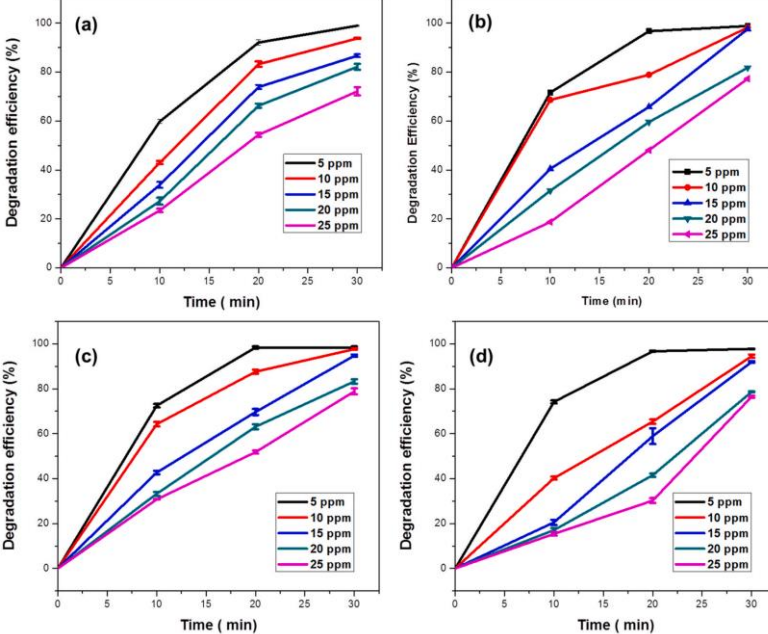
Maximum degradation of 55.35%, 93.65%, and 98.19% was observed for 30 min treatment at 2 kV, 4 kV, and 6 kV, respectively.

The degradation efficiencies of various dyes at an applied voltage of 6 kV

The degradation efficiencies of 98.91%, 98.79%, 98.43%, and 97.85% were achieved for CV, OG, CR, and CB, respectively in the 30 min treatment.



Effect of initial dye concentration on the degradation:

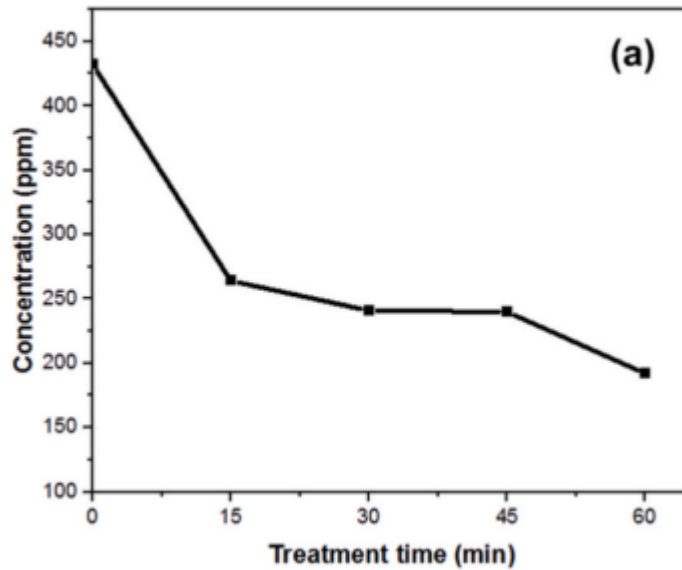


Effect of initial dye concentration on degradation of four different dyes in aqueous solution (a) CV, (b) OG, (c) CR, and (d) CB (6 kV).

- With the increase in the concentration of dye from 5 to 25 ppm, CV degraded from 98.91% to 72.14%, OG from 98.79% to 81.34%, CR from 98.43% to 78.85%, and CB from 97.85% to 76.49% and also

The kinetic constants of CV, OG, CR, and CB decreased from 0.15677 to 0.04085 min⁻¹, 0.1349 to 0.04867 min⁻¹, 0.13881 to 0.05094 min⁻¹, and 0.1209 to 0.04758 min⁻¹.

The water hardness:



The water hardness, which means the concentration of metals in water, **dropped significantly from 432 to 144 ppm** with increasing the treatment time.

The result:

- Nearly **99%** degradation efficiency (at 5 ppm concentration) could be achieved in **30 min** treatment time **for all dyes**.
- Degradation efficiency showed a direct relationship with applied voltage and an inverse relationship with the initial dye concentration.
- The **water hardness** was dropped by **55.5%** after **60 min** of plasma treatment.

Oxygen-mediated dielectric barrier discharge plasma for enhanced degradation of chlorinated aromatic compounds ⁽⁴⁾

the motivation: degradation of chlorinated aromatic compounds, 2,4-dichlorophenol (2,4-DCP), o-Nitrochlorobenzene (o-NCB) and chlorobenzene (CB), which are a kind of refractory pollutants, has a potential risk to the environment and human health, from water by dielectric barrier discharge plasma with flow of oxygen gas.

The process:

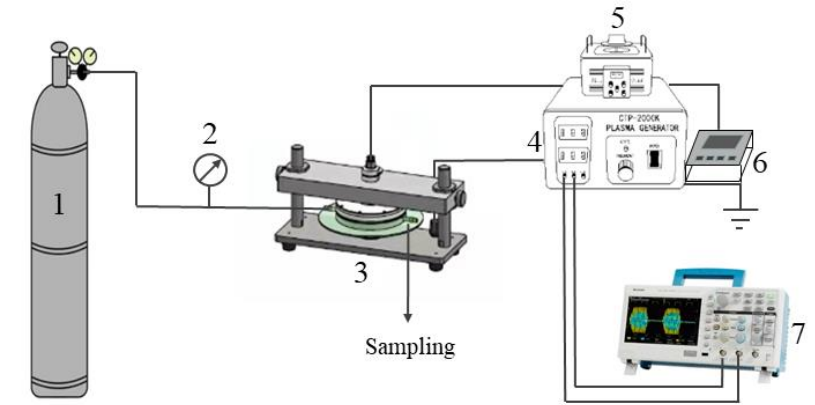
- 2,4-DCP degradation was exhibited in DBD plasma system with different working gases (air, N₂, O₂, and Ar) and then various flow rates of O₂.

Then for different types of pollutants (2,4-DCP, o-NCB, CB), the degradation rates and efficiencies in the DBD and DBD/O₂ plasma systems were compared.

- the degradation rate constant (k_{obs}) could be $\ln\left(\frac{C_t}{C_0}\right) = -k_{obs} \cdot t$

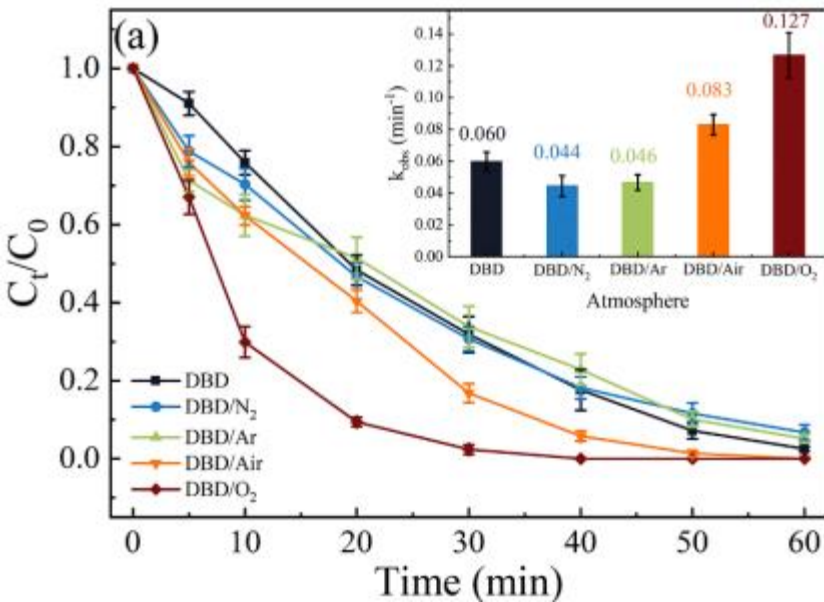
The DBD plasma reactor:

The dielectric barrier discharge plasma reactor consists of two electrodes connected to power supply and a dielectric of glass contain the solution on it with flowing gas of O_2 .



1. Steel cylinders; 2. Flowmeter; 3. Reaction units; 4. High-voltage power supply; 5. Voltage regulators; 6. pulse generator; 7. Oscilloscope.

The use of different working gases to degrade 2,4-DCP:



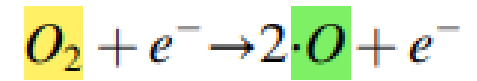
-oxygen presented the strongest contribution to the DBD plasma system.

2,4-DCP was completely degraded within 40 min, and the corresponding degradation rate k_{obs} reached 0.127 min^{-1} .

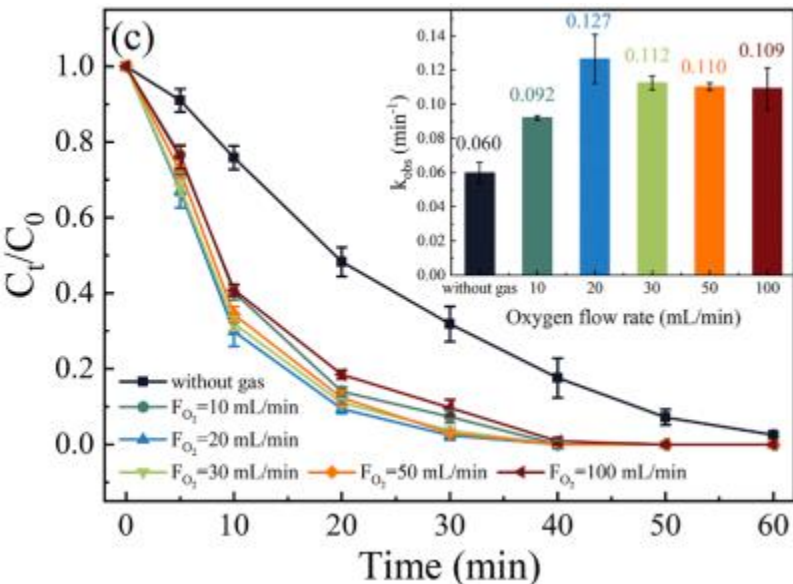
-The introduction of oxygen could accelerate the production of $\cdot OH$ and H_2O_2 and lead to the production of O_3 , which resulted in the rapid degradation of 2,4-DCP.

$\cdot\text{O}$ (atomic oxygen radical) could react with O_2 to produce O_3 and $\text{O}(^1\text{D})$ (the electronically excited singlet oxygen atom) could react with H_2O to produce $\cdot\text{OH}$ and H_2O_2 .

-When **oxygen was used as the working gas**, O_3 , $\cdot\text{OH}$ and H_2O_2 were continuously generated during the discharge process **at higher amounts than the other groups**.



The effect of oxygen flow rates on 2,4-DCP degradation:

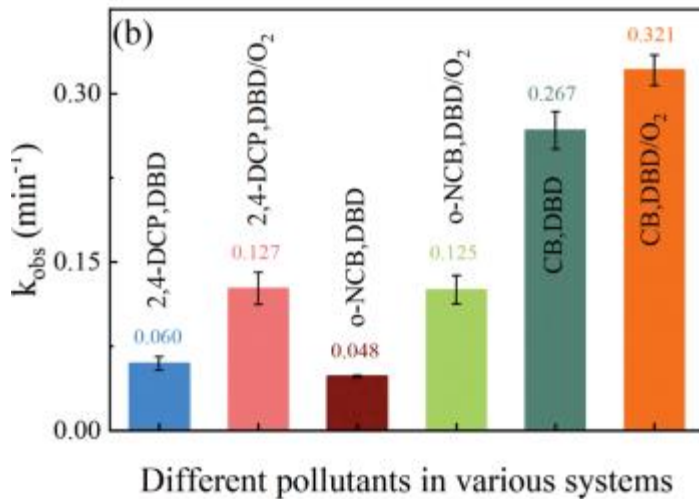
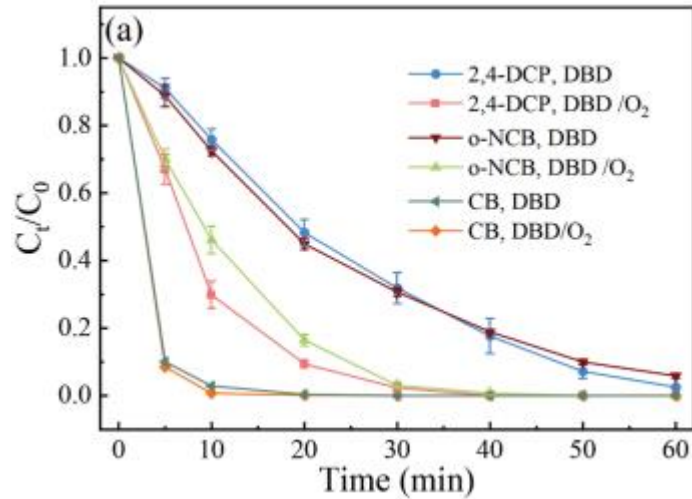


-the k_{obs} of 2,4-DCP peaked at 0.127 min^{-1} when the oxygen flow rate was **20 mL/min** where **O_3** was at its peak too.

The experimental results indicated that **O_3** was the active species leading to 2,4-DCP degradation.

- **An excessive oxygen flow rate** resulted in a short residence time in the discharge region, leading to insufficient ionization of oxygen and thus a reduction in **O_3** production.

Degradation of various CACs in the DBD and DBD/O₂ plasma systems:



- Compared to the DBD plasma system alone, the DBD/O₂ plasma system had improved the degradation efficiency and k_{obs} of them to different degrees.

-- The k_{obs} for 2,4-DCP, o-NCB and CB were increased from 0.060, 0.048 and 0.267 min^{-1} to 0.127, 0.125 and 0.321 min^{-1} , respectively.

-- The introduction of oxygen increased the dechlorination efficiency of 2,4-DCP, o-NCB, and CB from 71.28 %, 65.13 % and 80.63 % to 93.23 %, 88.56 % and 98.30 % at 30 min, respectively.

After 1 h, the dechlorination efficiency of 2,4-DCP and o-NCB was both up to 100 %, and the dechlorination efficiency of CB was up to 99.09 %.

Degradation of diclofenac and 4-chlorobenzoic acid in aqueous solution by cold atmospheric plasma source ⁽⁵⁾

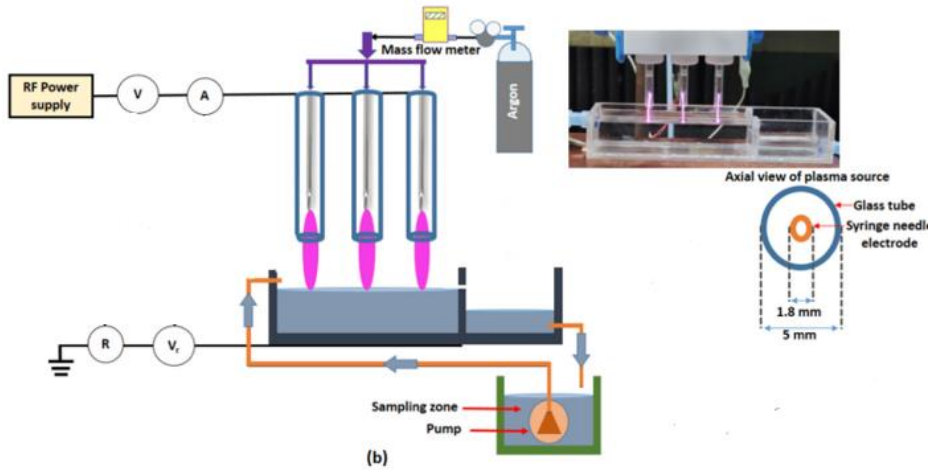
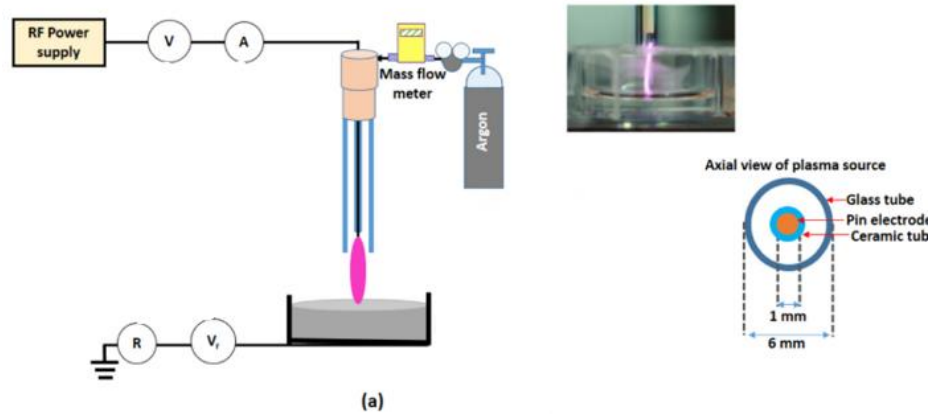
the motivation: the degradation of organic pollutants, Diclofenac sodium (DCF) and 4-Chlorobenzoic acid (pCBA), from water by Atmospheric pressure plasma jets (APPJs) with a 1 pin-electrode and multi-needle electrodes (3 pins).

The process:

- two different initial concentrations of each DCF, 25 mg/L and 50 mg/L, and pCBA, 25 mg/L and 40 mg/L, are investigated.
- Treatments were conducted with **two different volumes** (5 mL and 250 mL) of contaminated water samples.
- **the degradation rate constant (k)** was obtained from $\ln \frac{C}{C_o} = -kt$
- **the removal efficiency** could be obtained from $Removal (\%) = \frac{C_o - C \times d}{C_o} \times 100$
- Consequently, the half-life ($t_{1/2}$) decomposition time was determined as

$$t_{1/2} = \frac{0.693}{k}$$

Atmospheric pressure plasma jets (APPJs) with a 1 pin-electrode and multi-needle electrodes (3 pins)



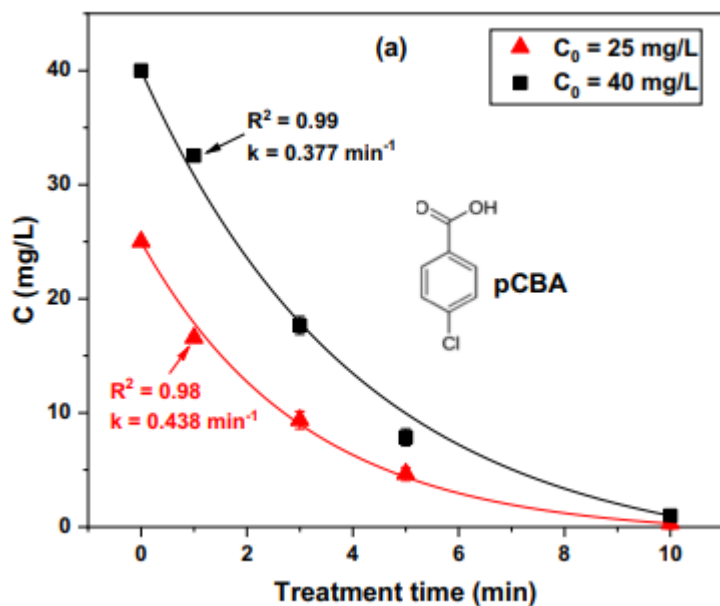
-The plasma source consists of a concentrically placed glass tube, a ceramic tube and a stainless steel wire with a sharpened tip is used as a **high-voltage electrode**.

-**The other grounded electrode** is the solution placed in a vessel with **copper tape** glued to the outer bottom side of the vessel and connected to the ground.

-plasma was generated **between the electrode tip and stagnant liquid surface** using **argon** as a working gas.

-The plasma generated using **argon** as working gas was touching a stationary liquid surface in the case of pin electrode-APPJ while for multi-needle electrodes-APPJ the liquid sample was flowing during treatment.

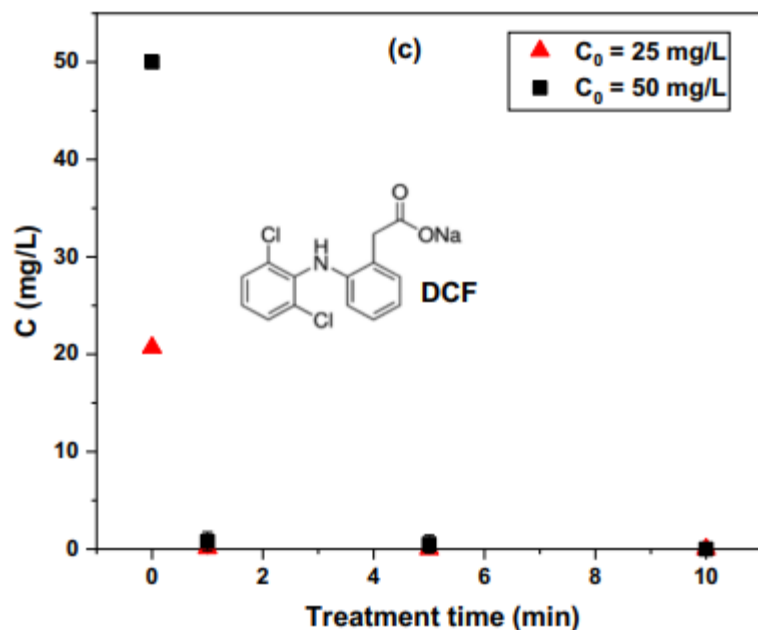
The results of APPJs with a 1 pin-electrode



- After 10 min of treatment, both degradation curves merged, resulting in the complete removal of 5 mL pCBA at the initial concentration of 25 mg/L and 40 mg/L.

- The degradation rates were 0.377 min^{-1} for 40 mg/L and 0.438 min^{-1} for 25 mg/L.

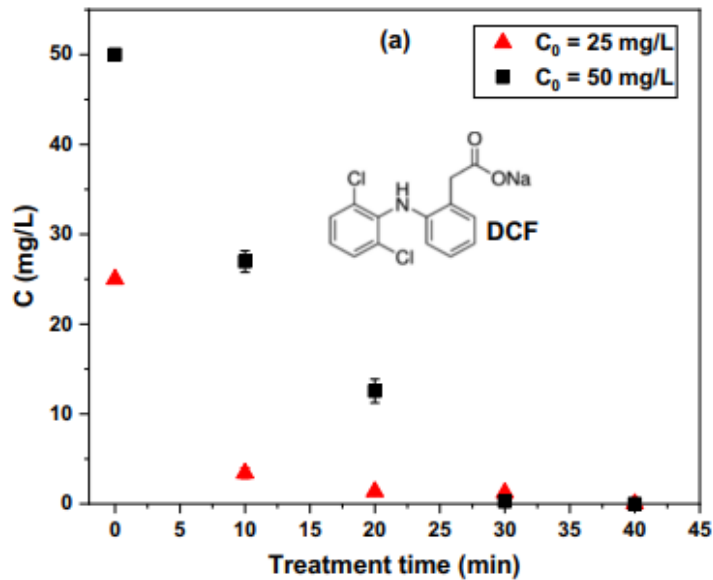
- The half-life ($t_{1/2}$) pCBA decomposition time required to remove 50 % of the pCBA was 1.58 min for 25 mg/L and 1.83 min for 40 mg/L.



- When treated with pin-APPJ, almost complete degradation of 5 mL DCF occurred in 1 min with the initial concentration of 25 mg/L and 50 mg/L.

- due to the short time, The degradation kinetics of DCF was not established.

The results of APPJs with a multi-needle electrodes (3 pins)

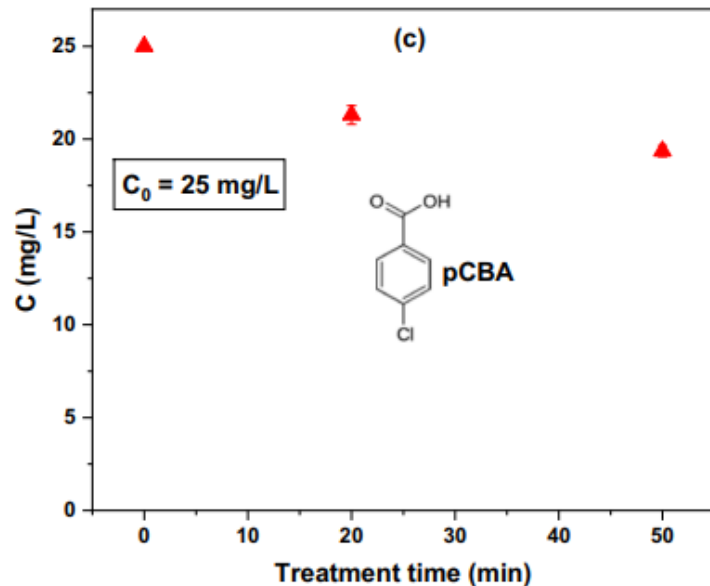


-The complete removal of DCF was seen with both initial concentrations in 30 min.

- When the treatment was performed at an initial concentration of 25 mg/L, the rate of degradation of DCF was 0.145 min^{-1} .

- DCF degradation is governed by a zero-order equation for rich initial concentrations, such as 50 mg/L and the rate of degradation was $1.636 \text{ mg/L min}^{-1}$

- The half-life ($t_{1/2}$) time required to degrade 50 % of DCF was roughly 5 min for lower initial concentrations and three times longer for higher concentrations.



-During the treatment of pCBA, slow degradation was observed, about 24 % removal of pCBA after 50 min of plasma treatment.

-The rate of degradation for pCBA was 0.00497 min^{-1} .

-Because here we had a better mixing of the contaminated sample, This could lead to a higher competition for the reactive oxygen species (HO^\bullet radicals for example).

References:

- (1)** Mari´a Hijosa-Valsero, Ricardo Molina, Hendrik Schikora, Michael Mu¨ller, Josep M. Bayona, Removal of cyanide from water by means of plasma discharge technology, Elsevier, 47 (2013) 1701-1707.
- (2)** Amit Kumar, Nikola Škoro, Wolfgang Gernjak, Dragan Povrenović and Nevena Puač, Direct and Indirect Treatment of Organic Dye (Acid Blue 25) Solutions by Using Cold Atmospheric Plasma Jet, Frontiers in Physics, 10 (2022) 835635.
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THANK YOU !