Degradation of m-cresol in aqueous solution by dielectric barrier discharge

B Jaramillo-Sierra², A Mercado-Cabrera¹, R López-Callejas¹,², R Peña-Eguiluz¹, S R Barocio¹†, R Valencia-Alvarado¹, B Rodríguez-Méndez¹, A Muñoz-Castro¹, A De la Piedad-Benitez²

¹ Instituto Nacional de Investigaciones Nucleares, Plasma Physics Laboratory AP 18-1027, 11801 México D. F., México.
² Instituto Tecnológico de Toluca, AP 890, Toluca, México
† In Memoriam
E-mail: antonio.mercado@inin.gob.mx

Abstract. It was carried out a theoretical and experimental study of the m-cresol degradation in aqueous solution using a non-thermal plasma induced by dielectric barrier discharge. For the experimental setup a coaxial reactor vertically placed was used. Wherein a liquid solution flowing inside the internal electrode was impelled by a peristaltic pump and falling over the external surface of the internal electrode. Working gas was applied in a parallel direction respect to the surface of the liquid and inside of the quartz tube. Non-thermal plasma was generated at the gas-liquid interface in Ar-O₂ gas mixtures with a high-voltage power supply system. The electric power applied ranged from 10-60W at a 3.0 kHz frequency. The initial concentration of m-cresol was of 5×10⁻³ mol/L, and the removal efficiency up to 97.3% was obtained after 1 h of treatment. For the theoretical study a simplified model of the chemical kinetics was developed where the temporary evolution of the compounds generated in the process of degradation of the m-cresol was analyzed. Byproducts as oxalic acid and CO₂ were found.

1. Introduction
Cresols are organic compounds obtained from petroleum, wood tar or coal tar and they have a great variety of applications in chemical, petrochemical, cosmetic and pharmaceutical industries [1,2]. Conventionally treatments as biological and physical methods are used for their degradation. Nevertheless, because cresols are chemically stable, they are not totally eliminated thus noxious byproducts as chlorocresols can be generated. For this reason they represent a source of pollution of the water. The non-thermal plasma is an alternative for the degradation of pollutants in the wastewater and its effectiveness has already been demonstrated for dyes [3], organic compounds as phenol [4], as well as bacteria deactivation. In this work non-thermal plasma induced by dielectric barrier discharge was intended to carry out the m-cresol degradation. For that, an experimental development was made, where several variables of the process like gas composition and released electric power were analyzed, with the objective of deciding the best operating conditions for the degradation as well as the determination of generated byproducts. A simple theoretical kinetics model was developed. It included only the liquid phase in order to determine in function of the time the final products of the degradation of the m-cresol.
2. Experimental setup and theoretical model

2.1. Experimental procedure

The experimental device shown in Figure 1 is composed by (1) plasmagen gases, which are supplied to the reactor according to the selected gas mixture, (2) a quasi-sinusoidal high-voltage power supply working at a repetition frequency of 3.0 kHz and released power ranged from 10 to 60 W, (3) a reactor of treatment with coaxial configuration is constituted by a stainless steel hollow tube inner electrode with external diameter of 12.0 mm, a quartz tube as a dielectric material and a fine mesh of copper working as outer electrode, (4) for the analysis of the collected samples a gas chromatography/mass spectrometry (GC/MS) system from Agilent Technologies was used, it meets the GC 5973N and the MSD 6890, which uses a column HP-5MS (30 m × 0.25 mm × 0.25 µm).

![Figure 1. Experimental apparatus](image)

The experimental procedure consisted on the treatment of synthetic aqueous solutions of m-cresol with an initial concentration of 5.0×10^{-3} mol/L. The treatment time was 1h for 500 mL of solution. The cylindrical reactor was placed vertically and the solution was impelled inside of the internal electrode, made of a hollow tube of stainless steel, using a submersible pump; when the liquid arrives to the top overflows on the external wall of the internal electrode and forms a thin layer of liquid establishing a gas-liquid interface as is showed in Figure 2. The residence time of the liquid was estimated of approx. 1.47 seg. Non-thermal plasma was generated in the gas phase using a gas mixture of Ar-O₂. During the treatment (1h), every five minutes solution samples were collected and analyzed by gas chromatography/mass spectrometry (GC/MS) system. The power supply working at a constant frequency of 3.0 kHz and a constant difference of potential was imposed during all treatment time. This procedure was repeted imposing a different electric potential scanning from 15 kV up to 23 kV.
2.2. Kinetics Model

The theoretical model is constituted by 33 reactions and 23 chemical species only for the liquid phase [5]-[11], and was developed from the equation of continuity of the species. It was neither considered the diffusion effect nor the convection effect. In this way the equation of continuity can be simplified (1), where \( n_i \) is the density of the \( i \) species, \( S_i \) represents the generation and decomposition of the \( i \) species.

\[
\frac{dn_i}{dt} = S_i \tag{1}
\]

3. Results and discussion

3.1. Theoretical study

In Figure 3 the theoretical degradation in liquid phase of the \( m \)-cresol is shown, the simulations were carried out at the atmospheric pressure with an initial concentration of \( 5 \times 10^{-3} \) mol \( m \)-cresol/L. The \( m \)-cresol degradation is carried out by combined chemical ways in gas and liquid phases. In gas phase electrons generated during the electric discharge react with \( O_2 \), \( Ar \) and vapour of water, producing active species like \( O_3 \), \( OH \) and \( O \) (2)-(5). Moreover, mass transfer mechanism is established in both phases, when some of the species in gas phase transfer to the liquid phase and vice versa [12] by diffusion process, Figure 2.

\[
e + Ar \rightarrow Ar^* + e \tag{2}
\]
\[
e + O_2 \rightarrow e + O^* + O \tag{3}
\]
\[
e + H_2O \rightarrow OH + H \tag{4}
\]
\[
O + O_2 + O_2 \rightarrow O_3 + O_2 \tag{5}
\]
\[
Ar^* + Ar^* \rightarrow Ar^+ + Ar^{**} + e \tag{6}
\]
\[
Ar^{**} + O_2 \rightarrow Ar + O + O \tag{7}
\]

The elimination mechanism starts when active species diffused in water \( O \), \( H_2O_2 \), \( OH \) and other
generated in liquide phase due to the dissociation of $H_2O$ (7)-(11), react with the $m$-cresol generating primary products (12)-(13).

\[
\begin{align*}
&H_2O \rightarrow H + OH \\
&H_2O + H_2O \rightarrow H_2O_2 + H_2 \\
&H_2O_2 \rightarrow OH + OH \\
&O_3 + H_2O \rightarrow H_2O_2 + O_2 \\
&m - cresol + 2OH \rightarrow 2 - methyl - hydroquinone + 2H_2O \\
&2 - methyl - hydroquinone + 2OH \rightarrow 2 - methyl - p - benzoquinone + 2H_2O
\end{align*}
\]

Later on, the $m$-cresol and his derived react with each other and OH in the solution producing smaller molecules such as oxalic acid and acetic acid. Finally, these species are oxidized to $CO_2$ and $H_2O$ following the way shown in [11].

**Figure 3.** Theoretical degradation of $m$-cresol

### 3.2. Experimental Results

a) Gas mixture: [90% Ar - 10% $O_2$]

Figure 4 makes evident that the increments of the applied electric power and the time of treatment had a positive effect on $m$-cresol degradation. In liquid phase, chemical reactions are carried out generating active species like $OH$ and $H_2O_2$ (8)-(11), (14)-(16). Radical $OH$ reacts with the $m$-cresol and starts its oxidation, based on the mechanism proposed by Da Silva Pimentel [11], the primary by-products are generated, as they are chemically unstable break down generating intermediate species as oxalic acid and acetic acid, which react successively in the solution producing $CO_2$ and $H_2O$ like final products.

\[
\begin{align*}
&H_2O + O_3 \rightarrow 2OH + O_2 \\
&H + O + O \rightarrow HO_2
\end{align*}
\]
Figure 4. Efficiency of $m$-cresol degradation (90% Ar - 10% O$_2$)

b) Gas mixture: [80% Ar - 20% O$_2$]
In Figure 5 the effect of the time of treatment and electric power supplied are shown. The tendency is the same as in the previous case (Fig. 4). However from powers beyond of 23.7 W a significant influence of the power is not clearly observed, efficiencies were obtained of up to 92.2% after 60 minutes of time of treatment. Comparing Fig. 5 with Fig. 4 a lower degradation efficiency is observed, two causes were possible. The first one attributed to an increase of the O$_2$ quantity. Indeed, at 10% O$_2$, the released power was consumed mainly by Ar. At 80% Ar - 20% O$_2$, the energy should be shared with O$_2$. Therefore Ar does not participate efficiently in the dissociation of O$_2$ (7), and the power consumption is increased as it is displayed on legend curves in Figures 4, 5 and 6. If the oxygen quantity increase the electron attachement and the power consumtion too. The second one may comes from the power consumption, as it becomes higher reactor and aqueous solution temperatures increase. This augment of temperature (results not shown) was measured at the end of the experiment and a value up to 64°C was observed. Temperature increasing rises humidity in the gas phase and therefore instabilities in the discharge were observed affecting the efficiency. As a consequence, the elimination process finishes prematurely, indeed when free radicals as OH are generated in excess, they associate with each other finishing the reaction path (17)-(18) [13].

\[
H + HO_2 \rightarrow OH + OH 
\] (16)

\[
H + OH \rightarrow H_2O \] (17)

\[
OH + OH \rightarrow H_2O_2 \] (18)
c) Gas mixture: [70% Ar - 30% O₂]
Treatment time and applied power effects are shown in Figure 6. Here, efficiencies were obtained up to 91.0% after 60 minutes of time of treatment. Comparing the three last figures, one can observe a decrease tendency of the degradation efficiency.

![Figure 5. Efficiency of m-cresol degradation (80% Ar - 20% O₂)](image)

**Figure 5. Efficiency of m-cresol degradation (80% Ar - 20% O₂)**

d) Gas mixture: [0% Ar - 100% O₂]
In Figure 7 is depicted, as the applied power was increased the efficiency of m-cresol degradation was augmented as in the previous cases. For this gas mixture the efficiencies were obtained up to 97.3%.
Due that the gas mixture was constituted totally by O₂, the whole energy was consumed by O₂ and competition was not exist with Ar. The presence of O₂ was propitious to the generation of active species as O and O₃, which contribute to the formation of radical OH, (to see reactions

![Figure 6. Efficiency of m-cresol degradation (70% Ar - 30% O₂)](image)

**Figure 6. Efficiency of m-cresol degradation (70% Ar - 30% O₂)**
5, 10, 11, 14 and 15) and therefore in the m-cresol degradation.

![Graph showing efficiency of m-cresol degradation.](image)

**Figure 7.** Efficiency of m-cresol degradation (0% Ar - 100% O₂)

### 3.3. Identification of by-products

In the liquid phase were identified oxalic acid, glyoxal, 4-hydroxy-2-pentanone, methyl alcohol, ethanol-2-methoxy-acetate, formic acid-methyl ester and ethanol-2-methoxy-acetate using gas chromatography and mass detection. Figure 8(a) shows the variation in time of oxalic acid, which can be explained by the formation of CO₂.

Furthermore, exhausted gases were also analyzed, the main compound found was CO₂. m-cresol in the exhausted gases was not detected. Figure 8(b) shows the variation of CO₂ during one hour of treatment. It can be seen in the figure that CO₂ generation rises as the treatment time is increased. CO₂, according to [11] comes from the oxidation of oxalic acid and formic acid.

![Graphs showing identification of oxalic acid and CO₂.](image)

a) Identification of oxalic acid  
b) Identification of CO₂

**Figure 8.** Identification of by-products
Furthermore, color alteration of the residual liquid was special noticed to be function of the treatment time. It can be observed that the sample without treatment (showed as 0, Figure 9) after some minutes of treatment becomes sepia color and in some cases it turns to a light yellow color. According to some authors [14]-[15] the color change is attributed to the presence of acids as for example: oxalic acid and acetic acid generated during the process of degradation of \(m\)-cresol. When the residual liquid presents a light yellow color, it indicates a higher mineralization and when it has practically a light color the by-products have been transformed almost completely in \(CO_2\) and \(H_2O\). This treatment time evolution is described in the Figure 9.

![Figure 9. Changes of color of the residual liquid [0% Ar - 100% \(O_2\)], 54.7 W](image)

The pH variation as a function of applied power and time of treatment is shown in Figure 10. As an exemple, in the case of 100% \(O_2\) initial pH measured was 7.5. It was observed an augmentation in acidity as the treatment time was increased. The acidity measured is explained by the carboxylic acids generated after the oxidation of \(m\)-cresol. Inversely a pH value increasing indicate that some carboxylic acids are oxidized to \(CO_2\) and water, as it is shown in Figure 10 when applied power was 54.7 W.

![Figure 10. pH variation](image)

4. Conclusion
Theoretically, it was possible to determine the main products of oxidation of \(m\)-cresol, the water and dioxide of carbon are among the final products. Another intermediate product as oxalic acid was also observed theoretically. Experimentally, during oxidation process as the oxygen
proportion in the gas mixture was increased the efficiency of removal of \textit{m}-cresol was diminished, a higher power was consumed and an increasing of temperature of the aqueous solution was measured. Nevertheless, a 97.3\% of efficiency of \textit{m}-cresol removal was obtained using 100\% \textit{O}_2. It shows the effectiveness of the non-thermal plasma for the degradation of compound organic in water and the dielectric barrier discharge process was able to oxidize compound organic in aqueous solution. Oxalic acid and carbon dioxide were determined in liquid and gas phase respectively. Measurements of pH had confirmed the organics acids formation.

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\textbf{References}

[1] Duu-Jong L, Kuo-Ling H and Yu-You C 2011 \textit{Appl. Microbiol. Biotechnol.} 89 209-15
[2] Abdollahi Y, Abdullah A H, Zainal Z and Yusof N A 2011 \textit{Int. J. Chem.} 3 31-43
[3] Tang Q, Jiang W, Zhang Y, Wei W and Lim T M 2009 \textit{Plasma Chem. Plasma P.} 29 291-305
[4] Jaramillo-Sierra B, Mercado-Cabrera A, López-Callejas R, López-Fernández J A, Peña-Eguiluz R, Barocio S R, Valencia-Alvarado R, Rodríguez-Méndez B, Muñoz-Castro A and de la Piedad-Beneitez A 2011 \textit{Eur. Phys. J. Appl. Phys.} 56 24026
[5] Hoigné J and Bader H 1976 \textit{Water Res.} 10 377-86
[6] Hoigné J and Bader H 1983 \textit{Water Res.} 17 173-83
[7] Hoigné J and Bader H 1983 \textit{Water Res.} 17 185-94
[8] Devlin H R and Harris L J 1984 \textit{Ind. Eng. Chem. Fund.} 23 387-92
[9] Dors M, Nichipor G V and Mizeraczyk J 2005 \textit{IEEE International Conference on Dielectric Liquids} 95-98
[10] Grymonpré D R, Finney W C and Locke B R 1999 \textit{Chem. Eng. Sci.} 54 3095-105
[11] Da Silva Pimentel M A 2008 PhD. dissertation Université Paris-Est Marne-La-Vallée
[12] Ogier S, Iya-sou D, Fourmond C and Cavadias S 2009 \textit{Plasma Chem. Plasma P.} 29 261-73
[13] Joshi A A, Locke B R, Arce P and Finney W C 1995 \textit{J. Hazard. Mater.} 41 3-30
[14] Tomizawa S and Tezuka M 2006 \textit{Plasma Chem. Plasma P.} 26 43-52
[15] Kavitha V and Palanivelu K 2005 \textit{Water Res.} 39 3062-72