

EFEITO DA ADIÇÃO DE PERSULFATO OU H₂O₂ SOBRE A DEGRADAÇÃO DE FENOL POR TiO₂ DOPADO COM Ce

EFFECT OF THE ADDITION OF PERSULFATE OR H₂O₂ ON THE DEGRADATION OF PHENOL BY Ce-DOPED TiO₂

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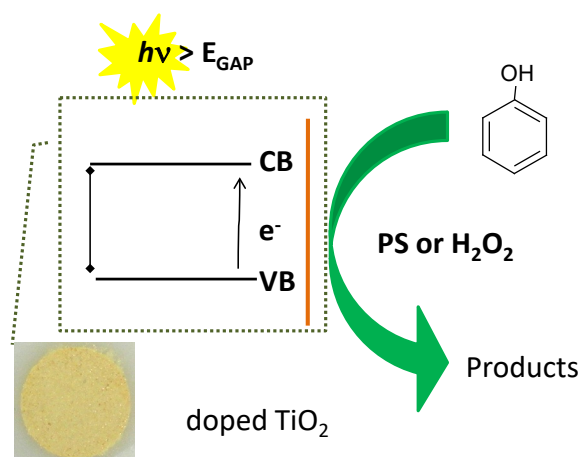
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ABSTRACT

Degradation of phenol was used as a model reaction to investigate the photocatalytic properties of cerium-doped (0.1% atomic nominal) TiO₂ catalyst, in the absence and presence of oxidants: persulphate (PS) or hydrogen peroxide (H₂O₂). Parallel experiments have been performed using either artificial ultraviolet and visible light or sunlight during spring-summer seasons in La Plata city (34.90°S, 57.92°W, 15masl) in a batch reactor.

The best result was found with doped material and 7.0mM of PS: total mineralization (250μM phenol) after 5 hours of solar exposition. Different intermediates were identified for the studied treatments.



INTRODUCTION

Increased water pollution is a major concern worldwide. The application of heterogeneous photocatalytic water purification processes has gained wide attention due to its effectiveness in degrading and mineralizing recalcitrant organic compounds, such as phenolic compounds [1]. By far, titania has played a much larger role in this scenario compared to other semiconductor photocatalysts due to its low cost, effectiveness, inert nature and photostability. However, applying TiO₂ as catalysts for treating polluted water presents a number of technical challenges. Modification of TiO₂ doped with Ce shows a significant potential to overcome the limitations of absorption of visible light and high recombination that pristine TiO₂ particles present [2]. Another strategy has been combined the UV/TiO₂ degradation process with either physical or chemical

operation. In combined with TiO₂, inorganic additive such as H₂O₂ and PS are added to trap electrons and generate more •OH [3].

The objective of this work is the study of the degradation of phenol using Ce-doped TiO₂ catalysts, combined with oxidants (PS and H₂O₂) under artificial light or solar exposure.

METHODOLOGY

Synthesized cerium-doped TiO₂ catalyst (*0.1Ce*) was prepared by sol-gel method as previously described [4].

Oxidation of phenol (50μM) in catalyst suspensions (1gL⁻¹) was carried out in a glass reactor at 25°C, in air and with continuous stirring. The effect of the addition of oxidants (PS and H₂O₂) to the reaction medium was evaluated (1.4mM). A Rayonet photochemical reactor RPR-100 with interchangeable lamps of different wavelengths (350 or 575nm) was used.

The phenol concentration and intermediate products (catechol, hydroquinone and *p*-benzoquinone) were determined using HPLC (HP1050) and the degree of mineralization was evaluated by total organic carbon analysis (Shimadzu TOC5000).

Solar photocatalytic oxidation of phenol (50, 100 and 250μM) was carried out in glass batch reactors with 250mL capacity and cylindrical geometry type (9 cm diameter), in air and with continuous stirring to ensure that the material was in suspension. These experiments were performed in the absence and presence of PS and H₂O₂ using sunlight under outdoor conditions. All experiments were conducted during the spring-summer period in La Plata, Argentina (34.90°S, 57.92°O, 15masl), for 5 hours (10a.m. to 3p.m.). Spectral solar radiation has been measured with a high-resolution Avantes spectrometer (AvaSpec-ULS3648 model) [5]. To calculate the UV solar irradiance, measurements in the range 310-400nm were integrated considering the transmittance (due to the glass cover) as a function of wavelength. Its maximum value (E_{UV}^{max}) at solar noon was reported for each day of measurement.

RESULTS AND DISCUSSION

Based on assays with 350 and 575nm lamps, the experimental conditions for solar experiments were selected. Control experiments were performed to evaluate others factor such as photodecomposition, adsorption and thermal degradation.

Main results for solar exposure experiments are shown in **Table 1**.

Table 1. Percentages of degradation and mineralization of phenol ([phenol]₀ = 250μM) in presence of 1.0Ce, $E_{UV}^{max} = 38.01Wm^{-2}$, without oxidant and with PS and H₂O₂ after 5 hours of reaction.

Treatment	% Degradation ^a	% Mineralization ^b
<i>0.1Ce</i>	75 ± 2*	44 ± 2
3.5mM PS + <i>0.1Ce</i>	83 ± 2	62 ± 2
7.0 mM PS + <i>0.1Ce</i>	100 ± 2	99 ± 2
3.5mM H ₂ O ₂ + <i>0.1Ce</i>	71 ± 2	67 ± 2
7.0mM H ₂ O ₂ + <i>0.1Ce</i>	82 ± 2	78 ± 2

^a Percentages calculated from values phenol concentrations determined by HPLC.

^b Percentages calculated from the measured values of total organic carbon (TOC).

*Experiment performed with $E_{UV}^{max} = 49.07Wm^{-2}$ and normalized.



For both oxidants, the best results were obtained for the degradation as well as the mineralization of phenol using 7.0mM of oxidant. The PS was more effective than H₂O₂ in the two conditions. For systems with H₂O₂ and for the system with 7.0mM of PS, the degraded phenol is completely mineralized at the end of treatments.

As the experiments performed using artificial light, the solar experiments with 0.1Ce and 0.1Ce /H₂O₂ showed the formation of hydroquinone, catechol and *p*-benzoquinone as reaction intermediates. However, with PS it was also observed other peaks with longer retention time, possibly due to the formation of dimers (biphenyls or phenylphenol), indicating differences in reaction mechanisms.

CONCLUSIONS

The use of the catalyst doped with Ce (0.1 % atomic nominal) is suitable for the degradation of phenol in aqueous phase, with sunlight (October to February, Southern Hemisphere). Adding oxidizing (PS and H₂O₂) increase process efficiency, achieving both degradation and mineralization of the contaminant. The best result was obtained working with 7.0mM of PS: total mineralization of 250μM phenol in 5 hours of exposure to the sun.

The identification of by-products in the treatments indicates differences in reaction mechanisms, whose analysis is in development.

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REFERENCES

- [1] BAHNEMANN, D. Photocatalytic water treatment: solar energy applications. *Solar Energy*, v. 77, n. 5, p. 445–459, 2004.
- [2] SILVA, A. M.T.; SILVA, C. G.; DRAŽIĆ, G.; FARIA, J. L. Ce-doped TiO₂ for photocatalytic degradation of chlorophenol. *Catalysis Today*, v. 144, n 1-2, p. 13–18, 2009.
- [3] GAYA, U.I.; ABDULLAH, A.H. Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, v. 9, p. 1–12, 2008.
- [4] MARTIN, M. V.; VILLABRILLE, P. I.; ROSSO, J. A. The influence of Ce doping of titania on the photodegradation of phenol. *Environmental Science and Pollution Research*, 2015. DOI: 10.1007/s11356-015-4667-4.
- [5] IPIÑA, A.; CASTAÑO, C.; DÁNTOLA, M. L.; THOMAS, A. H. Solar radiation exposure of dihydrobiopterin and biopterin in aqueous solution. *Solar Energy*, v. 109, p. 45-53, 2014.