

CATALYTIC OZONATION OF METOLACHLOR UNDER CONTINUOUS OPERATION USING NANOCARBON MATERIALS GROWN ON A CERAMIC MONOLITH

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Abstract: The catalytic ozonation of the herbicide metolachlor (MTLC) was tested using carbon nanomaterials as catalysts. Multiwalled carbon nanotubes were used in semi-batch experiments and carbon nanofibres grown on a honeycomb cordierite monolith were tested in continuous experiments. The application of the carbon catalyst was shown to improve the mineralization degree of MTLC and to decrease the toxicity of the solution subject to ozonation. Degradation by-products were also followed in order to compare the two processes. The application of the carbon coated monolith to the continuous ozonation process was shown to have potential as it improved the TOC removal from 5% to 20% and decreased the inhibition of luminescent activity of *Vibrio Fischeri* from 25% to 18%.

Keywords: catalytic ozonation, monolith, carbon nanomaterials, metolachlor, emerging organic micropollutants

INTRODUCTION

The use of pesticides in modern agriculture, including herbicides, is considered essential to avoid loss of cultures by infestations, which would render the large scale exploration impracticable. However, since the 1960s, preoccupations have escalated regarding the negative effects of such agents on human health and on the ecosystems.

Metolachlor (MTLC) is a chloroacetanilide selective herbicide extensively used in various cultures, and elevated concentrations in surface and groundwater have been reported, as well as some of its degradation products [1-5]. The structure of the molecule can be found in [Figure 1](#).

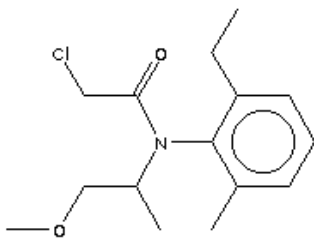


Figure 1 - Structure of the metolachlor molecule.

Currently, this pesticide is listed on the Contaminant Candidate List 3 (CCL3) by USEPA, together with its main degradation by-products [6]. The World Health Organization drinking water quality guideline suggests a value of 10 µg/L as a limit for MTLC [7]. Additionally, the pesticide and its aniline metabolites are suspected or confirmed carcinogens [1].

Conventional treatments are rather effective in the removal of MTLC from water [8, 9]. However, these processes are not capable of completely mineralizing the pesticide, yielding several by-products, including several organic acids and aromatic compounds. It has been shown that these compounds may present a more severe-harmful effect to the environment [1]. Thus, it is important to study novel treatment processes aiming at the complete mineralization of this type of water contaminants.

Recently, research in Advanced Oxidation Processes (AOP) has been target of attention from the scientific community due to their potential to further mineralize organic pollutants [10-15], and some studies have been published regarding MTLC [16-19]. These processes consist in the enhancement of the oxidation potential of conventional oxidants by producing other compounds that are capable of further mineralizing water contaminants. Catalytic ozonation is included in this category and is the focus of this study.

Conventional ozonation treatment consists in the oxidation of organic compounds and in the elimination of microorganisms present in wastewater or drinking water [20]. On the other hand, the catalytic ozonation process consists in the enhancement of the oxidation potential of ozone by the production of highly-reactive radicals, namely hydroxyl radicals (OH \cdot), which is achieved by the application of a catalyst. In the present study, the catalysts selected were Multiwalled Carbon Nanotubes (MWCNT) and Carbon Nanofibers (CNF), which have already been reported to be effective for this type of reaction [21, 22].

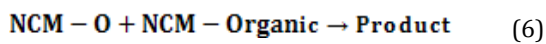
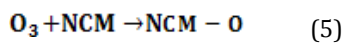
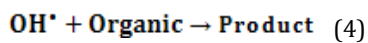
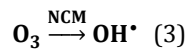
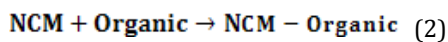
The mechanism of catalytic ozonation in the presence of carbon materials has been described as a combination of bulk and surface reactions [23-25]. A similar mechanism

should occur when nanocarbon materials (NCM) are used as catalyst [21, 26]. The mechanism for the formation of highly-reactive radicals and how they react with the organic pollutants has been described in the literature [23, 25, 27, 28]:

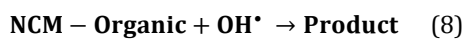
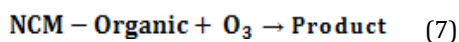
In aqueous solution ozone decomposes into hydroxyl radicals, process that is initiated by the presence of OH⁻ (eq. 1).



In the presence of carbon materials, the organic pollutant can be adsorbed (eq. 2). Dissolved ozone either reacts with the surface of the catalyst to yield free radical species released to the solution (eq. 3), which will react with the organic pollutant in the bulk (eq. 4), or ozone is adsorbed on the surface of the catalyst, yielding active surface groups (eq. 5), which will in turn react with the adsorbed pollutant (eq. 6).



It is also viable that the adsorbed pollutants react with aqueous species (eq. 7 and 8).



The application of a monolithic catalyst for reactions simultaneously involving gas and liquid phase has been subject to recent attention [29-33]. The two-phase flow through the monolith channels, under expected hydrodynamic conditions, develops into Taylor flow hydraulic regime. This regime is characterized by the formation of gas slugs, or long bubbles, of length several times larger than the diameter of the channels. Between these gas slugs and the walls of the monolith a thin film of liquid is formed (typically between 5 and 50 μm, depending on the viscosity of the fluid and the bubble velocity). The increased interfacial area and the short diffusion path greatly increase the mass transfer from the

gas phase to the solid phase. The films are renewed by the movement of the bubbles and the mixing inside the liquid slugs [34-38].

Most studies focusing in carbon materials as ozonation catalysts used powder catalysts. In the present study the potential of the carbon materials is transposed onto a macrostructure as a prospective solution for practical application in water treatment facilities. Besides the potential to enhance the oxidation potential of catalytic ozonation by facilitating mass transfer across the different phases, the ease of operation of a macrostructure is seen as a very important advantage of this technology. The process eliminates the need for filtration of catalyst particles, while reducing pressure drop when compared to packed bed reactors. The mechanisms for ozone decomposition and reactions with organic pollutants are expected to be similar to the described above [22].

The growth of CNF on the surface of a ceramic monolith has already been reported in the literature [39, 40], as well as the application of the system to catalysis, including catalytic ozonation [22, 39].

In summary, this study focuses on the development of a system for the oxidation of the herbicide Metolachlor using CNF grown on a honeycomb ceramic monolith under continuous operation. The main goal is to improve the mineralization of the pollutant, while reducing the acute toxicity. Semi-batch experiments were also made in a stirred tank reactor to gather data about the degradation mechanisms.

EXPERIMENTAL

MATERIALS AND CHEMICALS

Commercial Multiwalled Carbon NanoTubes (MWCNT) were used as supplied (Nanocyl 3100). Monolithic catalysts (see [Figure 2](#)) were prepared to fit inside the bubble column used for the catalytic tests. They consist of a commercial honeycomb cordierite structure, upon which carbon nanofibers (CNF) were grown after coating the monolith with an alumina wash coat impregnated with nickel, which acts as a catalyst for the carbon growth. CNF were formed under a gas flow of ethane and hydrogen (50:50). The detailed preparation method is described elsewhere [40]. The specific monolith used for the experiments here described had a diameter of 22 mm and a height of 60 mm, with square channels of 1 mm diameter. The loading of CNF on the catalyst was 10.22 wt%, and the total mass was 10.2 g.

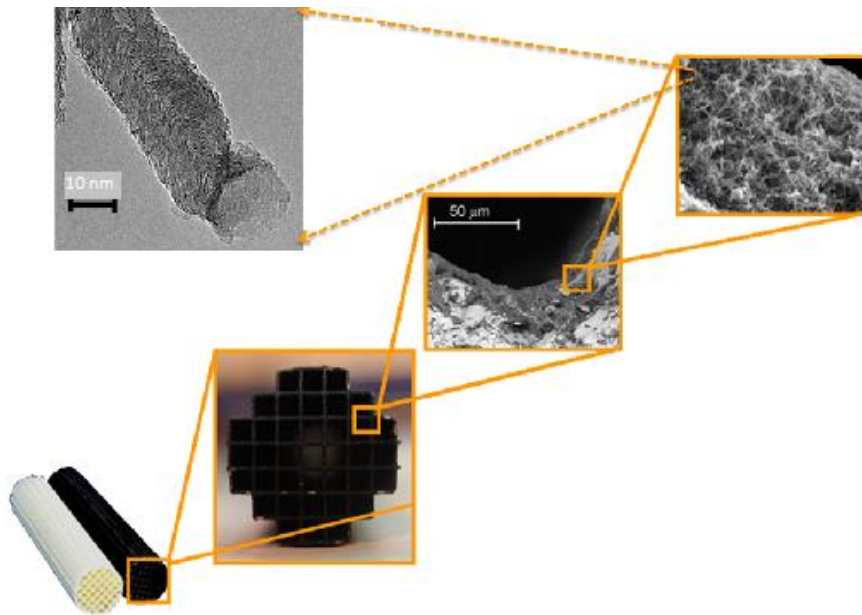


Figure 2 - Honeycomb monolith covered with CNF.

Metolachlor was acquired from Sigma-Aldrich (PESTANAL Analytical Standard). Oxalic ($\geq 99\%$), oxamic ($\geq 99\%$) and pyruvic acids ($\geq 98\%$) were also acquired from Sigma-Aldrich.

SEMI-BATCH OZONATION WITH MULTIWALLED CARBON NANOTUBES

The semi-batch ozonation experiments were made in a conventional stirred tank reactor presented in a previously published paper [22]. A volume of 700 mL of solution was used, with 20 ppm of MTLC prepared with milliQ ultrapure water. Ozone was generated from pure oxygen using a BMT 802X ozone generator and bubbled into the bulk of the solution using a diffusor (total flow rate = $150 \text{ cm}^3/\text{min}$; ozone concentration = $50 \text{ g O}_3/\text{m}^3$). Ozone in the gas phase was analyzed using a BMT 964 ozone analyzer. The powdered catalysts were introduced (100 mg) into the solution before ozone and kept suspended using a stirrer at 200 rpm. Blank (no catalyst) and adsorption (no ozone) tests were also performed. In the adsorption experiment pure oxygen was kept flowing to maintain the mixing conditions of the ozonation tests.

CONTINUOUS OZONATION WITH MONOLITHIC CATALYST

Continuous experiments were performed in a bubble column reactor with internal loop, presented in a previously published paper [22], inside which a monolithic catalyst can be lodged. Ozone was fed through a diffusor in the bottom of the column, and MTLC solution (20 ppm) was introduced near the bottom using a peristaltic pump. The monolith is placed

inside the column and both the gas phase and the liquid phase go through the channels, concurrently in upflow. Experiments were made using 1 and 4 monoliths in series, thus varying the contact time with the catalyst between approximately 1.9 min and 7.6 min respectively. A biphasic experiment was made by placing the monolithic catalyst inside the reactor's internal loop, thus separating the gas-liquid interface from the liquid-gas interface.

Liquid phase was pumped at 12 cm³/min and the gas phase at 15 cm³/min. Ozone was generated from pure oxygen at 50 g O₃/m³ using a BMT 802N ozone generator. The internal recirculation loop was kept at 60 cm³/min using a peristaltic pump.

These conditions were optimized in order to obtain the best homogeneous distribution through the channels of the monolith. For large bubble sizes (2-3 mm diameter) it was found that the bubbles coalesced beneath the monolith, eventually breaking through the channel that offered a smaller pressure drop. However, for bubble sizes with diameters inferior to the channel diameter, a bubbly flow develops inside the channels of the monolith, putting away any advantage in using a three-phase system [36]. Thus, a bubble size with approximately the diameter of the monolith channels was chosen as a compromise between the two situations. The mean superficial liquid velocity (~0.30 cm/s) and the bubble rise velocity (~10 cm/s [41]) used should place the hydrodynamic regime as Taylor flow [36, 38, 42]. The bubble column has a diameter of 22 mm and the liquid column has a height of 60 cm, leaving free head room inside the column.

ANALYTICAL METHODS

Several different techniques were used to obtain data from the ozonation experiments. The removal of MTLC was followed by HPLC, using a Hitachi Elite LaChrom apparatus equipped with a diode array detector. The separation of MTLC was achieved using a Lichrocart C18-RP Puroshper Star (250 mm × 4.6 mm, 5 μm) column and an isocratic 60%ACN-40%H₂O mobile phase at 1 mL/min. Quantification of MTLC was made at 198 nm. Likewise, the formation and concentration of organic acids, typical end-of-chain degradation products, was followed using a Hitachi Elite LaChrom HPLC equipped with an UV-Vis detector. Separation of the organic acids was achieved using an Alltech OA-1000 chromatography column using an isocratic 5mM H₂SO₄ mobile phase at 0.5 mL/min. Quantification of the organic acids was made at 200 nm.

The release of ionic compounds into the solution was followed using a HPLC system equipped with a conductivity detector to measure both anions and cations. The separation

was achieved with a Dionex ICS-2100 Ion Chromatography System using a Dionex IonPac AS11-HC column (250 mm × 4 mm), under an isocratic elution with a solution of NaOH 30 mM at a flow rate of 1.5 mL/min, and a Dionex DX-120 Ion Chromatography System using an IonPac CS12A column (250 mm × 4 mm) working with a solution of methanesulfonic acid 20 mM as the mobile phase at a flow rate of 1.0 mL/min, for anions and cations respectively. The system was equipped with a conductivity detector, which performance was improved by electrolyte suppression using ASRS 300 or CSRS ULTRA II self-regeneration suppressors for anions and cations, respectively.

Acute toxicity analyses were performed using an Azure Environment Microtox apparatus and procedure ISO/DIS 11348-3. The microorganisms used were the luminescent bacteria *Vibrio Fischeri* from Hach Lange, which is used as representative of aquatic environments [17, 43]. The bacteria were exposed to samples after activation and 15 minutes incubation at 15 °C, and the decrease in activity as function of the luminescence was measured after 30 minutes. The standard index used to evaluate acute toxicity, the EC₅₀, was not calculated because, at the concentrations used in this study, a large number of the samples did not reach 50% of inhibition of the luminescent activity. Instead, the inhibition of activity measured is presented.

Total organic carbon, measured with a Shimadzu TOC-5000A apparatus, was used to assess the mineralization of MTLC.

RESULTS AND DISCUSSION

SEMI-BATCH OZONATION OF METOLACHLOR

In ~~Figure 3~~ [Figure 3](#) the evolution of the dimensionless concentration of MTLC during the semi-batch catalytic ozonation experiment, together with the results obtained for the blank and the adsorption tests, are presented.

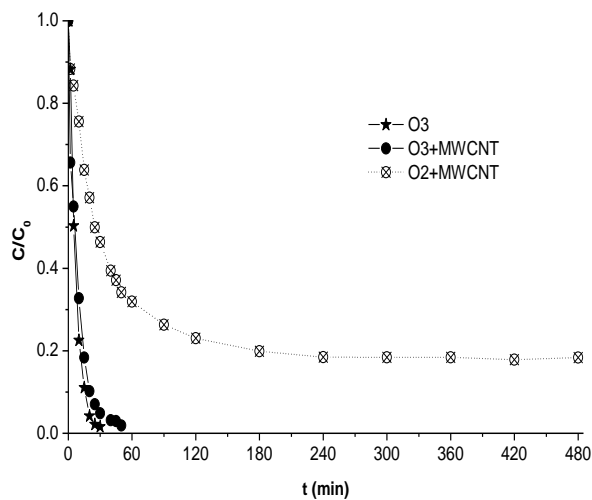


Figure 3 - Dimensionless concentration of Metolachlor during semi-batch ozonation experiments.

It is noticeable that the addition of MWCNT did not accelerate the decomposition of the pesticide when compared with single ozonation, which suggests that the degradation of MTLC is mainly due to the direct reaction with ozone. The formation of the non-selective hydroxyl radicals might have a negative effect on the degradation of the parent pollutant, since less ozone is available to directly react with MTLC. However, the difference between the two experiments is negligible when only the parent compound is considered.

Although adsorption on MWCNT is rather extensive, as seen in the experiment with no ozone ([¡Error! No se encuentra el origen de la referencia.Figure 3Figure 3](#)), the main mechanism for the catalytic ozonation of metolachlor is by oxidation. Furthermore, there are several operational setbacks for adsorption processes, namely it is a water treatment process where the pollutant is just transferred from liquid to solid. In this study, we are trying to achieve the mineralization of the pollutant.

Although MTLC is easily degraded, total mineralization is not readily achieved, as can be seen in [Figure 4Figure 4](#), where the dimensionless TOC concentration is shown.

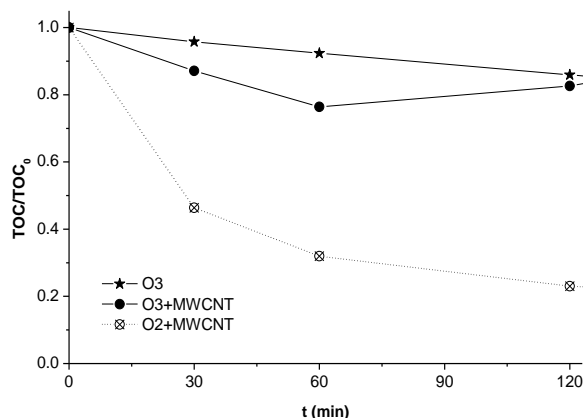


Figure 4 - Evolution of dimensionless TOC concentration during the semi-batch ozonation experiments.

In [Figure 4](#) it is noticeable the influence of the presence of MWCNT. Further mineralization of the organic carbon in solution is attributed to hydroxyl radicals, which production is enhanced by the presence of the catalyst. However, it is noticeable that the degradation of the organic matter slows down after 60 minutes of reaction. This occurs because the by-products of the oxidation of MTLC are less reactive with the oxidants in solution than MTLC. However, there is also a contribution of the powder material to TOC concentration that cannot be disregarded [25]. Additional tests (without pollutant) were carried out, but this contribution was found to be dependent on the composition of the solution. Then, it was not possible to discount the mentioned effect on TOC values.

The decrease in the value of TOC for the experiment without ozone corresponds to the adsorption of MTLC, while for the ozonation experiments it corresponds to the mineralization of pollutant and its by-products.

The evolution of three identified organic acids is presented in [Figure 5 \(oxalic acid\)](#), [Figure 6 \(pyruvic acid\)](#) and [Figure 7 \(oxamic acid\)](#), for ozonation and catalytic ozonation.

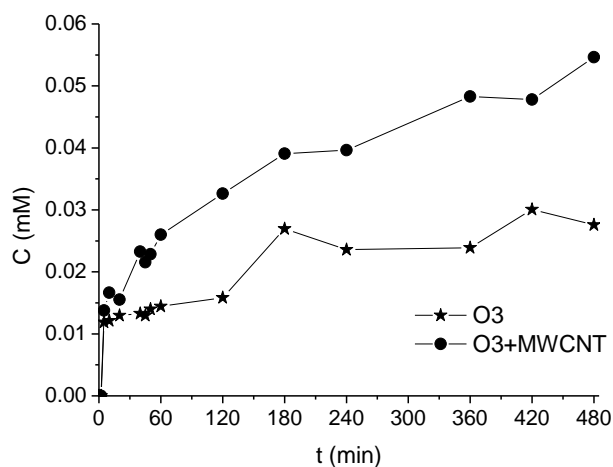


Figure 5 - Concentration of oxalic acid measured during the semi-batch ozonation experiments.

It is known that the catalytic ozonation process, using carbon materials, greatly improves the oxidation of oxalic acid when compared to single ozonation [21, 23]. In Figure 5 there seems to be a constant increase in the concentration of oxalic acid in both experiments. Furthermore, the concentration of this acid was higher for the catalytic ozonation experiment. This indicates that the accumulated TOC during the ozonation experiments is due to more complex organic compounds, which are formed between the primary degradation of MTLC and the appearance of low molecular weight organic acids. The more extensive degradation of these products during catalytic ozonation increases the amount of oxalic acid found in solution [16, 17, 44-46]. Oxalic acid is probably accumulated due to a combination of its continual formation with the competition with the several other organic compounds present in solution. Since the pH of solution decreases during the semi-batch experiments (from ~6 to ~4 in 3 hours), the production of hydroxyl radicals due to the natural decomposition of ozone in water also decreases [44]. Thus, the degradation of the formed intermediates during single ozonation is slowed down.

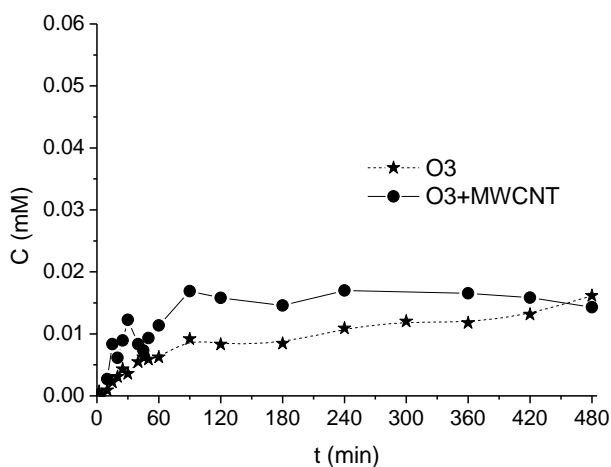


Figure 6 - Concentration of pyruvic acid measured during the semi-batch ozonation experiments.

The formation of pyruvic acid, depicted in [Figure 6](#), is in accordance with what is proposed above for oxalic acid. In this case, after 6 hours of reaction, a decrease in the concentration during the catalytic ozonation experiment is observed. For the single ozonation experiment the acid accumulated continuously during the 8 hours of reaction, as mentioned above for oxalic acid.

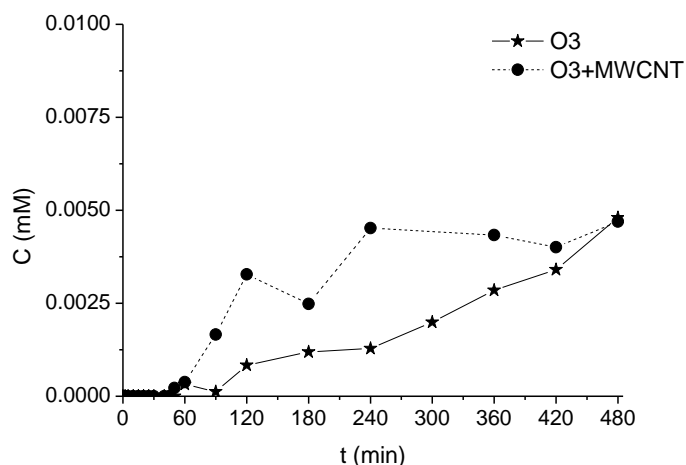


Figure 7 - Concentration of oxamic acid measured during the semi-batch ozonation experiments.

Oxamic acid is also recalcitrant to direct ozonation. However, the reaction with the highly-reactive radicals produced during the catalytic ozonation experiment is not as fast as for oxalic and pyruvic acids [23], which explains why it accumulates in solution during single

and catalytic ozonation, as seen in [Figure 7](#). It is noticeable that the amount detected in solution is far smaller when compared to the other quantified acids.

In Table 1 the mass balance of the carbon measured in the quantified organic compounds in relation to the measured TOC value is presented. The values of inorganic carbon in solution were residual and are negligible in this case. The identified TOC was calculated following equation 9. Mineralized carbon ($TOC_{\text{mineralized}}$) was calculated from the removal of TOC from solution.

$$TOC_{\text{identified}} = TOC_{\text{MTLC}} + TOC_{\text{organic acids}} + TOC_{\text{mineralized}} \quad (9)$$

Table 1 - Mass balance of TOC measured in solution during the semi-batch ozonation experiments.

t (min)	TOC _{MTLC} (mg/L)		TOC _{organic acids} (mg/L)		TC _{identified} /TOC ₀	
	O ₃	O ₃ +MWCNT	O ₃	O ₃ +MWCNT	O ₃	O ₃ +MWCNT
0	9.2	9.1	0	0	1	0
30	0.14	0.44	0.0049	0.013	0.05	0.18
60	0	0	0.0063	0.011	0.07	0.23
120	0	0	0.0076	0.020	0.14	0.27

Observing Table 1, it is noticeable that there is a large percentage of organic carbon not detected. In fact, it is expected that large amounts of organic compounds are still present in solution, even after 8 hours of reaction [16, 17, 44-46]. In addition, other peaks were detected in the chromatogram resulting from the analysis by HPLC-UV. However, since it was not possible to unmistakably identify the corresponding compounds, they were not quantified in this study. It is, however, important to notice in Table 1 that the contribution of unidentified TOC to what is measured in solution is decreasing after the first 60 minutes, when the parent compound is completely degraded. For the first 60 minutes, the larger contribution to the quantifiable TOC is from the MTLC still present in solution. This suggests that, for longer reaction times, a larger amount of the total organic carbon is present in the end-of-chain degradation products [16, 17]. A slightly larger increase in the fraction of identified TOC is seen in the catalytic ozonation experiment. This difference between the two experiments indicates that the catalytic ozonation experiment is degrading the top-of-chain formed intermediates at a faster rate, yielding a larger amount of carbon containing organic acids. This, combined with a larger portion of the initial TOC

mineralized, justifies the more extensive increase in identified TOC in the case of the catalytic ozonation experiments.

~~Figure 8~~ and ~~Figure 9~~ present the concentration of inorganic ions found during semi-batch ozonation experiments.

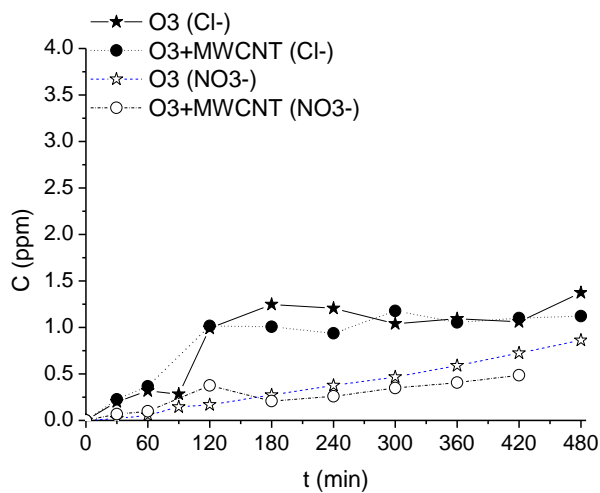


Figure 8 - Concentration of chloride and nitrate during the semi-batch ozonation experiments.

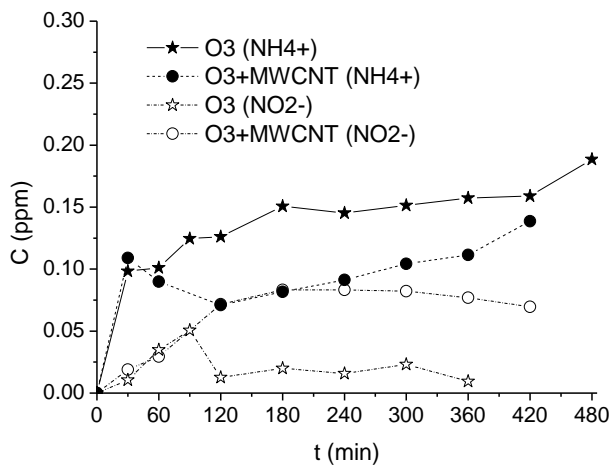


Figure 9 - Concentration of ammonium and nitrite during the semi-batch ozonation experiments.

The release of ions during the experiments is very similar whether the catalyst is present or not. The main difference regards the production of ammonium and nitrite. The catalytic

ozonation experiment produced a larger amount of nitrite, while decreasing the amount of released ammonium. This may be due to the different reaction pathways followed by ozone and hydroxyl radicals to degraded organic compounds.

A mass balance of chlorine and nitrogen quantified during the semi-batch ozonation experiments is presented in [Figure 10](#). The concentration of chlorine was calculated by adding the mass of chlorine in the measured MTLC and what was found in solution by ion chromatography. The concentration of nitrogen was calculated by adding the mass of nitrogen in the measured MTLC with that found in solution by ion chromatography as nitrite, nitrate and ammonium and with the mass of nitrogen in the measured oxamic acid.

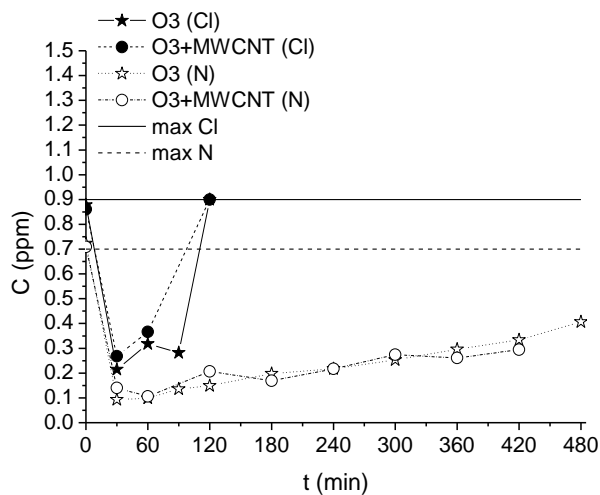


Figure 10 - Dimensionless concentration of quantified chlorine and nitrogen during semi-batch ozonation experiments.

It is noticeable in [Figure 10](#) that all chlorine present in MTLC is very quickly released to the solution. The initial decrease indicates that the primary degradation of MTLC does not involve dechlorination. In fact, a large part of chlorine is present in the intermediates formed in the beginning of the degradation of MTLC. However, it is clear that these chlorine containing compounds are oxidized directly by ozone, since this appears to occur similarly in both experiments [17]. After 120 minutes, the chlorine contained in MTLC was completely released into solution. Nitrogen presents a similar behaviour to chlorine, suddenly decreasing in the beginning of the reaction, due to the degradation of MTLC, and then gradually increasing during the experiments. This suggests that intermediate nitrogen containing by-products are being formed and slowly being mineralized. However, nitrogen increases much slower throughout the experiments. In

fact, a great part of the expected by-products formed contain nitrogen in their structure[16, 17].

The measurements of acute toxicity in terms of inhibition of the luminescent activity of the bacteria are presented in [Figure 11](#)~~Figure 11~~.

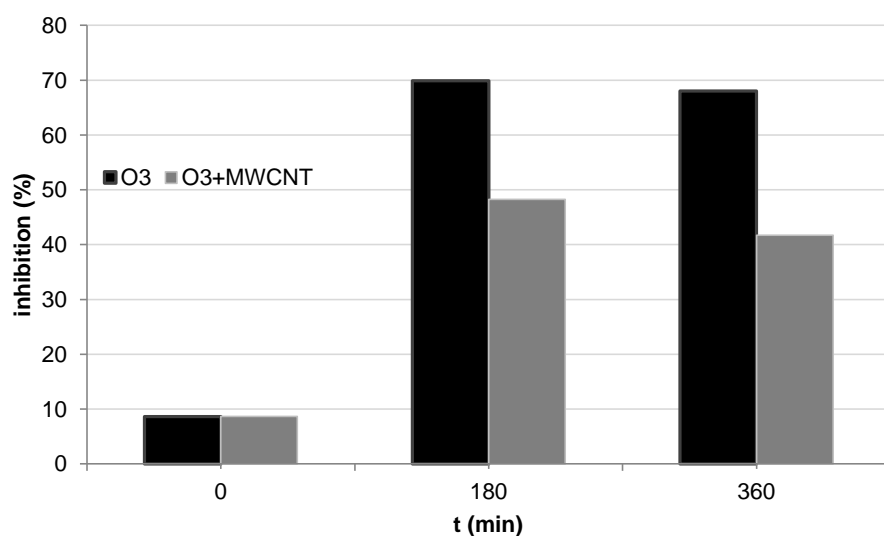


Figure 11 - Inhibition of luminescent activity of *Vibrio Fischeri* during the semi-batch ozonation experiments.

The oxidation of the parent compound results in by-products, which are more toxic for *Vibrio Fischeri* than MTLC itself. The possibility of a synergistic effect among the by-products cannot be excluded [1, 17, 43]. Nevertheless, the presence of the catalyst diminishes the effect of ozonation on toxicity. This may be due to a smaller amount of compounds toxic to this bacteria presented in solution due to a more complete and less selective oxidation of MTLC [17].

CONTINUOUS OZONATION OF METOLACHLOR

Since the system is being operated continuously, several samples were taken at steady state (after 2 hours) and the average values are presented with the respective standard deviations (see Table 2). These include the removal of MTLC and TOC, as well as the release of inorganic ions and organic acids into the liquid phase.

Table 2 - Characterization of the outlet at steady state for continuous ozonation experiments.

Effluent at steady state	Single Ozonation	Catalytic Ozonation	
T_{contact} (min)	n/a	1.9	7.6
Removal of MTLC (%)	73.4 ± 0.1	81.9 ± 0.1	78.0 ± 0.1
Removal of TOC (%)	5 ± 1	20 ± 1	35 ± 1
$C_{\text{oxalic acid}}$ (mg/L)	0.195 ± 0.001	0.139 ± 0.001	0.111 ± 0.001
$C_{\text{pyruvic acid}}$ (mg/L)	0.079 ± 0.001	0.206 ± 0.001	0.255 ± 0.001
$C_{\text{oxamic acid}}$ (mg/L)	0.0280 ± 0.0003	0.0298 ± 0.0003	0.057 ± 0.0003
C_{Cl^-} (mg/L)	0.7 ± 0.2	0.6 ± 0.2	0.8 ± 0.2
$C_{\text{NO}_2^-}$ (mg/L)	<LOQ*	<LOQ*	<LOQ*
$C_{\text{NO}_3^-}$ (mg/L)	0.55 ± 0.01	0.43 ± 0.01	0.32 ± 0.01
$C_{\text{NH}_4^+}$ (mg/L)	0.091 ± 0.007	0.127 ± 0.007	0.11 ± 0.007
$\text{TOC}_{\text{identified}}/\text{TOC}_0$	0.52 ± 0.03	0.58 ± 0.03	0.84 ± 0.03
Quantifiable N/ N_0	0.2475 ± 0.0002	0.1992 ± 0.0002	0.1791 ± 0.0002
Quantifiable Cl/ Cl_0	1.0 ± 0.3	0.70 ± 0.3	0.9 ± 0.3

*below the limit of quantification

In **¡Error! No se encuentra el origen de la referencia.** [Table 2](#) a trend similar to that found during the semi-batch ozonation experiments is observed for the removal of MTLC and its mineralization. In this case, since the carbon material is well fixed to the structured support (previously tested by ultra-sonication), the TOC measurements were not affected by the release of carbon material to the solution. Thus, the difference between the single ozonation and the catalytic ozonation experiments, regarding the TOC values, is accentuated, when compared to the semi-batch experiments. The percentage of identified TOC clearly rises with the inclusion of the monolithic catalyst. This percentage is further increased when the contact time is risen. This agrees with the trend that was found during the semi-batch experiments.

Additional tests were made using a biphasic system by putting the catalyst inside the internal loop of the reactor. It was seen that the TOC removal decreased from 25 % to 17%. This decrease is due to the improvement of the mass transfer between the different phases

when the triphasic system is used. This type of system allows the operation of the reactor under flow conditions, namely Taylor flow, that enhance the mass transfer between the phases, and thus the effectiveness of the catalytic process [30, 31].

An important difference is found in the organic acids and inorganic ions released into solution when compared to those found in the semi-batch ozonation experiments. It is likely that, given the residence (~20 minutes) and contact times (~1.9 minutes) at which the system is being operated, the mineralization of MTLC is still in its early stages, as can be attested by the values of the parent compound still present in the effluent. It is known that the hydroxyl radicals produced during catalytic ozonation are less selective than ozone [25]. It is probable that ozone is attacking specific locations of the molecule, which would explain the larger amounts of oxalic acid and chloride released into solution during the single ozonation experiment. Nevertheless, the high relative errors associated with the measurement of chloride suggest that the occurrence of different concentrations of this ion might be due to experimental errors.

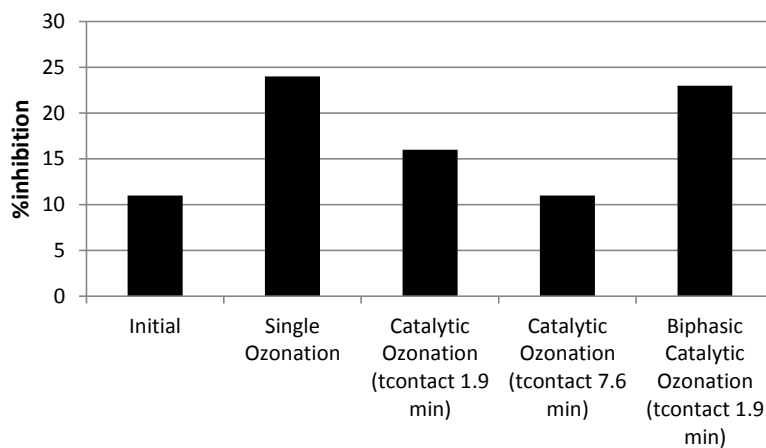


Figure 12 - Inhibition of luminescent activity of *Vibrio Fischeri* in the continuous ozonation experiments.

The toxicity values obtained at steady state (Figure 12) corroborate the suggestion that the compounds formed present higher toxicity for *Vibrio Fischeri* than the pesticide being studied [1, 17]. The presence of the monolithic catalyst during the reaction reduced the toxicity values when compared to the single ozonation experiment. Longer contact times with the catalyst produced further reduced toxicity levels. On the other

Comentario [eb1]: It would be better in the legend of 3 and 4th column to include the world triphasic

hand, the placing of the catalyst as to operate under biphasic conditions diminished the reduction of the toxicity when compared to the triphasic system.

CONCLUSIONS

The catalytic ozonation of the herbicide Metolachlor was studied in a semi-batch conventional stirred tank reactor, using MWCNT in powder form and in a continuous bubble column reactor, using CNF grown on the surface of honeycomb cordierite monoliths.

The degradation of MTLC was easily achieved with or without the application of a catalyst. However, it was shown that it was not the case for the mineralization of the pollutant. In fact, large quantities of organic matter are still present in solution even after 8 hours of reaction in the semi-batch reactor. The presence of MWCNT in solution catalyzed the oxidation of the organic matter. The mineralization degree achieved in semi-batch reactions was higher, and the reaction was shown to be placed further down on the degradation chain of the herbicide when compared with the single ozonation experiments.

The application of a structured catalyst in the continuous ozonation experiments was shown to have potential as a solution for practical applications. The presence of the catalyst enhanced the mineralization of the organic matter in solution. The increase of the contact time with the catalyst further increased the mineralization of the organic matter in solution.

The ozonation of MTLC was shown to increase the toxicity to the bacteria used to simulate the effect on an aquatic environment of the effluents produced in this study. However, it was shown that the addition of a catalyst to the system reduces the impact of the ozonation process.

The application of CNF grown on a structured support was shown to be a potential solution for the mineralization of MTLC.

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