

**IBUPROFEN DEGRADATION UNDER LED VISIBLE LIGHT, USING SELF DOPED
CARBON MESOPOROUS TiO₂.**

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Resumen

Nanopartículas de TiO₂ se obtuvieron de un método simple de síntesis sol-gel. Los sólidos sintetizados se caracterizaron por XRD, espectroscopía UV-Vis DR, adsorción-desorción con N₂ y TEM. Los estudios permitieron confirmar la naturaleza mesoporosa de todas las muestras y la existencia de una fase cristalina que consiste en anatasa pura. Como no se usó un agente molde durante la síntesis, no fue necesario someter los catalizadores a tratamientos finales con altas temperaturas. Sin embargo, se estudió el efecto de la temperatura de calcinación sobre el rendimiento fotocatalítico de los materiales, en términos de la degradación del ibuprofeno (IBF) en solución acuosa bajo luz LED visible. Se confirmó que la ausencia de calcinación permite que el sólido permanezca auto-dopado con especies de carbono, que provienen de la misma fuente utilizada para el titanio, y sería responsable de la absorción hacia las longitudes de onda correspondientes al rango visible del espectro. Además, podría determinarse que a 200 ° C mejora la actividad fotocatalítica, ya que la recombinación positiva electrón / agujero se retrasa y entra más carbono en la matriz. De esta manera, se especificaron las condiciones óptimas para obtener un material mesoporoso capaz de ser activado bajo luz visible.

Abstract

TiO₂ nanoparticles were obtained from a simple sol-gel synthesis method. The synthesized solids were characterized by XRD, UV-Vis DR spectroscopy, N₂ adsorption-desorption, and TEM. The studies allowed confirming the mesoporous nature of all samples and the existence of a crystalline phase consisting of pure anatase. Since a template agent was not used during the synthesis, it was not necessary to subject the catalysts to final treatments with high temperatures. However, the effect of calcination temperature on the photocatalytic performance of the materials was studied, in terms of the degradation of Ibuprofen (IBF) in aqueous solution under visible LED light. It was confirmed that the absence of calcination allows the solid to remain self-doped with carbon species, which come from the same source used for titanium, and would be responsible for absorption towards wavelengths corresponding to the visible range of the spectrum. In addition, it could be determined that at 200 ° C the photocatalytic activity improves, since the positive electron / hole recombination is delayed and more carbon enters the matrix. In this way, the optimal conditions for obtaining a mesoporous material capable of being activated under visible light were specified.

Keywords: self-doped, titania, non-metal, organic pollutants, visible light.

We would be willing to submit our work to an evaluation process for publication in an international journal.

1. Introduction

There are numerous for superficial and underground water contaminated with organic substances of refractory nature and persistent nature, which cannot be eliminated from the environment through conventional treatment methods [1].

In this sense, the study of new technologies that respond to Advanced Oxidation Processes (PAOs) is in development. Within the variety of methods, photocatalysis is one of the alternatives that only involves the presence of a solid semiconductor that, when activated with radiation of a certain wavelength, is capable of inducing the formation of radical species. These will be, due to their high oxidizing power, which will attack the organic substrates, leading to their degradation and consequent mineralization [2].

Given its low toxicity and cost, high chemical and mechanical stability, titanium dioxide (TiO_2) is one of the most used photocatalyst. However, its use under visible radiation is limited because the high band gap (3.2 eV) that only makes possible the activation with UV radiation, which represents 5% of the solar radiation [3]. Therefore, recent research has been pointed on shifting the absorption range towards longer wavelengths. These reports confirm that doping the material with nonmetals and metals, the semiconductor absorption capacity is improved. The presence of carbonaceous species generates a photo sensitizing effect on the solid, which improves the absorption capacity to wavelengths greater than 400 nm [4]. Moreover, given the recent concern regarding energy use, there is a tendency to replace conventional lamps with LED lamps as radiation sources [5]. This implies the development of compact, low-cost, and environmentally friendly systems. Avoiding the use of mercury lamps (high toxicity) solves the problem of final disposal. In turn, it is known that photocatalytic systems are more efficient when the used solids offer a high specific area and have a mesoporous nature [6]. In this sense, the present work proposes the synthesis of a mesoporous TiO_2 material and the study of the synthesis conditions (such as calcination temperature) that allows the self-doped titania with carbon. The materials were tested in photocatalytic degradation tests of Ibuprofen (IBF) under visible radiation, coming from high-power LED modules, white light emitters in the 400-700 nm range.

2. Experimental

The material was synthesized by dissolving 6 mL of titanium n-butoxide ($\text{Ti}(\text{OBU})_4$) in ethanol. Hydrothermal treatment involves subjecting the system under self-generated pressure at 180 °C. The formed solid is recovered by filtration, and dried at 60 °C. In order to study the influence of calcination, the material is subjected to 200 °C and 400 °C. The photocatalysts were called MT-x, where "x" indicates the temperature of the final treatment. The absence of "x" indicates absence of calcination.

The absorption range of solids was analyzed by UV-Vis spectrometry, using a Jasco V-650 device with integrating sphere. X-ray diffraction studies were carried out on a PANalytical X'Pert Pro diffractometer in the range of $2\theta = 20-80^\circ$. The specific area (BET) and pore diameter (BJH) were determined from the N_2 adsorption-desorption study with nitrogen in a Micromeritics ASAP 2020 equipment. Transmission electron microscopy (TEM) images were obtained from a JEOL Model equipment 21 JEM-1200 EXII (120 kV).

The catalysts were tested in photocatalytic reactions of degradation of IBF in aqueous solution. All tests were performed under visible radiation, coming from LED modules located towards the sides of the reactor. It consists of a stirred and aired glass container.

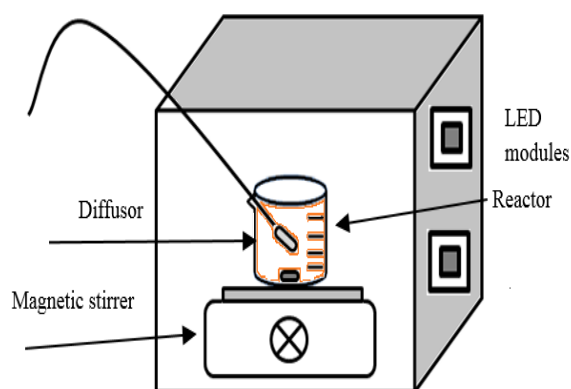


Figure 1. Photocatalytic reactor

The pollutant concentration ([IBF]) was measured through high performance liquid chromatography (HPLC). The mobile phase was composed of 40% acidified water (3% V/V with acetic acid) and 60% acetonitrile. IBF has a retention time of approximately 3 min.

Results and discussion

The XRD study (Fig. 2) confirms the existence of 100% anatase as crystalline phase. It is important to notice that this phase presents better photocatalytic activity than brookite and rutile [7]. At the same time, the MT catalyst exhibits good crystallinity despite not having been subjected to a final treatment at high temperature. Fig. 4 shows the N₂ adsorption-desorption isotherms with nitrogen of the samples. They correspond to isotherms of type IV, characteristics of mesoporous materials [8]. Mesoporosity arises because of the particles agglomeration process during hydrothermal treatment at 180 °C [9]. The space that results from these confinements are the mesopores. It can be observed in TEM image (Fig. 3) for the MT-200 solid that monodispersed nanoparticles lead to a mesoporous structure.

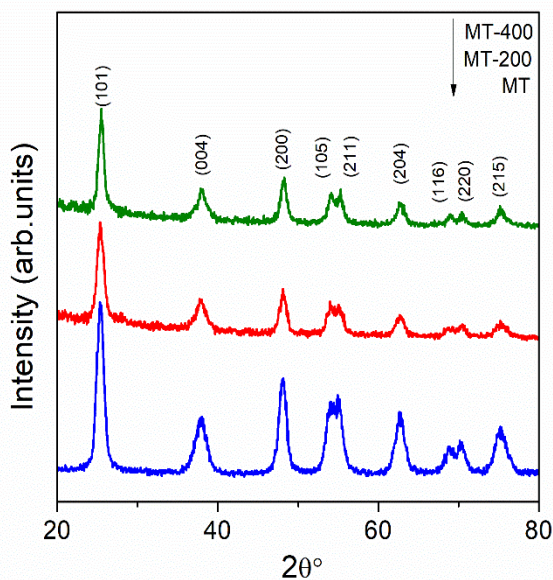


Figure 2. XRD analysis for the solids.

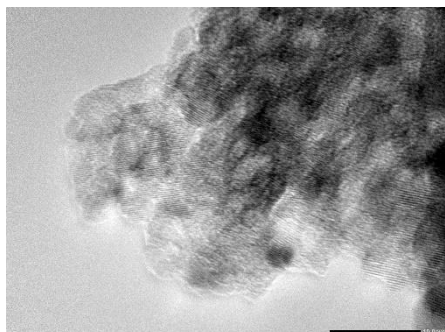


Figure 3. TEM image for MT-200 solid.

The UV-Vis DR spectra of the synthesized solids (Fig. 5) shows the null absorption capacity of the

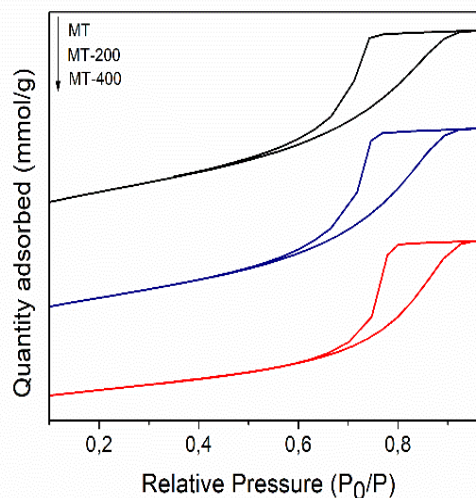


Figure 4. N₂ adsorption-desorption analysis

calcined material at 400 °C. The MT and MT-200 solids have a shift towards greater wavelengths. This can be attributed to the presence of carbon species, as a result of the material not having been subjected to high temperatures as final treatment. The carbon in the material acts as a photosensitizer [8]. Temperatures above 200 °C contribute to the expulsion of this nonmetal, and for that MT-400 sample does not absorb radiation beyond 400 nm.

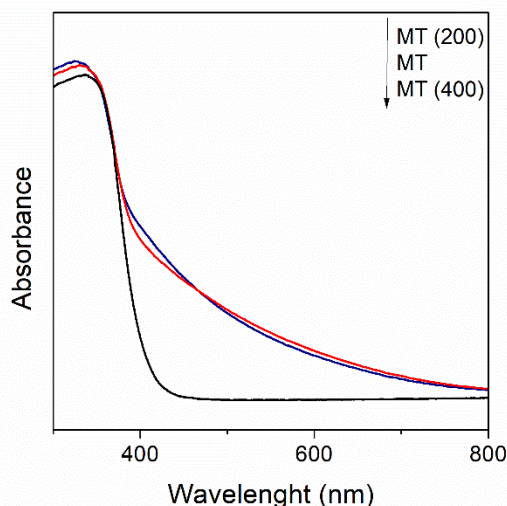


Figure 5. UV-Vis DR spectra of the samples

Table 1 shows the value of the specific areas (S_{BET}), pore diameter (P_D) and band gap of the obtained solids. MT has an area visibly greater than MT-400. In photocatalysis, high area values contribute to better activity, since the reactions take place on the surface. In addition, the larger the area,

greater the amount of available active sites to interact with the substrates molecules. It can also be observed that the band gap is smaller in the solid without calcining and in the calcined at 200 °C, due precisely to the photosensitizing carbonaceous species presence. Then, high temperatures (> 400 °C) promote the carbon loss in titania, and contribute to the collapse of some mesopores [10]. Therefore the specific area decreases in MT-400.

Table 1: Texturales properties and band gap

Photocatalyst	S_{BET} ($m^2 g^{-1}$)	P_D (nm)	Band gap (eV)
MT	150	6.2	3.1
MT-200	139	6.6	3.1
MT-400	93	7.9	3.3

Fig. 6 shows the photocatalytic activity of the obtained materials, under visible light LED radiation, and after five hours of reaction.

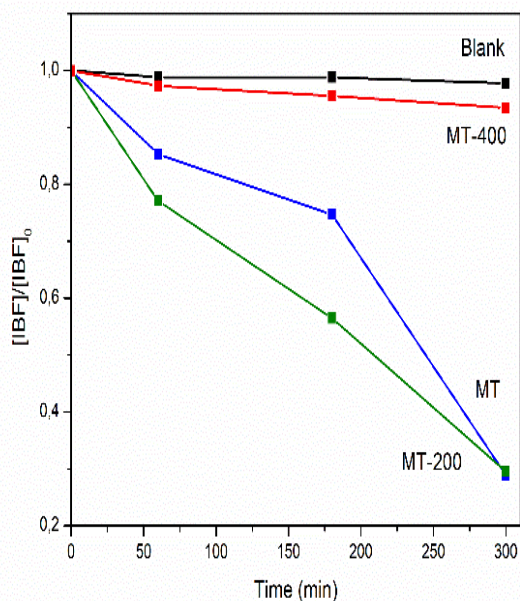


Figure 6. Photocatalytic activity of the solids, under visible light LED irradiation.

With MT and MT-200 catalysts, it was reached a degradation of 77%. This represents an improvement in relation to the percentage observed without catalyst (blank), where the concentration of the IBF remained the same. The improvement in photocatalytic activity is attributed, precisely, to the presence of carbon traces, whose

photosensitizing effect allows the solid to be activated with less energy (longer wavelengths - visible range). In turn, it can be noted that with MT-400 solid, the activity was null as in the Blank reaction. The poor performance of this solid is related to the null absorption capacity in the visible range, as a consequence of the removal of carbon at 400 °C.

Moreover, although with both MT and MT-200 solids, the degradation percentage was the same, the reaction rate was higher with the second one. At 200 °C, a greater diffusional effect of carbon through the matrix is promoted. This can be attributed to the intermediate treatment temperature, at which the surface defects are corrected [10, 11].

3. Conclusions

Through a simple method, titanium dioxide mesoporous nanoparticles self-doped with carbon could be obtained without using a template agent or an external (additional) source of the nonmetal. By manipulating the synthesis conditions such as the final calcination temperature, the presence of carbon in the titania structure of the titania is possible.

Given that it was not used a molding agent or structure director, it was not necessary to subject the solids to final treatments at high temperatures in order to remove organic impurities. This allows the catalyst to contain carbon traces, coming from the same titanium source. The presence of these species generates a photosensitizing effect on the semiconductor solid, improving its absorption capacity in the visible range of the electromagnetic spectrum. The carbon expulsion could be verified by subjecting the solid to a 400 °C. At intermediate treatment temperatures, 200 °C, a greater diffusion of carbon is induced to the TiO₂ network. In turn, efficient separation of the positive electron/hole pair is guaranteed. These factors, in synergy with the high value of the specific area and the radiation absorption capacity at greater wavelengths, imply that the solid treated at 200 °C has presented the highest level of degradation of IBF, 77%. As expected, the lowest photocatalytic activity was achieved with the solid treated at 400 °C. In this way, a reaction system that uses visible radiation from LED modules (replacing the use of conventional lamps) was developed.

4. Acknowledgement

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5. References

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