Research article

Diclofenac Photodegradation Under Visible Light With (La,Ba)(Fe,Ti)O_3 Perovskites

Ana Sofia Rodrigues, Lurdes Ciríaco, Maria José Pacheco, and Ana Lopes

FibEnTech and Departament of Chemistry, University of Beira Interior, Rua Marquês d'Ávila e Bolama, 6201-001, Covilhã, Portugal

Abstract.
Perovskites $BaTiO_3$ and $BaFeO_3$ were prepared by the ceramic and complex polymerization methods and the substituted perovskites $La_{0.2}Ba_{0.8}TiO_3$, $BaFe_{0.8}Ti_{0.2}O_3$, and $BaFe_{0.6}Ti_{0.4}O_3$ were prepared by the ceramic method. All of them were used as photocatalytic material for the degradation of the pharmaceutical diclofenac under visible light. The best diclofenac degradation results were obtained with the substituted perovskite $La_{0.2}Ba_{0.8}TiO_3$ (46%), prepared by the ceramic method, and with the non-substituted perovskite $BaFeO_3$ (43%), prepared by the complex polymerization method.

Keywords: visible light, perovskites, photocatalysis, (La,Ba)(Fe,Ti)O_3, diclofenac

Corresponding Author: Ana Sofia Rodrigues; email: ana.sf.rodrigues@ubi.pt

Published 10 August 2022

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the FibEnTech21 Conference Committee.

1. Introduction

Perovskites are a class of compounds with the general formula ABX_3, where A is an alkali or alkaline earth metal or a member of the lanthanides' family, B is a transition metal, X is an anion, frequently an oxygen ion [1]. Perovskite oxides are characterized by their flexible chemical composition, structural stability, and elemental abundance. Approximately 90% of the Periodic Table metal elements can be accommodate in the perovskite structure, modifying the catalytic properties, without destroying the matrix structure [1,2].

Perovskite-type metal oxides are being increasingly investigated in various areas, namely as photocatalysts for water decontamination [2]. Photocatalysts are semi-conductors with band gap energy (Eg) between 1.4 and 3.8 eV, being activated by UV light for Eg<3 eV and by visible light for Eg>3 eV. However, perovskites optical properties may be changed by doping, inducing visible light absorption, allowing their utilization with visible light or even sunlight, a green, safe, and sustainable energy. Thus, for good-environmental practices, it is important to develop photocatalysts activated by visible light, to use the maximum potential of solar energy.

In this work, perovskites of the family (La,Ba)(Fe,Ti)O_3, namely $BaTiO_3$, $BaFeO_3$, $La_{0.2}Ba_{0.8}TiO_3$, $BaFe_{0.8}Ti_{0.2}O_3$ e $BaFe_{0.6}Ti_{0.4}O_3$ were synthetized and tested as photocatalysts. The influence of the chemical composition and of the preparation method on their

How to cite this article: Ana Sofia Rodrigues, Lurdes Ciríaco, Maria José Pacheco, and Ana Lopes, (2022), "Diclofenac Photodegradation Under Visible Light With (La,Ba)(Fe,Ti)O_3 Perovskites " in *1st International FibEnTech Congress (FibEnTech21) New opportunities for fibrous materials in the ecological transition*, KnE Materials Science, pages 100–107. DOI 10.18502/kms.v7i1.11613

photocatalytic properties was assessed, using synthetic solutions of a model compound – Diclofenac (DIC). This pharmaceutical drug is of great environmental concern due to its occurrence and fate, and also due to the metabolites from its degradation in the human body [3]. Diclofenac was already detected in reservoirs for drinking water, and the European media of diclofenac occurrence in wastewater is 0.174 μg/L [3,4]. Diclofenac can be removed by many ways: biodegradation [5], sorption [6]; solar photo-Fenton reaction [7]; bioaugmentation [8]; ultrasound [9], electro-oxidation using BDD [10], electro-Fenton process [11]; pyrite catalysed Fenton oxidation [12], and activation of peroxymonosulfate by $LaFeO_3$ [13].

2. Material and methods

Perovskites $BaTiO_3$, $BaFeO_3$, $La_{0.2}Ba_{0.8}TiO_3$, $BaFe_{0.8}Ti_{0.2}O_3$ and $BaFe_{0.6}Ti_{0.4}O_3$ were synthetized by the ceramic method (MC) and $BaTiO_3$, $BaFeO_3$ were also synthesized by the complex polymerization method (PC).

For the synthesis using the ceramic method, stoichiometric amounts of commercial La_2O_3 (Acros Organics, +99.9%), $BaCO_3$ (Fluka, +99.0%), Fe_2O_3 (Merk, +99.0%) and TiO_2 (Aldrich, +99.8%) were weighed and milled for 30 min, pre-calcined at 900 °C for 6 h in a tubular furnace and calcined at 1130 °C for 4 h (adapted from [14]).

The perovskites synthesized by the complex polymerization method (adapted from [15,16]) were prepared with stoichiometric amounts of commercial $BaCO_3$ (Fluka, +99%), $C_{12}H_{28}O_4Ti$ (Acros Org., +98%) or $FeN_3O_9\cdot 9H_2O$ (Sigma-Aldrich, 99.95%). For the preparation, $C_{12}H_{28}O_4Ti$ or $FeN_3O_9\cdot 9H_2O$ are weighed, dissolved in ethylene glycol (Carlo Erba, +99,5%). After that, citric acid (Aldrich, +99%) is added, being ethylene glycol/ citric acid volumetric ratio 1:4. $BaCO_3$ is then added and the resulting mixture is submitted to successive heating: 50 °C, 90 °C, 150 °C; finally, at 400 °C, for 2 h, in a tubular furnace, with a heating rate of 5 °C/min, for the formation of a black precursor powder. The powder is then calcined at 900 °C, for 3 h (5 °C/min), milled for 15 min, calcined again at 900 °C, for 3 h (5 °C /min), and milled again for 15 min.

All the synthetized perovskites were characterized by X-ray diffraction, XRD, using a Rigaku diffractometer, model DMAX III/C, with automatic data acquisition (MDI, Materials Data), equipped with a monochromatized Cu kα radiation (λ = 0.15406 nm), operating at 40 mA and 30 kV. Dispersive energy spectroscopy (EDS) and scanning electron microscopy (SEM) were done in a Hitachi (S-3400N)/ Bruker system, operating at 20 keV.

In a setup [17] that allows simultaneous assays (Fig. 1), 10 mL diclofenac (25 ppm) aqueous solutions were submitted to photocatalytic degradation assays, performed in batch mode, with orbital stirring, for 6 h, under visible light (OSRAM, 300W).

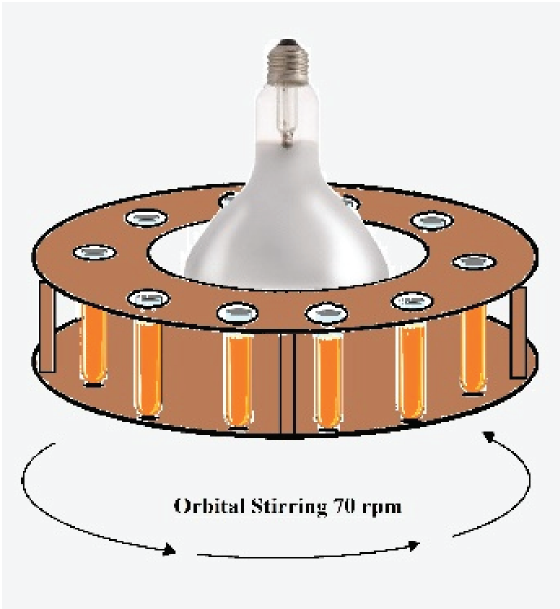

Figure 1: Setup for the photocatalytic assays [17].

The perovskites concentration in suspension was 250 ppm. After the photocatalytic assays, solutions were centrifuged, and the diclofenac degradation was monitored by UV/visible absorption spectrophotometry, with the spectra performed in a Shimadzu UV-1800 spectrophotometer. To determine ban gap energies for the different perovskites, diffuse reflectance spectra of the perovskite films were also obtained, in an UV–vis spectrometer Shimadzu UV-2600PC, equipped with an integrating sphere ISR 2600plus, over the spectral range 200–900 nm. Kubelka–Munk function was used to analyze the diffuse reflectance spectra. $BaSO_4$ was utilized as reflectance standard.

3. Results and discussion

The diffractograms of the prepared perovskite powders are presented in Fig. 2. Both $BaTiO_3$ MC and PCpresent cubic symmetry in a Pm3m space group. However, for $BaTiO_3$ PC there is evidence of another phase, an orthorhombic secondary phase of Ba_2TiO_4, probably due to the lower synthesis temperature utilized in the PC method.

$BaFeO_3$ MC presents a predominant tetragonal phase, with traces of secondary hexagonal and cubic phases. On the other hand, $BaFeO_3$ PC has a predominance of a cubic structure, although with traces of hexagonal and tetragonal secondary phases.

$La_{0.2}Ba_{0.8}TiO_3$ is the only one that exhibit monoclinic structure, and traces of reagent La_2O_3.

$BaFe_{0.8}Ti_{0.2}O_3$ and $BaFe_{0.6}Ti_{0.4}O_3$have hexagonal structure,but a new phase of $BaO(TiO_2)_2$ can be detected. This perovskite, without Fe may be the responsible for an higher EDS signal in Ti, indicating a higher concentration in Ti in the intended perovskite.

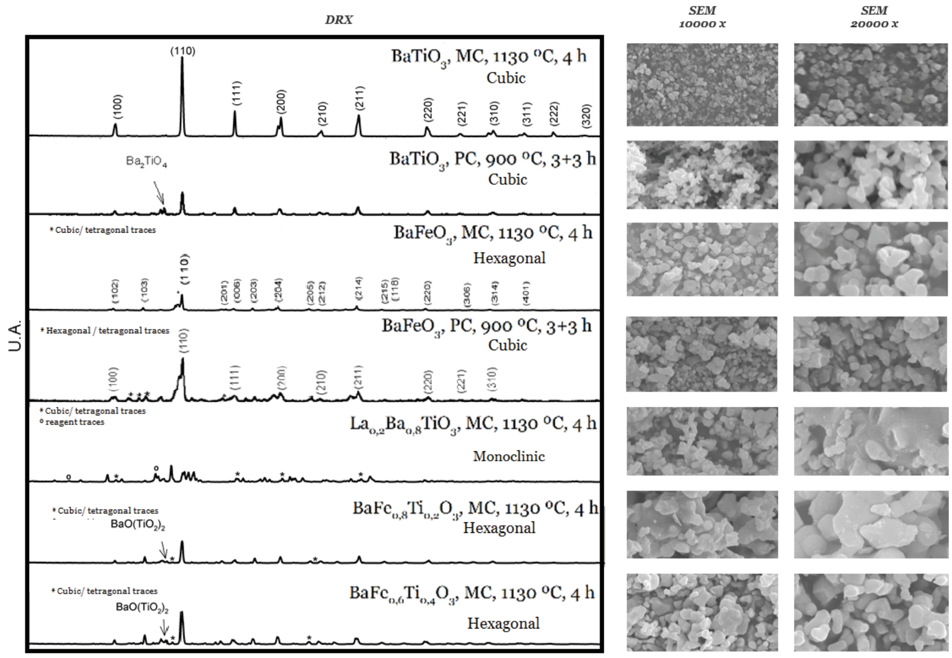

Figure 2: Results of the perovskites powders characterization by DRX and SEM.

Table 1 shows the crystallite size, cell parameters, band-gap energies (Eg) and EDS results for the perovskites prepared. $BaTiO_3$MC and $BaTiO_3$PC present cubic structure, with a cell parameter of approximately 0.4 nm. For this peroveskite, it seems that the preparation method does not to have any influence on the unit cell. Regarding $BaFeO_3$MC and $BaFeO_3$PC, the later perovskite presents a crystallite size of approximately half of the former perovskite. This must be due to the calcination temperature since higher temperature will allow the formation of a more developed crystallite.

Peroveskites presenting Eg<3 eV are $BaFeO_3$ MC, $BaFe_{0.8}Ti_{0.2}O_3$ MC and $BaFe_{0.6}Ti_{0.4}O_3$ MC, being promising for use in photocatalytic assays activated by visible light; the other perovskites present Eg>3 eV, being technically only activated by UV light. However, the existence of secondary phases, forming heterostructures, may sometimes allow their activation by visible light.

Figure 3 shows the results for DIC photocatalytic degradation tests. BaFeO3 PC, presents the best results for the non-substituted perovskite. Regarding the perovskites

Table 1: Physical properties of perovskite powders prepared at different experimental conditions.

Perovskite	Crystallite size /nm	Cell param. / nm*	Eg / eV	EDS
$BaTiO_3$, MC, 1130, 4h	55.16	a=4.007	3.24	$Ba_{0.85}Ti_{1.00}O_{3.15}$
$BaTiO_3$, PC 900, 3+3h	55.76	a=4.014	3.24	$Ba_{1.00}Ti_{1.05}O_{2.94}$
$BaFeO_3$, MC, 1130, 4h	36.37	a=3.989; c=4.067	2.96	$Ba_{1.14}Fe_{1.07}O_{2.79}$
$BaFeO_3$, PC 900, 3+3h	19.87	a=4.005	3.61	$Ba_{1.04}Fe_{1}O_{2.96}$
$La_{0.2}Ba_{0.8}TiO_3$, MC, 1130, 4h	55.28	a=3.997	3.47	$La_{0.23}Ba_{0.63}Ti_{0.94}O_{3.20}$
$BaFe_{0.8}Ti_{0.2}O_3$, MC, 1130, 4h	49.93	a=5.690; c=13.984	2.57	$Ba_{1.18}Fe_{0.64}Ti_{0.37}O_{2.81}$
$BaFe_{0.6}Ti_{0.4}O_3$, MC, 1130, 4h	46.60	a= 5.702; c=14.00	2.65	$Ba_{1.10}Fe_{0.36}Ti_{0.70}O_{2.84}$

*Determined using Holland TJB, Redfern SAT. Unicell, computer program, developed at the University of Cambridge, in 1995.

that underwent substitutions, it was found that 20% substitution of Ba by La causes an increase in the photocatalytic activity, surpassing the DIC removal value with $BaTiO_3$ and even with $BaFeO_3$. This perovskite maintained the cubic structure of $BaTiO_3$and the size of the crystallites did not vary significantly.

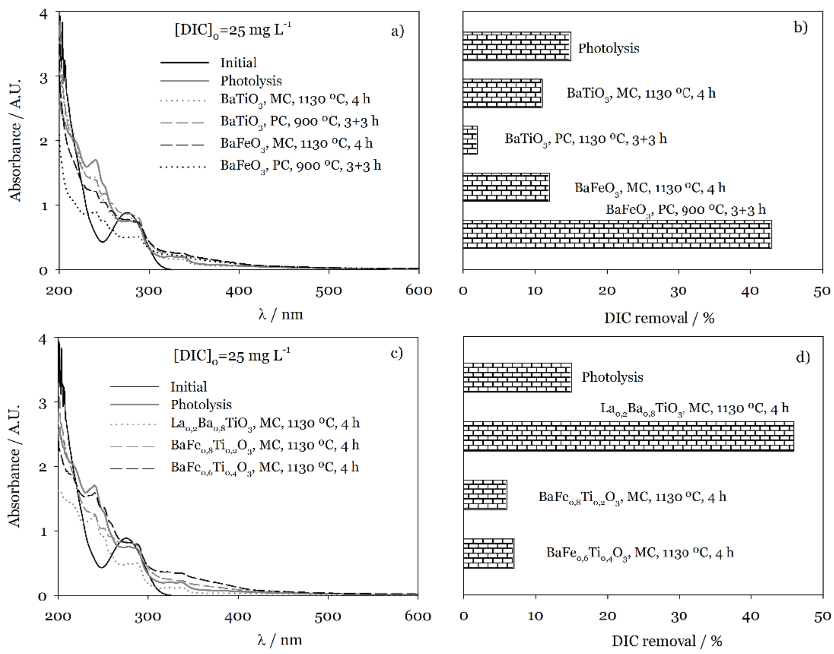

Figure 3: Results of Diclofenac degradation tests, after 6 h in a circular set-up, using different perovskites: (a,c) – UV-Vis absorbance spectra; (b,d) – DIC removal. [perov]=250ppm.

Removal of diclofenac was calculated based on its absorbance at 276 nm, where DIC presents an absorption maximum. The UV-Vis spectra show the formation of by-products that absorb at 240 nm, probably acetophenone [18]. However, this by-product also suffers degradation since the absorbance at this wavelength decreases as the assay proceeds.

4. Conclusions

Results show that perovskites of the family (La,Ba)(Fe,Ti)O_3 can be utilized as visible light-driven photocatalysts for diclofenac degradation, as well as for the degradation of the DIC by-products. The best DIC removal rates were attained with $La_{0.2}Ba_{0.8}TiO_3$ (46%), prepared by the ceramic method, and with $BaFeO_3$ (43%), prepared by the complex polymerization method. The results evidence that synthesized perovesquites are promising for use with natural sunlight for depuration of natural waters.

Acknowledgments

The authors acknowledge the financial support from Fundação para a Ciência e a Tecnologia, FCT, through the funding of the UID Fiber Materials and Environmental Technologies (FibEnTech), project UIDB/00195/2020, and for the grant SFRH/BD/109901/2015 awarded to A.S. Rodrigues.

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