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Lanthanum-based perovskites as catalysts for the ozonation of selected organic compounds

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ABSTRACT

The ozonation of two model compounds (oxalic acid and dye C. I. Reactive Blue 5) was carried out in the presence of La containing perovskites prepared by the citrate method. With the exception of LaFe_{0.9}Cu_{0.1}O₃, all samples are active in the catalytic ozonation of oxalic acid, some of them allowing fast degradation of the compound. The presence of lattice vacancies on the perovskites surface and tuning of oxidation ability by the B cation play a key role in oxalic acid removal. Sample LaCoO₃ was considered the best catalyst in oxalic acid degradation; in addition to its high activity, no metal leaching was observed. Regarding colour removal from the dye solution, single ozonation was slightly more efficient than catalytic ozonation in the presence of LaCoO₃. On the other hand, ozonation catalyzed by LaCoO₃ improved the TOC removal, allowing almost complete mineralization of the solution after 3 h of reaction under the conditions tested.

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1. Introduction

Perovskite have a general formula ABO₃, where A is usually a rare earth cation and B a transition metal cation [1]. This kind of material can tolerate substitutions at both cation sites without modification of the crystal structure. The substitution at A site with ions having lower valence can allow the formation of structural defects such as anionic or cationic vacancies and/or a change in the oxidation state of the transition metal cation to maintain the electroneutrality of the compound. When the oxidation state of B cation increases, the redox process generates larger amounts of available oxygen at low temperature and the overall oxidation activity is enhanced. Moreover, the oxygen vacancies favour the catalytic activity in oxidation reactions because they increase the lattice oxygen mobility [2]. The preparation method of perovskites is important both in defining suitable textural characteristics for catalysis and in achieving phases of great purity. The literature describes numerous synthesis methods, most of them producing materials for applications other than catalysis, and allowing incorporation of cations into the functional perovskite structure due to the high calcination temperatures used. The most commonly technique used to overcome the problem of purity is the sol–gel citrate method. This method allows to obtain catalysts with high surface areas, but it has the drawback of sintering, which depends

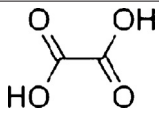
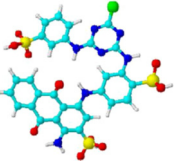
on the temperature [3]. Metal oxides with a perovskite structure have been consistently proposed during the last two decades as alternative catalysts for the total oxidation of methane and volatile organic compounds. The use of these materials has been especially promoted in applications involving high temperatures and oxygen steam-rich atmospheres, where their thermal stability comes into play [4].

Heterogeneous catalytic ozonation is gaining an increasing interest in the drinking water and wastewater treatment field [5]. The main advantages of this technique are the ability to enhance the rate of oxidation of organic compounds and especially to improve the mineralization degree achieved at the end of the process [6]. Carbon materials, metal oxides and supported metal oxides have been proposed as effective heterogeneous ozonation catalysts, but only a few studies addressed the catalytic activity of perovskites in ozonation processes. Perovskite LaTi_{0.15}Cu_{0.85}O₃ was successfully used in the ozonation of pyruvic acid, a refractory substance typically generated after oxidation of phenol-like compounds [7], and in the ozonation of gallic acid [8]. The same perovskite was evaluated in the ozonation of different phenolic wastewaters, and the catalytic stability were confirmed by consecutive experiments [9]. More recently, a perovskite containing copper was appointed as a very efficient catalyst to improve TOC removal in the ozonation of sulfamethoxazole, a sulfonamide type synthetic antibiotic [10].

In this work, a wide range of La-containing perovskites prepared by the citrate method and characterized by different techniques were used to investigate the catalytic ozonation of

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Table 1
Main characteristics of selected pollutants.

Compound	M (g mol ⁻¹)	pKa	λ_{\max} (nm)
Oxalic acid (C ₂ H ₂ O ₄) 	90.04	1.23, 4.19	–
CI Reactive Blue 5 Cibacron Blue BR (C ₂₉ H ₂₀ ClN ₇ O ₁₁ S ₃) 	74.16	–	597

oxalic acid and the reactive dye C. I. Reactive Blue 5 for the first time.

2. Experimental

2.1. Catalysts preparation and characterization

Perovskites were prepared by the citrate method as described by Merino et al. [1]. Briefly, aqueous solutions of the metal nitrates were added to the solution of citric acid, and then stirred for 15 min. The resulting solution was concentrated by slowly evaporating water under vacuum in a rotavapor at 75 °C until a gel was obtained. The gel was dried in an oven, slowly increasing the temperature to 200 °C and maintaining this temperature overnight, in order to produce a solid amorphous citrate precursor, which was then milled and calcined in air at 700 °C for 2 h.

Perovskites were characterized by a wide range of techniques as reported elsewhere [1]. Briefly, BET specific surface areas were calculated from N₂ adsorption isotherms at –196 °C, obtained in a Micromeritics Accusorb 2100E apparatus. The elemental composition was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). XRD patterns were recorded at room temperature with a Rigaku diffractometer operated at 30 kV and 20 mA and Ni-filtered Cu-K α radiation (λ = 0.15418 nm). Temperature-programmed reduction (TPR) experiments were performed in a quartz reactor with a TCD detector; samples were pretreated in helium and the temperature was increased from room temperature to 700 °C under a reducing atmosphere of 5% H₂/N₂. XPS spectra were recorded on a VG Scientific ESCALAB 200A spectrometer and XPS data were fitted using the software XPSpeak.

2.2. Kinetic experiments

Two organic molecules were selected for this study: a carboxylic acid (oxalic acid, 99%, Sigma–Aldrich) and a textile dye (CI Reactive Blue 5). Their main characteristics are shown in Table 1.

Ozonation of pollutants was investigated in a slurry lab-scale reactor equipped with agitation under optimal operation conditions, previously determined. In each experiment the reactor was filled with 700 cm³ of pollutant solution (C_{0,oxalic acid} = 1 mM, C_{0,dye} = 50 mg L⁻¹) at the natural pH (pH_{0,oxalic acid} = 3.0, pH_{0,dye} = 5.5). In the catalytic ozonation experiments, 100 mg of catalyst (dp < 100 μ m) were introduced in the reactor. Ozone was produced from pure oxygen in a BMT 802X ozone generator. The experiments were performed at constant gas flow rate (150 cm³ min⁻¹) and constant inlet ozone concentration (50 g m⁻³). The concentration of ozone in the gas phase was monitored with a BMT 964 ozone analyzer. Ozone in the gas phase leaving the reactor was removed in a series of gas washing bottles filled with iodide potassium solution. The agitation was maintained constant in order to keep the reactor

content perfectly mixed. In adsorption experiments, the ozone-containing stream (mixture of ozone and oxygen) was replaced by an oxygen stream, in order to maintain the experimental conditions and to remove the effect of ozone. In the experiments carried out in the presence of *tert*-butanol, a concentration of 10 mM of this radical scavenger was used [11]. All experiments were carried out at room temperature and atmospheric pressure.

The concentration of oxalic acid was followed by a Hitachi Elite Lachrom HPLC 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 H₂SO₄ 4 mM. The concentration of dye in the solution was followed by UV–vis spectrophotometry with a JASCO V-560 UV/Vis spectrophotometer. The degree of mineralization was determined by total organic carbon (TOC) analysis in a Shimadzu TOC-5000A Analyser.

3. Results

3.1. Catalysts characterization

Table 2 presents the BET surface areas and the percentages of lattice oxygen species (O²⁻) on the surface of the prepared perovskites. La-containing perovskites have BET surface areas between 7 and 15 m² g⁻¹. LaFeO₃ presents the highest BET surface area, which decreases with the introduction of Cu. The study of the catalysts by XPS was carried out as described in [12]. XPS analyses of selected samples allow to conclude that oxygen vacancies are present on perovskite surfaces, except in the case of LaFeO₃. Sample LaAl_{0.9}Cu_{0.1}O₃ has the largest amount of lattice oxygen species on surface.

Fig. 1 shows the TPR profiles of La-containing perovskites. LaMnO₃ has a splitted signal with a maximum at around 400 °C. LaCoO₃ has two reduction stages, one between 350 and 450 °C and the other at around 600 °C [1]. Sample LaNiO₃ presents two peaks, the first corresponding to the reduction of Ni³⁺ to yield the La₂Ni₂O₅ phase, with a loss of oxygen from the structure, and the second with

Table 2
BET surface areas and percentage of lattice oxygen species of La-containing perovskites.

Perovskite	S _{BET} (m ² g ⁻¹)	% O ²⁻ (lattice) ^a
LaFeO ₃	15.2	0
LaNiO ₃	9.8	N.D.
LaCoO ₃	7.4	39.4 ^b
LaMnO ₃	14.6	N.D.
LaFe _{0.9} Cu _{0.1} O ₃	10.5	46.3
LaFe _{0.7} Cu _{0.3} O ₃	11.5	41.8
LaAl _{0.9} Cu _{0.1} O ₃	6.9	57.4
LaAl _{0.7} Cu _{0.3} O ₃	8.4	48.1

^a Determined by O 1s XPS peak deconvolution.

^b Value from [12].

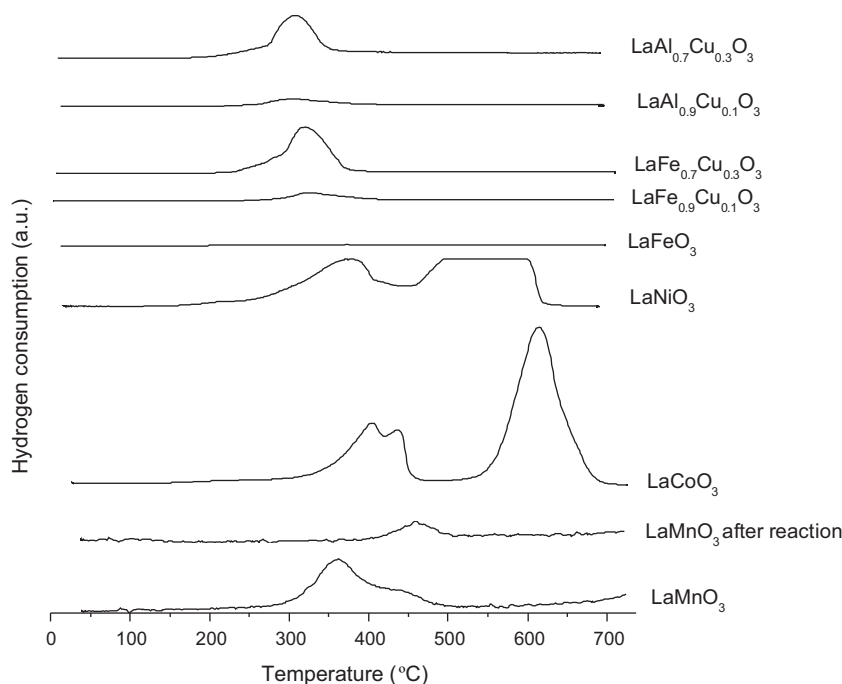


Fig. 1. Temperature programmed reduction profiles of La-containing perovskites.

a maximum consumption of H_2 between 500 and 600 °C leading to nickel deposited on lanthanum oxide [13]. $LaFeO_3$ does not show any reduction peak in the temperature range analyzed. Samples $LaFe_xCu_{1-x}O_3$ and $LaAl_xCu_{1-x}O_3$ present a signal at approximately 300 °C, which corresponds to the reduction of copper ions.

The XRD diffractograms of the prepared catalysts are depicted in Fig. 2. $LaFe_xCu_{1-x}O_3$ samples present the same diffraction peaks as $LaFeO_3$, but a shift to higher angles is observed. This displacement suggests that Cu may be present as Cu^{3+} , since the diameter of Fe^{3+} is bigger than Cu^{3+} . As the diameter of Fe^{3+} is smaller than Cu^{2+} [14], the shift would be to lower angles in this case. $LaAl_xCu_{1-x}O_3$ samples have a diffractogram similar to $LaAlO_3$, but displacement of peaks to lower angles is verified, which suggests that Cu is present as Cu^{2+} , whose diameter is bigger than Al^{3+} . The sample $La_{0.8}Ce_{0.2}Al_{0.7}Cu_{0.3}O_3$ is amorphous.

3.2. Oxalic acid removal

Oxalic acid was selected for this study because it is one of the most important final products of non-catalytic oxidation processes, with a high refractory character relatively to single ozonation [15]. The ozonation of oxalic acid was carried out at the natural pH of solutions, which is ca. 3. Fig. 3 presents the results obtained for its degradation by single ozonation and catalytic ozonation in the presence of perovskites. Adsorption of oxalic acid was also evaluated. For that purpose, sample $LaFeO_3$ was selected as an example and the adsorption kinetic was included in Fig. 3.

With the exception of $LaFe_{0.9}Cu_{0.1}O_3$, all catalysts allow better performances than single ozonation, and practically complete removal was achieved after around 1 h in the presence of $LaMnO_3$, $LaCoO_3$, $LaNiO_3$ and $La_{0.8}Ce_{0.2}Al_{0.7}Cu_{0.3}O_3$. Perovskites with La and a transition metal (open symbols) show higher catalytic activities than the other samples, except $LaFeO_3$, which is the only sample without lattice oxygen species on the surface. $LaMnO_3$ presents the best performance; however, a small amount of metal leaching during the reaction was observed. In spite of the low BET surface area, $LaCoO_3$ presents a high performance, since it has oxygen vacancies on its surface. Comparing samples $LaAl_{0.7}Cu_{0.3}O_3$

and $La_{0.8}Ce_{0.2}Al_{0.7}Cu_{0.3}O_3$, it is verified that the catalytic activity increases when part of lanthanum is exchanged with cerium. The higher performance verified with $La_{0.8}Ce_{0.2}Al_{0.7}Cu_{0.3}O_3$ may be explained by the presence of different amorphous phases in its structure. Although $LaAl_{0.9}Cu_{0.1}O_3$ presents better initial catalytic activity than $LaAl_{0.7}Cu_{0.3}O_3$, no differences were observed after 3 h of reaction. $LaFe_xCu_{1-x}O_3$ perovskites show a worse performance than $LaFeO_3$, which means that the introduction of Cu has a negative effect in the catalytic activity. Adsorption of oxalic acid on $LaFeO_3$ allows a maximum removal of 24% after 3 h.

In spite of perovskites containing Cu had a high amount of lattice oxygen species (see Table 2), they presented low catalytic activity. Comparing the TPR profiles of $LaFe_xCu_{1-x}O_3$ perovskites with $LaFeO_3$, a reduction signal at low temperature was observed, especially in the sample with more Cu (results depicted in Fig. 1). Identical performance was verified with samples $LaAl_xCu_{1-x}O_3$. Then, the presence of Cu or the increase of its charge provides a catalyst with a higher oxidation ability, which probably prevents the activation mechanism of the oxygen adsorbed species. Therefore, it is suggested that not only is required the presence of oxygen adsorption sites, such as the vacancies, but also that the tuning of the oxidation ability by the B cation plays an important role in the capacity of selectively activate the adsorbed molecules.

The ozonation of organic compounds involves a number of complex reactions and many mechanistic approaches have been presented in the literature. In general, the proposed mechanisms of ozonation catalyzed by metal oxides assume that the adsorption of organic molecules and ozone takes place on the surface of the catalyst [16]. Ozone interaction with the metal oxide surface results in the formation of free radicals that can initiate a radical chain type reaction, both on the surface of the catalyst and in the liquid phase, leading to the production of HO^* radicals [5,17]. There is few reported information about catalytic activity of perovskite type catalysts in ozonation processes. Rivas et al. observed a positive effect in pyruvic acid removal when the radical scavenger *tert*-butanol was added in the ozonation catalyzed by $LaTi_{0.15}Cu_{0.85}O_3$, and then they suggested that the reaction took place on the solid surface [7]. This was experimentally confirmed by direct measurements of

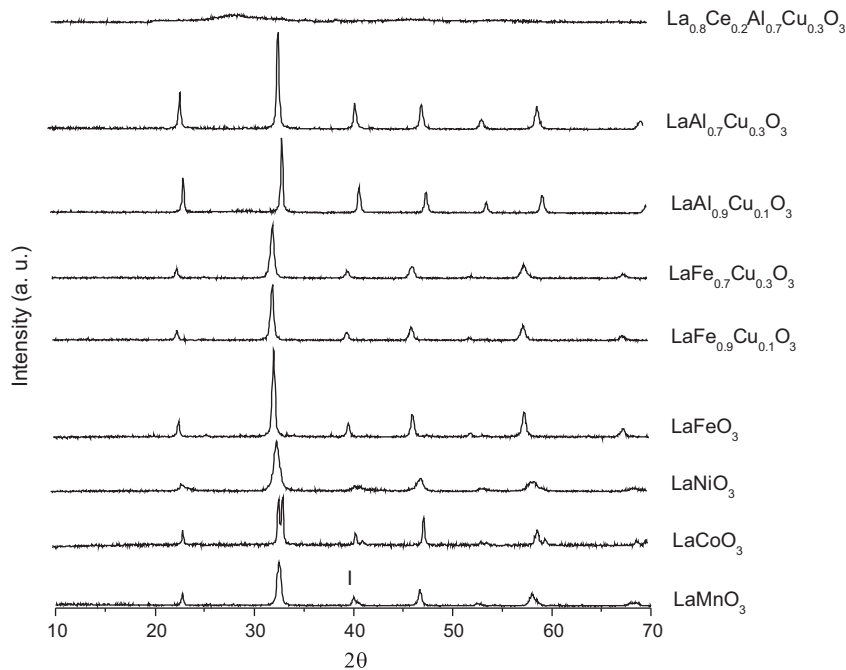


Fig. 2. X-ray diffractograms of samples.

dissolved ozone in the presence and absence of the scavenger. Addition of *tert*-butanol had no effect in gallic acid removal in ozonation catalyzed by the same perovskite, although its presence decreases the mineralization degree achieved [8]. Thus, it was suggested that free radicals play an important role in the

mineralization process and/or the scavenger adsorbs onto the solid hindering the adsorption of gallic acid and intermediates. Beltrán et al. considered a possible mechanism to explain the TOC removal of sulfamethoxazole solutions observed in the ozonation catalyzed by $\text{LaTi}_{0.15}\text{Cu}_{0.85}\text{O}_3$ and $\text{LaTi}_{0.15}\text{Co}_{0.85}\text{O}_3$ [10]. Ozone adsorption on

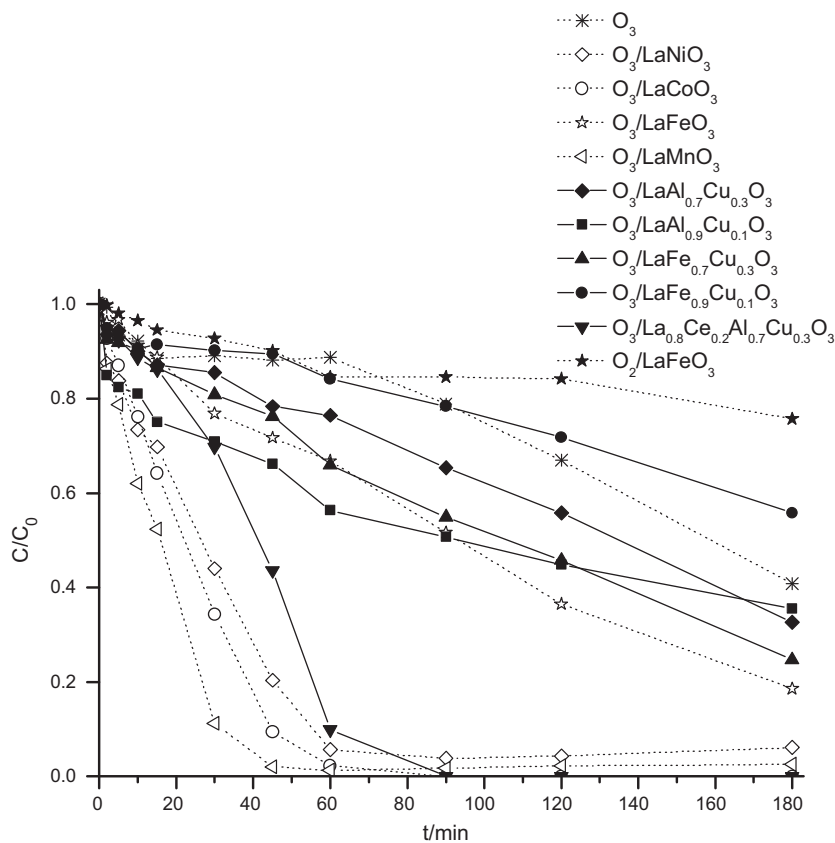


Fig. 3. Oxalic acid removal by single ozonation, catalytic ozonation in the presence of perovskites and adsorption on LaFeO_3 ($C_0 = 1 \text{ mM}$, $m_{\text{catalyst}} = 100 \text{ mg}$).

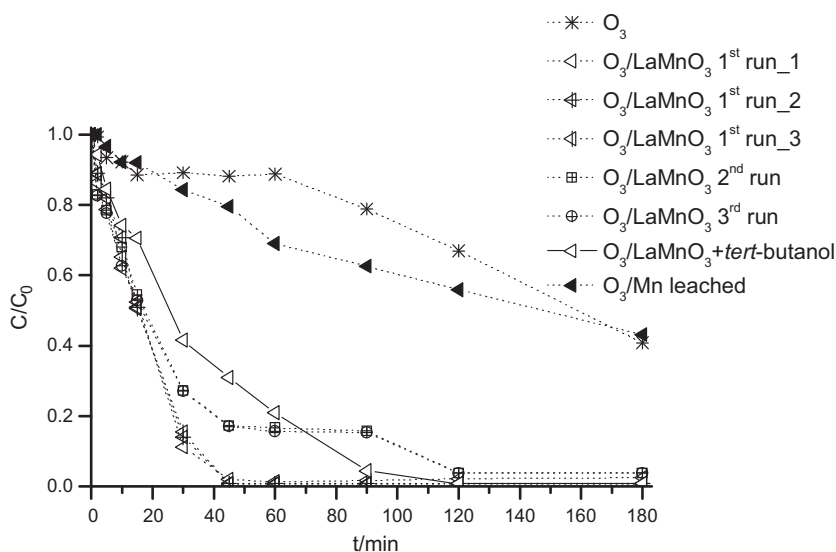


Fig. 4. Evolution of dimensionless concentration of oxalic acid during catalytic ozonation, effect of *tert*-butanol, successive experiments and reproducibility tests using LaMnO_3 ($C_0 = 1 \text{ mM}$, $m_{\text{catalyst}} = 100 \text{ mg}$, $C_{\text{tert-butanol}} = 10 \text{ mM}$).

the catalyst surface to yield superoxide ion species (by metal–ozone electron transfer), which eventually lead to hydrogen peroxide or react with ozone to generate hydroxyl radicals [18], was considered in the kinetic study.

Additional experiments were performed in order to investigate the catalytic activity and the mechanism of oxalic acid ozonation in the presence of perovskites. LaMnO_3 was chosen for these additional tests, since it allowed complete oxalic acid degradation in less than 1 h. With the aim of evaluating the eventual deactivation of the sample during the ozonation experiments, three consecutive runs were carried out with fresh oxalic acid solutions. The kinetic results presented in Fig. 4 show that a slightly decrease in the catalytic activity of LaMnO_3 from the first to the second run was observed, while no differences were noticed between the second and third runs (total removal was achieved after 2 h of reaction). Concluding, sample LaMnO_3 is stable after the first run. To a certain extent, this may be caused by some leaching, which was in fact observed.

Replicated experiments of oxalic acid removal in the presence of LaMnO_3 were carried out. The corresponding curves in Fig. 4 confirm the reproducibility of the results, since practically no differences were observed.

Since a small metal leaching was observed during ozonation catalyzed by LaMnO_3 , an experiment using the aqueous solution obtained after the catalytic reaction was carried out with the aim of evaluating the contribution of the leached metal in the catalysis of oxalic acid removal. No major differences were observed relatively to single ozonation (see Fig. 4), which suggests that the Mn leached is not the principal responsible for the catalytic activity observed with sample LaMnO_3 .

In order to study if the ozonation of oxalic acid in the presence of perovskites involves only HO^\bullet radicals in the liquid phase, one experiment was carried out in the presence of *tert*-butanol, a well known HO^\bullet radical scavenger. The results show that ozonation catalyzed by LaMnO_3 is slightly inhibited in the presence of *tert*-butanol; nevertheless, the catalyst still has significant activity, leading to complete mineralization after about 2 h of reaction. These experimental observations indicate that, in these conditions, oxidation via HO^\bullet radicals in the liquid bulk occurs, but it is expected that surface reactions play also an important role in catalytic ozonation. Therefore, it is believed that the reaction

mechanism comprises both surface reactions and liquid bulk reactions involving HO^\bullet radicals.

The TPR of sample LaMnO_3 collected after reaction was carried out. As previous reported, LaMnO_3 presented a splitted signal at around 400°C (see Fig. 1). According to the literature, two zones may be distinguished in the TPR curve of LaMnO_3 [19]. Firstly, a zone between 260 and 390°C that corresponds to the removal of the excess oxygen of the perovskite, and secondly a region between 390 and 550°C that represents the reduction of Mn^{4+} to Mn^{3+} . Analyzing the TPR profile of LaMnO_3 after ozonation (see Fig. 1), the first zone was not observed. This result suggests that no excess of oxygen exists on the perovskite after ozonation. The loss of Mn during ozonation experiments could be the responsible for the formation of cation vacancies, and consequently the electronic unbalance caused by the presence of these cation vacancies led to the formation of Mn^{4+} . Since the nonstoichiometric oxygen was not interstitial, but it is due to the presence of cation vacancies, it is proposed that the perovskite structure changed after reaction with the decrease of vacancies. This may justify (at least in part) the decrease of catalytic activity verified from the first to the second run, as shown in Fig. 4. On the other hand, from the second to the third run no differences were observed, which suggests that the new structure is stable.

3.3. Reactive dye ozonation

Research on the decolourisation of textile effluents has been often focused on reactive dyes for three reasons. First, reactive dyes represent an increasing market share; second, a large fraction of the applied reactive dyes is wasted because of dye hydrolysis in the alkaline dyebaths; and third, conventional wastewater treatment plants have a low removal efficiency for reactive and other anionic soluble dyes, which leads to coloured waterways, and public complaints [20]. Therefore, there is a demand for the development of practical and highly efficient technologies for treatment of dye-containing wastewater [21]. The use of ozone in textile effluent treatment appears as a very attractive alternative with considerable application potential. Ozone is a powerful oxidizing agent ($E^\circ = 2.08 \text{ V}$), and can react with several classes of compounds by direct or indirect reactions. Chromophore groups generally correspond to conjugated double bonds that can be broken by ozone

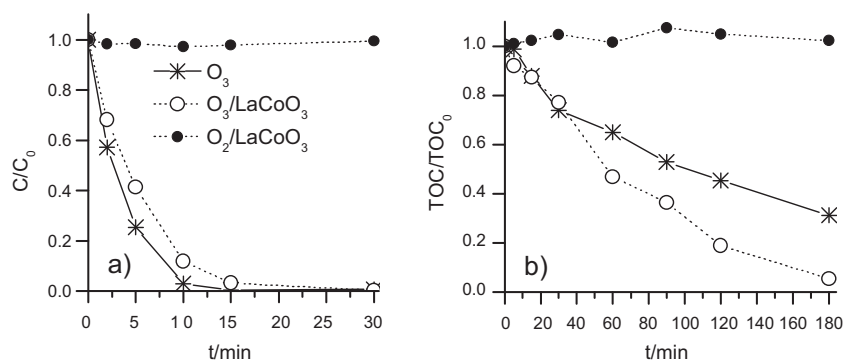


Fig. 5. Colour removal (a) and dimensionless TOC concentration (b) for the reactive dye during single ozonation and ozonation and adsorption using $LaCoO_3$ as catalyst.

(directly or indirectly) forming smaller molecules, which decreases the colour intensity of textile effluents [22,23].

As reported in the previous section, oxalic acid is a small molecule and it has been identified as one of the most common final oxidation products refractory to single ozonation. In order to evaluate the catalytic activity of perovskites with bulky molecules, the dye C. I. Reactive Blue 5 was selected as model. The best catalyst in oxalic acid degradation was chosen. According to the data depicted in Fig. 3, $LaMnO_3$ presented the best performance; however, as mentioned before, some metal leaching was observed during catalytic ozonation. Therefore, sample $LaCoO_3$ was selected for this study, since it also presented high catalytic activity and no leaching was observed during oxalic acid mineralization. Fig. 5 shows the kinetic results of single ozonation and catalytic ozonation in the presence of $LaCoO_3$ for the decolourisation and mineralization of the reactive dye C. I. Reactive Blue 5 solution. Adsorption of the reactive dye on $LaCoO_3$ was also evaluated, and it was observed that dye adsorption on $LaCoO_3$ is negligible.

The complete decolourisation of solution can be accomplished by single ozonation in a short reaction period (approximately 10 min). Ozonation catalyzed by $LaCoO_3$ presented a slightly slower decolourisation rate, but complete colour removal was achieved after ca. 15 min of reaction. Ozone is a strong oxidant that selectively attacks the chromophore groups of dye molecules, and colour removal is easily attained by single ozonation [24,25]. However, the mineralization rate of solutions of this type of compounds is generally low [25,26]. When a catalyst is added, the formation of HO^\bullet radicals is promoted, but this strong oxidant is less selective than ozone. Thus, in the catalytic ozonation, the HO^\bullet radicals formed attack both dye and intermediates, while in single ozonation, ozone is selective to chromophore groups, which originates a faster decolourization. Single ozonation also originates a decrease in the amount of TOC in solution, leading to a mineralization degree close to 70% after 3 h of reaction. Nevertheless, this mineralization is lower than colour removal, which is an indication that some of the dye degradation products (colourless) still remain in solution. The advantage of using a catalyst is seen in the TOC removal, which is faster than that obtained in non-catalytic ozonation. Catalytic ozonation in the presence of $LaCoO_3$ allowed an almost complete mineralization after 3 h of reaction.

4. Conclusions

In this study, the use as ozonation catalysts of lanthanum containing perovskites synthesized by the citrate method was reported.

With the exception of $LaFe_{0.9}Cu_{0.1}O_3$, the perovskites tested in oxalic acid ozonation showed better performances than single ozonation. Non-substituted perovskites of the type $LaBO_3$

presented higher catalytic activities than the other samples, with the exception of $LaFeO_3$. The presence of lattice oxygen vacancies plays an important role in the catalytic activity, due to the ability to activate adsorbed species. It is suggested that reactions in the liquid phase and surface reactions are responsible for the catalytic activity observed. $LaCoO_3$ was considered the best catalyst, since it allowed fast oxalic acid degradation, complete mineralization of the dye solutions, and no leaching of metal was observed. On the other hand, sample $LaMnO_3$, which also presented a good performance, suffers from some lixiviation.

Single ozonation allowed a complete colour removal of the reactive dye in a few minutes. Catalytic ozonation in the presence of $LaCoO_3$ enhanced the mineralization rate of the dye solution, leading to a TOC removal close to 100% after 3 h.

Acknowledgments

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References

- [1] N.A. Merino, B.P. Barbero, P. Grange, L.E. Cadús, *Journal of Catalysis* 231 (2005) 232–244.
- [2] B.P. Barbero, J.A. Gamboa, L.E. Cadús, *Applied Catalysis B: Environmental* 65 (2006) 21–30.
- [3] N.A. Merino, B.P. Barbero, P. Ruiz, L.E. Cadús, *Journal of Catalysis* 240 (2006) 245–257.
- [4] G. Pecchi, P. Reyes, R. Zamora, C. Campos, L.E. Cadús, B.P. Barbero, *Catalysis Today* 133–135 (2008) 420–427.
- [5] B. Legube, N.K.V. Leitner, *Catalysis Today* 53 (1999) 61–72.
- [6] F.J. Beltrán, *Ozone Reaction Kinetics for Water and Wastewater Systems*, Lewis Publishers, Boca Raton, FL, 2004.
- [7] F.J. Rivas, M. Carbajo, F.J. Beltrán, B. Acedo, O. Gimeno, *Applied Catalysis B: Environmental* 62 (2006) 93–103.
- [8] M. Carbajo, F.J. Beltrán, F. Medina, O. Gimeno, F.J. Rivas, *Applied Catalysis B: Environmental* 67 (2006) 177–186.
- [9] M. Carbajo, F.J. Beltrán, O. Gimeno, B. Acedo, F.J. Rivas, *Applied Catalysis B: Environmental* 74 (2007) 203–210.
- [10] F.J. Beltrán, P. Pocostales, P.M. Álvarez, F. López-Piñeiro, *Applied Catalysis B: Environmental* 92 (2009) 262–270.
- [11] F.J. Beltrán, F.J. Rivas, L.A. Fernández, P.M. Álvarez, R. Montero-de-Espinosa, *Industrial and Engineering Chemistry Research* 41 (2002) 6510–6517.
- [12] N.A. Merino, B.P. Barbero, P. Eloy, L.E. Cadús, *Applied Surface Science* 253 (2006) 1489–1493.
- [13] G. Pecchi, M.G. Jiliberto, E.J. Delgado, L.E. Cadús, J.L.G. Fierro, *Journal of Chemical Technology and Biotechnology* 86 (2011) 1067–1073.
- [14] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallographica Section A: International Union of Crystallography A* 32 (1976) 751–767.
- [15] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Applied Catalysis B: Environmental* 79 (2008) 237–243.
- [16] F.P. Logemann, J.H.J. Année, *Water Science and Technology* 35 (1997) 353–360.
- [17] C. Cooper, R. Burch, *Water Research* 33 (1999) 3695–3700.
- [18] K.M. Bulanin, J.C. Lavalley, A.A. Tsyganenko, *Journal of Physical Chemistry* 99 (1994) 10294–10299.

- [19] W.P. Stege, L.E. Cadús, B.P. Barbero, *Catalysis Today* 172 (2011) 53–57.
- [20] P.C. Vandevivere, R. Bianchi, W. Verstraete, *Journal of Chemical Technology and Biotechnology* 72 (1998) 289–302.
- [21] Y. Peng, D. Fu, R. Liu, F. Zhang, X. Xue, Q. Xu, X. Liang, *Applied Catalysis B: Environmental* 79 (2008) 163–170.
- [22] E. Oguz, B. Keskinler, Z. Çelik, *Dyes and Pigments* 64 (2005) 101–108.
- [23] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Applied Catalysis B: Environmental* 88 (2009) 341–350.
- [24] P.C.C. Faria, D.C.M. Monteiro, J.J.M. Órfão, M.F.R. Pereira, *Chemosphere* 74 (2009) 818–824.
- [25] C.A. Orge, J.J.M. Órfão, M.F.R. Pereira, A.M. Duarte de Farias, M.A. Fraga, *Chemical Engineering Journal* 200–202 (2012) 499–505.
- [26] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Water Research* 39 (2005) 1461–1470.