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Solvothermal synthesis and photocatalytic evaluation of TiO_2/ZnO based nanoparticles

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Abstract
Herein the synthesis and evaluation of potential photocatalyst particles having ZnO to TiO_2 ratios of 0.005, 0.01, 0.03, 0.05, 0.10, 0.30, 0.50 and 1, using solvothermal method is described.Titanium butoxide (IV) and zinc acetate were used as sources for Ti and Zn respectively, anhydrous ethanol worked as solvent while nitric and acetic acids catalyzed the particles production. The synthesis was carried out by mixing solutions of chemical precursors, solvent and catalysts in adequate proportions and later transferring them to the autoclave type reactors, where the solutions reactedduring 6h at a temperature of 200ºC, the produced crystals were ground in agate mortars. Characterizationwas performed by FT-IR spectroscopy, X-ray diffraction (DRX), physical gas adsorption (BET) and UV-Vis spectroscopy. The FT-IR spectra showed the presence of TiO_2 and ZnO in all composites, results obtained by DRX showed the formation of the Anatase phase with tetragonal structure of $TiO_2$for the ratios of 0.005-0.50, however, for the 1 to 1 TiO_2/ZnO ratioamorphous particles were obtained. Crystallite sizes vary from 7.4 to 10.6 nm, surface areas from 127-287 m^2/g, energy values of the prohibited bandwidth from 2.98-3.5 eV, increasing as the ZnO content increases. The particles were used in the degradation of methylene blue by ultraviolet light, resultingthat sample with 0.10 ZnO to TiO_2 ratiohad the best performance, degrading 80% of the pollutant in 120 min.

Keywords: *Solvothermal, precursor, blue methylene, photocatalyst.*

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I. Introduction.

With the accelerated growth of the textile industry, the emission of pigments and other pollutants into bodies of water has increased, those pollutants must be eliminated to avoid environmental damage, economic losses, and even social repercussions. Therefore, various physical and chemical methods have been developed, being the photocatalysis one of the most promising for the treatment of industrial effluents.

Photocatalysis is one of the methods known as advanced oxidation processes (AOP´s) and it works though the generation of hydroxyl radicals (OH-) by the interaction of high energy photons and the metal oxide surface, these radicals are highly reactive species with an elevated oxidation potential, capable of reacting with most of the organic compounds non-selectively [1]. Once that photocatalysis has occurred, oxidized pollutants can be transformed to biodegradable compounds through a subsequent biological treatment.

According to many authors [2-5], TiO_2 microparticles are among the most effective photocatalysts for organic oxidation, that is in part due to its electronic properties as well as its chemical stability and high reactivity, in the other hand, ZnO is also a promising photocatalyst, due to its low cost and its chemical properties, therefore mixing both materials should integrate their advantages, at least between some efficiency boundaries. But not only they can be used for water treatment, their uses go farther, including self-cleaning materials, coats for textile materials and even biomedical implants.

In the present study, the effect in the photocatalytic capacity expressed as pollutant removal efficiency is analyzedfor different ZnO/ TiO_2 ratios, being the dependent variable the removal efficiency and the independent one the aforementioned ratio.

Solvothermal synthesis is the process in which chemical precursors are dissolved in the solvent (ethanol for this paper) to be heated using a rigid container such as an autoclave, where evaporation of solvent occurs producing a very high pressure in the system that in conjunction with high temperature and solvent behavior produces the metal oxidesaggregationand itscrystallization.

Although the synthesis method has been extensively studied, little has been reported in the literature about the photocatalytic evaluation of TiO2 composites with ZnO using the solvotermal technique. The objective of this article is to know the effects of the variation of the concentration of ZnO in TiO2 base compounds by means of the solvothermal synthesis technique in the photocatalytic activity of titanium dioxide.

II. METODOLOGY

Materials

The synthesis of microparticles of titanium dioxide is carried out in autoclaves with a capacity of 100ml, this equipmentis made up of an internal Teflon container, an external stainless-steel casing and a screw cap of the same material, figure 1 shows the equipment and configuration of liquid inside the reactor.

Figure 1 Autoclave reactor for solvothermal synthesis

The preparation referred to in the solvothermal technique developed corresponds to a mixture of titanium butoxide$Ti(OCH_2CH_2CH_2CH_3)_4$97% pure, anhydrousethanol CH_3CH_2OH and 65.5% concentrated nitric acid HNO_3in a molar proportion of 2: 30:2, while precursor for ZnO was prepared using ethanol, zinc acetate and acetic acid in proportions 2:25:2.

The reagents were mixed with continuous stirring at 40 °C for 2 hours to achieve homogenization, the appearance of the precursor solution was semi-transparent with an amber color, Figure 2 shows this preparation during the homogenization stage.

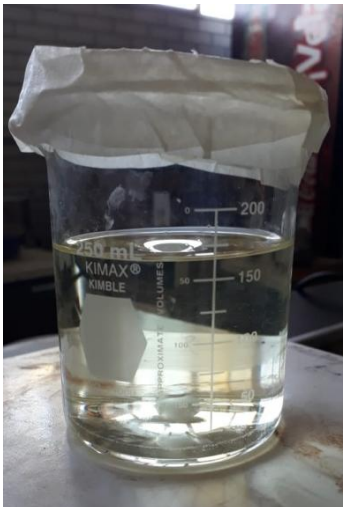

Figure 2 Precursor solution during homogenization stage

Preparation of titanium and zinc oxide precursors was conducted separately and then proportions of both solutions were mixed to achieve the specific proportions of ZnO to TiO_2 of 0.005, 0.01, 0.03, 0.05, 0.10, 0.30, 0.50 and 1.

Specific proportions and characteristics of the reagents are summarized in table 1.

Table 1 Specification and proportion of reagents

Substance	M [g/mol]	Density [kg/l]	Grade	Vol. Fracc. [mL/mL]	Reactive [g/mL]
$TiOBu_4$	340.322	1	97%	0.275	0.26663
EtOH	46.07	0.807	99%	0.671	0.54142
HNO_3	63.01	1.39	65.5%	0.054	0.04937
$ZnC_4\ H_6\ O_4$	183.48	1.74	99.9%	*	*
CH_3COOH	60.05	1.05	99.5%	*	*

* Depending on requirements

After homogenization, solutionswere tempered to ambient conditions and subsequently transferred to the autoclave to be heated at 200° C for 6h, as shown in figure 3.

Figure 3Autoclaves ready for heating stage

After 6 hours of heating the crystals were treated to obtain the reduced size particles, this process was performed using agate mortar as shown in figure 4.

Figure 4 Ground crystals in an agate mortar

IV. RESULTS

BRUKER AXS D8 ADVANCE diffractometer operated at 35 kV and 25 mA, with a speed of 4 ° / minute, was used to measure the X-ray diffraction (DRX) of TiO_2 and determine its crystalline structure.

UV-vis spectrophotometer (liquids) J. Spectra UV-3100 to obtain absorption wavelengths of TiO2 particles and Bruker Alpha FT-IR spectrometer to perform additional characterization.

Figure 5 shows the diffractograms of TiO_2 obtained experimentally and the reference standard PDF 21-1272 of TiO_2 in its crystalline phase of anatase.

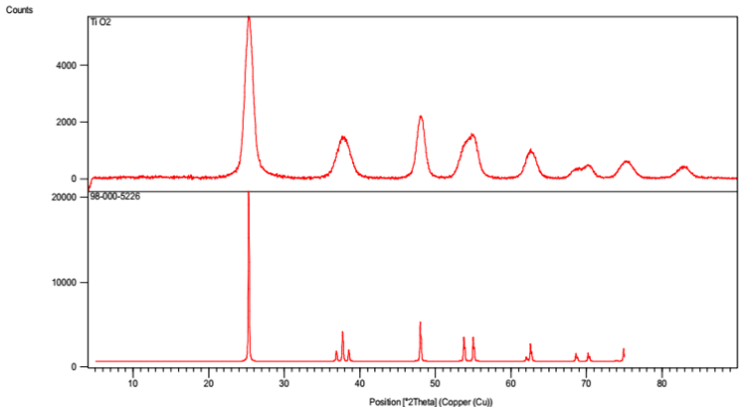

Figure 5Comparison of synthesized TiO_2(upper) diffractograms with respect to the Anatase crystalline phase reference pattern

In the diffractograms of figure6, comparisons between diffraction peaks for TiO_2 compounds with addition of ZnO at different concentrations, with respect to TiO_2 and ZnO are shown,all synthesized in the laboratory.

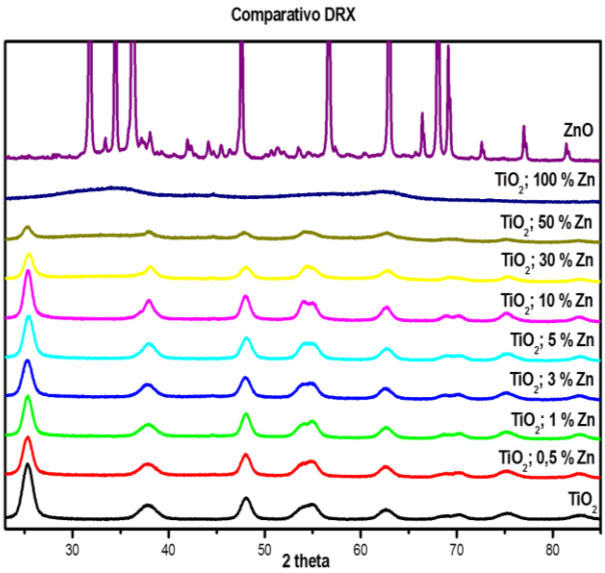

Figure 6 Amorphous behavior of composites with a high percentage of ZnO

It is observed that for the TiO_2 sample, the diffraction peaks correspond to the anatase phase, which has a tetragonal structure. The ZnO sample corresponds to the Zincita phase, with its hexagonal structure. Similarly, it is possible to observe the diffractograms of the TiO2 compounds added with different atomic ratios of ZnO with respect to the TiO_2.

Using the Miller indices obtained from the TiO_2 samples and by applying the Debye-Scherrer method, the crystallite size values are shown without considering the error in the following table.

Table 2Crystallite size

Composite	Crystallite size [nm]
TiO_2	8.8
TiO_2:0.005 ZnO	7.7
TiO_2:0.01 ZnO	9.6
TiO_2:0.03 ZnO	7.4
TiO_2:0.05 ZnO	8.7
TiO_2:0.10 ZnO	10.6
TiO_2:0.30 ZnO	9.2
TiO_2:0.50 ZnO	9.1
TiO_2:1.00 ZnO	Amorphous
ZnO	>100

Figure 7 shows the optical absorption spectra. With the absorbance values of the TiO_2 spectrogram, the calculations of the prohibited bandwidth were performed, yielding a value of 3.47 eV per indirect transition [6].

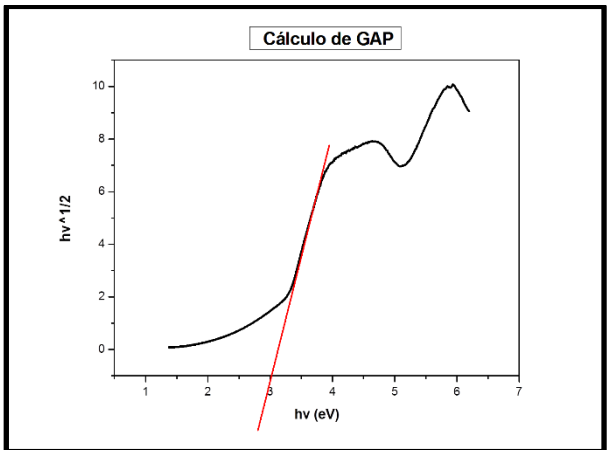

Figure 6Calculation of GAP by indirect transition for TiO_2

Using UV-vis spectroscopy, the results of the photocatalytic evaluation were measured by determining the concentration of the contaminant as an effect of its degradation by being exposed to UV irradiation in contact with the samples as the pressure varied. The results of this characterization in the photocatalytic degradation tests for the different concentrations are shown in Table 3.

Table 3 shows the results of the evaluation of photocatalytic degradation for the different TiO2 / ZnO combinations by UV-Vis spectroscopy, determining the concentration of the contaminant as an effect of its degradation when exposed to UV irradiation in contact with the composites.

Table 3Photocatalytic degradation results

Time	**Concentration % at specified ZnO/TiO2 ratio**							
[min]	**0.005**	**0.01**	**0.03**	**0.05**	**0.1**	**0.3**	**0.5**	**1**
-30	100	100	100	100	100	100	100	100
0	100	96	97	98	99	99	96	98
5	96	90	96	96	98	96	96	97
10	88	87	93	91	98	95	95	91
15	80	78	93	89	93	94	95	90
20	78	78	90	85	84	86	86	86
30	74	73	79	79	72	84	79	83
60	63	57	76	61	54	74	73	65
90	51	43	65	48	37	63	62	37
120	32	33	61	35	22	45	52	24

The behavior of the degradation tests in the previous table is shown in Figure 7, showing the best performance for the 0.1 and 1 zinc to titanium ratio, as well as a pseudo-first order kinetics.

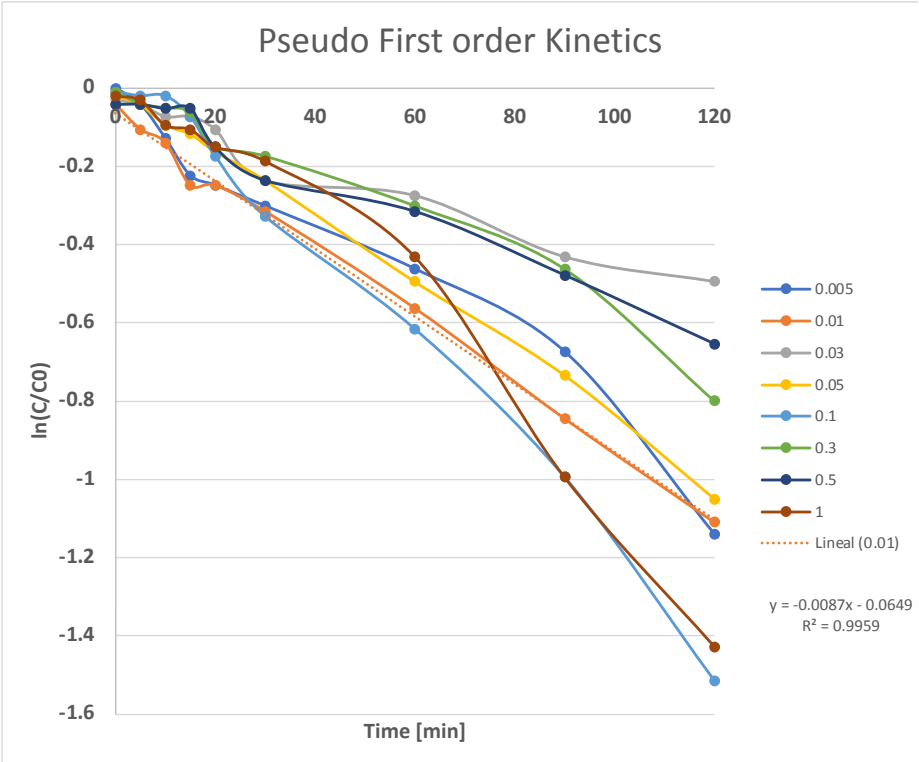

Figure 7Pseudo-first order kinetics

Methylene blue degradation results can be seen even by visual inspection in figure 8.

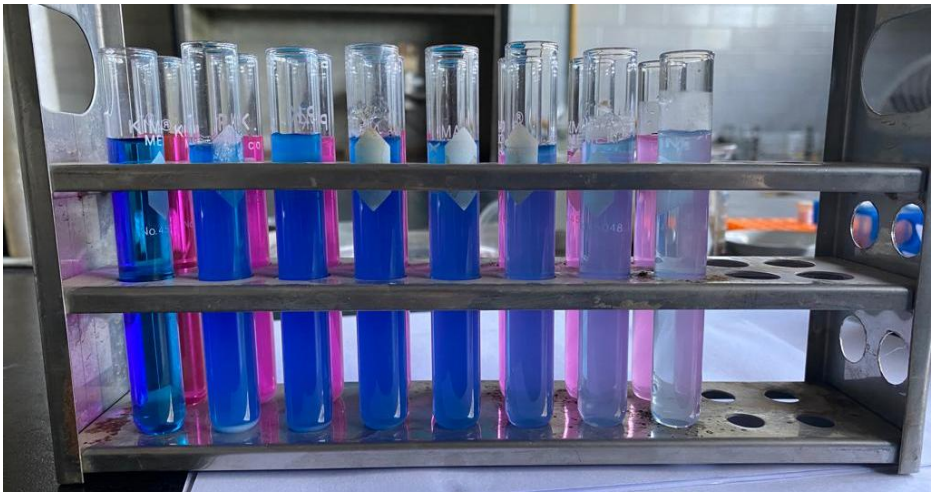

Figure 8Methylene blue degradation

DISCUSION

When comparing the diffraction patterns of Figure 5 it is possible to observe that the peaks of the TiO_2 diffractogram coincide with the reference pattern; indicating that the samples obtained in the laboratory have an anatase phase tetragonal structure. In the diffractograms of Figure 6 with atomic ratios from 0.005 to 0.30 ZnO, it can be seen how the crystallinity remains unchanged in the anatase phase and it is also observed that there are no peaks corresponding to ZnO indicating that it is in an amorphous state [7].

Likewise, it is clearly perceived how the intensity in the diffraction peaks goes down as the ZnO increases. An indication that composites tend to the amorphous phase [8]. It is possible to observe in Figure 7 that the material with the percentage of 10% ZnO degrades more contaminant than any other of the materials used in the study.

VI. CONCLUSION

This paper demonstrates the presence of the proposed materials in the synthesized composites for the entire range of ZnO variations. In composites with variations from 0.005 to 0.30 of ZnO, their surface area increases with the increase of ZnO in TiO_2 composites. TiO_2 has anatase structure and amorphous ZnO.

Absorption bands are observed in wavelengths from 280 nm to 358 nm with a band gap of 3.7 eV and that increases as the ZnO content increases in the ZnO/TiO_2 compounds.

The degradation constant (k) was higher for the compound with the ratio of 0.10 of ZnO; with a value of k = 0.542 although the sample with the 1 to 1 ratio of TiO2 / ZnO had a degradation constant (k) like that of 0.10 even though the materials are amorphous. Indicating that the materials have a short-range crystallographic arrangement.

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