Generation of OH radicals using an argon non-thermal microwave plasma jet

E. Casado¹, A.Rodero²¹ and ²M.C. Garcia²

¹Department of Physics, Universidad de Córdoba, Córdoba, Spain. ²Department of Applied Physics, Universidad de Córdoba, Córdoba, Spain.

Abstract: The ability to generate OH species of a non-thermal microwave plasma reactor designed for liquid treatment was tested. Different plasma conditions including microwave power, argon flow rate, treatment time and geometry were explored. The oxidation of toluene with this plasma reactor was also investigated, by using Gas Chromatography – Mass Spectrometry (CG-MS) analysis.

Keywords: OH radicals, CG-MS, Plasma, Fluorimetry.

1. Introduction

In the last years, design of plasma reactors capable to generate reactive oxygen and nitrogen species has become a main task in the development of both environmental and bio-medical applications.

In this work, the ability for hydroxyl radicals generation of a non-thermal microwave argon jet while it is being used for water treatment, has been investigated. The OH radical production was studied under different plasma conditions (including microwave power, argon flow rate, treatment time, geometry).

Also, the way in which a small toluene layer on the surface of water is oxidized *via* these radicals, was analyzed. OH radicals play an important role in the degradation of aromatics. Products resulting from the interaction plasma-toluene were identified and quantified using Gas Chromatography – Mass Spectrometry (CG-MS) analysis.

2. Materials and method

2.1. Plasma generation

An argon plasma was created using a *surfatron* microwave power coupling device [1]. Surfatron was originally designed to generate cylindrical plasma columns inside straight dielectric tubes (TM_{00} surface wave mode). In this case, a T-shaped quartz tube (1.5 and 4 mm of inner and outer diameter) with one of its ends opened to the air was used (Fig. 1). This configuration forced the plasma column to go down through the vertical part of the T-tube and approach the water.

The sample suffered a remote plasma exposure and plasma-water distance was changed from 0.5 to 4.5 cm. Microwave power was set at different levels from 30 to 90 W, and argon flow rate ranged between 0.5 and 1.7L/min. Different treatment times of the sample were also explored.





Fig.1: Experimental set-up.

2.2. Liquid samples.

All the liquid samples were placed in cylinder shaped glass containers (2 cm diameter and 4 cm high).

In OH generation studies, 4 ml of miliQ water with 3-Coumarin Carboxylic acid dissolved was used. The concentration of the solution was 0.003 M. In the second part of this work, 1 ml of toluene was added to the miliQ water, staying on the top.

2.3. Analysis of samples.

OH radicals generation rate was measured from the fluorimetric method proposed by Newton and Milligan [2] based on the use of 3-Coumarin Carboxylic acid dissolved

in water. This component reacts with OH radicals, being 7-Hydroxycoumarin Carboxylic acid (which is fluorescent) one of the resulting products. Thus, the method consist of treating water samples with 3-Coumarin Caboxylic acid dissolved and see how much 7-Hydroxycoumarin Carboxylic acid is produced, using a spectrofluorometer. From the rate formation of this compound and taking into account that the yield per OH radical of this fluorescent product is about 4.7%, the rate formation of OH radicals can be measured [3]. A PTI, Quanta Master 40 UC/VIS Steady State Spectrofluorometer was used to measure the concentration of the fluorescent product.

Solutions of toluene treated with this plasma reactor were analysed using a GC-MS (Thermo Finnigan, Thermo-Quest Trace GC/MS–Trace DSQ) and changes of product concentrations in this solution were obtained. Evaporation produced in the sample due to high volatility of toluene was taken in to account in terms of changes in concentration.

3. Results

3.1. OH generation

Solutions with 3-Coumarin Caboxylic acid were treated with the plasma reactor under different experimental conditions, and formation of 7-Hydroxycoumarin Carboxylic acid was studied. Typical fluorometric spectra measured for plasma treated samples are shown in Fig. 2. The height of the peak is measured from the maximum at 443 nm with the minimum at 400 nm subtracted. Three different measurements were made for each power, however, in Fig. 2 mean values are represented.



Fig.2: Typical fluorometric spectra measured for plasma treated samples using different microwave powers.

Changes in concentration of this compound under different experimental conditions were analysed. In first instance, the dependency on the microwave power injected to the plasma was studied (see Fig. 3). Microwave power was set at 30, 50, 70 and 90 W levels, while treatment time, gas flow rate and distance were kept constant. A linear relationship was found between 7-Hydroxycoumarin Carboxylic acid concentration and power with a rate of 0.02 ppm/W, which could be ascribed to a higher OH production by plasma for higher microwave power.



Fig.3: Concentration in ppm of 7-Hydroxycoumarin Carboxylic acid for different powers.

A similar study was made changing gas flow rate conditions (from 0.5 to 1.7 L/min), keeping constant treatment time, microwave power and distance (see Fig. 4). In this case, a maximum of OH formation is observed around 1 L/min.



Fig.4: Concentration in ppm of 7-Hydroxycoumarin Carboxylic acid for different flow rates.

Figure 5 depicts changes in 7-Hydroxycoumarin Carboxylic acid concentration of the sample after different treatment times (1, 1.5, 2 and 2.5 min), for a distance, microwave power and gas flow rate 1.5 L/min fixed. In this case, a linear dependency was also found with a rate of 0.61 ppm/min.

Results corresponding to changes in plasma-sample distance are shown in Fig. 6. An exponential decrease was found in this case.



Fig.5: Concentration in ppm of 7-Hydroxycoumarin Carboxylic acid for different treatment times.



Fig.6: Concentration in ppm of 7-Hydroxycoumarin Carboxylic acid for different distances.

3.2. Oxidation of Toluene pollutant

Products resulting from the interaction plasma-toluene were identified and quantified using CG-MS analysis. In the present case, Benzyl radicals Benzaldehyde, Benzyl Alcohol, o-cresol and p-cresol were identified in the chromatograms (see Fig. 7). These products came from toluene oxidation (see Fig. 8) and have been previously studied [4].



Fig.7 Chromatogram measured for P = 50 W, F = 0.8 L/min, t = 1 min and d = 2 cm.



Fig.8: Oxidation products of Toluene and OH radicals.

Formation of these products under different experimental conditions was studied. The areas of their corresponding GC-MS peaks were measured.

Figure 9 shows changes in Benzaldehyde, Benzyl Alcohol, o-cresol and p-cresol content of the treated sample for different microwave power conditions. A linear relationship was found between the content of these products and power, which could be ascribed to a higher OH production by plasma at higher microwave power.



Fig.9: Benzaldehyde, Benzyl Alcohol, o-cresol and p-cresol GC-MS peak area for different powers (F = 1.5 L/min, t = 1 min, d = 2 cm).

Figure 10 depicts changes in Benzaldehyde, Benzyl Alcohol, o-cresol and p-cresol content of the treated sample for different gas flow rate conditions (0.5, 0.8, 1.1, 1.4 and 1.7 L/min), keeping constant treatment time, microwave power and distance. In this case, the interdependency showed an exponential trend.



Fig.10: Benzaldehyde, Benzyl Alcohol, o-cresol and p-cresol GC-MS peak area for different gas flow rate conditions (P = 50 W, t = 1 min, d = 2 cm).

Figure 11 shows changes Benzaldehyde, Benzyl Alcohol, o-cresol and p-cresol content of the sample after different treatment times (1, 1.5, 2 and 2.5 min), for a distance, microwave power and gas flow rate 1.5 L/min fixed. In this case, a linear dependency was found.



Fig.11: Benzaldehyde, Benzyl Alcohol, o-cresol and p-cresol GC-MS peak area for different treatment times (P = 50 W, F = 1.5 L/min, d = 2 cm).

Finally, results corresponding to changes in plasmasample distance are shown in Fig. 12. A maximum in the 4 products was measured for 2 cm.



Fig.12: Benzaldehyde, Benzyl Alcohol, o-cresol and p-cresol GC-MS peak area for different plasma-sample distances (P = 50 W, F = 1.5 L/min, t = 1 min)

4. Conclusions

This work proves the generation of OH radicals when an argon microwave plasma jet is being used for water treatment, in a remote exposure. The amount of OH radical generated depends upon plasma parameters (microwave power, gas flow rate), treatment time and distance plasmawater.

Oxidation products resulting from the interaction plasma-toluene were identified and quantified, showing again that OH radicals have been generated by this plasma reactor. The oxidation of toluene is also determined by plasma conditions, treatment time and distance plasmawater.

5. Acknowledgements

Authors thank the European Regional Development Funds program (EU-FEDER) and the MINECO (project MAT2016-79866-R) for financial support. The authors also are grateful to Andalusian Regional Government (Research Group FQM-136) for their technical and financial support.

6. References

[1] M. Moisan and J. Pelletier (1992) Microwave excited plasmas, Plasma Technology, Elsevier, Amsterdan, (Chap. 3).

[2] G.L. Newton and J.R. Milligan, Radiation Physics and Chemistry, 75, 473-478 (2006)

[3] F.J. Bosi et al, Plasma Processes and polymers, 15 (2018).

[4] B. Bohn, The Journal of Physical Chemistry, 105, 6092-6101 (2001).