

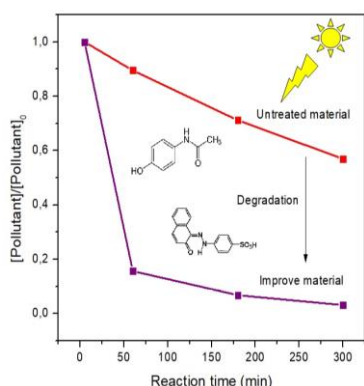
**Active TiO₂ under visible light, as a key material for photoremediation.**

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TiO₂ nanoparticles were obtained from a simple sol-gel method, which not involve the use of structure directing agents neither a high final calcination temperature. The solids were characterized by XRD, UV-Vis, N₂ adsorption-desorption, and TEM. These materials were tested in photocatalytic degradation of two organic substrates: acid orange acid 7 (AO7) and paracetamol (PCT). LED lamps were used as sources of visible radiation. The parameters evaluated were the final calcination temperature as a post-synthesis treatment, and the presence of iron along carbon. A complete degradation of the two tested pollutants was achieved, using the catalysts modified with iron, carbon, and calcined only at 200 °C. In this way, it was possible to activate the synthesized mesoporous material with visible light, to be applied in an advanced oxidation process, as is heterogeneous photocatalysis.

Introduction

Recently, it is important the study of new technologies in order to solve the problem of water contamination with organic substances of a refractory and persistent nature. These species can not be eliminated from an aqueous medium through conventional methods of treatment [1]. One of the promising alternative methods includes the Advanced Oxidation Processes (AOPs). Within the wide variety of methods, photocatalysis is the one that only involves the presence of a semiconductor solid, such as titanium dioxide (TiO₂). This material, when it is activated with radiation of a certain wavelength, is capable to induce the formation of radical species. These will be the ones that would attack organic substrates, leading to their degradation and subsequent mineralization [2]. For TiO₂ to be photoactive under visible light, it is necessary to dope it with other elements, whose presence allows to reduce the band gap, delay the recombination process of the positive electron/hole pair, and displace the absorption of the solid towards longer wavelengths [3].

Already reports indicate that this is achieved by doping the material with metals and non-metals, such as iron and carbon [4]. At the same time, with the purpose of designing compact, energy-sustainable photocatalytic systems, there is a tendency to replace conventional lamps (such as mercury lamps) with LED lamps as sources of radiation. This would allow to start up processes and systems more friendly with the environment [5]. In addition, the photocatalytic efficiency is greater when the used catalysts offer a high specific area and have a mesoporous nature [6].

Given the above considerations, in this work we propose the synthesis of a mesoporous TiO₂ material and the study of the synthesis and doping conditions. That is, the calcination temperature, which enables or not the self-doping of the solid with carbon (non-metal) species; and the presence of iron which is incorporated in the synthesis gel. The materials were tested in photocatalytic degradation assays of Acid Orange 7 (AO7) and Paracetamol (PCT), pollutants present in effluents that come from the textile and pharmaceutical industry respectively. Visible radiation was used, coming from high power LED modules, white light emitters in the range of 400-700 nm.

Material and Methods

The material was synthesized by dissolving 6 mL of titanium n-butoxide (Ti(OBu)₄) in ethanol. The hydrothermal treatment is 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 final calcination temperature, the material is subjected to 200 °C or 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 materials modified with iron were obtained from the incorporation in the synthesis gel of a sufficient amount of iron (III) acetylacetonate, in order to obtain a material doped at 0.1% wt. These materials were denominated Fe-MT (x).

Results and Discussion

The study by X-ray diffraction allowed to affirm that all the catalysts presented a crystalline phase constituted only by anatase. It is important to note



the convenience of the presence of this phase in all materials, given its better photocatalytic activity compared to that presented by other phases such as rutile [7]. On the other hand, isotherms of N₂ adsorption-desorption correspond to type IV which are characteristics of mesoporous materials [8]. Here it is important to consider that to-obtain these nanoparticles, it was not used a template agent. Then, mesoporosity was formed as a consequence of the agglomeration process suffered by the particles during the applied hydrothermal treatment at 180 °C. Therefore, the space that results from these confinements gives rise to the existence of mesopores [9].

The UV-Vis diffuse reflectance spectra (Fig. 1) give account for Fe doped samples showed the highest capacity absorption shifted towards longer wavelengths. The presence of iron contributes to the formation of new electronic states intra band gap [10]. Whereas it can be seen that MT (400) did not show any absorption beyond 400 nm.

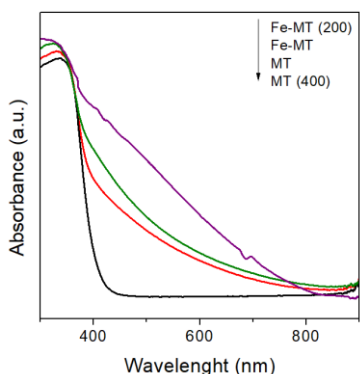


Figure 1. UV-Vis DR spectra of the solids

The catalysts were tested in photocatalytic degradation reactions of AO7 and PCT in aqueous solution. All the tests were carried out under visible

radiation, coming from LED modules, located towards the sides of the reactor which consists of a stirred glass container, with an air diffuser. The temperature was kept constant and equal to 35 °C.

The initial concentration of pollutant and catalyst was 20 ppm and 1 g/L, respectively.

The concentration value of [AO7] was measured following the absorbance at 485 nm using a Jasco V650 equipment. As for paracetamol, the reaction samples were first filtered through a NY filter of 0.45 µm, and then analyzed by high-performance liquid chromatography in order to determine the PCT concentration. It was used a C-18-5 column, with a flow rate of 1 mL/min. The mobile phase was 25% methanol and 75% miniQ water.

For both substrates the reached degradation level is calculated as $X = (C_0 - C) \times 100 / C_0$.

Table 1 shows the results of the photocatalytic activity of the materials obtained, after five hours of reaction. Degradation of around 36% can be obtained with MT catalyst for both pollutants. The highest degradation, 100%, was obtained using the solid Fe-MT (200). The low activity of MT (400), in relation to the others samples, can be related with its null absorption capacity already observed in the analysis by UV-Vis DR, and also with the lower value of its specific area. Otherwise, at 200 °C, more carbon is able to enter the titania network, as its diffusion process is facilitated. In addition, a treatment at this intermediate calcination temperature conduces to inhibit or delay the recombination process of the generated electron/hole positive pair [11]. Finally, this fact added to the presence of carbon and iron photosensitizing species [12] (which increase the capacity of absorption of visible radiation by decreasing the band gap) and the high value of specific area (which allows a greater contact with substrates by making more available the active sites), are the main factors to which the high photocatalytic activity achieved with the Fe-MT solid (200) is attributed.

Table 1. Degradation percentage under visible LED irradiation.^a

Photocatalyst	AO7	PCT
MT	36%	37%
MT (400)	5%	2%
Fe-MT	76%	60%
Fe-MT (200)	99%	100%

^a[pollutant]=20 ppm; [catalyst]=1 g/L.

Conclusions

Through a simple and cheap method, mesoporous titanium dioxide nanoparticles could be obtained. Given the fact that a template agent was not used, it is not necessary to submit the solid to high calcination temperatures. This allowed the solid to remain self-doped with carbon species, coming from the same source of titania. It could be verified that at 400 °C, the carbon is expelled from the material, so there is no absorption in the visible range, and the catalytic activity is null.



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Intermediate treatment temperatures, 200 °C, favor the diffusion of carbon into the titania matrix, while certain surface defects were corrected. This implies an improvement for photocatalytic activity. In order to study the synergy effect of co-doped solids, it was incorporated iron in some samples. The presence of the metal improves the visible light absorption, and decrease the band gap given new electronic states along the forbidden band. These factors, and with the high specific area of the material, convert the Fe-MT (200) into the most photoactive, reaching complete degradation for AO7 and PCT under visible light. In this sense, this catalyst is a good option for advanced oxidation process systems with LED irradiation.

Acknowledgments

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