Catalytic Removal of Phenolic Compounds by Ozone using Manganese and Cerium Oxides

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Abstract — The ozonation of a mixture of six phenolic acids present in Olive Mill Wastewaters enhanced by Manganese and Cerium oxides based catalysts was studied. The activity of MnO_2, CeO_2 and the bimetallic catalyst with a ratio Mn/Ce of 70/30 was studied. No significant differences were observed concerning the initial phenolic compounds degradation, however, when total organic carbon removal was studied it was observed a synergetic effect between Mn and Ce, thus the best results were obtained when the catalyst where these two metals were present was used. The increase of the calcination temperature leads to a decrease in the Bruaneur-Emmet-Teller area resulting in a inhibitory effect over the total organic carbon removal, pointing out a higher importance of the catalyst in the reaction intermediates mineralization that in the parent phenolic compounds degradation. By the comparison between the ozonation and the catalytic ozonation in the presence of the Mn-Ce-O (70/30) catalyst, a high enhancement was observed in both total phenolic content and total organic carbon. After 120 min of reaction low carbon adsorption was detected in the recovered catalyst meaning that the pollutants removal occurred by oxidation and not by adsorption to the solid phase, moreover low Mn was detected in the liquid phase confirming the stability of the catalyst in what concerns leaching behaviour of the active phase to the liquid. Therefore, Mn-Ce-O showed to be an interesting catalyst to be applied to improve the efficiency of ozonation in the treatment of phenolic wastewaters.

Index Terms — **Catalytic ozonation, Environment protection, Phenolic acids, Wastewater reaction engineering.**

I. INTRODUCTION

Public concern for environmental problems arising from industrial effluents is increasing and as consequence environmental legislation is nowadays imposing more restrictive regulations for effluents discharge. In Mediterranean area countries, Olive Mill Wastewaters (OMW) constitute an important source of pollution due to the increasing volume of such effluents produced (estimated at 7-30 million m^3 each year) [1]. These wastewaters have a high pollutant character, mainly due to the large organic fraction which includes sugars, tannins, acids, pectins, lipids, and especially phenols and polyphenols. In some cases, these effluents are directly dumped into the environment untreated. When treated, the most common processes applied are: a) evaporation ponds where the effluents are retained for water removal by solar energy; however, this procedure causes unpleasant odours and the possibility of ground waters contamination; b) direct application in soil which is an inexpensive way of disposing and recycling nutrients and organic matter, however this procedure can have an unfavourable environmental impact, since the toxic bio-refractory pollutants present may reach the water beds [2] c) an alternative is incineration due the high organic load of the olive mill wastewaters though inherent disadvantages have to be balance like: fuel costs, gas emissions and the fact that some by-products still remain; d) other applications deal with the use of these effluents as a source of fermentation products, such as fat and oils preservatives. Most of the studies related with olive mill wastewater treatment were focused on biological depuration systems. However, many problems due the high toxicity and low biodegradability mainly related to the phenolic content of the OMW, since these compounds are known bio-refractory agents, lead to unsatisfactory results. Therefore, other techniques have to be implemented in order to achieve the depuration degree needed to accomplish environmental regulations. In this context, ozone is very efficient to remove phenolic compounds with high reaction rates due to the strong electrophilic nature of molecular ozone which is able to react with the nucleophilic sites of the aromatic rings. Therefore, ozonation shows to be an interesting pre-treatment for biological depuration. However, when the objective is the wastewater mineralization, single ozonation is not a suitable process due to the formation of refractory saturated intermediates during the process, therefore, Total Organic Carbon (TOC) is kept practically unchanged leading to a low mineralization level of the effluent. Within this scenario, ozonation enhanced by an heterogeneous catalyst reveals to be a feasible treatment technique due to its potentially effectiveness in the degradation of refractory organic pollutants. In what

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concerns phenolic wastewaters, gallic acid catalytic ozonation was studied using perovskite [3] and activated carbon [4] as catalyst. In the former the presence of the catalyst reduced the time required to gallic acid elimination, enhancing TOC reduction even when used at low concentrations, whereas in the later, the contribution of activated carbon is mostly noticed in the intermediate products evolution and low advantage was gained with the use of the catalyst during ozonation to remove gallic acid itself. Perovskite showed also to be an active and stable catalyst when used in ozonation of complex simulated phenolic acids mixture and real wastewaters as well [5].

The aim of this research work addresses the study of the efficiency of ozonation enhanced by a catalyst prepared in our laboratory (Mn-Ce-O) in a model effluent degradation. To the best of our knowledge this is the first study regarding the catalytic ozonation treatment using the bimetallic Mn-Ce-O catalyst, which showed to be very active in the catalytic wet oxidation of phenolic compounds [6] as well as of low weight carboxylic species [7], [8].

II. EXPERIMENTAL

A. Materials and Catalysts

Syringic acid, vanillic acid, 3,4,5-trimethoxybenzoic acid, veratric acid, protocatechuic acid and 4-hydroxybenzoic acid were obtained from Sigma-Aldrich and used as received without further purification. These six phenolic acids typically found in OMW were used to prepare the synthetic effluent with a concentration of 100 mg/L of each compound. Mn-Ce-O catalyst was prepared by co-precipitation of a mixed aqueous solution of metals nitrates as precursors (Riedel-de-Häen and Labsolve) by the procedure described elsewhere [9]. The metals salts solution was poured into 200 mL of a 3 M NaOH solution. The precipitate was filtrated and washed five times with 500 mL of ultra pure water and dried at 100ºC over night, followed by calcination during 3h, at 300ºC or 450ºC. Before calcination the catalysts were crushed into fine powder in order to provide maximum specific surface area for reaction.

B. Oxidation procedure

Ozonation and catalytic ozonation were carried out in a semi-batch mode being the liquid pollutant charged at the beginning of the experiment and the gas continuously fed. The reactor consisted in a glass vessel (1 L of capacity) provided with magnetic stirring and four top inlets for bubbling the gas feed, by means of two gas diffusers placed in the liquid bulk, sampling and venting. In every experiment, the reactor was filled with 500 mL of the model solution. Ozone was produced from a pure oxygen stream (99.999% Praxair, Portugal) in an ozone generator (MICROLAB 1579, SPO_3, Portugal) with a flow rate of 2 gO_3/h, the remaining ozone was trapped into a gas absorption bottle containing 10% (w/v) KI solution. The catalytic experiments where carried out in slurry conditions with 1.5 g of powder catalyst (3 g/L) introduced into the reactor just before turn on the ozone generator. The stirring speed was maintained at 750 rpm, in order to maintain the external mass transfer resistances negligible and during the experiments, samples were withdrawn periodically and immediately filtered with 0.45 µm disposable filters for further analysis.

C. Analytic techniques

Total Organic Carbon (TOC) was determined with a *Shimadzu 5000A Analyser*, which operates based on the combustion /non-dispersive infrared gas analysis method. Total carbon (TC) was first measured followed by the measurement of the inorganic carbon (IC) and TOC was then determined by subtracting IC from TC. Total Phenolic Content (TPh) was measured colourimetrically using a Folin-Ciocalteu reactant obtained from Fluka. The procedure used is described elsewhere [10]: 20 µL of sample were introduced in a 2 mL cuvette and 100 µL of the Folin-Ciocalteu reagent as well as 1.58 mL of water were added. After 3-6 min, 300 µL of a saturated sodium carbonate solution was introduced and the resulting solution was left in the dark for 2 h. The absorbance was determined in a spectrophotometer (T60 U, PG instruments) at 765 nm against a blank solution containing 20 µL of water instead of 20 µL sample. The calibration curve was prepared using gallic acid at different concentrations and therefore the phenols content values are reported as gallic acid equivalent. pH was monitored with a HANNA instrument-HI8711E. *Elemental analysis* was used to detect carbon adsorption in catalysts with a *Fisons Instruments EA 1108 1108* CHNS-O equipped with a pre-packed ox/red quartz reactor, operating with a flash combustion and using a thermal conductivity detector (TCD). *Atomic absorption* was used to measure the leaching of manganese to the liquid phase and the analysis was performed in a spectrometer *Perkin-Elmer 3300*, with hollow cathode lamps (Cathodeon). The catalyst *Brunauer-Emmett-Teller (BET) surface area analysis* (S_{BET}) was determined with an accelerated surface area and porosimetry analyzer (ASAP 2000) from Micrometrics using nitrogen at a constant temperature (-196ºC).

III. RESULTS AND DISCUSSION

A. Mn/Ce based catalysts

The use of Mn as an active homogenous or heterogeneous catalyst in the catalytic ozonation of organic pollutants is well spread in literature: Andreozzi *et al.* (1996) [11] studied the applicability of MnO_2 as heterogeneous catalyst in catalytic ozonation of oxalic acid, a known refractory compound to ozone oxidation; Andreozzi *et al.* (1998) [12] showed that the reactivity of pyruvic acid with ozone was strongly enhanced by both suspended MnO_2 and dissolved Mn ions. Villaseñor *et al.* (2002) [13] tested different catalysts of MnO_2 supported in TiO_2

for phenol catalytic and photocatalytic ozonation of phenol. The enhancement in the mineralization achieved in the ozonation treatment of precursors of trihalomethanes using MnO_2 was studied by Alsheyab and Muñoz (2007) [14]. Also cerium was used with satisfactory results as homogeneous catalyst in the ozonation of phenol solutions [15]. Moreover, the use CeO_2 as support to a Ru catalyst in catalytic ozonation of succinic ozonation was studied by Delanöe and co-workers (2001) [16] using two different catalyst preparation methods: impregnation and acid exchange. However the use of a bimetallic catalyst using both Manganese and Cerium oxides was never performed in catalytic ozonation field. As the Mn-Ce-O catalyst with relative proportion between Mn and Ce of 70/30 has, recently, showed good results when used in catalytic wet oxidation of several organic pollutants [6]-[9], the efficiency of this catalyst in the catalytic ozonation of a complex simulated mixture of phenolic acids presents in OMW was compared with MnO_2 and CeO_2 as it can be observed in Fig. 1 for both TPh and TOC reduction. The difference of using different catalysts for the catalytic ozonation of the pollutants is more evident in the case of TOC reduction. In fact, concerning to TPh removal (Fig.1a), all the catalysts led to total degradation and though the initial times of reaction were similar, the instants where total phenolic content degradation is achieved were different, since TPh is totally removed after 60 min of reaction using Mn-Ce-O 70/30, whereas 75 min with MnO_2 and almost 120 min were required when ozonation is enhanced by CeO_2. The difference between the activity of the three catalysts in the ozonation of the phenolic wastewater is more evident in what concerns TOC degradation (Fig.1b), meaning that the presence of the catalyst is more important in the ozonation of the intermediates than for the degradation of the parent phenolic compounds, since ozone by himself is highly reactive concerning the degradation of benzenic derivates as the case of the phenolic compounds [17-18] the problem is that from the degradation of these acids occurs the formation of saturated intermediates which are no further reactive with ozone, therefore the differences between the activities of the catalysts will be more evident in what respects the intermediates degradation and as consequence in TOC depletion that in the initial acids decompositions. Fig. 1b shows that for the initial times of the process, both Mn-Ce-O (70/30) and CeO_2 allow a pronounced TOC reduction while MnO_2 has a lower degradation rate. However at higher reactional times, TOC removal by cerium oxide tends to lower values leading to the lowest mineralization degree achieved for the three catalysts tested after 120 min (50 %). The reactional system with ozone and manganese oxide reaches up to 56 % of mineralization after 2 h of catalytic ozonation. Indeed, a synergetic effect between Mn and Ce is highlighted by the fact that the best result for TOC degradation was observed for the system where the catalyst was composed by the two metals with 66 % of mineralization achieved at the end of the experiment. In fact, it is reported in literature than in Mn-Ce composites, the concentration of Ce^{4+} is higher than Ce^{3+} and the remain electrons seem to be transferred to Mn, which improves the mobility of electrons, therefore the higher activity of the bimetallic catalyst can be explained by an efficient equilibrium of the electrons transfer which enhance the oxidation reactions leading to higher treatment performances [19].

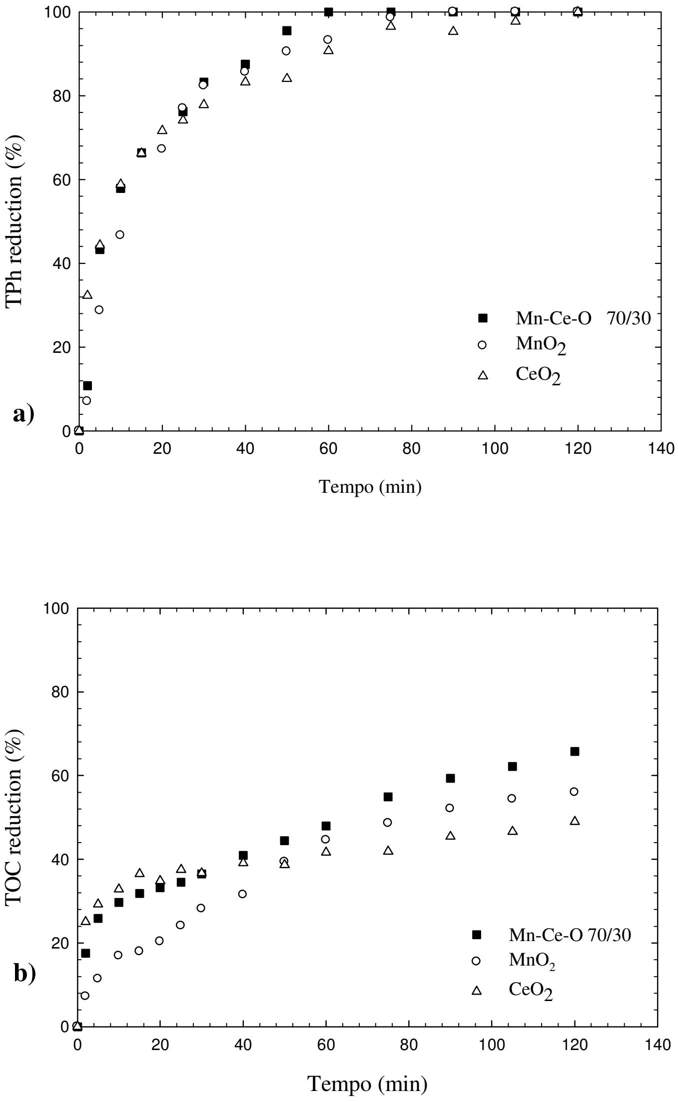

Fig. 1. (a) Total Phenolic Content, TPh and (b) Total Organic Carbon, TOC abatement for catalytic ozonation over different catalysts. 3 g/L of catalyst, 2 gO_3/L and pH=3.

In order to analyse the influence on the Brunauer-Emmet-Teller (S_{BET}) areas of the calcination temperatures, Mn-Ce-O 70/30 was prepared with two different calcinations temperatures, namely 300ºC and 450ºC, and the area of BET decreased from 102.48 to 98.52 m^2/g. In what regards the activity of the catalyst in the catalytic ozonation of the phenolic mixture concerning TPh no significant difference was detected (Fig.2a). However, as shown in Fig. 2b, a slight inhibitory effect is observed in TOC removal when the catalyst calcinated at a temperature of 450ºC is used. In fact, after 120 min of reaction the catalyst calcinated at 300ºC led to a mineralization degree 6% higher than the catalyst calcinated at 450ºC, which may be explained by the decrease in the BET area. Moreover, the similar results for catalysts performance in TPh removal while differences are observed in what concerns

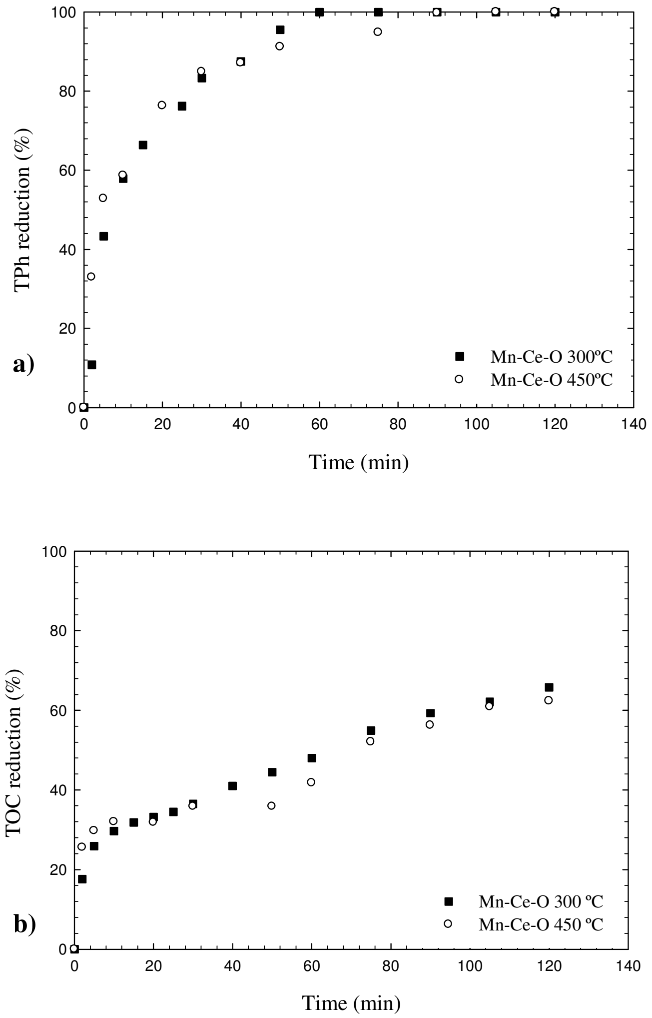

Fig. 2. (a) Total Phenolic Content, TPh and (b) Total Organic Carbon, TOC abatement for catalytic ozonation over the Mn-Ce-O (70/30) catalyst calcinated at different temperatures. 3 g/L of catalyst, 2 gO_3/L and pH=3.

TOC degradation, points out once more that the presence of the catalyst is more important in the oxidation of the reaction intermediates until total mineralization than in the initial phenolic acids degradation.

B. Ozonation versus Catalytic ozonation

Within these results, a comparison between the performance of single ozonation and catalytic ozonation enhanced by Mn-Ce-O (70/30) calcinated at a temperature of 300ºC is show in fig. 3 for both TPh (fig.3a) and TOC (fig. 3b). As it can be observed, single ozonation is an efficient technology to eliminate the phenolic content of the effluent with a reduction up to 88% of the TPh after 120 min. However whit these conditions, only a slight mineralization degree is achieved with less that 24% of TOC removed after the same period of time. It is well known that ozone is very efficient in benzenic compounds degradation, especially when the aromatic ring is activated with electron-donating groups, as is the case of hydroxyl (OH) and methoxy (CH_3O) groups in the specific case of the phenolic acids used in this work, since the ozone molecule preferentially attacks with an electrophilic pathways, therefore the reaction is enhanced when the benzenic ring is provided with a high electronic density. In fact due to the strong electrophilic nature of ozone molecule, this oxidant specie reacts quickly with the nucleophilic positions of the activated rings [4]. Nevertheless, the accumulation of different refractory intermediates (mostly aliphatic saturated carboxylic acids) during the ozonation process keeps TOC concentration practically unchanged leading, therefore, to a low level of mineralization. The addition of Mn-Ce-O truly enhanced the performance of ozone in the degradation of the pollutants, specially concerning to the mineralization degree achieved, confirming that the importance of the presence of the catalyst is higher for the oxidation of the intermediates than for the degradation of the parent phenolic compounds. Even at 2 min of

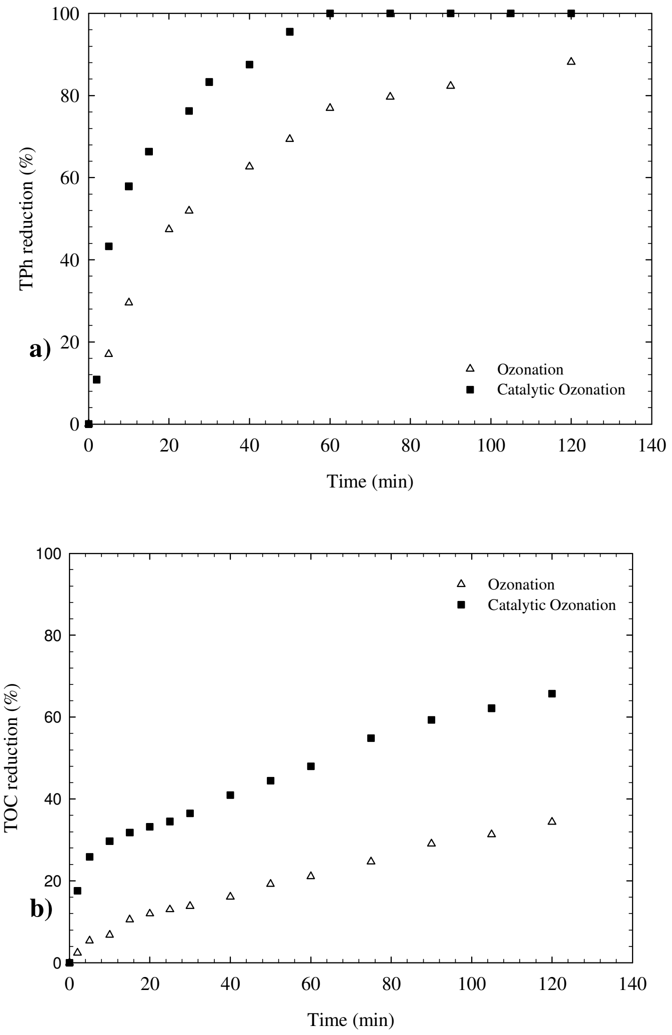

Fig. 3. Comparison between Ozonation and Catalytic Ozonation in the (a) reduction of the Total Phenolic Content, TPh and (b) Total Organic Carbon, TOC. 3 g/L of Mn-Ce-O (70/30) catalyst with a calcination temperature of 300ºC, 2 gO_3/L and pH=3.

reaction the degradation of TOC was already 17%, and at the end of 120 min more than 66% of removal was achieved, corresponding to an improvement higher that 42% when comparing with single ozonation at the same experimental time. Even if non-catalytic ozonation showed to be appropriated for TPh abatement, the use of the catalyst enhanced the process leading to total removal after 60 min while for single ozonation total degradation is not achieved even after 120 min of reaction.

The TOC was removed mainly by oxidation and not by adsorption in the solid Mn-Ce-O catalyst since low carbon adsorption was detected by elemental analysis after the experiment (less than 8% of the total carbon load into the reactor). This is important since catalyst deactivation may occur due to the formation of carbonaceous deposits in the catalyst surface irreversibly adsorbed on the active sites. Another important issue which has to be taken into account concerning to the chemical stability of ceramic catalysts involves the analysis of the leaching behaviour of the active metals to the liquid phase during reaction. The occurrence of this phenomenon may also lead to the deactivation of the catalyst due the irreversible loss of the catalytic species. Besides, diffusion of metals from the solid matrix may contaminate the liquid wastewater being then required a post-treatment to separate the metals from the final effluent. However in our studies, less than 1 mg Mn/L was detected by atomic absorption after 120 min of oxidation, which corresponds to a leaching lower than 0.05% of the total Mn charged at the reactor. Catalytic ozonation using a Mn-Ce-O catalyst seems then to be an interesting pre-treatment technique for biological processes in order to enhance the ozone degradation of phenolic compounds which are known to cause severe problems in OMW treatment.

IV. CONCLUSIONS

The aim of this work addressed the study of the activity of a laboratorial catalyst (Mn-Ce-O) in the catalytic ozonation of a complex synthetic wastewater composed by a mixture of six phenolic acids present in Olive Mill Wastewaters. The comparison between the activity of a bimetallic catalyst (Mn-Ce-O 70/30) and the respective metal oxides (MnO_2 and CeO_2) was performed. No significant difference was observed between the three catalysts concerning to TPh degradation; nevertheless, Mn-Ce-O led to total degradation after 60 min, whereas MnO_2 and CeO_2 needed 75 min and around 120 min, respectively. The synergetic effect between Mn and Ce is more evident when TOC removal is analyzed. Thus, the following order of mineralization was achieved after 120 min of reaction: Mn-Ce-O (66 %) > MnO_2 (56 %) > CeO_2 (50 %). Therefore, the presence of the catalyst is more important in intermediates total mineralization than in the parent phenolic acids degradation. The calcination temperature is an important parameter in the catalyst conception; the increase of the calcination temperature from 300ºC to 450ºC showed no influence on TPh degradation and a slight inhibitory effect over TOC removal. Comparing ozonation with catalytic ozonation enhanced by Mn-Ce-O (70/30) calcinated at a temperature of 300ºC it was possible to notice that, whereas ozonation achieved 88% of TPh degradation after 120 min, catalytic ozonation allowed total degradation after 60 min of reaction. Concerning TOC, an improvement of more than 42% in the removal of this parameter is obtained when the ozonation of the pollutants is performed in the presence of the Mn-Ce-O catalyst. Less than 8% of the total carbon loaded at the reactor was found adsorbed at the catalyst after 120 min of reaction, meaning that TOC was indeed removed by oxidation and not by adsorption into the solid phase. Moreover less that 1 mg/L of Mn was detected at the liquid after the treatment process, pointing out that the catalyst is stable in what concerns diffusion of the active metal from the solid matrix to the liquid effluent. Therefore, Mn-Ce-O showed to be an interesting catalyst for the enhancement of ozonation of organic pollutants.

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