# Decomposition of methylene blue by a cold atmospheric pressure plasma jet source

E.C. Stancu, D. Piroi, M. Magureanu, G. Dinescu

*National Institute for Lasers, Plasma and Radiation Physics, Atomistilor Str. 409, PO Box MG-36, 077125 Bucharest-Magurele, Romania; email: dinescug@infim.ro*

***Abstract:*** Operation of a cold plasma jet submerged in liquids opens the way of degradation of pollutants in aqueous media. In this contribution we present results describing the decomposition of the dye methylene blue in water using a cold atmospheric pressure radiofrequency (13.56 MHz, 15 W) argon plasma jet, in presence of oxygen. The degradation process was monitored by visible absorption spectrophotometry. The plasma jet was placed: submerged into the solution (5 mm below the surface), just above the solution surface and at 15 mm above the surface. The highest decomposition efficiency was obtained when the plasma jet was submerged into the solution.

***Keywords:*** plasmas in liquids; atmospheric pressure plasma jet; plasma depollution

## 1. Introduction

The degradation of organic pollutants from contaminated water using atmospheric non-thermal plasmas has been intensely investigated in the last years [1]. Such plasmas have the ability to generate active species such as ozone, hydroxyl radicals, atomic oxygen, hydrogen peroxide etc., in absence of significant heating. These strong oxidizing species are highly effective in degradation and removing of organic compounds [2]. The decomposition efficiency in diverse plasma configurations has been studied mainly for corona discharges and dielectric barrier discharges. The investigations have been focused mostly on the effects of the applied power and frequency, the treatment time and gas composition [3,4].

Some of these plasma configurations are suitable to be operated with both electrodes submerged in water (to create reactive species directly in water), or with one of the electrodes submerged in water and the other one placed above the surface of water to create plasma in the gas phase and in water [5,6]. In this contribution we describe experiments and report results obtained by application of a cold atmospheric pressure plasma jet source with bare electrodes for degradation of organic contaminants in water. Previously, this plasma jet source was used for applications like surface treatment and modification of plastic foils for interaction with cells [7]. This atmospheric pressure plasma jet is a special one because it may operate not only in open atmosphere, but also submerged under liquid, being thus possible to be used for sterilization or pollutants removing from the liquid phase.

Methylene blue was selected as model organic contaminant for the present experiments. Due to its molecular structure, this typical dye cannot be degraded by conventional methods [8].

## 2. Experimental

More details on the RF atmospheric plasma jet source can be found elsewhere [9]. It has small size: a total length of less than 100 mm and a diameter of 8 mm at the main body (Figure 1). It is easily operated in argon without significant gas heating at RF power values in the range 5-20 W and gas flow rates of 2000-3000 sccm. The jet source produced cold plasma, as has been proved by thermocouple

***Figure 1.*** *Image depicting the size of the plasma source*

measurements and the fitting of the experimental OH radical bands with simulated spectra [10]. The temperature was around 380 K.

The decomposition of the methylene blue in solution was monitored by optical absorption spectroscopy in the visible spectral range. The assembled experimental setup is presented in Figure 2. It consists in a glass vessel (plasma reactor) which was half-filled with a solution of methylene blue in water (130 ml). For experiments, an initial concentration of 25 $mgl^{-1}$ of methylene blue solution was prepared. The vessel is closed at the top end with a teflon plate which allows the plasma source to pass inside. Vertical displacement of the plasma source under tight conditions is possible, allowing the change of the distance between the source tip and the liquid level. In addition, the atmosphere above the liquid can be controlled by introducing a selected gas through another tube. During the present decomposition experiments $O_2$ was maintained as additional gas.

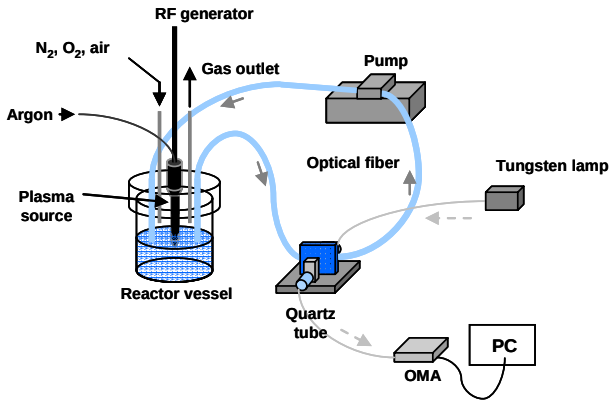


***Figure 2.*** *Schematic representation of the experimental set-up for methylene blue decomposition*

To maintain the discharge, the RF power has been set to 15 W. The plasma sustaining gas, argon, was fed into the plasma source at a constant gas flow rate of 3000 sccm. The reactive gas, oxygen, was introduced in the reaction chamber at 50 sccm.

In order to perform the optical measurements the methylene blue solution was forced by a liquid pump to recirculate continously, in a closed flow loop, through a small optical absorbtion cell. As light source a stabilized tungsten lamp was used. The light passing through the cell was collected and analyzed by an Ocean Optics spectrometer. The absorption curve has been recorded continuously during the exposure of the solution to RF plasma jet expanding in oxygen ambient.

## 3. Results and discussions

By increasing the treatment time of methylene blue solution, the color of the collected samples changed from dark blue through light blue until to completely colorless in 120 minutes. An image which illustrates the effect of plasma treatment on solution is shown in Figure 3.

***Figure 3.*** *A comparison between untreated (left) and plasma treated (right) methylene blue solution*

Figure 4 shows the visible spectra of methylene blue solution at various moments, for plasma treatments in the range 0-60 min.

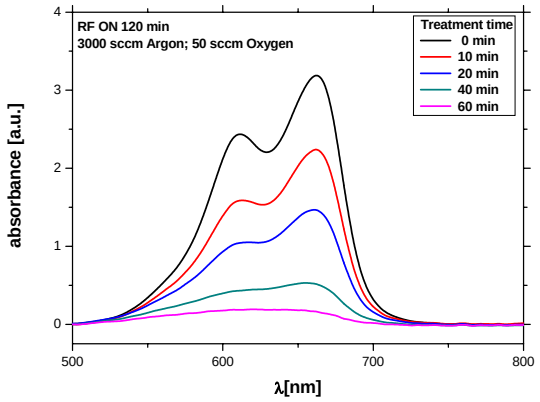


***Figure 4.*** *Visible spectra of methylene blue solution, untreated and treated in plasma for 10-60 min*

The methylene blue decomposition process is characterized by conversion and yield. The conversion parameter is defined as:

$$conv\,(\%) = \left(1 - \frac{[MB]_{out}}{[MB]_{in}}\right) \times 100$$

where:

$[MB]_{in}$ − the initial concentration of methylene blue

$[MB]_{out}$ − the concentration of methylene blue after plasma treatment

The yield is defined as the ratio between the amount of methylene blue removed during plasma treatment and the energy spent is:

$$Y(\frac{g}{kWh}) = \frac{V(l)\times[MB]_{in}(g/l)\times conv(\%)/100}{P(kW)\times t_{tr}(h)}$$

where:

V − the methylene blue solution volume

$t_{tr}$ − the treatment time

P – RF supplied power

In the present study we were interested to evaluate the importance of plasma jet tip position with respect to the liquid surface. Thus, we have compared the rate of methylene blue degradation by the atmospheric pressure plasma jet above the solution, just at the solution surface level, and submerged into solution, Figure 5 illustrates the conversion obtained for all plasma jet positions investigated.

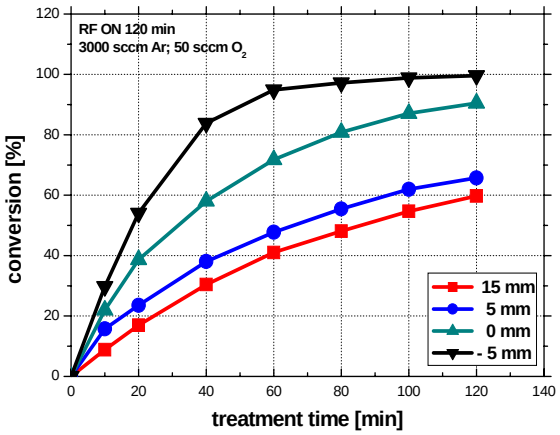


***Figure 5.*** *Methylene blue conversion by plasma treatment in argon with addition of $O_2$ for different positions of the plasma jet*

A conversion of 48% of methylene blue in 80 min has been obtained when the plasma jet was placed 15 mm above the surface.

The highest decomposition efficiency was obtained when the plasma jet was submerged into the solution, when 97% conversion in 80 min has been recorded.

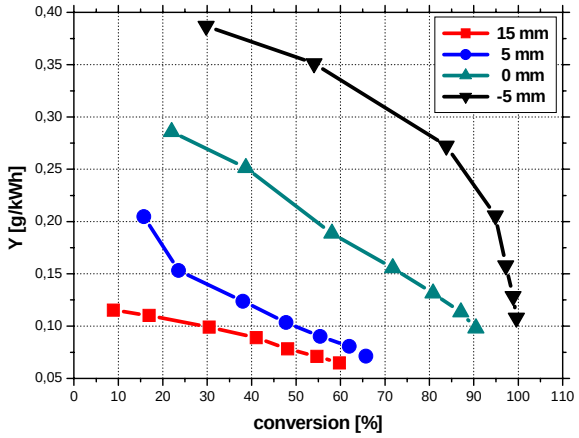


***Figure 6.*** *Yields obtained for methylene blue decomposition as a function of conversion, for different positions of the plasma jet relative to the solution*

Figure 6 shows the yields as function of the methylene blue conversion. In the case of submerged plasma jet the corresponding yield was 0.2 g/kWh.

Therefore, comparing to plasma jet working outside of solution, the submerssion of the argon jet creates better conditions for decomposing species to interact with methylene blue molecules.

Moreover we investigated the importance of plasma presence for the decomposition process. Two experiments were performed with plasma jet submerged in the liquid and $O_2$ maintained as additional gas. In one of them the treatment was maintained until complete conversion, in the other one plasma was switched off after 40 minutes of operation, but maintaing the gases (argon, oxygen) flows.

The conversion curves, shown in Figure 7, indicate that without plasma the conversion process stops rapidly, which indicate that long lasting species which might continue the decomposition during plasma absence are not created in significant amount or are rapidly transported outside the decomposition vessel.

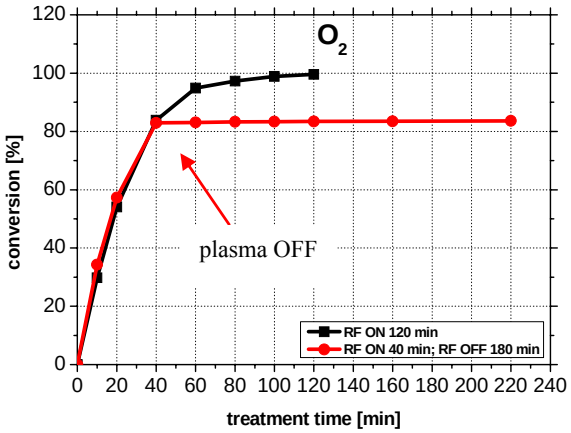


***Figure 7.*** *The effect of switching plasma OFF on the conversion rate*

## 4. Conclusion

We have investigated the decomposition of methylene blue in solution by exposure to a low power, atmospheric pressure argon plasma jet in presence of oxygen ambient. The comparison of decomposition characteristics indicates that the dye conversion due to the plasma jet is much faster and more energy efficient when the plasma was submerged into solution. The decomposition process is strictly connected to the plasma presence.

## Acknowledgments

The financial support of the CNCSIS-UEFISCDI under the project number IDEI 1999/2008 is gratefully acknowledged.

## References

[1] J.E. Foster et al., Plasma Sources Sci. Technol. 19 (2010) 025001 (9pp).

[2] P. Lukes et al., J. Phys. D: Appl. Phys. 38 (2005) 409–416.

[3] M. Magureanu et al., Plasma Chem Plasma Process 28 (2008) 677-688.

[4] Y.S. Mok, J-O. Jo, C. Whitehead, Chem. Eng. J. 142 (2008) 56-64.

[5] M.A. Malik et al., Plasma Sources Sci. Technolog. 10 (2001) 82-91.

[6] Petr Lukes et al., J. Phys. D: Appl. Phys. 38 (2005) 409–416.

[7] E.R. Ionita et al., Applied Surface Science 255 (2009) 5448–5452.

[8] I.K. Konstantinou et al. Appl Catal B: Environ 49 (2004) 1-14.

[9] G. Dinescu et al., Pure and Applied Chemistry 80 9(2008) 1919-1930.

[10] M. Teodorescu et al., Proceedings of 20th ESCAMPIG Conference, 13-17 July 2010, Serbia http://www.escampig2010.ipb.ac.rs/papers/P2.07.pdf