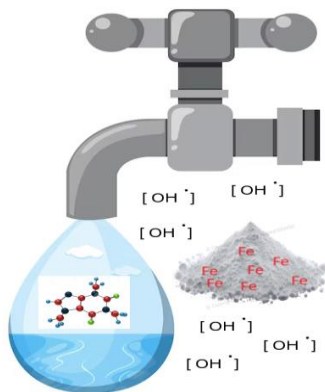


Study of the incorporation of Fe into TiO₂ and ZnO in the photodegradation of caffeine in aqueous solutions.

POSTER

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The aim of this study was to evaluate the performance of iron-doped and undoped ZnO and TiO₂ oxide catalysts in the photocatalytic degradation of caffeine. To this end, 5%Fe/TiO₂ and 5%Fe/ZnO catalysts were synthesised using the excess solvent impregnation method. The prepared catalysts were characterised by N₂ physisorption measurements and scanning electron microscopy with energy dispersive X-rays (SEM/EDS). Of the catalysts investigated in this study, the ones with the greatest potential, with degradations of over 90% for caffeine, were ZnO (cal and ncal) and the 5% Fe/TiO₂ non-calcined catalyst.

Introduction

Contaminants of emerging concern have been frequently detected, even in low concentrations, in water bodies. In this context, caffeine stands out, since 5% of all caffeine consumed is excreted by the body. This organic can be found in foods, medicines and especially drinks, such as coffee [1].

Advanced oxidative processes are a very promising alternative for the application in environmental remediation of these toxic compounds of anthropogenic origin, given that POAs allow the total mineralization of these organics, thus allowing the obtaining of a better quality effluent [2].

Therefore, the objective of this work was to evaluate the potential that pure oxides such as TiO₂ and ZnO have in the photodegradation of caffeine when present in aqueous solutions. Furthermore, the study was also concerned with evaluating the influence of doping these oxides with iron on the photocatalytic activity of these photocatalysts.

Material and Methods

To prepare the metal catalyst supported on TiO₂ or ZnO, 5% iron by mass, the classic impregnation method was used, in which 20 g of TiO₂ (5%Fe/TiO₂) or 20 g of ZnO (5%Fe/ZnO) were transferred to a round-bottomed flask (1000 mL) adjustable to the rotaevaporator system and 3 mL of pure water was added, enough to form a paste. Afterwards, 7.76 g of iron (III) nitrate nonahydrate [Fe(NO₃)₃·9H₂O, previously dissolved in 5 mL of Pure water was mixed, under gentle stirring, with titanium

dioxide or zinc oxide, inside the flask. The flask containing the resulting mixture remained under constant stirring in the rotary evaporator, rotating at 80 rpm, for a period of 14 hours. Afterward, the catalysts were dried, and the calcination process was carried out in a muffle furnace at 400°C for a period of 4 hours, following a heating ramp with a speed of 3°C/minute. All catalysts (calcined and uncalcined) were characterized by N₂ physisorption and SEM/EDS.

For the photocatalytic assays, a batch reactor with a capacity of 1000 mL, equipped with magnetic stirring, was used. The mass of catalyst used in all reactions was 0.05 g, and the volume of effluent to be treated was 6 mL. At predetermined times, aliquots of 3 mL of the effluent were collected, filtered using a stainless steel support and 0.22 µm membranes, and then sent for analysis to monitor the reaction in the UV-VIS spectrophotometer.

Results and Discussion

For the results of N₂ physisorption (Table 1), it is observed that the thermal calcination treatment decreased the specific surface area of TiO₂ and increased the area value for ZnO. The pore volume found for the uncalcined TiO₂ was higher than the value found for uncalcined ZnO. For the catalysts doped with iron, it was possible to observe that the supported catalyst 5%Fe/TiO₂ presented significantly smaller specific surface area and pore volume than those obtained for pure TiO₂. Regarding the average pore diameter, the addition

of iron caused a slight increase in the values found. Hernandez *et al.* (2017) evaluated the effect of metal doping (Cu, Ag, Eu) on the surface areas of TiO₂. The authors observed a decrease in area for all doped samples calcined at 500°C, compared to the pure oxide. This behavior was justified by the agglomeration that occurs in the particles after doping with metals [2].

Regarding iron catalysts based on ZnO, similar specific surface area values to the pure form were observed, regardless of the thermal calcination treatment. Similar results were obtained by Coelho *et al.* (2017) when studying ZnO as a catalyst in mercury reduction [3].

Through SEM/EDS analysis, it was possible to observe that the catalysts have a porous, non-uniform structure, and that calcination does not cause apparent modifications in the morphology of the particles. A similar morphology was found by Ananpattarachai *et al.* (2009) and Al-Johani *et al.* (2015) [4,5]. Additionally, EDS allowed determining the mass composition of the iron dosage for each produced catalyst. Values of 5% and 4.2% were found for the catalysts 5% Fe/TiO₂ ncal and cal, respectively, and 5.10% and 5.70% for the ncal and cal catalysts referring to 5% Fe/ZnO.

Figure 1 presents the results of the photocatalytic study for the pure oxides ncal and cal. According to the obtained results, it is observed that the type of semiconductor oxide and the thermal calcination treatment influenced the amount of degraded

caffeine. The degradation percentage followed the following order: Calcined ZnO (97%) > Uncalcined ZnO (94%) > Calcined TiO₂ (36%) > Uncalcined TiO₂ (27%).

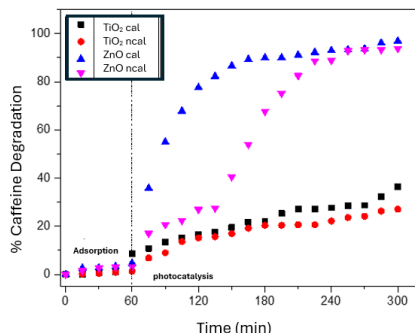


Figure 1. Influence of the oxide on caffeine degradation.

For the catalysts doped with 5% iron, the obtained results were: 94% (5% Fe/TiO₂ ncal), 90% (5% Fe/ZnO cal), 52% (5% Fe/TiO₂ cal), and 47% (5% Fe/ZnO cal). With the results found, except for the ncal ZnO, all maintained or had an increase in their photocatalytic activity with Fe doping. In fact, according to Ellselami *et al.* (2017), the addition of metals to oxides promotes an increase in the separation efficiency, favoring the formation of active species that inhibit the recombination of electron-hole pairs, thus improving the photocatalytic activity [6].

Table 1. N₂ physisorption results

Catalyst	S _o (m ² /g)		V _p (cm ³ /g)		d _p (nm)	
	ncal	cal	ncal	cal	ncal	cal
TiO ₂	26	19	0.05	0.04	7.33	6.77
ZnO	12	25	0.02	0.04	8.52	7.65
5%Fe/TiO ₂	11	28	0.02	0.04	8.43	5.60
5%Fe/ZnO	12	12	0.02	0.04	8.30	5.80

Conclusions

The main results of this study show that doping oxides with iron modifies the photocatalytic potential of oxides in the degradation of caffeine. This result was particularly significant for TiO₂, where the addition of Fe to its composition increased its degradation activity from 27% for TiO₂ ncal to 94% for 5% Fe/TiO₂ ncal, highlighting the importance of adding the metal to this oxide.

Acknowledgments

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