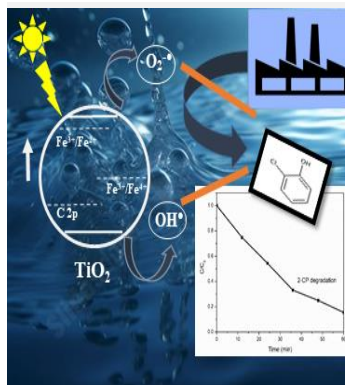


Determination of the quantum efficiency in 2-chlorophenol degradation processes under LED visible light, using doped TiO₂.

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In the present work, the photocatalytic activity of mesoporous TiO₂ doped with iron and self-doped with carbon, obtained from a more environmentally friendly synthesis route, is reported. The tests were performed on 2-chlorophenol degradation processes, under LED visible light (40 W total power). The beneficial effect of calcining the solids at 150 °C was confirmed, since it improves their optical properties, favors the location of the dopants in the titania matrix, and new electronic states are generated. Thus, with these catalysts, it was possible to degrade the contaminant by 80% at 60 min of reaction. Likewise, after 180 min the mineralization was around 50%. Due to these results, the calculated quantum efficiency was the highest for the Fe-MT-150 material.

Introduction

In recent decades, the environmental crisis has focused the point on the develop of innovative and sustainable technologies to resolve the problem associated with the contamination of water resources with refractory organic substances, called emerging contaminants [1]. Unfortunately, conventional water treatment methods often fail to effectively remove these non-biodegradable contaminants. For this reason, new technologies such as Advanced Oxidation Processes (AOPs) have emerged. Particularly, titanium dioxide (TiO₂) photocatalysis represents a promising and environmentally friendly alternative. The photocatalytic process involves the generation of photogenerated species that participate in redox reactions with water, oxygen and contaminants adsorbed on the surface, generating the reactive radicals than can degrade and mineralize pollutants. However, some applications are still limited due to the low absorption that TiO₂ presents in the visible range. In this sense, numerous attempts have been made to expand this capacity [2]. The high rate of degradation and mineralization of Acid Orange 7 (AO7), Paracetamol (PCT) and Ibuprofen (IBU) has previously reported, using calcined and not-calcined doped iron and autodoped carbon mesoporous titania as photocatalysts [3]. On the other hand, it is important to calculate the quantum efficiency, since it considers other factors such as the radiation flux and the geometry of the reactor. [4]. Thus, in this work the degradation of 2-chlorophenol (2-CP), under LED visible radiation is

proposed, using mesoporous titania doped with iron and carbon. The impact of the calcination temperature on the photocatalytic activity was verified, correlating it with the quantum efficiency corresponding to each test.

Material and Methods

The titanium oxide photocatalysts were synthesized using an eco-compatible sol-gel method previously reported [3]. The catalysts were called Fe-MT-x, where "x" indicates the calcination temperature, and its absence, that the material was not calcined. The tests were carried out in a 100 mL borosilicate photoreactor, irradiated from its sides by high-power LED visible modules (40 W). The determination of the concentration (C_t) of 2-CP in the reaction samples was by HPLC. The starting point was C₀ = 20 ppm 2-CP.

Results and Discussion

Regarding the characterization of the synthesized solids [5], X-ray diffraction (XRD), N₂ adsorption-desorption studies, UV-Vis Diffuse Reflectance spectrophotometry (UV-Vis DR), and X-ray photoelectron spectroscopy were carried out. (XPS). Through the first technique, the presence of anatase phase in all catalysts was verified, while through the second one, the existence of mesoporosity could be determined, due to the type of isotherms (type IV) resulting. The UV-Vis DR spectra obtained show the greater absorption in the visible range by the Fe-MT-150 catalyst compared to the other solids capacity. The presence of carbon

and iron in the interstitial and substitutional sites of the TiO₂ matrix photo-sensitize the material through the generation of new electronic levels, which reduce the band gap. Although the same active species are found in the Fe-MT solid, as it is not calcined at 150 °C, they do not completely diffuse towards the previously mentioned sites of the structure (XPS analysis), and could remain on the surface. Finally, the Fe-MT-400 material has the lowest absorption in the same wavelength range, due to carbon loss as a consequence of the high calcination temperature. In accordance to this, with the Fe-MT-150 material, the highest level of degradation of 2-CP (80%) was reached after 60 min (t_i) under LED visible light. Meanwhile, the activity was lower for Fe-MT and Fe-MT-400, 60 and 16% respectively at the same reaction time (Fig. 1). This catalytic behavior can be directly correlated with the properties demonstrated by the solids when characterizing them. The Fe-MT-150 catalyst, due to the synergistic presence and diffusional effect of both carbon and iron, presents the greatest capacity to absorb visible radiation. For this same reason, the higher levels of degradation of 2-CP were achieved with it. Furthermore, as expected, the lowest activity levels were for Fe-MT-400 material. It is possible to calculate the quantum efficiency (ε), considering reaction volume (V_R), and incident radiation flux (q) at the reactor window averaged over the window area (A_w) (Table 1). This efficiency is defined as the relationship between the number of molecules of 2-CP degraded at t_i and the number of photons that actually reaches the reactor (Eqs. 1 and 2) [4]. The q value was measured using a miniature spectrophotometer with an optical fiber, 4.69 x 10⁻⁹ Einstein cm⁻² s⁻¹.

Conclusions

Iron-doped and carbon self-doped TiO₂ mesoporous materials were synthesized. Dopants photosensitize titania, since they generate new electronic states along its band gap. It could be corroborated that this effect is more pronounced when these species can diffuse to specific sites of the mesoporous matrix, beyond the surface level. This was achieved by calcining the catalysts at 150 °C. For this reason, with the Fe-MT-150 material, the highest levels of degradation of 2-CP were achieved at 60 min of reaction. In this way, this catalyst is proposed as a promising alternative for the treatment of aqueous effluents contaminated with refractory substances. This finds its support in the quantum efficiency parameter, which considers the versatility of the different geometric configurations existing for photoreactors, and the characteristics of the different radiation sources that can be used. The Fe-MT-150 catalyst presents the highest quantum efficiency value, compared to the other solids tested.

Acknowledgments

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References

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$$\varepsilon = (\text{reaction rate of 2-CP}) / (\text{rate of photon arriving reactor}) \quad \text{Eq. 1}$$

$$\varepsilon = (C_0 - C_t) \cdot V_R / (t_i) \cdot q \cdot A_w \quad \text{Eq. 2}$$

In accordance with the behavior observed in Figure 1, Fe-MT-150 has the highest efficiency value (Table 1). It is important to mention that after three hours of reaction with both Fe-MT-150 and Fe-MT, 100% degradation of the contaminant is achieved.

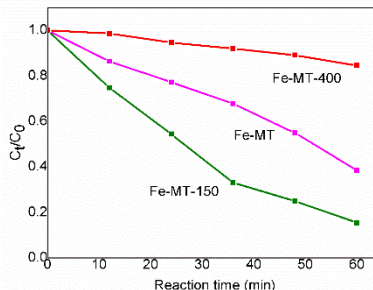


Figure 1. Photocatalytic activity of the synthesized solids, for 60 min of reaction under LED visible light.

Table 1. Photonic efficiency for the 2-CP degradation.^a Efficiency values (ε) calculated considering A_w = 152.2 cm² and V_R = 100 cm³.

Catalyst	(C ₀ -C _t)x10 ⁸ (molxcm ⁻³)	εx10 ³ (molxEin ⁻¹)
Fe-MT	8.88E-08	34.81
Fe-MT-150	1.27E-07	49.84
Fe-MT-400	2.69E-08	10.59