Preliminary Study on the Treatment of Benzene Contaminated Water using an Argon Microwave Plasma Jet

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Abstract. In this work, the ability of a microwave induced plasma jet to treat water contaminated with benzene was investigated. It studies the formation of hydroxyl (OH) radicals by the plasma jet and reactions between benzene and these radicals, under different experimental conditions (including microwave power and treatment time). Products resulting from the interaction plasma-sample were identified and quantified using Gas Chromatography – Mass Spectrometry (CG-MS) analysis.

1. Introduction
In the last years, the use of plasma technology to induce Advances Oxidation Processes for water treatment purposes has notably grown [1-3]. Plasmas generate charged particles, excited species, radicals and UV radiation, among others, each of which are advanced oxidation techniques themselves. These species are able to degrade contaminants through mineralization [4-8]. In this work we report on the degradation of benzene by an argon microwave induced plasma jet.

2. Materials and method
2.1. Plasma generation
An argon plasma was created using a surfatron microwave power coupling device [9]. 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 (see figure 1). This configuration forced the plasma column to go down through the vertical part of the T-tube making it easier to control the plasma-liquid distance.

2.2. Liquid samples.
Liquid samples suffered a remote plasma exposure and plasma-sample distance was fixed at 2 cm. The argon flow rate was set at 1.5 L/min, and the microwave power was changed from 30 to 60 W. Different treatment times of the sample were also explored. 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, 1.5 ml of benzene was added to the miliQ water, staying on the top.
2.3. Analysis of samples.
OH radicals generation rate was measured from the fluorometric method proposed by Newton and Milligan [3] 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 consists of treating water samples with 3-Coumarin Carboxylic 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 [10]. A PTI, Quanta Master 40 UC/VIS Steady State Spectrofluorometer was used to measure the concentration of the fluorescent product.
Solutions of benzene 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 into account in terms of changes in concentration.

![Figure 1. Experimental set-up.](image)

3. Results

3.1. OH radical generation
Solutions with 3-Coumarin Carboxylic acid were treated with the plasma reactor under different experimental conditions, and formation of 7-Hydroxycoumarin Carboxylic acid was studied. Changes in concentration of this compound were analysed.

![Figure 2. Concentration in ppm of 7-Hydroxycoumarin Carboxylic acid for different powers.](image)
In first instance, the dependency on the microwave power injected to the plasma was studied (see figure 2). 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.

Figure 3 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.

Figure 3. Concentration in ppm of 7-Hydroxycoumarin Carboxylic acid for different treatment times.

3.2. Oxidation of Benzene

Products resulting from the interaction plasma-benzene were identified and quantified using CG-MS analysis. In the present case, the attention was focused on two products resulting from oxidation of benzene, phenol and 1,2-benzenediol, whose peaks appeared at 3.31 min and 5.76 min, respectively.

Phenol and 1,2-benzenediol came from benzene oxidation. Formation of these products under different experimental conditions of microwave power and treatment time was also studied. The areas of their corresponding GC-MS peaks were measured for this purpose.

Figure 4 shows changes in phenol and 1,2-benzenediol content of the treated samples under different microwave power conditions (from 30 to 60 W). An increasing trend was found according to the dependence on the microwave power of OH radical formation measured (Figure 2).

Figure 5 shows changes of phenol and 1,2-benzenediol content after different times of treatment (0.5, 1, 1.5 and 2 min), for a plasma-sample distance, microwave power and gas flow rate 1.5 L/min fixed. A linear dependency was found, which agrees with results shown in figure 3 for 3-Coumarin Carboxylic acid oxidation.

Figure 4. Phenol and 1,2-benzenediol GC-MS peak area for different microwave powers (F = 1.5 L/min, t = 1 min, d = 2 cm).
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 radicals generated depends upon plasma microwave power and treatment time.

Interaction plasma-benzene cause oxidation of benzene, being phenol and 1,2-benzendiol the main products identified. This oxidation is controlled by OH production. These preliminary results show that the microwave plasma jet is a promising technology for treatment of benzene contaminated water.

Acknowledgements
As part 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. This work was also partially financed from the project BUT InterAcademic Partnerships (PPI/APM/2018/1/00033/DEC/1).

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