



## Composites of manganese oxide with carbon materials as catalysts for the ozonation of oxalic acid

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### ARTICLE INFO

#### Article history:

Received 24 November 2011  
Received in revised form 5 January 2012  
Accepted 20 January 2012  
Available online 27 January 2012

#### Keywords:

Catalytic ozonation  
Manganese oxide  
Carbon materials  
Composites  
Oxalic acid

### ABSTRACT

Manganese oxide and manganese oxide–carbon composites were prepared and tested as catalysts for the removal of oxalic acid by ozonation. Their performances were compared with the parent carbon material (activated carbon or carbon xerogel) used to prepare the composites. Oxalic acid degradation by carbon materials is slower than that attained with manganese oxide or manganese oxide–carbon composites. A complete degradation after 90 and 45 min of reaction was obtained for carbon materials and for the catalysts containing manganese, respectively. The ozonation in the presence of the prepared composites are supposed to occur mainly by surface reactions, following a direct oxidation mechanism by molecular ozone and/or surface oxygenated radicals.

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### 1. Introduction

Metal oxides represent one of the most important and widely employed classes of solid catalysts, either as active phases or supports [1]. Several reported studies have shown that metal oxides and supported metal oxides can be efficient for the catalytic ozonation of a vast range of organic contaminants. Supported and unsupported oxides of transition metals are frequently studied ozonation catalysts [1].

Heterogeneous catalytic ozonation aims to enhance the removal of highly refractory compounds by the transformation of ozone into more reactive species and/or by adsorption and reaction of the pollutants on the surface of the catalyst [1–3]. The efficiency of catalytic ozonation depends on the solution pH, the chemical nature of the reactants and the surface properties of the catalyst.

Ozone, a powerful oxidizing agent ( $E(\text{O}_3/\text{O}_2) = 2.07 \text{ V}$ ), is effective for the conversion of refractory organic compounds. However, generally it does not cause the complete mineralization of solutions. In the presence of an appropriate catalyst or in combination with UV or  $\text{H}_2\text{O}_2$ , the ozonation process becomes more efficient in the degradation of organic compounds [4].

Magnesium oxides are the most widely studied metal oxides as ozonation catalyst, and they are reported to be the most efficient in ozone decomposition in gaseous medium. Manganese salts and

oxides have been used as active catalysts in the homogeneous and heterogeneous catalytic ozonation systems and its efficiency has been proved for several organic compounds [1]. Nevertheless, there is a lack of understanding of the mechanisms governing their use in catalytic reactions [5].

Manganese, cobalt and cerium oxides were also tested as ozonation catalysts for aniline and sulfanilic acid removal. However, the highest efficiency was reported in the case of composites of metal oxides such as Ce–Mn and Co–Ce catalysts [6].

Faria et al. obtained excellent results in the catalytic ozonation of oxalic acid with a ceria–activated carbon composite, as a result of a strong synergic effect between activated carbon and cerium oxide [7]. In order to better understand this effect, composites of carbon materials and cerium oxide with different compositions (between 10 and 90 wt% of carbon) were prepared in a recent work, and it was verified that most of the composites had better performances than the parent carbon materials, i.e. a synergic effect clearly occurs. The reaction mechanism was believed to comprise both surface reactions and also liquid bulk reactions involving  $\text{HO}^\bullet$  radicals. It was assumed that the existence of delocalized electrons on the basal planes of carbon materials contributes to the formation of Ce(III) species, which are active for the decomposition of  $\text{O}_3$  into  $\text{HO}^\bullet$  radicals [8].

Considering the reported good catalytic performances of the cerium oxide–carbon materials composites in ozonation, there was a high expectation about the simultaneous used of carbon materials and manganese oxides. In the present work, the preparation of composites of manganese oxide–carbon materials with different compositions was carried out with the aim of evaluating their

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**Table 1**  
Properties of manganese oxide, carbon materials and composites.

| Samples       | % carbon material <sup>a</sup> | $S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) | $S_{\neq \mu\text{pore}}$ ( $\text{m}^2 \text{g}^{-1}$ ) | $V_{\mu\text{pore}}$ ( $\text{cm}^3 \text{g}^{-1}$ ) | $d^{\text{b}}$ (nm) |
|---------------|--------------------------------|-------------------------------------------------|----------------------------------------------------------|------------------------------------------------------|---------------------|
| Mn-O          | –                              | 44                                              | 44                                                       | 0                                                    | 55                  |
| AC0           | –                              | 897                                             | 254                                                      | 0.285                                                | –                   |
| XC            | –                              | 603                                             | 238                                                      | 0.191                                                | –                   |
| ACoxid        | –                              | 843                                             | 245                                                      | 0.313                                                | –                   |
| AC0–Mn–O.1    | 12                             | 71                                              | 46                                                       | 0.012                                                | 65                  |
| AC0–Mn–O.2    | 35                             | 269                                             | 88                                                       | 0.094                                                | –                   |
| AC0–Mn–O.3    | 63                             | 417                                             | 166                                                      | 0.132                                                | –                   |
| AC0–Mn–O.4    | 78                             | 732                                             | 273                                                      | 0.228                                                | 90                  |
| XC–Mn–O.1     | 25                             | 96                                              | 60                                                       | 0.018                                                | –                   |
| XC–Mn–O.2     | 50                             | 278                                             | 109                                                      | 0.089                                                | –                   |
| XC–Mn–O.3     | 75                             | 495                                             | 102                                                      | 0.201                                                | –                   |
| ACoxid–Mn–O.1 | 25                             | 81                                              | 58                                                       | 0.012                                                | –                   |
| ACoxid–Mn–O.2 | 50                             | 254                                             | 109                                                      | 0.077                                                | –                   |
| ACoxid–Mn–O.3 | 75                             | 564                                             | 207                                                      | 0.187                                                | –                   |

<sup>a</sup> Determined by thermogravimetry.

<sup>b</sup> Crystallite diameters determined by XRD analyses.

performance as ozonation catalysts for the mineralization of oxalic acid and to investigate the reaction mechanism. The carbon materials used were an activated carbon, as received and oxidized with  $\text{HNO}_3$ , and a carbon xerogel. Then, the influence of composition, surface chemistry and textural properties of carbon materials in the composites was evaluated. The results obtained were compared to those previously obtained for composites of carbon materials and cerium oxide [8].

## 2. Experimental

### 2.1. Materials and their characterization

Oxalic acid (99%) was obtained by Sigma–Aldrich.

A commercial activated carbon, Norit GAC 1240 Plus (sample AC0), was used as received.

The synthesis of the carbon xerogel (sample XC) started by the polycondensation of resorcinol (99%, Aldrich) with formaldehyde (37%, Aldrich), at an initially controlled pH ( $\text{pH} = 6.0$ ), in order to promote the mesoporosity [9]. Polymerisation was carried out at  $85^\circ\text{C}$  during 3 days. Then, the gel was ground and dried in an oven during 4 days at  $120^\circ\text{C}$ . Finally, the material was carbonised under nitrogen flow ( $100 \text{ cm}^3 \text{ min}^{-1}$ ) at  $800^\circ\text{C}$ .

The activated carbon was submitted to a chemical treatment to obtain a material with a different surface chemistry: oxidation with nitric acid 6 M at boiling temperature during 3 h in a Soxhlet (sample ACoxid).

Manganese oxide (Mn-O) was prepared by precipitation, according to the procedure described by Imamura et al. [10], using an aqueous solution of  $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ . In each batch, 200 mL of a sodium hydroxide 3 M solution was added drop wise to the metal salt solution (ca. 15 g/100 mL  $\text{H}_2\text{O}$ ) under continuous stirring. The resultant precipitate was thoroughly washed with distilled water, dried at  $100^\circ\text{C}$  for 24 h and calcinated in air ( $50 \text{ cm}^3 \text{ min}^{-1}$ ) at  $450^\circ\text{C}$  for 3 h. Composites of carbon materials and manganese oxide were prepared by a similar procedure to that described for the oxide, where a selected amount of carbon material was dispersed in the metal solution before addition of NaOH. After precipitation, the suspension was shaken for 5 h at room temperature. Then, it was filtered and thoroughly washed and dried in an oven for 24 h at  $100^\circ\text{C}$ . This material was thermally treated at  $450^\circ\text{C}$  for 3 h under a flow of  $\text{N}_2$  ( $50 \text{ cm}^3 \text{ min}^{-1}$ ). All catalysts were sieved to a particle size of 100–300  $\mu\text{m}$  prior to reaction studies in order to minimize mass transfer effects.

The textural characterization of materials was based on the corresponding  $\text{N}_2$  equilibrium adsorption isotherms, determined at  $-196^\circ\text{C}$  with a Quantachrome Instruments NOVA 4200e

apparatus. The BET surface areas ( $S_{\text{BET}}$ ), the mesopores surface areas ( $S_{\neq \mu\text{pore}}$ ) and the micropore volumes ( $V_{\mu\text{pore}}$ ) of the samples were calculated, using appropriate procedures (the *t*-method for the last two parameters). The relative amounts of manganese oxide in the composites were determined by thermogravimetric analysis under air in a STA 409 PC/4/H Luxx Netzsch thermal analyser. XRD spectra were recorded on a Philips X'Pert MPD diffractometer ( $\text{Cu K}\alpha = 0.15406 \text{ nm}$ ) and XPS analyses were performed with a VG Scientific ESCALAB 200A spectrometer. The morphology and semi-quantitative elemental analysis of the catalysts were determined by SEM and energy dispersive X-ray spectroscopy (EDS) on a JEOL JSM 35C/Noran Voyager system.

The amounts of manganese leached during reaction were measured in a GBC 932 Plus atomic absorption spectrometer (AAS), using the remaining solution after stopping the reaction.

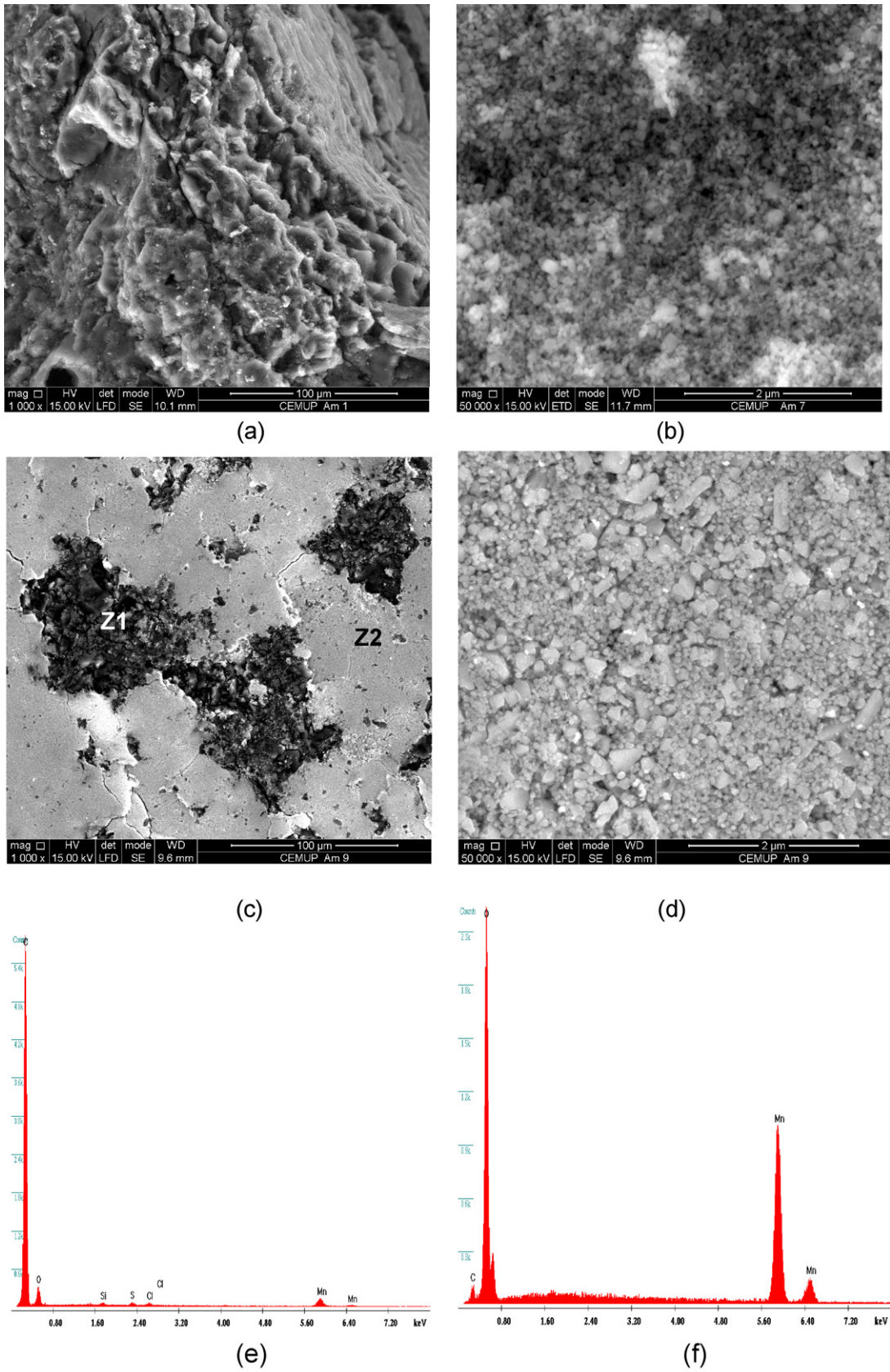
### 2.2. Kinetic experiments

The removal of pollutants was investigated in a slurry lab-scale reactor equipped with stirring. In each experiment the reactor was filled with  $700 \text{ cm}^3$  of solution of oxalic acid 1 mM at the natural pH ( $\text{pH}_{\text{oxalic acid}} \approx 3.0$ ) and 350 mg of catalyst (particle size = 100–300  $\mu\text{m}$ ). Ozone was produced from pure oxygen in a BMT 802X ozone generator. The experiments were performed at constant gas flow rate ( $150 \text{ cm}^3 \text{ min}^{-1}$ ) and constant inlet ozone concentration ( $50 \text{ g m}^{-3}$ ). The concentration of ozone in the gas phase was monitored with a BMT 964 ozone analyser. Ozone in the gas phase leaving the reactor was removed in a series of gas washing bottles filled with potassium iodide solution. Ozone was introduced in the reactor by a diffuser with 1 cm of diameter and porosity #2 (pore size between 40 and 100  $\mu\text{m}$ ). In the experiments carried out in the presence of *tert*-butanol, a concentration of 10 mM of this radical scavenger was used [11]. The concentration of oxalic acid was followed by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was an Aminex HPX-87H column (300 mm  $\times$  7.8 mm) working at room temperature, under isocratic elution with  $\text{H}_2\text{SO}_4$  4 mM.

## 3. Results and discussion

### 3.1. Catalysts characterization

Three sets of composites of manganese oxide and carbon materials (activated carbon, oxidized activated carbon and carbon xerogel) with different compositions were prepared. The properties of the prepared materials are presented in Table 1. Thermal analysis revealed the relative amounts of both materials in the composites.



**Fig. 1.** SEM micrograph of: (a) AC0, (b) Mn-O, (c) AC0-Mn-O.2, and (d) magnification of zone Z2; EDS analyses of zones Z1 (e) and Z2 (f).

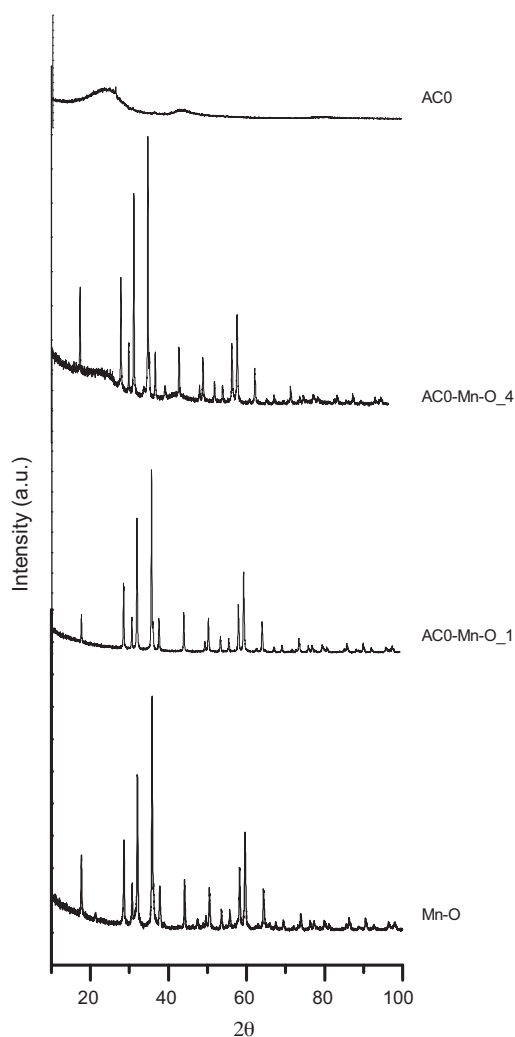


Fig. 2. X-ray diffractograms of selected samples.

BET surface areas, mesopore surface areas and micropore volumes of composites increase with the amount of carbon material present. This was expected and occurs due to the contribution of the carbon introduced.

SEM and EDS analyses of samples (Fig. 1) revealed the morphology and the semi-quantitative elemental composition of the particles. It is possible to identify carbon areas (dark zones, Z1) and Mn enriched zones (clear zones, Z2) in the same composite particle.

In order to identify the phases of manganese oxide present in the composites and determine the crystallites diameters, selected samples were analysed by X-ray diffraction. The XRD patterns of Mn-O, AC0-Mn-O.1 and AC0-Mn-O.4 are shown in Fig. 2. For selected catalysts the reflections are characteristic of hausmannite ( $Mn_3O_4$ ). It is observed that the crystallite diameter (d) in the composites AC0-Mn-O.1 and AC0-Mn-O.4 are higher than that obtained in the single oxide (estimated values obtained by Scherrer equation are shown in Table 1).

With the aim of verifying the chemical states of the manganese species on the surface, selected samples were analysed by XPS (Fig. 3). In the Mn  $2p_{3/2}$  region two peaks were identified at 641.7 and 644.2 eV for sample Mn-O and at 642.7 and 645.5 eV for sample AC0-Mn-O.1. For sample AC0-Mn-O.2 three peaks were observed in the same region (643.1, 645.6 and 648.1 eV). Thus, according to the literature, Mn(II) and Mn(III) co-exist on the surface of samples

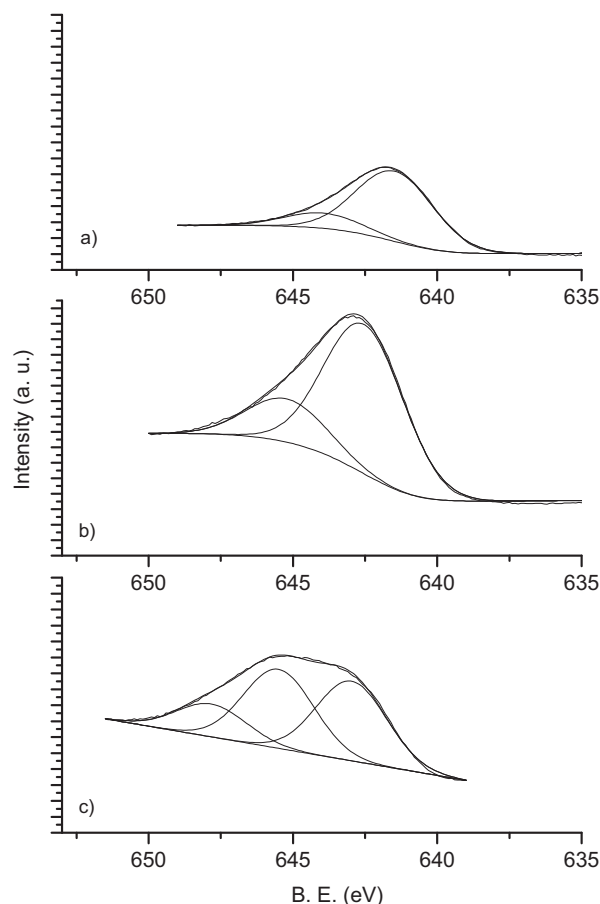


Fig. 3. Experimental and fitted Mn 2p XPS spectra of samples: (a) Mn-O, (b) AC0-Mn-O.1, and (c) AC0-Mn-O.2.

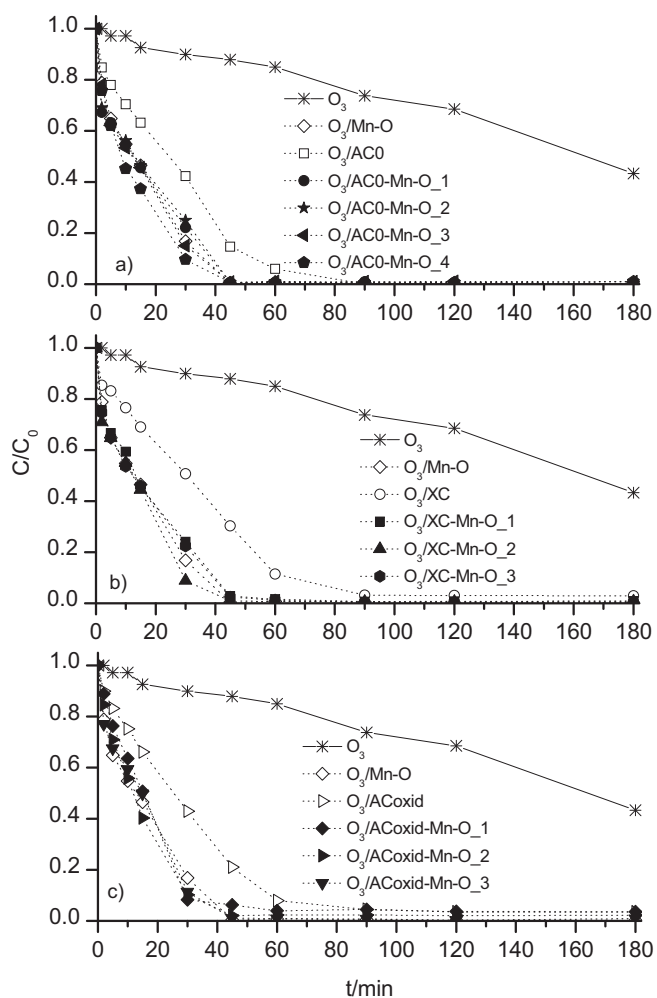
Mn-O and AC0-Mn-O.1, but Mn(IV) is also present on the surface of AC0-Mn-O.2 [12].

### 3.2. Ozonation of oxalic acid

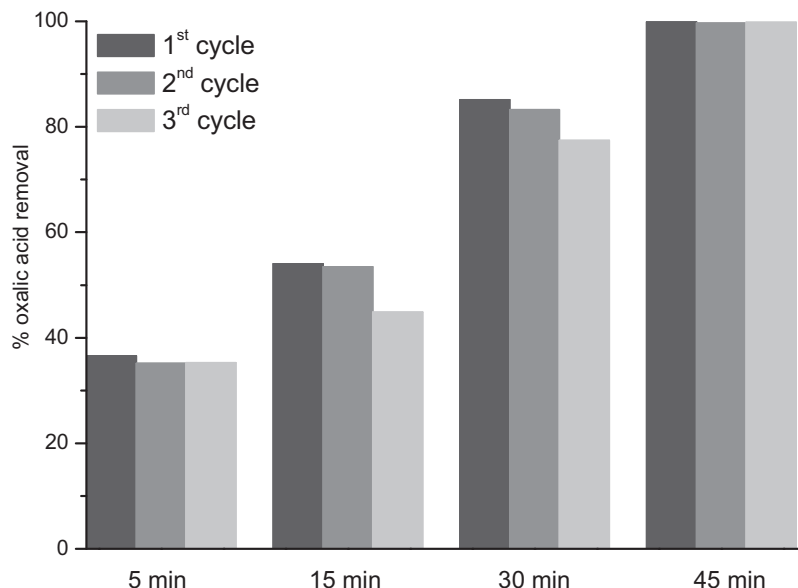
Oxalic acid was selected for this study because it is one of the most important final products of oxidation processes, with a high refractory character relatively to single ozonation [7]. Fig. 4 presents the results obtained for its degradation by catalytic ozonation in the presence of manganese oxide-carbon composites. Data obtained with AC0, XC, ACoxid and Mn-O are also included, as well as single ozonation. It is observed that in acidic conditions oxalic acid is not efficiently removed by single ozonation, but its mineralization degree is enhanced by the addition of any of the catalysts tested. The ozonation of oxalic acid in the presence of carbon materials present worse results than ozonation catalysed by manganese oxide or by the prepared composites. The catalytic activity of manganese oxide-carbon composites practically does not change with the increase of the amount of carbon present. These results are significantly different from those obtained in a similar study using cerium oxide-carbon composites as catalysts [8], where it was observed that carbon materials performed better than cerium oxide, and the catalytic activity increased with the amount of carbon material present in the corresponding composites. The reasons for these different performances are discussed below.

Analyses of Mn by atomic absorption spectrometry in the remaining solutions after reaction in the presence of Mn-O and AC0-Mn-O.3 were carried out with the aim of determining the percentage of leached metal; values of 2.3% and 2.8% of the Mn initially present were detected, respectively. Summarizing, the prepared

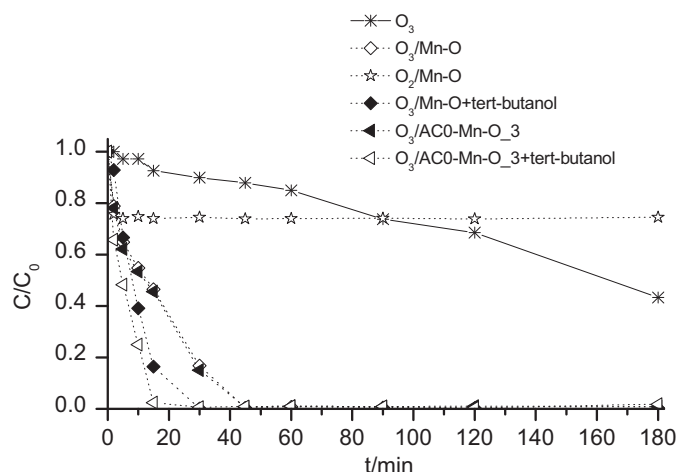




**Fig. 4.** Oxalic acid removal by single ozonation and catalytic ozonation in the presence of: (a) AC0-Mn composites, (b) XC-Mn composites, and (c) ACoxid-Mn composites ( $C_0 = 1$  mM,  $m_{cat} = 350$  mg,  $V_{sol.} = 700$  mL).



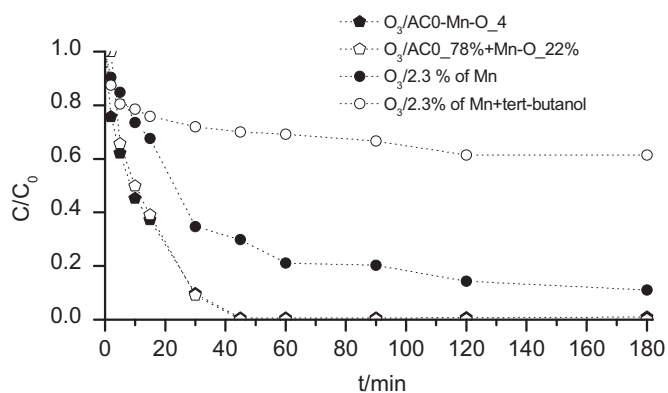
**Fig. 6.** Evolution of oxalic acid removal during cyclic experiments ( $C_0 = 1$  mM,  $m_{cat} = 350$  mg,  $V_{sol.} = 700$  mL).



**Fig. 5.** Evolution of dimensionless concentration of oxalic acid during adsorption on Mn-O, single ozonation and catalytic ozonation with Mn-O and AC0-Mn-O<sub>3</sub>, and effect of *tert-butanol* ( $C_0 = 1$  mM,  $m_{cat} = 350$  mg,  $V_{sol.} = 700$  mL,  $C_{tert-butanol} = 10$  mM).

materials presented excellent results in the mineralization of the selected pollutant, and only a small metal leaching was observed during the experiments.

In order to improve the understanding of the reaction mechanism, experiments in the presence of *tert-butanol*, a well known  $HO^\bullet$  radical scavenger, were carried out. This compound reacts very quickly with hydroxyl radicals ( $k = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) and very slowly with ozone ( $k = 0.03 \text{ M}^{-1} \text{ s}^{-1}$ ) [13]. The adsorption kinetic of oxalic acid on manganese oxide was also determined. The results obtained are presented in Fig. 5. Adsorption of oxalic acid on Mn-O is very fast, allowing a maximum removal of about 25% after a few minutes. The results show that ozonation catalysed by Mn-O and AC0-Mn-O<sub>3</sub> in the presence of *tert-butanol* favoured the oxalic acid removal (see Fig. 5). This is similar to what was reported for brucite as catalyst, where an increase of phenol [14] or azo dye [15] degradation rates were observed when *tert-butanol* was added. Therefore, it was proposed that catalytic ozonation with brucite probably proceeds according to direct oxidation by ozone, instead of the radical pathway by reactions with hydroxyl radicals generated in the ozone decomposition. Thus, it is suggested that catalytic ozonation in the



**Fig. 7.** Evolution of dimensionless concentration of oxalic acid during ozonation catalysed by AC0–Mn–O.4 and the corresponding physical mixture of activated carbon and manganese oxide, and catalytic ozonation with a solution of the manganese precursor with or without *tert*-butanol ( $C_0 = 1 \text{ mM}$ ,  $m_{\text{cat}} = 350 \text{ mg}$ ,  $V_{\text{sol.}} = 700 \text{ mL}$ , percentage of Mn = 2.3%,  $C_{\text{tert-butanol}} = 10 \text{ mM}$ ).

presence of the materials prepared in this work does not follow the radical pathway by reactions with hydroxyl radicals in solution.

In order to evaluate the eventual deactivation of manganese oxide during the ozonation experiments, three consecutive runs were carried out with fresh oxalic acid solutions. The kinetic results presented in Fig. 6 show that there is a slightly decrease in the catalytic activity, especially from the second for third run, but the total removal is still achieved after 45 min of reaction.

Experiments with an aqueous solution of manganese precursor with the equivalent amount of Mn leached during ozonation catalysed by manganese oxide, with or without *tert*-butanol, were carried out (Fig. 7). A slower removal of oxalic acid in the ozonation with the solution of manganese precursor compared with the ozonation catalysed by Mn–O is observed, and after 3 h of reaction 11% of the pollutant still remains in solution. The results in the presence of *tert*-butanol show that the homogeneous catalysed ozonation of oxalic acid is strongly inhibited. This experimental observation indicates that, under these conditions, the oxidation mechanism of oxalic acid occurs predominantly via HO• radicals in the liquid phase. In heterogeneous catalysed ozonation the effect of *tert*-butanol is completely different, since the presence of the radical scavenger enhances the oxalic acid removal, as discussed before. Therefore, these results indicate that reactions in the liquid phase are not responsible for the performances observed with the catalysts containing manganese. Thus, it is proposed that surface reactions play an important role in catalytic ozonation in the presence of manganese catalysts, which is in accordance with the literature. Adsorption of organic molecules on the surface of oxide and subsequent attack of ozone was the mechanism initially proposed by Andreozzi et al. [16], and after defended by Tong et al. [17]. In general, the proposed mechanisms of metal oxides catalytic ozonation assume that the adsorption of organic molecules and ozone takes place on the surface of the catalyst [18].

An experiment using a physical mixture of activated carbon and manganese oxide (in the same proportion as in sample AC0–Mn–O.4) was carried out and the corresponding result is also presented in Fig. 7. The physical mixture was prepared using activated carbon and manganese oxide, previously synthesised by the precipitation method, with particle size between 100 and 300  $\mu\text{m}$ . No differences between ozonation catalysed by the physical mixture or the intimate mixture (composite) were observed, which confirms that in the manganese oxide–carbon composites there is no synergic effect for the ozonation reactions, contrarily to what was previously observed for ceria–carbon composites [8].

In fact, the obtained results with manganese oxide are very different from the results reported in that work with cerium oxide prepared by precipitation [8]. Contrary to manganese oxide, which has better performance than carbon materials, cerium oxide has lower catalytic activity, leading to an 83% conversion of oxalic acid after 180 min of reaction. Adsorption on manganese oxide allows a maximum removal of 25% in a few minutes. On the other hand, adsorption on cerium oxide was not so high and fast, leading to a maximum removal of 19% after 3 h under the conditions tested. The effect of *tert*-butanol is also completely different in ozonation catalysed by cerium oxide or manganese oxide. While the addition of *tert*-butanol in the catalytic ozonation in the presence of manganese oxide has a positive effect, since it favours the oxalic acid removal, in the ozonation catalysed by cerium oxide the influence of the radical scavenger is negative, decreasing the removal of oxalic acid. Therefore, in the case of cerium oxide the reaction mechanism of oxalic acid occurs predominantly via HO• radicals in solution, since the presence of *tert*-butanol strongly inhibits the removal of oxalic acid. According to the results, the reaction mechanism in the presence of manganese oxide is different. The adsorption of oxalic acid on the surface of Mn–O is relevant and ozone and/or surface oxygenated radicals react directly with adsorbed molecules of oxalic acid. Thus, HO• radicals have a negative effect, since they decompose ozone producing new HO• radicals and decreasing the amount of ozone available for surface reactions, which was demonstrated by the increase of oxalic acid removal when *tert*-butanol was added.

The results obtained for physical mixtures of carbon material and cerium oxide are also very different from the results observed with physical mixtures of activated carbon and manganese oxide. It was shown that ozonation of oxalic acid in the presence of physical mixtures was less efficient than ozonation in the presence of the corresponding composites of cerium oxide–carbon material [8]. This indicates that the intimate mixture between cerium oxide and carbon materials results in a strong synergic effect for ozonation reactions. In addition, it was observed that the catalytic activity increases with the amount of carbon material present in the composites, and there is a minimum amount of carbon material in the composite in order to have a synergic effect. Therefore, the reaction mechanism of cerium oxide–carbon composites is believed to comprise both surface reactions and also liquid bulk reactions involving HO• radicals, while the proposed reaction mechanism of manganese oxide–carbon involves predominantly surface reactions, following a direct pathway through oxidation with molecular ozone and/or surface oxygenated radicals.

#### 4. Conclusions

The results obtained in this study for the mineralization of oxalic acid show that manganese oxide prepared is an effective ozonation catalyst and its catalytic activity is better than that of carbon materials. Synergic effects between manganese oxide and carbon materials in the prepared composites were not observed, contrarily to what was previously observed for ceria–carbon composites. The reaction mechanism is believed to occur mainly by surface reactions, following a direct oxidation of adsorbed molecules by molecular ozone and/or surface oxygenated radicals.

#### Acknowledgements

This work is supported by project PEst-C/EQB/LA0020/2011, financed by FEDER through COMPETE - Programa Operacional Factores de Competitividade and by FCT - Fundação para a Ciência e a Tecnologia. C.A.O. thanks FCT for the research fellowship BD/45809/2008. The authors are indebted to Dr. Carlos M. Sá (CEMUP) for assistance with SEM and XPS analyses.

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