

Enhanced Photocatalytic Degradation of Ibuprofen in Aqueous Solution under Visible-Light Irradiation: Effects of LaFeO₃ and Cu/LaFeO₃

Renato Pelosato, Veronica Carrara, Isabella Natali Sora*

University of Bergamo, Department of Engineering and Applied Science, viale Marconi 5, Dalmine, Italy.
 isabella.natali-sora@unibg.it

The efficiency of LaFeO₃ and Cu-doped LaFeO₃ nanopowders in the photocatalytic degradation of ibuprofen (IBP) has been investigated. Aqueous solutions of IBP were irradiated under visible-light in the presence of the catalyst and H₂O₂. The experiments were carried out on aqueous suspensions containing 5.0×10^{-5} M of IBP, 0.003 M of H₂O₂, 0.130 g L^{-1} (5.0×10^{-4} M) of catalyst. The composition of the reaction solution was monitored during the experiments by UV-Vis spectroscopy and HPLC. The results showed a higher photocatalytic activity of Cu-doped LaFeO₃ (5 and 10 mol%) compared to pure LaFeO₃. The concentration of 4-isobutylacetophenone (4-IBAP), an harmful by-product of the degradation of IBP was the lowest when using 5 mol% Cu-doped LaFeO₃ catalyst, i.e. ~ 2 % and << 1 % of the initial IBP concentration after 5 h and 24 h of irradiation, respectively. The chloride water matrices decreased the degradation percentage of IBP and 4-IBAP.

1. Introduction

In a photocatalytic process, a chemical reaction is initiated when a semiconductor photocatalyst is irradiated by light with an energy that matches or exceeds the band gap energy of the semiconductor, generating excited electron-hole pairs that can be active for the production or degradation of a compound (Hoffmann et al, 1995). The AOP (Advanced Oxidation Process) combined with a photocatalytic process can be extremely beneficial and effective for the degradation of certain categories of pollutants such as pharmaceuticals (PhCs) and their metabolites, which are generally recalcitrant and, due to continuous discharge in the effluents, persistent. PhCs were detected worldwide at low concentrations (from ng L⁻¹ to µg L⁻¹ levels) in surface water bodies in different areas (Calamari et al, 2003; Verlicchi et al, 2012). The photodegradation of PhCs under photocatalytic conditions has been already carried out efficiently through the use TiO₂ and UV-light,. However, in wastewater treatment plants the application of AOP systems utilizing the TiO₂ photocatalyst is infrequent, limited by a certain low photonic efficiency of the technology and by the use of energy-consuming ultraviolet (UV-A) lamps as radiation source. To achieve a wider application of AOPs combined with photocatalysis, a non-toxic and efficient catalyst, activated with visible light, should be used.

LaFeO₃ (hereafter LF) with a typical ABO₃-type perovskite structure (A is usually a rare earth and B is a transition metal) is effective on catalytic reactions, combined with chemical stability and nontoxicity. LF-based materials have applications in essential components such as electrodes (Zurlo et al, 2016), chemical sensors (Tulliani et al, 2015) and catalysts (Spinicci et al, 2001; Turkten et al, 2018). LF is a charge-transfer-type semiconductor and exhibits a narrow band-gap energy between 2.1 eV (for dense polycrystalline samples) and 2.6 eV (for nanopowdered samples) (Köferstein et al, 2013; Natali Sora et al, 2013). LF was proposed as visible-light photocatalyst since 2007 (Iervolino et al, 2016; Li et al, 2007; Parida et al, 2010), although most of these photodegradation studies were focused on organic dyes in aqueous solution (Su et al, 2010), often combined with a Fenton-like reaction (Wang et al, 2017). However, tests with dyes are not appropriate in photocatalysis, because they do not distinguish between a pure photocatalytic process, a dye sensitization or both, as underlined in recent literature (Barbero & Vione, 2016). Recently, the photocatalytic degradation of ibuprofen (IBP, a widely used non-steroidal anti-inflammatory drug) in the presence of LF photocatalyst and

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aqueous H₂O₂ using visible-light irradiation has been reported (Natali Sora & Fumagalli, 2017). After 24 h irradiation about 80 % of the initial IBP concentration (10.0 mg L⁻¹) was removed from an aqueous solution; however, it was found that the photodegradation products of IBP induced toxic effects on aquatic organisms (*D. magna* and *P. subcapitata*) and bacteria (*V. fischeri*). These results suggested that an incomplete detoxification of the starting solution was obtained, and that the toxicity of photoproducts was higher than that of IBP itself. The higher toxicity was due to the presence of 4-isobutylacetophenone (4-IBAP), which is known to be formed from IBP when heated, or under oxidative conditions (Caviglioli et al, 2002), and photochemically upon direct photolysis, reaction with ·OH and chromophoric organic matter (Ruggeri et al, 2013).

We have previously studied the crystal structure of LaFe_{1-x}Cu_xO₃, through the Rietveld method applied to X-ray powder diffraction data (Caronna et al, 2009). Up to x = 0.20 the compounds exhibited the orthorhombic symmetry and crystallize in the perovskite-like cell of LaFeO₃, with octahedral sites occupied by a mixture of Fe and Cu and lanthanum atoms twelve-fold coordinated. The amount of Fe⁴⁺ was negligible, as measured by redox titration. In this study, the photocatalytic degradation of IBP by visible-light and in the presence of H₂O₂ by LaFe_{1-x}Cu_xO₃ suspensions was investigated. The effect of Fe partial substitution by Cu, reaction time, as well as water matrices on the yields of 4-IBAP from IBP, was assessed.

2. Experimental section

2.1. Materials

Lanthanum ferrite nanopowders LaFe_{1-x}Cu_xO₃, with x = 0, 0.05 and 0.10 (LF, LFC05 and LFC10), were prepared by citrate auto-combustion of dry gel obtained from a solution of the corresponding nitrates poured into citric acid solution, as described in our previous work (Caronna et al, 2009). Analytical grade La₂O₃, Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·2.5H₂O, citric acid, nitric acid and aqueous NH₃ were used as the starting materials. A specific amount of dried La₂O₃ was dissolved in a nitric acid solution to prepare La(NO₃)₃·6H₂O. Cu substituted powders were green-blackish coloured. Ibuprofen (IBP, purity grade 98 %), 4-isobutylacetophenone (4-IBAP, purity grade 97 %) and H₂O₂ (3 wt%) were used as purchased from Sigma-Aldrich. Table 1 shows the chemical structures and the main characteristics of IBP and 4-IBAP.

2.2 Water matrices

IBP solutions were prepared in distilled water (pH = 5.9) and in synthetic water matrices, distilled water in the presence of potassium chloride (177 mg L⁻¹ chlorides). Reference 4-IBAP solutions were prepared in distilled water.

Table 1: Main characteristics of the investigated PhCs

	Ibuprofen	4-isobutylacetophenone
Structure		
Formula	C ₁₃ H ₁₈ O ₂	C ₁₂ H ₁₆ O
CAS-No	15687-27-1	38861-78-8
Molecular weight (g/mol)	206.28	176.25
Solubility in water	Slightly soluble	Soluble

2.3. Photocatalytic oxidation experiments

The photocatalytic degradation reactions were carried out using a Rayonet reactor equipped with 8 lamps (8 W, GE lighting 10055-F8T5/D) emitting in the visible region (irradiance 50 W m⁻²). Irradiation of aqueous suspensions containing 5.0 × 10⁻⁵ M (10.3 mg L⁻¹) of IBP, 0.003 M H₂O₂, 130 mg L⁻¹ LF (or LFC05, LFC10) (5.0 × 10⁻⁴ M) were carried out in magnetically stirred Pyrex glass tubes at constant temperature of 30 ± 1 °C. The molar concentration of 4-IBAP in reference solutions was 5.0 × 10⁻⁵ M, corresponding to 8.8 mg L⁻¹. The concentration of H₂O₂ corresponded to a mole amount that largely exceeded the mole amount of IBP, but was about 1/30 than that used in typical studies on the heterogeneous Fenton-like process. It is worth noting that in this study we used an initial concentration of IBP which is much higher than that found in the effluents of the wastewater treatment plants (143 - 4 ng L⁻¹) (Petrie et al, 2015), so as to reach a significant spectrophotometric signal. The analyses were performed on aqueous samples taken at regular intervals of irradiation and centrifuged for 10 min to separate the solid fraction.

The absorption spectra were measured using an ultraviolet-visible (UV-Vis) spectrophotometer (Jasco V-650), with 10 mm light path. Full spectra were taken in the range 200-800 nm. High performance liquid chromatography HPLC (Agilent Technologies 1200 Series) with variable wavelength detector, isocratic pump and a Chrompack C8 (3.0 x 100 mm) column was also used. The mobile phase consisted in an isocratic method of ultrapure water (30 %) and acetonitrile (70 %). The IBP absorbance peaked at 220 nm, 4-IBAP absorbance peaked at 258 nm, as determined from the respective UV-Vis absorption spectrum. The solvent flow rate was 1 mL min⁻¹. The normalized concentration C_t/C_0 of IBP was calculated, where C_0 and C_t are the total concentrations of the pollutant solution before irradiation, and after an irradiation time t , respectively. Each experiment was repeated at least two times.

3. Results and discussion

3.1 Photocatalytic degradation tests with Cu-doped LF

We have previously reported that the optical absorption edge energy values E_g for Cu-doped LF are in the range 2.5 ± 2.6 eV (Parrino et al, 2016). The substitution of Fe³⁺ by Cu²⁺ in LFC05 and LFC10 caused: (i) elimination of oxygen atoms, and (ii) variation of the Fe⁴⁺/Fe_{tot} atomic ratio, which was measured by redox titration as 0.13, 0.12 and 0.16 mol% for LF, LFC05 and LFC10 respectively (Caronna et al, 2009). The surface composition of Cu-doped LF nanopowders was richer in copper than the bulk. The Fe/Cu surface molar ratios measured by EDX analyses were much lower than the nominal ones: 5.80 compared to 19.0 and 5.00 compared to 9.00 for LFC05 and LFC10, respectively (Parrino et al, 2016). The specific surface area was about 13 m² g⁻¹ for all samples (Parrino et al, 2016).

As a first step, the photocatalytic degradation of IBP was investigated by UV-Vis spectrometry. As a reference, in Figure 1 are shown the UV-Vis absorption spectra of reference aqueous solutions of IBP and 4-IBAP, in presence of H₂O₂ and LF, after centrifugation. The main absorption peaks were detected at 220 nm for IBP and 258 nm for 4-IBAP. A small absorption in the 250-270 nm region was detected also in the spectra of IBP, and it was attributed to the presence of some impurities or decomposition products of IBP in the pristine solution (e.g. 4-IBAP and others). Upon irradiation, an increase of the signal at 258 nm was observed in the spectrum of IBP solutions that reached a maximum intensity after 5 h and then decreased at longer irradiation times.

The use of UV-Vis spectrophotometry is experimentally convenient, but it is prone to spectral interferences. For this reason, HPLC measurements were also performed. The chromatograms of IBP in the presence of different catalysts + H₂O₂ after 5 h visible-light irradiation confirmed the degradation of IBP revealed via UV-Vis spectrometry. The HPLC quantitative analyses showed that IBP was degraded in the presence of the catalyst following the trend LFC05 > LFC10 >> LF.

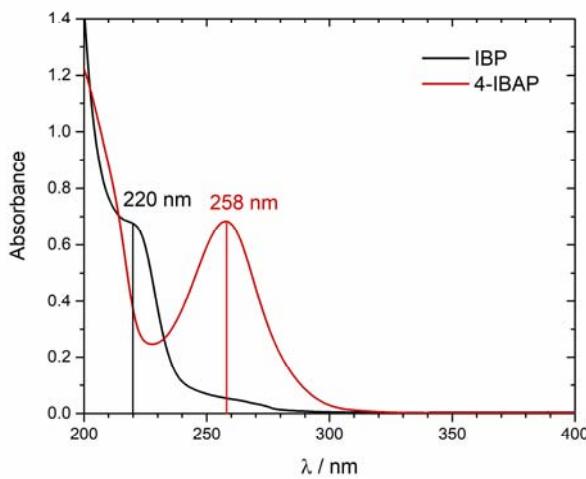


Figure 1: UV-Vis spectra of aqueous solutions of 5.0×10^{-5} M IBP (—) and 5.0×10^{-5} M 4-IBAP (—), both in presence of 130 mg L^{-1} LF catalyst and $0.003 \text{ M H}_2\text{O}_2$, after centrifugation.

As already reported (Natali Sora & Fumagalli, 2017) the direct photolysis of IBP after 5 hours of visible light irradiation is negligible in these experimental conditions; the same applies in solutions containing IBP and

H_2O_2 . Figure 2A shows the obtained results reported as concentration of Ibuprofen at the irradiation time t respect the initial Ibuprofen concentration ($C_t^{\text{IBP}}/C_0^{\text{IBP}}$): after 5 h irradiation, LFC05 catalyst achieved the most extensive degradation of IBP, i.e 85 % ($C_t^{\text{IBP}}/C_0^{\text{IBP}} = 0.15$), while LFC10 degraded 76% of initial IBP and LF 58%. These results were excellent; considering that we have previously found that after 5 h visible-light exposure the degradation of IBP in presence of H_2O_2 only was less than 4 % (Natali Sora & Fumagalli, 2017). LFC05 and LFC10 are way more efficient catalysts than LF also after 24 h visible-light irradiation: both reached a complete transformation of IBP, while LF degraded 87% of the initial IBP.

The formation yields of 4-IBAP from IBP were also evaluated using HPLC technique. The relevant results are shown in Figure 2B, which reports the concentration values of 4-IBAP divided by the initial IBP concentration $5.0 \times 10^{-5} \text{ M}$ (10.3 mg L^{-1}) as $C_t^{\text{4-IBAP}}/C_0^{\text{IBP}}$. A small concentration of 4-IBAP was detected in the starting solution of in the three samples. Noteworthy, a higher concentration was found in LFC05 and LFC10 solution respect to the LF containing one, as a confirmation of the higher activity of the two former catalysts. As expected, 4-IBAP increased with time in the first hours of irradiation, being 4-IBAP a product of the decomposition of IBP. After 5 h of irradiation the amount of 4-IBAP exceeded 2% of the initial IBP in the three solutions. The maximum concentration value of 4-IBAP was found when using LF + H_2O_2 ($\sim 3\%$ of C_0^{IBP}). This value correspond to $1.5 \times 10^{-6} \text{ M}$, which is a concentration that would cause environmental concern (Natali Sora & Fumagalli, 2017). By the way, 4-IBAP itself was subsequently decomposed in the reaction mixture, and its amount sharply decreased after 24 h of irradiation. The final 4-IBAP concentrations followed the trend LF ($\sim 1\%$ of C_0^{IBP}) > LFC10 ($< 1\%$ C_0^{IBP}) > LFC05 ($<< 1\%$ C_0^{IBP}).

The results of 4-IBAP degradation further support the higher activity of LFC05 and LFC010 catalysts respect to LF.

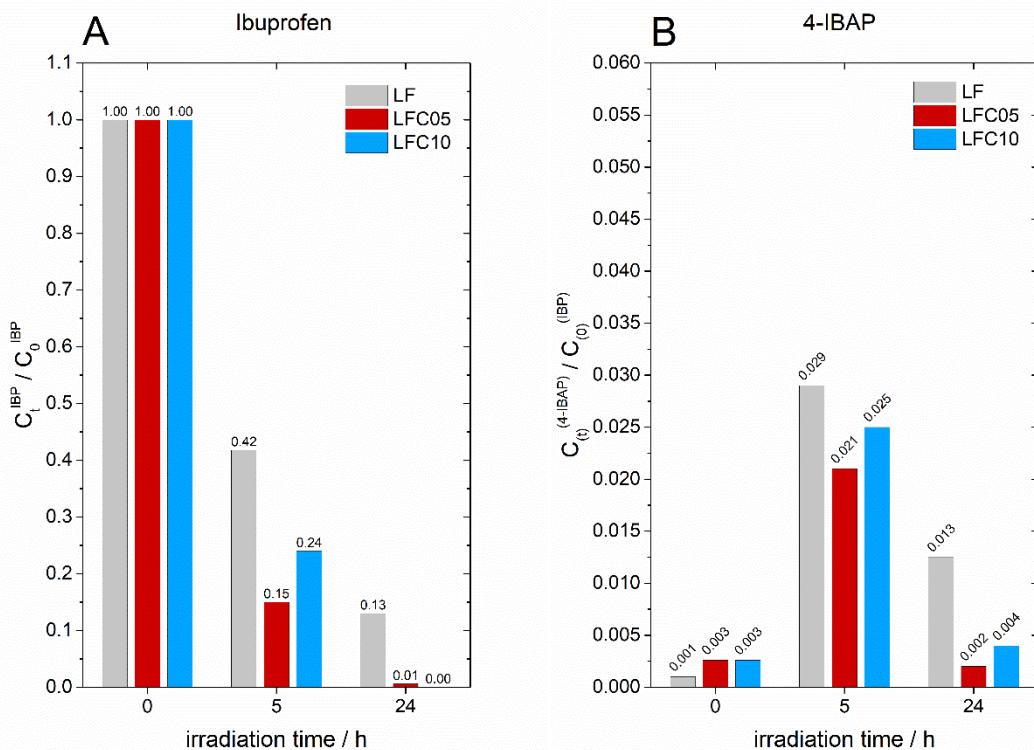


Figure 2: Concentration values of IBP (C_t^{IBP} , panel A) and 4-IBAP ($C_t^{\text{4-IBAP}}$, panel B) divided by the initial IBP concentration(C_0^{IBP}) in solutions irradiated with visible-light for 5 and 24 h. Initial conditions: $5.0 \times 10^{-5} \text{ M}$ IBP, 130 mg L^{-1} catalysts, 0.003 M H_2O_2 .

The Fe partial substitution by Cu clearly influenced the photocatalytic activity of LF. The enhanced photocatalytic activity of LFC05 and LFC10 catalysts may be ascribed to the presence of both Cu(II) and oxygen vacancies, which through trapping of conduction band electrons could slow the recombination of charge carriers.

3.2 Degradation of IBP in water matrices containing chloride

The effect of chloride anions on the IBP transformation and 4-IBAP formation in the presence of LF + H₂O₂ was assessed with the same initial concentration of contaminant, catalyst and H₂O₂ used above. Chlorides decreased the degradation kinetic of IBP as shown in Figure 3A. The degradation of IBP was strongly decreased/slowed down. After 5 hours of irradiation, a residual of 72% of pristine IBP was detected in the solution with chloride ions, respect to the 42% found in the chlorine free solution. This trend was confirmed also after 24 hours irradiation, with 42% of initial IBP left in the chlorine containing solution, respect to the 13% detected in the chlorine free one. The photodegradation was so slowed down that in the case of chlorine containing solution, the amount of the degradation product 4-IBAP (Figure 3B) was found to increase also after 24 hours of irradiation. It has been suggested in the literature that Cl⁻ ions could interfere by competing for the active sites on the catalyst, given that the catalyst surface is positively charged in the experimental conditions (pH < Point of Zero Charge, which is around 8.9, according to Rusevova et al, 2014), or, less likely, act as a scavenger for the OH radicals (Krivec et al, 2014).

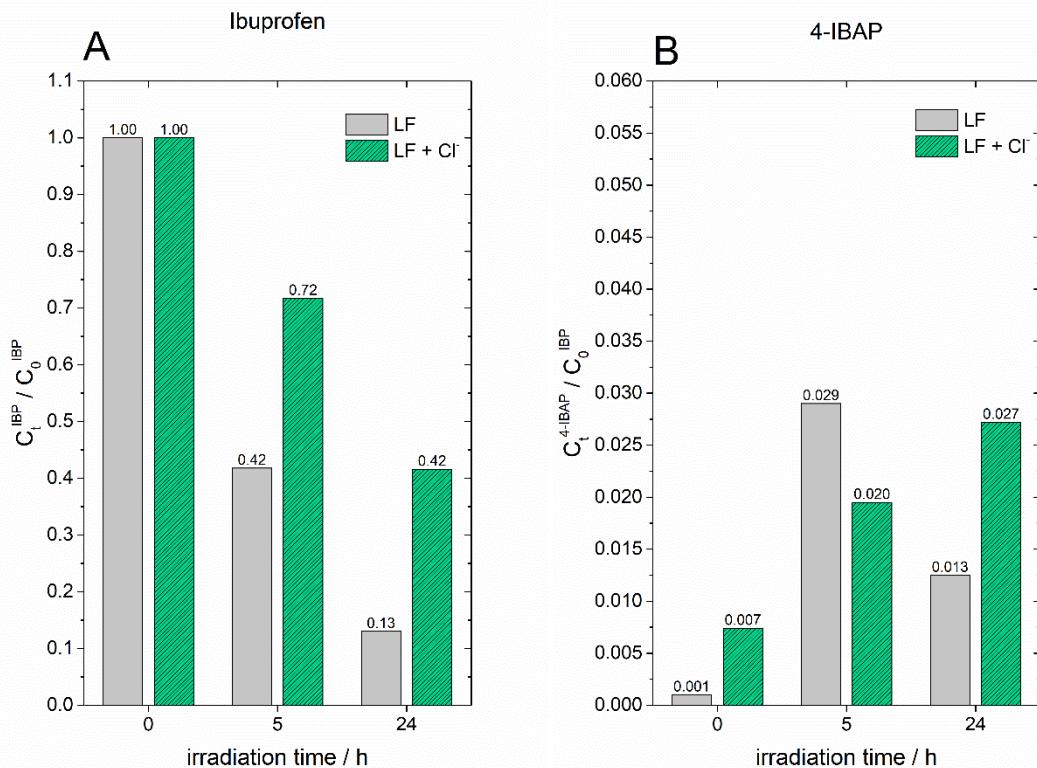


Figure 3: Concentration values of IBP (C_t^{IBP} , panel A) and 4-IBAP ($C_t^{\text{4-IBAP}}$, panel B) divided by the initial IBP concentration (C_0^{IBP}) in solutions irradiated with visible-light for 5 and 24 h. Initial conditions: 5.0×10^{-5} M IBP, 130 mg L^{-1} LF, $0.003 \text{ M H}_2\text{O}_2$, 177 mg L^{-1} chlorides.

4. Conclusions

The Fe partial substitution by Cu strongly influenced the photocatalytic activity of lanthanum ferrite. Using visible-light irradiation and in the presence of LFC05 and aqueous H₂O₂ an excellent photocatalytic degradation of IBP (85 %) was observed already after 5h. Nevertheless, even in the case of the most efficient catalyst (LFC05) the harmful by-product 4-IBAP from IBP was found in the mixture at a concentration of ~ 2 % after 5 hours irradiation. Its amount decreases to safe levels << 1 % of the initial IBP after 24 h irradiation. Chloride water matrices could interfere with the process, as in the performed experiments decreased the amount of degraded IBP and increased the yield of the harmful degradation product 4-IBAP.

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