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DEVELOPMENT OF PHOTOCATALYSTS FOR THE DEGRADATION OF EMERGING CONTAMINANTS IN WATER

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INTRODUCTION

The presence of emergent contaminants (EC), such as pharmaceuticals, in aqueous media is a serious and unresolved concern. Carbamazepine (CBZ) is a highly persistent antiepileptic drug that is resistant to biodegradation. The effect of CBZ on aquatic life has been evaluated as dangerous[1].

The use of ZnO as a photocatalyst has been widely used for the degradation of contaminants in water due to its low toxicity, low relative cost and wide bandgap. However, it presents a rapid recombination of photogenerated electrons and holes, which added to photocorrosion, could decrease its photocatalytic activity[2-4].

Modifying ZnO with metals allows to overcome these limitations, as well as visible light absorption.

OBJECTIVES

- Perform the synthesis and characterization of undoped and Ce-doped ZnO by sol-gel method, at pH 4 and pH 8.
- Evaluate the photocatalytic activity of the as prepared materials for the degradation of phenol (as model of organic pollutant) and carbamazepine using UV and visible irradiation.

MATERIALS AND METHODS

Synthesis

Sol-gel method

Zinc Oxide: ZnO
Zinc oxide doped with 5 at% Ce (pH4): **CeZnOa**
Zinc oxide doped with 5 at% Ce (pH8): **CeZnOb**

Characterization

- RAMAN
- FTIR
- SEM
- HRTEM

Photocatalytic Activity

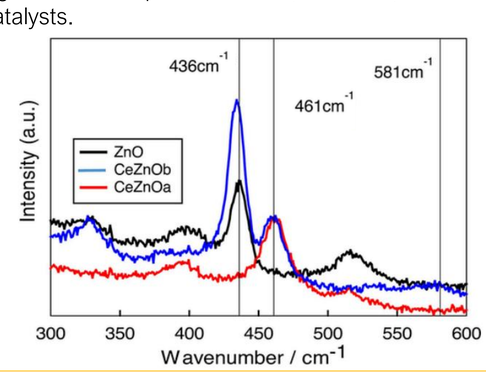
3 h of photolysis - Contaminants evolution by HPLC

- Phenol $1x10^{-4}$ M
- Carbamazepine (CBZ) $6.3x10^{-5}$ M
- Catalyst 1g / L

Photolysis Rayonet Reactor
- 8 UV lamps (365 nm)
- 8 Visible lamps (575 nm)

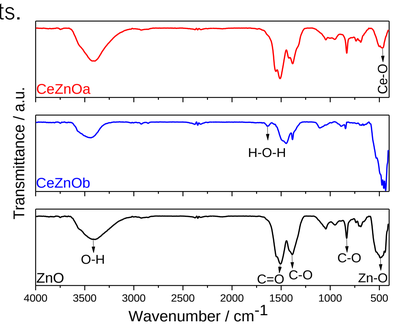
RESULTS AND DISCUSSION

Fig. 1. Raman spectra of ZnO, CeZnOa, and CeZnOb catalysts.



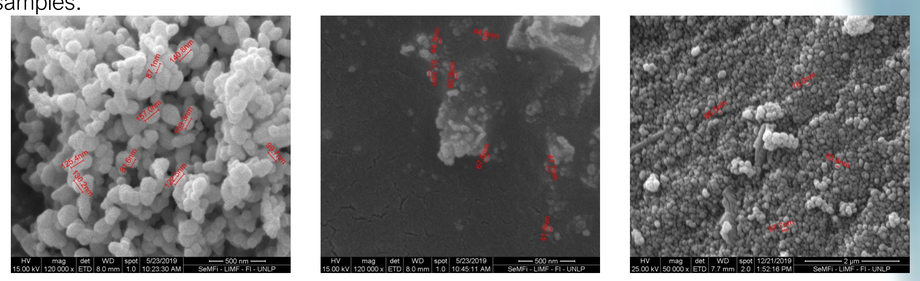
436.3 cm^{-1} wurtzite phase of ZnO
461 cm^{-1} cubic structure of CeO_2 fluorite
581 cm^{-1} defects such as oxygen vacancies and interstitial Zn

Fig. 2. FTIR spectra of ZnO, CeZnOa, and CeZnOb catalysts.



Intense band in the range of 600–400 cm^{-1} : contributions from the stretching modes of Zn–O and Ce–O.

Fig. 3. SEM images of undoped and Ce-doped ZnO samples.

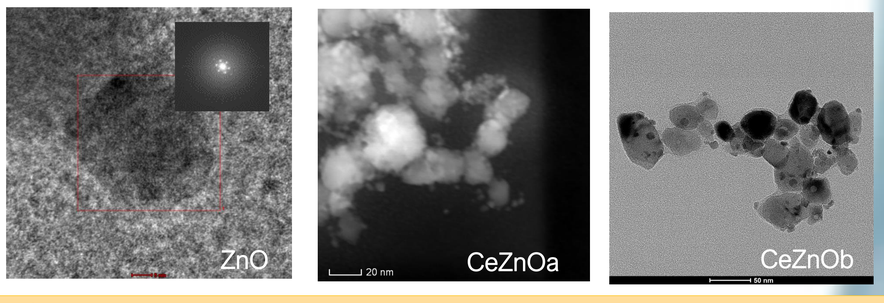


ZnO
Average size 110 + 34 nm

CeZnOa
Average size 87 + 19 nm
By EDS analysis
Ce content: 3.4 at%

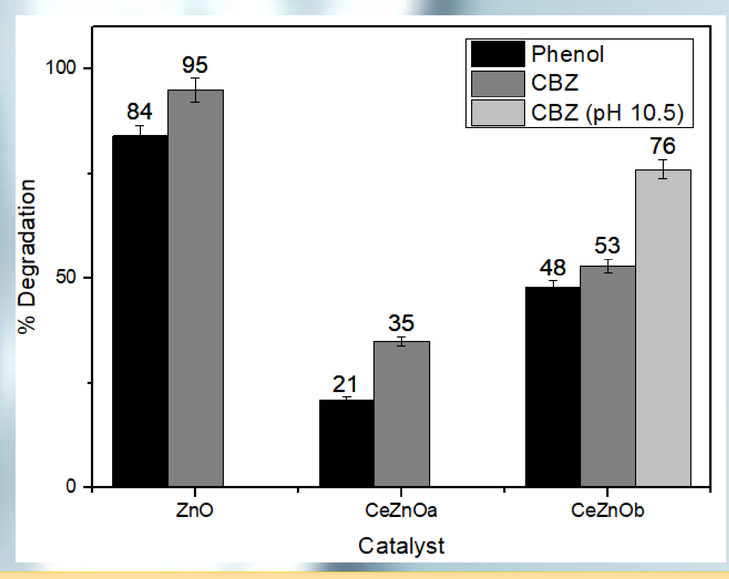
CeZnOb
Average size 51 + 10 nm
By EDS analysis
Ce content: 0.4 at%

Fig. 4. TEM images of undoped and Ce-doped ZnO samples.



ZnO TEM images mainly show polyhedral particles with sizes in the range of 100-50 nm, an essentially crystalline nature is observed.
Ce-doped ZnO: ZnO particles with a diameter of ~ 50 nm and smaller particles of size 5 nm, which are identified as CeO_2, At acid pH some of them forming agglomerates.

Fig. 5. Percentage of phenol and CBZ degradation with the prepared catalysts after 3 h of irradiation with 575 nm lamps



- Phenol was used as a test compound.
- The higher photocatalytic performance of CeZnOb compared to CeZnOa could be explained taking into account the surface to volume ratio, cerium content and crystallinity.
- Control experiments showed neither contaminants adsorption on the solids nor direct photolysis in the absence of catalysts.

Photodissolution (ICP/MS)

Essays	Zn (mg/L) (ε 0,6%)
ZnO (dark)	2.8
ZnO (575nm)	9.2
CeZnOa (575nm)	5.7
CeZnOb (575nm)	8.6
CeZnOb+NaOH (pH 10.5) (575nm)	4.8

CONCLUSIONS

Two Ce-dopped ZnO photocatalysts were prepared at pH 4 and 8 using a simple wet method, with different structural, morphological, and surface properties.
They decrease the photodissolution of zinc in the aqueous media with respect to the undoped catalyst, in the experimental conditions described[5].
The Ce-doped ZnO catalyst synthesized at pH 8 showed a good photocatalytic performance for carbamazepine and phenol degradation (> 45 %) after 3 h of irradiation with visible light.

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