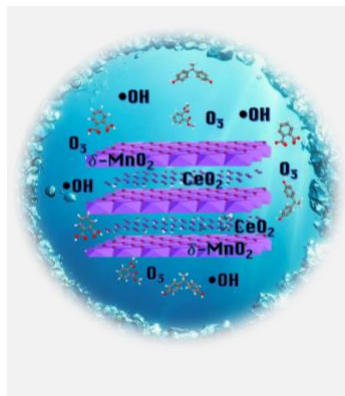


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The present work deals with the study of the degradation of phthalic acid and dimethyl phthalate in an aqueous system with ozone. An ozone-oxygen flow rate and concentration at 0.2 Lmin<sup>-1</sup> and 15 mgL<sup>-1</sup> respectively. The experimental conditions were constant for all experiments. The  $\delta$ -MnO<sub>2</sub>/CeO<sub>2</sub> were synthesized by hydrothermal treatment. The ozonation results showed that the model mixture in aqueous solution decomposes, obtaining a higher removal in catalytic ozonation.

## Introduction

The use of plastics or polymers is part of the modernity that has transformed homes and other environments and in order to obtain a wide range of materials with diverse properties and applications, different kinds of additives are introduced into plastics, among which we can mention bulking agents, antioxidants, flame retardants and plasticisers. These agents widely used in the manufacture of adhesives, plastic containers, lubricants, wrappings, coatings, varnishes, thinners, etc., include low molecular weight phthalates, some phthalic acid (PA) esters, e.g. dimethyl phthalate (DMP) [1,2].

Phthalates are a pollutant with harmful effects and depending on the different alkyl chains, the physicochemical attributes of phthalates tend to change but they have been reported to mimic and disrupt the functioning of hormones in the body and are therefore categorised as endocrine disruptors[2,3]. Advanced oxidation processes (AOPs) have been applied for the elimination of pollutants in water. Different oxidant agents generate species such as the hydroxyl radical, which has a high oxidation potential (2.80 V). Among the AOPs is catalytic ozonation where the catalyst promotes the decomposition of ozone to promote the formation of highly reactive radicals where a wide range of catalysts have been employed for the removal of various toxic organic compounds [4]. One of the catalysts with promising results is MnO<sub>2</sub> and CeO<sub>2</sub> because it can be obtained with diverse morphologies varying synthesis conditions in order to modify the particle size and surface area of the catalyst.

Based on the widespread detection of AP and DMP in the environment, the main objectives of this study are: to evaluate the removal of these contaminants during ozone and ozone-catalyst treatment and to know the effect of manganese oxide supported on cerium oxide and the synergy of the two metal oxides.

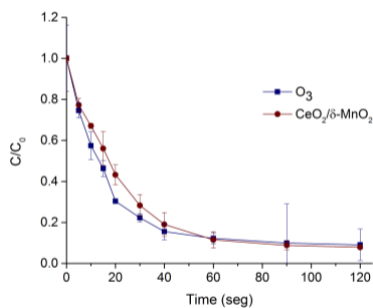
## Material and Methods

The material was obtained in two stages: a) first the synthesis of  $\delta$ -MnO<sub>2</sub>, was carried out with 4.3 g of KMnO<sub>4</sub> and 9.8 g of CO(NH<sub>2</sub>)<sub>2</sub> in 70 ml of distilled water to form the precursor solution After stirring for 30 min, the solution was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 100 ml. The autoclave was maintained at 90 °C for 24 h and then cooled to room temperature. The precipitates were filtered and subjected to washes with deionized water and ethanol, followed by drying at 60°C for 24 h. b) Precursors and conditions for CeO<sub>2</sub> synthesis were then placed in the presence of a certain amount of previously synthesized  $\delta$ -MnO<sub>2</sub>. The precursor solution was prepared with 0.26 g of cerium nitrate hexahydrate, 2.25 g of urea and 70 ml of deionized water, plus 2.6554 g of the previously synthesized and dried  $\delta$ -MnO<sub>2</sub> catalyst. The resulting mixture was stirred for 30 min, and then placed in the reactor for hydrothermal synthesis. The synthesis temperature was 160 °C for 24 h, then allowed to cool to room temperature. The material was washed in a similar way as in the first stage as well as the drying, finally the dried material was crushed in an agate mortar, until a fine powder was obtained to be calcined in the muffle at 300 °C for 3 h. The catalysts were evaluated by conventional (O<sub>3</sub>) and

catalytic ( $O_{3\text{cat}}$ ) ozonation; this was carried out in a glass reactor (capacity approximately 460 ml). The reactor is charged with 300 ml of a model mixture solution at a concentration of 50 mg L<sup>-1</sup> and a catalyst concentration of 0.1 mg L<sup>-1</sup>. Ozone was produced from extra dry oxygen at a flow rate of 0.2 L min<sup>-1</sup> using a corona discharge type generator to obtain an ozone concentration of 15 mg L<sup>-1</sup>. The degradation of the pollutant during treatment was monitored using the High Performance Liquid Chromatography (HPLC) technique was used to monitor the formation and/or degradation of the reaction-intermediates.

## Results and Discussion

The decomposition of the PA and DMP mixture (Figure 1) presents a degradation profile for both conventional and catalytic ozonation, achieving 95% removal of the main compounds in both processes in 120 min. The presence of the catalyst did not show a significant difference in the removal rate of the model mixture, however, the catalytic effect was observed in the removal of the by-products generated during the ozonation process or in the overall efficiency of the system.



**Figure 1.** PA and DMP degradation by conventional and catalytic ozonation.

Figure 2 shows the generation and removal profiles of the by-products generated during the degradation process of the model mixture (AP and DMP). For oxalic acid (Figure 2a) the conventional treatment shows an

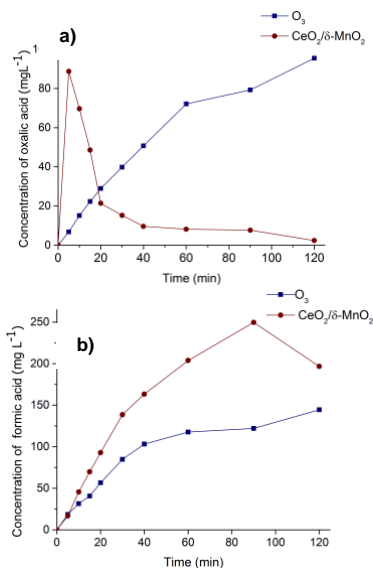
## Conclusions

The ozonation process with and without catalyst achieved 95% removal of PA and DMP during 120 min of treatment. Catalyst efficiency was obtained in TOC removal levels, achieving 71% in the catalytic system compared to 10% in conventional ozonation. The difference is due to the probable formation of oxidizing species generated from the decomposition of ozone, as well as the presence of oxygen vacancies of the metal oxides, which are active sites in the catalytic ozonation process.

## References

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- [2] Liu, Xiaoge, et al. "Application of metal organic framework in wastewater treatment." *Green Energy & Environment* (2022).
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accumulation of this by-product while the catalytic treatment shows a maximum accumulation at 5 min and after 120 min almost complete removal is observed. For formic acid an accumulation profile was obtained, however for the catalytic system it has a slight removal.



**Figure 2.** Reaction-intermediate profiles.

The TOC removal percentages for the conventional and catalytic ozonisation systems at 120 min of treatment. In the case of catalytic ozonation, only 10% mineralisation was obtained, which indicates that a large amount of organic matter is still present in the solution, possibly short-chain organic acids (such as oxalic acid) because they are recalcitrant to ozone and only accumulate in the reaction medium. On the other hand, in the presence of  $CeO_2/\delta-MnO_2$  a 71% mineralisation was achieved, which is 7 times higher than that obtained in conventional ozonation. This result indicates that the formation of reactive oxygen species is being generated between the catalyst and ozone favouring ozone decomposition.

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