

Heterogeneous Photo-Fenton Oxidation on Nanosized Pt/Perovskites as Efficient Process for Organic Pollution Removal in Wastewaters

D. Sannino^{1,2}, Lyubov A. Isupova³, P. Ciambelli^{1,2}, V. Vaiano¹

¹University of Salerno, Via Ponte Don Melillo, 84084, Fisciano (Salerno), Italy

Tel. and Fax: 0039089964151 e-mail : pciambelli@unisa.it

²NANO_MATES, Research Centre for NANOMaterials and nanoTEchnology at University of Salerno, 84084, Fisciano (SA), Italy

³Boreskov Institute of Catalysis, SB RAS, pr. Lavrentieva, 5, 630090 Novosibirsk, Russia

ABSTRACT

Photo-Fenton oxidation of organic compounds in wastewaters based on heterogeneous catalysts is a promising advanced oxidation process (AOP) in wastewater treatment that permits to overcome the main drawbacks related to the use of Fe as homogeneous catalyst. In this work we compare the performances of perovskites in the presence or in the absence of supported Pt in the photo-Fenton oxidation of acetic acid. The heterogeneous process showed higher total organic carbon (TOC) removal with lower consumption of H₂O₂ with respect to the homogenous reaction. No significant leaching phenomena were observed. Monolith catalysts were stable and reusable. The realization of nanosized supported perovskites in the absence or in the presence of Pt nanoparticles well anchored to a “macroscopic” monolithic support permitted to match the improved catalytic activity to the easy and safe manipulation and separation from a treated wastewater.

Keywords: PhotoFenton oxidation, heterogeneous process, perovskites, monolith.

1 INTRODUCTION

Homogeneous photo-Fenton type oxidation is an attractive method for industrial wastewater treatment. It uses hydrogen peroxide, Fe²⁺ and UV light for the formation of highly reactive hydroxyl radicals. Heterogeneous photo-Fenton process, based on solid catalysts, is a promising advanced oxidation process (AOP) of pollutants that permits to overcome the main drawbacks related to the use of a Fe homogeneous catalyst, such as catalyst recovery [1], limited operational pH range (2-4) due to sludge formation in the “classical” photoFenton reaction [2].

In previous work we first found high photo-Fenton activity by using perovskites as catalysts [3-4].

In this work we compare the performances of LaMeO₃ perovskites with Me = Mn, Fe, as modified for the presence of supported Pt. Structured catalysts in honeycomb monolith shape were studied in photo-Fenton oxidation of acetic acid.

2 EXPERIMENTAL

LaMnO₃ and LaFeO₃ perovskite based catalysts were prepared by impregnation of thin (0.4 mm) wall monolithic honeycomb cordierite (triangular channels size = 2.5 mm, specific surface area = 2 m²/g, mean pore radius = 0.12 microns), followed by calcination at 900°C for 4 h. According to X-ray analysis the particle size of supported perovskites was in the range 30–40 nm. Pt at 0.1 wt % was added by wet impregnation of the perovskite pre-covered cordierite substrate. Bulk monolith perovskites LnFeO₃ (Ln = lanthanides) with triangular channels (4 mm side and 1.2 mm wall thickness) were obtained by mechanoceramic process [5]. Fe₂(C₂O₄)₃ was chosen as reference homogeneous catalyst.

Catalytic tests were carried out in a properly designed sealed stainless-steel batch photoreactor.

Acetic acid aqueous solutions containing total organic carbon concentration (TOC) of 500 mg/l (0.021 mol/l) (pH 3.9) and H₂O₂ of 0.083 mol/L were used. As UV source, a mercury vapours lamp at nominal power of 8W and emitting at 254 nm was used.

Monolithic catalysts were placed in the reactor. When the lamp was switched on, the reaction started. Very small samples of treated solution (500 µl) were taken for analyses every hour, to avoid changing in the contact time during the test.

TOC was evaluated as function of time from CO₂ obtained by catalytic combustion at T = 680°C. The H₂O₂ concentration was determined by H₂O₂/TiOSO₄ complex (λ = 405 nm) UV-Vis analysis.

Continuous mixing of model wastewater was achieved by gas fine bubbling under the monolith holder (Q = 250 (stp)cm³/min) and external recirculation.

Before re-entering into the reactor the solution was cooled by a cold trap. At the reactor outlet the gases pass through a cold trap (0°C) in order to assure water condensation, prior to the gas analysers for measurements of CO and CO₂ concentrations. The catalytic properties of monolithic samples were tested in the photo-Fenton reaction under atmospheric pressure at 25°C using samples mass comprised between 4.9 and 6.4 g.

3 RESULTS

The list of heterogeneous catalysts tested in the photo-Fenton oxidation with the active phase loading is reported in Table 1.

Table 1: List of catalysts with active phase loading.

Perovskite catalyst	Active phase loading, wt %
LaMnO ₃	2.7
LaMnO ₃	3.7
LaFeO ₃	2.2
Pt/LaMnO ₃	2.7
LnFeO ₃	88

TOC removal and H₂O₂ conversion for heterogeneous photo-Fenton on LaMnO₃ (2.7 wt %), LaFeO₃ and Pt/LaMnO₃ in comparison with homogeneous reaction are reported in Figure 1a and 1b, respectively

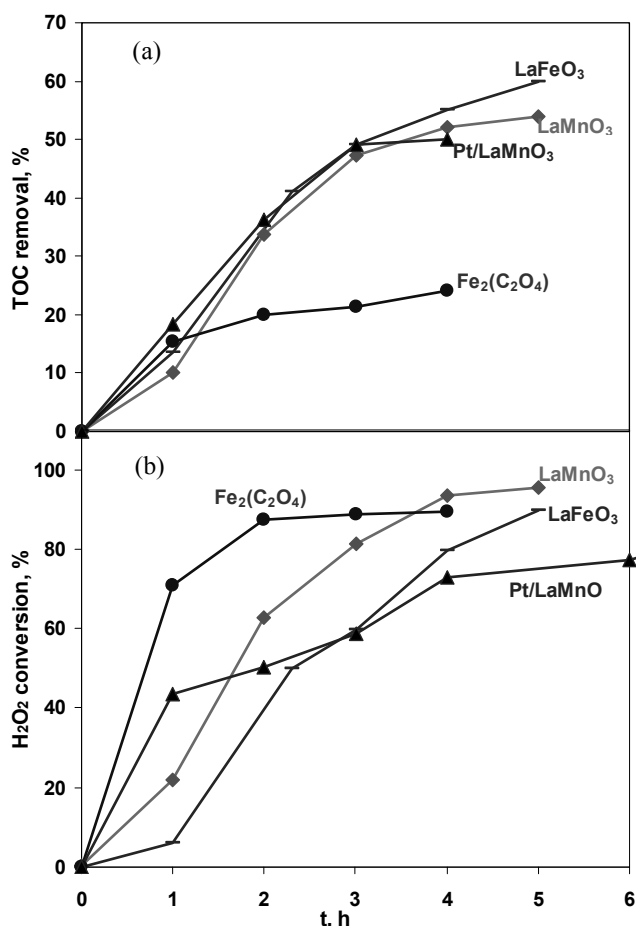


Figure 1: TOC removal (a) and H₂O₂ conversion (b) as a function of reaction time.

The homogeneous catalyst Fe²⁺ was faster than LaMnO₃ and LaFeO₃ perovskites (Fig.1a) at short reaction time (1

hour). The addition of well dispersed Pt nanoparticles enhanced the initial rate of acetic acid removal overcoming the Fe²⁺ performances. Fe²⁺ activity decreased after one hour, because of the very high H₂O₂ consumption (Fig. 1b), reaching the lower final degree of TOC removal (24 %).

Thus, for longer time, the heterogeneous catalysts showed higher TOC removal efficiency with lower H₂O₂ consumption. More particularly, the TOC removal after 5 hours reached the value of 60, and 54 %, respectively, for LaFeO₃ and LaMnO₃. The addition of Pt did not significantly enhance the catalytic performance of heterogeneous catalysts after five hours of reaction time, although on Pt/LaMnO₃ the value of TOC reduction after one hour of irradiation was the highest for all the catalysts (about 18 %).

The analysis of the gas evolved during run time from the sealed photoreactor allowed to evidence the presence of only CO₂. The total carbon mass balance, evaluated from the values of TOC removal and carbon dioxide amount evolved in gas phase, was about 98%, indicating that complete mineralization of acetic acid was obtained in photo-Fenton oxidation.

Leaching tests were carried out by ICP-AES analysis of the solution, in order to check the potential of metal leaching from perovskite during the catalytic test. ICP-AES allowed to determine the amount of metal ions in solution. The results showed a limited metal dissolution from the perovskite upon acetic acid oxidation for all the catalysts, (0.6 ppm for Mn and 0.03 ppm for Fe).

Figure 2 shows the effect of pH on the catalytic activity of LaMnO₃ (3.7 wt %) monolith.

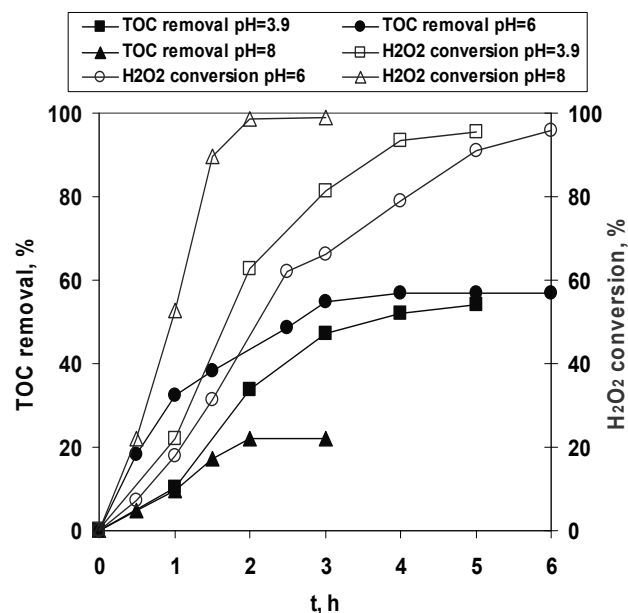


Figure 2: Effect of pH on the catalytic activity of LaMnO₃ (3.7 wt %).

By increasing the pH from 3.9 to 6, TOC removal increased from about 54 to 57 %, while at pH = 8 TOC removal decreased to 22 % after 3 hours of reaction time. At pH = 6, the H₂O₂ conversion was slower than at pH = 3.9, while in more basic conditions its decomposition was faster and complete after only 2 hours.

The data of H₂O₂ conversion suggest that the rate of TOC removal by photo-Fenton oxidation decreased because of H₂O₂ decomposition to O₂, subtracting the oxidant to the photo-Fenton reaction. Moreover, it is worthwhile to take into account that, in order to make the photo-Fenton process competitive with other AOPs, it is crucial to have low operation costs, which necessary implies to have low consumption of H₂O₂. Since a controlled concentration of H₂O₂ permits higher TOC reductions in shorter times, owing to the auto-scavenger effect of H₂O₂ that traps highly reactive hydroxyl radicals by photolysis, it is necessary to perform the reaction with an adjusted concentration of H₂O₂ during all of the reaction time. To this purpose we have tried to select the best operational dosage of H₂O₂ in photo-Fenton processes.

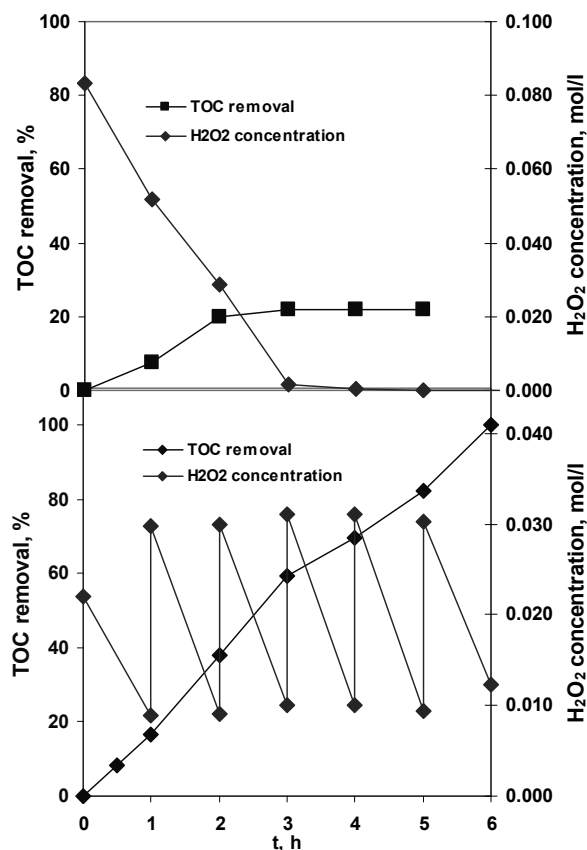


Figure 3: Photo-Fenton oxidation on LnFeO₃ without H₂O₂ dosage (a) and with an H₂O₂ dosage of 0.022 M/h (b)

Step addition of H₂O₂ was performed by adding small volumes of concentrated solution of H₂O₂ each hour. The influence of H₂O₂ dosage on TOC removal was investigated

for LnFeO₃ catalyst and the results are reported in Figure 3a and Figure 3b.

Without H₂O₂ dosage about 22 % of TOC removal was obtained after 3 hours, when a total H₂O₂ consumption was achieved. Also in this case the maximum TOC removal appears limited by H₂O₂ consumption.

Figure 3b reports the typical trend of H₂O₂ concentrations with its dosage into the reactor, resulting in a saw tooth profile. The values of H₂O₂ concentration lied in a range from 0.01 to 0.03 M. It is worthwhile that the overall average addition of H₂O₂ (0.022 M/h) increased the total organic removal from 29 % to 100 %.

Also in this case the analysis of the solution showed the presence of a very small concentration of Fe (about 0.03 ppm).

Table 2 reports a comparison of TOC removal and hydrogen peroxide consumption in the photo-Fenton on LnFeO₃ (88 wt %) with H₂O₂ dosage and in the photo/LnFeO₃ test with initial H₂O₂/CH₃COOH=4.

There is a smaller hydrogen peroxide consumption when hydrogen peroxide is dosed, compared with the photo/LnFeO₃ test at initial H₂O₂/CH₃COOH = 4. Moreover, 100 % organic carbon removal for dosed hydrogen peroxide can be achieved, while operating at initial molar ratio H₂O₂/CH₃COOH = 4, only 20 % TOC conversion is obtained.

By evaluating the specific H₂O₂ consumption with respect to the removed carbon at the same TOC conversion (20 %), we have found that it is reduced from 18.0 mol/mol (26.4 g_{H2O2}/g_C) in the test without dosage to 3.1 mol/mol, equivalent to 4.5 g_{H2O2}/g_C, by step H₂O₂ addition.

For total TOC removal 5.3 mol/mol are needed, being equivalent to 7.6 g_{H2O2}/g_C, a much lower amount than that obtained without H₂O₂ dosage.

Table 2 Comparison of hydrogen peroxide consumption of the photo-Fenton of LnFeO₃ (88 wt%) with dosage of H₂O₂ with respect to the photo/LnFeO₃ system with H₂O₂/CH₃COOH = 4.

TOC removal, %	Dosage H ₂ O ₂ cons. ppm	Dosage H ₂ O ₂ cons. g _{H2O2} /g _C	No dosage H ₂ O ₂ cons. ppm	No Dosage H ₂ O ₂ cons. g _{H2O2} /g _C
20	446	4.5	2604	26.4
60	2453	8.2	-	-
100	3814	7.6	-	-

cons.=consumed

The effectiveness of heterogeneous photo-Fenton process was tested for several organic compounds different from acetic acid, such as methanol, ethanol (Figure 4), and methyl tert-butyl ether (MTBE) (Figure 5)

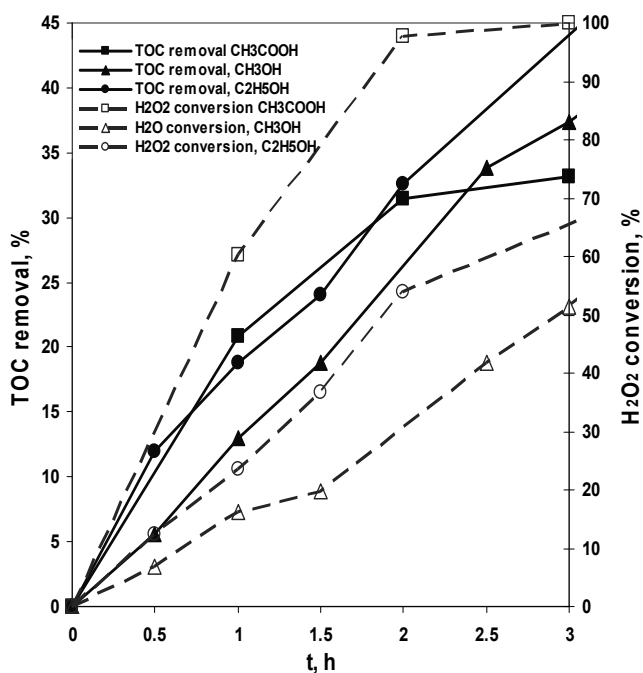


Figure 4: Photo-Fenton oxidation of acetic acid, methanol and ethanol on LaMnO₃ (3.7 %).

Figure 4 shows that about 33, 37 and 45 % TOC removal was obtained after 3 hours with acetic acid, methanol and ethanol, respectively. It is worthwhile to note that alcohols inhibited the H₂O₂ decomposition with respect to acetic acid since, at fixed reaction time, the H₂O₂ decomposition is the highest in the presence of acetic acid.

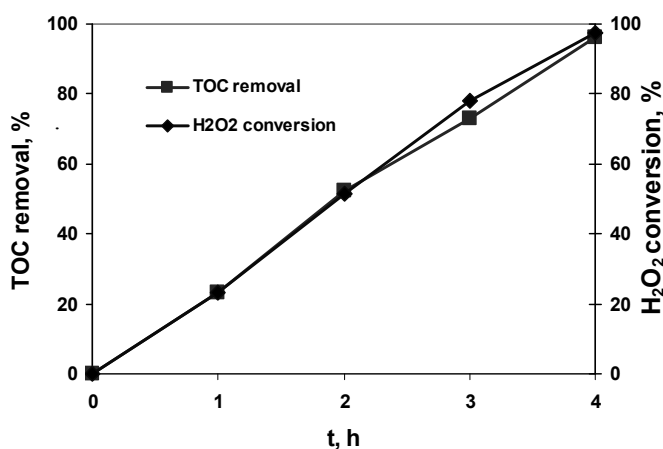


Figure 5: Photo-Fenton oxidation of MTBE on LaMnO₃ (3.7 wt %).

With regard to MTBE abatement (Figure 5), in the presence of perovskites based catalyst the TOC removal reached 100 % after 4 hours of reaction time, paralleling the

H₂O₂ conversion, while in the absence of catalyst a lower conversion with a higher H₂O₂ consumption was found.

4 CONCLUSIONS

Heterogeneous photo-Fenton process allows to obtain higher TOC removal efficiency with a lower consumption of H₂O₂ with respect to the homogeneous process.

No significant leaching phenomena were observed.

By dosing H₂O₂ to maintain its concentration to low values the TOC removal increased up to 100 %. Monolith catalysts were stable and reusable.

The preparation of nanosized supported perovskites, in the absence or in the presence of Pt nanoparticles well anchored to a “macroscopic” monolithic support, permitted to match improved catalytic activity to easy and safe manipulation and separation from a treated wastewater.

The heterogeneous process allows a deep oxidation of acetic acid and of several organic compounds, such as methyl tert-butyl ether, methanol and ethanol, to CO₂ and H₂O.

Concluding, heterogeneous photo-Fenton system on monolith perovskites can provide an effective technology of organic pollutants abatement without producing sludges and long start-up time, with low-cost, stable and reusable heterogeneous structured catalysts.

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