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D3.2 Preliminary evaluation of plasma parameters for atmospheric pressure plasma sources suitable for OMP removal

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Executive Summary

This deliverable contains a compilation of certificates confirming that appropriate health and safety procedures conforming to relevant local/national guidelines/legislation are followed for ESRs involved in this project.

Therefore, all beneficiaries confirm that any possible harm to the environment caused by the research due to use of potentially toxic materials will be prevented by the measures that will be taken to mitigate the risks.

1. Atmospheric pressure plasma jet (APPJ) with 1-pin electrode type configuration

For the preliminary evaluation of the 1-pin APPJ, the electrical characterisation of plasma has been studied in order to calculate discharge parameters, such as voltage, current and power deposition. Additionally, optical emission spectroscopy (OES) has been used to monitor the reactive species in the gaseous phase of plasma. The OES measurements show excited hydroxyl radicals, atomic oxygen, atomic hydrogen and nitrogen were generated in the gaseous phase of plasma system. In order to test the efficiency of the 1-pin APPJ for decontamination treatments of water contaminated with Acid Blue 25 dye was performed.

1.1. Characterisation

The starting point in the development of the multi-pin APPJ was construction and optimization of the 1-pin electrode type APPJ. This device was constructed and developed as one of the first tasks within ESR5 activities. The schematic diagram of the experimental setup is given in Figure 1.

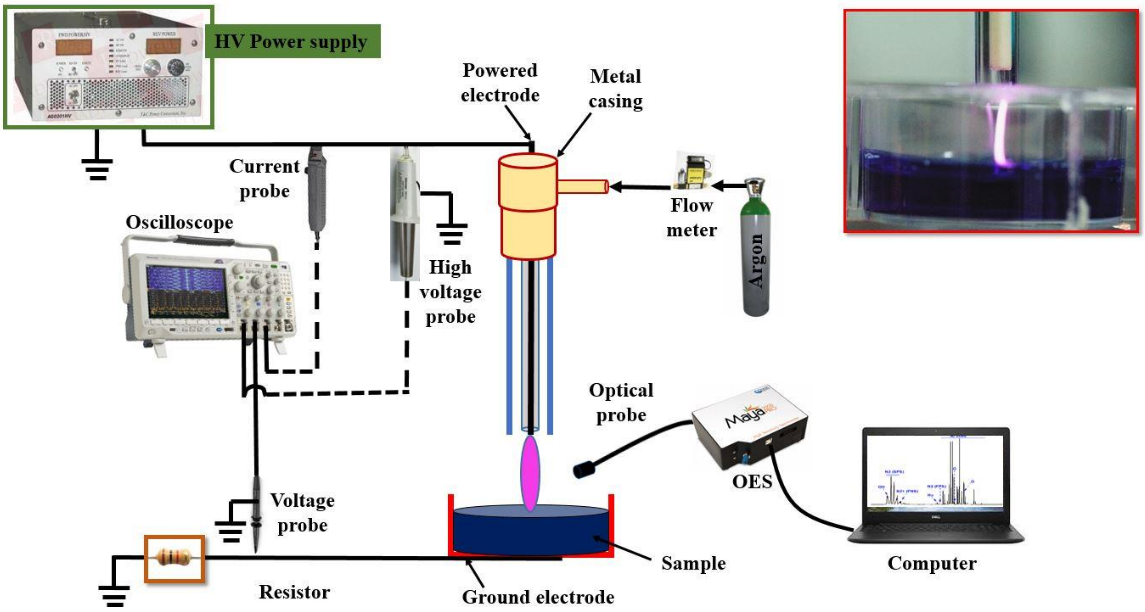


Figure 1. Schematic diagram (left) and picture (right) of the plasma jet over the liquid surface.

The APPJ consists of glass and ceramic tubes and a stainless steel electrode (powered electrode). The powered electrode is a 1 mm diameter stainless steel wire with a sharpened edge placed inside the ceramic tube. The distance between the tip of the powered electrode and the surface of the sample was 10 mm. The inner powered electrode is connected to the high voltage (HV) source. The grounded electrode is a copper tape placed on the sample vessel and connected to the ground via a 1 kΩ resistor. A commercial high voltage RF high voltage power supply was used as a plasma powered source. The frequency of the power supply was 336 kHz. Argon was used as a feed gas with a flow rate of 1 slm and the flow rate was controlled through a mass flow meter. The volume of the treated sample containing AB25 dye was 5 ml.

The plasma established with this plasma source is of streamer discharge. In all conditions of the experiment and the treatments, the streamer propagates through the entire discharge gap, i.e. between the tip of the powered electrode and the liquid sample. A conductive bright plasma channel is formed in the gap and operation of the channel is stable if observed in time domain that includes many sine-signal periods. The entire gap voltage is set across this conductive channel having strong ionization fronts within one half-period of supply signal. The conductive channel is characterized with very non-uniform radial field distribution. The interior of a streamer consists of a conducting, roughly quasi-neutral plasma while a thin and curved space charge layer at its tip is responsible for the screening of the inner ionized area and the strong field enhancement at the streamer head. In this type of discharge, apart excited atoms and molecules and their ions, there is also high concentration of highly energetic electrons in the field enhanced zone around the streamer head due to the field enhancement. Thus, this discharge is able to trigger variety of chemical reactions at the point of interaction with the liquid target. In this case, at the gas-liquid interface region at the point where the channel connects with the liquid sample, we observed branching of the streamer. This is probably due to dielectric property of the liquid target that enables formation of surface charges that influence formation of several conductive channels at the surface.

The voltage at the powered electrode was determined by a high voltage probe. The current at the powered electrode was measured with a current probe. The voltage drop across the 1 kΩ resistor was recorded by using a voltage probe. The power delivered from the power supply to the plasma source and the power in the grounded line connected to the sample, i.e. the power deposited from the plasma passing through the sample was calculated. The average power at the source was determined by averaging the instantaneous power (product of measured voltage and current) over the time interval of 6 periods.

$$P_{average} = \frac{1}{nT}\int_{T1}^{T2} V(t) \times Is(t) \times dt$$

Where, $P_{average}$: average power at the source; V: voltage signal at the source; I_S: current at the source: $nT = T_2 – T_1$. However, the average power at the ground was determined by averaging the instantaneous power (product of measured voltage and current) over the time interval of 6 periods.

$$P_{average} = \frac{1}{nT}\int_{T1}^{T2} V(t) \times Ig(t) \times dt$$

The current at the ground was calculated by dividing the voltage drop at the resistor and resistance.

$$I_g\ (t) = V_R(t)/R$$

Where $P_{average}$: average power at the sample; V_R: voltage drop at the resistor; R: resistance of the resistor (1kΩ); I_g: current at the ground.

Table 1. The range of parameters of 1-pin APPJ obtained by electrical characterisation.

	V_{RMS} (kV)	I_s^{RMS} (mA)	I_g^{RMS} (mA)	P_s^{mean} (W)	P_g^{mean} (W)
Plasma OFF	1-1.6	18-28	3-4	0.7-2	0-0.2
Plasma ON	1.1-1.3	24-28	6-13	7-13	5-11

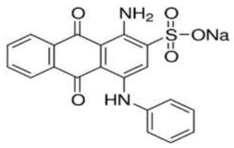
The voltage and current characterisation gave the linear dependency between voltage and current when plasma is not ignited with drop in voltage after the breakdown and appearance of the discharge. The current measured in the main part of the electrical circuit (I_s^{RMS}) several times larger than the current flowing through the ground part of the electrical circuit (I_g^{RMS}). The current flowing through the ground part of the electrical circuit is actually the current flowing through the sample since during the treatments plasma is in contact with the sample. The most important parameter for plasma treatments is power deposited in the plasma. For us this parameter is related to the power deposited in the part of the electrical circuit in contact with contaminated water sample. When plasma is ignited this power is in the range of 5 W-11 W.

Apart from electrical characterisation we have performed optical emission spectroscopy measurements in the wavelength range of 200-1100 nm. Since the argon is used as feeding gas several argon lines were detected. The plasma is ignited actually in the mixture of argon with the surrounding air so there is a presence of the nitrogen and oxygen lines. What is more important for the decontamination processes is the presence of oxygen atom lines as well as OH line.

1.2. Application of 1-pin APPJ in the decomposition of AB25 dye

AB25 (product number: 210684; purity: 45 %; chemical class: anthraquinone) was used as a target compound. It was purchased from Sigma Aldrich. The characteristics of the dye are given in Table 1 and operating conditions in Table 2. To prepare the experimental dye-containing aqueous sample, a stock solution with AB25 concentration of 50 mg/L was prepared by dissolving the required amount of analytical grade of AB25 in distilled water. The lower concentration was achieved by the addition of distilled water into the stock solution.

Table 1. Characteristics of AB25 dye.

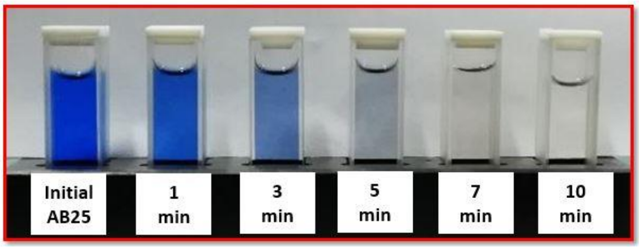
Chemical formula	Chemical structure	MW (g/mol)	λ_{max} (nm)
$C_{20}H_{13}N_2NaO_5S$		416.38	602

* λ_{max}: maximum absorbance

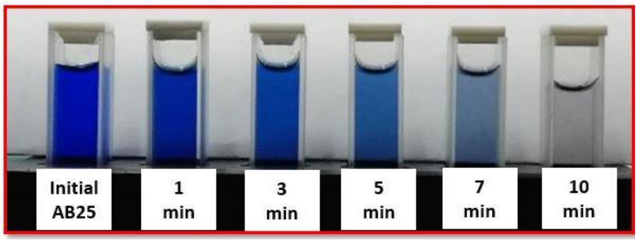
Table 2. Operating conditions.

Power (W)	Argon flow rate (SLM)	Discharge gap (mm)	Sample volume (ml)	AB25 concentrations (mg/L)	Treatment time (min)
11	1	10	5	25 and 50	1, 3, 5, 7 and 10

The pH of the treated solutions decreases with treatment time while conductivity increases. With the increase of treatment time the initial concentration of the AB25 dye decreases. In the case of lower initial concentration the destruction for the longest treatment time (10 min) is close to 100 %. For the two times greater initial concentration the removal efficiency is around 90 % for the 10 min treatment time. We can expect that for a longer time the initial concentration of AB25 would be removed completely. Visually, the change in the colouring of the sample is shown in Figure 2.



(a)



(b)

Figure 2. Dissapearance of AB25 with treatment time (a) Co = 25 mg/L (b) Co = 50 mg/L.

2. Conclusion

1-pin atmospheric pressure plasma jet producing streamer discharge is an efficient tool in removing pollutants from the water. We have presented electrical characterisation of 1-pin APPJ with calculations of mean power deposited to the discharge. The emission spectra of the discharge has abundance of the argon lines, but the most important is the presence of oxygen atom lines as well as OH line and the intensity of these lines increases with the increase of the deposited power in the discharge. As a test case we have chosen AB25 dye molecule. We have used two different initial concentrations. For both initial concentrations the degradation rates follow the first-order equation. Also, the removal efficiency increases with the deposited power into the discharge.