Diclofenac Photodegradation Under Visible Light With \((\text{La,Ba})(\text{Fe,Ti})\text{O}_3\) Perovskites

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Abstract.
Perovskites \(\text{BaTiO}_3\) and \(\text{BaFeO}_3\) were prepared by the ceramic and complex polymerization methods and the substituted perovskites \(\text{La}_{0.2}\text{Ba}_{0.8}\text{TiO}_3\), \(\text{BaFe}_{0.8}\text{Ti}_{0.2}\text{O}_3\), and \(\text{BaFe}_{0.6}\text{Ti}_{0.4}\text{O}_3\) 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 \(\text{La}_{0.2}\text{Ba}_{0.8}\text{TiO}_3\) (46%), prepared by the ceramic method, and with the non-substituted perovskite \(\text{BaFeO}_3\) (43%), prepared by the complex polymerization method.

Keywords: visible light, perovskites, photocatalysis, \((\text{La,Ba})(\text{Fe,Ti})\text{O}_3\), diclofenac

1. Introduction
Perovskites are a class of compounds with the general formula \(\text{ABX}_3\), where \(\text{A}\) is an alkali or alkaline earth metal or a member of the lanthanides’ family, \(\text{B}\) is a transition metal, \(\text{X}\) 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 semiconductors with band gap energy \((\text{Eg})\) between 1.4 and 3.8 eV, being activated by UV light for \(\text{Eg}<3\) eV and by visible light for \(\text{Eg}>3\) 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 \((\text{La,Ba})(\text{Fe,Ti})\text{O}_3\), namely \(\text{BaTiO}_3\), \(\text{BaFeO}_3\), \(\text{La}_{0.2}\text{Ba}_{0.8}\text{TiO}_3\), \(\text{BaFe}_{0.8}\text{Ti}_{0.2}\text{O}_3\) e \(\text{BaFe}_{0.6}\text{Ti}_{0.4}\text{O}_3\) were synthetized and tested as photocatalysts. The influence of the chemical composition and of the preparation method on their
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 synthesized 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$_2$O$_3$ (Acros Organics, +99.9%), BaCO$_3$ (Fluka, +99.0%), Fe$_2$O$_3$ (Merk, +99.0%) and TiO$_2$ (Aldrich, +99.8%) were weighed and milled for 30 min, pre-calcined at 900 ºC for 6 h in a tubular furnace and calcined at 1130 ºC 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$_4$Ti (Acros Org., +98%) or FeN$_3$O$_9$·9H$_2$O (Sigma-Aldrich, 99.95%). For the preparation, C$_{12}$H$_{28}$O$_4$Ti or FeN$_3$O$_9$·9H$_2$O 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 ºC, 90 ºC, 150 ºC; finally, at 400 ºC, for 2 h, in a tubular furnace, with a heating rate of 5 ºC/min, for the formation of a black precursor powder. The powder is then calcined at 900 ºC, for 3 h (5 ºC/min), milled for 15 min, calcined again at 900 ºC, for 3 h (5 ºC/min), and milled again for 15 min.

All the synthesized 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).

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 band 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. BaSO₄ was utilized as reflectance standard.

3. Results and discussion

The diffractograms of the prepared perovskite powders are presented in Fig. 2. Both BaTiO₃MC and PC present cubic symmetry in a Pm3m space group. However, for BaTiO₃ PC there is evidence of another phase, an orthorhombic secondary phase of Ba₂TiO₄, probably due to the lower synthesis temperature utilized in the PC method.

BaFeO₃ MC presents a predominant tetragonal phase, with traces of secondary hexagonal and cubic phases. On the other hand, BaFeO₃ PC has a predominance of a cubic structure, although with traces of hexagonal and tetragonal secondary phases.
La0.2Ba0.8TiO3 is the only one that exhibit monoclinic structure, and traces of reagent La2O3.

BaFe0.8Ti0.2O3 and BaFe0.6Ti0.4O3 have hexagonal structure, but a new phase of BaO(TiO2) 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.](image)

Table 1 shows the crystallite size, cell parameters, band-gap energies (Eg) and EDS results for the perovskites prepared. BaTiO3 MC and BaTiO3 PC present cubic structure, with a cell parameter of approximately 0.4 nm. For this perovskite, it seems that the preparation method does not have any influence on the unit cell. Regarding BaFeO3 MC and BaFeO3 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.

Perovskites presenting Eg<3 eV are BaFeO3 MC, BaFe0.8Ti0.2O3 MC and BaFe0.6Ti0.4O3 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
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](image-url)

**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]=250 ppm.

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.

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References

[1] Zhu J, Li H, Zhong L et al. Perovskite oxides: Preparation, characterizations, and applications in heterogeneous catalysis. Acs Catalysis. 2014;4(9):2917-2940. https:/ / doi.org/10.1021/cs500606g

[2] Grabowska E. Selected perovskite oxides: Characterization, preparation and photocatalytic properties - A review. Appl. Catal. B-Environ. 2016;186:97-126. https:/ / doi.org/10.1016/j.apcatb.2015.12.035

[3] Rigobello ES, Dantas ADB, Di Bernardo L, Vieira EM. Removal of diclofenac by conventional drinking water treatment processes and granular activated carbon filtration. Chemosphere. 2013;92(2):184-191. https:/ / doi.org/10.1016/j.chemosphere.2013.03.010

[4] Rabiet M, Togola A, Brissaud F, Seidel JL, Budzinski H, Elbaz-Poulichet F. Consequences of treated water recycling as regards pharmaceuticals and drugs in surface and ground waters of a medium-sized Mediterranean catchment. Environmental Science & Technology. 2006;40(17):5282-5288. https:/ / doi.org/10.1021/es060528p

[5] Gusmaroli L, Mendoza E, Petrovic M, Buttiglieri G. How do WWTPs operational parameters affect the removal rates of EU watch list compounds? Science of the Total Environment. 2020;714:136773. https:/ / doi.org/10.1016/j.scitotenv.2020.136773
[6] Pérez-Estrada LA, Malato S, Gernjak W et al. Photo-Fenton degradation of diclofenac: Identification of main intermediates and degradation pathway. Environmental Science & Technology. 2005;39(21):8300-8306. https://doi.org/10.1021/es050794n

[7] Vieno N, Sillanpää M. Fate of diclofenac in municipal wastewater treatment plant--A review. Environment International. 2014;69:28-39. https://doi.org/10.1016/j.envint.2014.03.021

[8] Toufexi E, Dailianis S, Vlastos D, Manariotis ID. Mediated effect of ultrasound treated diclofenac on mussel hemocytes: First evidence for the involvement of respiratory burst enzymes in the induction of DCF-mediated unspecific mode of action. Aquatic Toxicology. 2016;175:144-153. https://doi.org/10.1016/j.aquatox.2016.03.017

[9] Zhao X, Hou Y, Liu H, Qiang Z, Qu J. Electro-oxidation of diclofenac at boron doped diamond: Kinetics and mechanism. Electrochimica Acta. 2009;54(17):4172-4179. https://doi.org/10.1016/j.electacta.2009.02.059

[10] Sadeghi M, Mehdinejad MH, Mengelizadeh N et al. Degradation of diclofenac by heterogeneous electro-Fenton process using magnetic single-walled carbon nanotubes as a catalyst. Journal of Water Process Engineering. 2019;31:100852. https://doi.org/10.1016/j.jwpe.2019.100852

[11] Bae S, Kim D, Lee W. Degradation of diclofenac by pyrite catalyzed Fenton oxidation. Applied Catalysis B: Environmental. 2013;134:93-102. https://doi.org/10.1016/j.apcatb.2012.12.031

[12] Rao Y, Zhang Y, Han F et al. Heterogeneous activation of peroxymonosulfate by LaFeO3 for diclofenac degradation: DFT-assisted mechanistic study and degradation pathways. Chemical Engineering Journal. 2018;352:601-611. https://doi.org/10.1016/j.cej.2018.07.062

[13] Han F, Ye X, Chen Q, Long H, Rao Y. The oxidative degradation of diclofenac using the activation of peroxymonosulfate by BiFeO3 microspheres—Kinetics, role of visible light and decay pathways. Separation and Purification Technology. 2020;232:115967. https://doi.org/10.1016/j.seppur.2019.115967

[14] Shao S, Zhang J, Zhang Z et al. High piezoelectric properties and domain configuration in BaTiO3 ceramics obtained through the solid-state reaction route. Journal of Physics D: Applied Physics. 2008;41(12):125408. https://doi.org/10.1088/0022-3727/41/18/189801

[15] Vinothini V, Singh P, Balasubramanian M. Synthesis of barium titanate nanopowder using polymeric precursor method. Ceramics International. 2006;32(2):99-103. https://doi.org/10.1016/j.ceramint.2004.12.012
[16] Kakihana M, Okubo T, Arima M et al. Polymerized complex synthesis of perovskite lead titanate at reduced temperatures: Possible formation of heterometallic (Pb, Ti)-citric acid complex. Chemistry of Materials. 1997;9(2):451-456. https://doi.org/10.1021/cm9602353

[17] Rodrigues AS, Jorge MEM, Ciríaco L, Pacheco MJ, Lopes A. Perovskites (La,Ba)(Fe,Ti)O3: AO7 photocatalysis under visible light. Reviews on Advanced Materials Science. 2020;59(1):151-159. https://doi.org/10.1515/rams-2020-0012

[18] Silverstein R, Bassler GC, Morrill T. Identificação espectrofotométrica de compostos orgânicos E. LTC. São Paulo: Editora Guanabara Dois; 1994.