Surface modification of TiO$_2$ with a less expensive metal (iron) to exploit solar energy in photocatalysis: An ecological and economical solution

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Abstract

To degrade the tryptophan molecule through photocatalysis, the exploitation of solar energy in the present study necessitated the use of visible light active photocatalysts. Iron-transition metal nanoparticles were deposited on the surface of TiO$_2$ powders through an impregnation method to obtain X\%Fe-TiO$_2$ for the purpose of improving the optical absorption of TiO$_2$ in the visible light region. The effects of iron percentage (X\%: 2, 4 and 5), iron oxidation state and pH on the photocatalytic performance of TiO$_2$ modified under solar irradiation were thoroughly studied. The characterization results by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM-EDS) indicate that iron nanoparticles were successfully fixed on the TiO$_2$ surface. The absorption wavelengths of all X\%Fe-TiO$_2$ photocatalysts shifted towards the visible, confirming successful modification of the TiO$_2$ surface with iron. Based on the empirical results, X\%Fe-TiO$_2$ nanomaterials demonstrate a higher activity compared with the unmodified TiO$_2$ under solar irradiation. The 4\%Fe(III)-TiO$_2$ photocatalyst, in particular, displayed the highest photocatalytic activity at natural pH. The degradation was complete in 60 min. Therefore, it is interesting to note that iron had more functions and benefits than noble metals. The mechanism of the Fe-TiO$_2$ system has been proposed in detail.

1. Introduction

All the countries of the world are concerned about preserving freshwater resources because of water scarcity or pollution. Hence, it is necessary to develop highly effective treatment methods including chemical, biological and electrical or electrochemical processes. The advanced oxidation processes (AOPs) which are among the chemical processes belong to the latest generation of water treatment technologies and aim to convert pollutants into carbon dioxide, water and inorganic compounds (Elsellami et al. 2015; Martínez-Huitl et al. 2023; Ngo et al. 2017). They are based on the formation of highly reactive oxidizing species by light activation of a semiconductor. TiO$_2$, one of the semiconductors, is widely used and proves to be promising for UV photocatalysis (Elsellami et al. 2010; Ferreira et al. 2022). However, due to its wide band gap, inability to absorb visible light and high charge recombination rate, it results in a lower photocatalysis rate, which is a major drawback (Malato et al. 2002; Roccamante et al. 2022; Wang 2000). To overcome these disadvantages, various strategies are being implemented by researchers through the improvement of the light absorption and charge transfer characteristics of TiO$_2$. So far, different approaches have been widely developed including various anion and/or cation doping (Asiltürk et al. 2009; Cao et al. 2013), sensitization with absorbed molecules (Hachem 2001; Li et al. 2013), coupling with semiconductors (Elsellami and Djeridi 2022; Lv et al. 2011; Wu et al. 2010) and grafting of noble metals or transition metals (Cao et al. 2010; Li et al. 2006; Park et al. 2013). Among these methods, the surface modification of TiO$_2$ with metallic and/or non-metallic elements has been considered as one of the most promising strategies to develop visible light sensitive TiO$_2$ photocatalysts.
Compared to noble metals (Pt, Au, Ag, etc.), iron is the most abundant metal on earth (34.6% in mass fraction). Normally, noble metals acting as electron capture centers only play the role of efficient transfer of photo-generated electrons from the conduction band (CB) of photocatalysts (Elsellami et al. 2017). However, iron not only acts as a noble metal, but it can also facilitate wide band gap photocatalysts such as TiO$_2$ to directly absorb visible light. Furthermore, iron can reversibly change its oxidation state between the Fe(II) and Fe(III) forms but its most striking feature is its very low cost.

It is important to imagine and bring simple and inexpensive solutions into play for treating polluted water successfully. This study suggests an appropriate strategy that consists in coupling the photochemical and economical processes. Even more desirable in this period due to the sustained increase in its cost, solar photocatalysis seems to be a suitable option among the AOPs to save energy.

Nevertheless, it is interesting to note that works regarding iron-modified TiO$_2$ are little studied in spite of the availability of some papers on the photocatalytic treatment using TiO$_2$ modified by metals or non-metals. Wang et al. (2014) elaborated nitrogen-doped TiO$_2$ and then modified it with iron in the photocatalytic decolorization of methyl orange under visible light irradiation. In the photoelectrochemical process, Peng et al. (2022) studied the degradation of trichlorethylene by iron-modified TiO$_2$ nanotube networks. However, there is no study available in the scientific literature on the application of the photocatalysis in the presence of powdered TiO$_2$ only modified with iron mediated by solar irradiation. The present work intends to optimize the operating parameters for the purpose of reducing treatment costs.

This study focuses on the possibility of extending the photoresponse of TiO$_2$ in the visible light by modifying its surface with a variable percentage of Fe (X%: 2, 4 and 5) under optimal conditions to take advantage of the abundant solar radiation at the very most. The physicochemical properties of these photocatalysts were studied by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM-EDS). Tryptophan degradation was examined to evaluate the photocatalytic performance of X%Fe-TiO$_2$. Tryptophan was chosen as a model molecule for this study because of its widespread use in the pharmaceutical field.

2. Experiment

2.1. Chemical products

The precursor employed for the synthesis of TiO$_2$ was titanium tetrachloride (TiCl$_4$, 98%, Sigma−Aldrich). The source of the used Fe(III) was Fe(NO$_3$)$_3$.9H$_2$O (Sigma ≥ 99%) while that of Fe(II) was FeSO$_4$.7H$_2$O (Sigma ≥ 99%). Tryptophan (C$_{11}$H$_{12}$N$_2$O$_2$, 99%, Aldrich) was chosen as a pharmaceutical pollutant to test the photocatalytic performance of the materials. All these products were used as received.

2.2. Preparation of the X%Fe-TiO$_2$ photocatalyst
Pure TiO$_2$ was synthesized according to our previous studies (Elsellami et al 2017, 2018). Briefly, 3.9 ml of titanium tetrachloride was introduced into 10 ml of absolute ethanol. Then, ultra-pure water was added drop by drop to the mixture. After being stirred for 15 min at room temperature (0°C), the resulting gel was dried at 85°C for 15 h and then calcined at 600°C for 2 h to obtain pure TiO$_2$.

The surface modification procedure of the iron-synthesized TiO$_2$ was based on a simple impregnation method. In the empirical framework, 1 g of pure TiO$_2$ powder was dispersed in a 50 ml aqueous solution containing proportions of hydrated ferric sulphate (Fe(NO$_3$)$_3$.9H$_2$O) making it possible to get suspensions with an iron mass percentage of 2, 4 and 5% respectively. The solution was stirred for 24 h in the dark. Next, the solid-liquid phase separation was obtained by centrifugation. The recovered powder was washed with water several times and dried at 80°C for 2 hours. The acquired materials were named X%Fe(III)-TiO$_2$ where X% refers to the mass percentage of iron.

As far as the preparation of 4%Fe(II)-TiO$_2$ is concerned, the experimental protocol was exactly the same as the former. 1 g of TiO$_2$ was dispersed in a solution containing 4% of hydrated ferrous sulphate (Fe(SO$_4$).7H$_2$O). As for the sample labeled 4%Fe(III)-TiO$_2$-pH = 1.5, it was received after the impregnation process where an appropriate amount of nitric acid (HNO$_3$) was added to reach a pH of 1.5.

### 2.3 Characterization

X-ray diffraction (XRD) is an essential method for structural characterization in the field of materials. XRD measurements were carried out by a PANalytical X’Pert PRO device at room temperature with Cu-K$_\alpha$ radiation. The acquired diffractograms were used to verify the presence of crystalline impurities in the solid catalysts, to differentiate the phases and to calculate the crystallite size by the Scherrer method. The irradiance measurement was determined by diffuse reflection spectroscopy (DRS) using an Avantes AvaSpec-2048 fiber optic spectrometer equipped with a symmetric Czerny-Turner design with a 2048-pixel CCD detector array. The spectra were recorded from 250 nm to 800 nm. The scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) was also employed to get information on the morphology, the size distribution, and the quality of the chemical elements in the nanoparticles. The SEM images were taken by Marie-Line de Solan Bethmale (SAP-LGC) on a Leo 435 VP SEM equipped with an EDS detector (INCA system, Oxford Instruments).

### 2.4. Photocatalytic experiments

Photocatalytic assays were carried out in a glass beaker using a 100 mL aqueous solution of tryptophan (20 ppm) as a model pollutant and 100 mg of the prepared photocatalyst. To ensure the establishment of the adsorption/desorption equilibrium, the suspension was magnetically stirred in the dark for at least 60 minutes.

The photocatalytic degradation experiments of tryptophan under sunlight were conducted under similar conditions in an open terrace. 2 mL samples were taken from the suspension at regular time intervals. The photocatalysts were separated from the solution by means of centrifugation. The quantitative
determination of tryptophan was carried out by measuring its absorbance at 280 nm using a UV-Vis spectrophotometer (Shimadzu UV-3101).

3. Results And Discussion

3.1. Characterization of materials

3.1.1. X-ray diffraction analysis

Four catalyst powders were studied. Diffractograms of pure and X%Fe(III)-modified TiO₂ (X%: 2, 4 and 5%) are shown in Fig. 1. For pure TiO₂ calcined at 600 °C, it may be noticed that the X-ray diffractogram mainly showed the anatase phase (96%) characterized by the main peaks observed at 2θ = 25, 38, 48, 54, 56, 64.2 and 68° as reported in our previous work (Elsellami et al. 2018). The anatase phase was always stable, even when the TiO₂ powder was modified with iron. Nevertheless, it should be noted that the iron peak was not detected by the XRD analysis regardless of the percentage probably due to the lattice parameters that were identical for all the samples with a tetragonal crystal system. Moreover, there was no change in the mesh volume 136.30 Å³ noticed after surface modification.

Besides, as shown in Fig. 1, the diffractogram of the 5%Fe-TiO₂ composite revealed new peaks beyond 4%, showing the presence of an impurity phase at the TiO₂ interface. These peaks suggested that the crystallinity rate was 75% of the TiO₂ particles.

It is generally observed that the diffraction peaks of modified TiO₂ were broader and with lower intensity compared with pure TiO₂, proving that its crystallites were smaller. This can be clearly noticed on the XRD spectra. The average values of the crystal size of the samples were calculated by the Scherrer's equation and the width at half-peak height (1 0 1). The analysis results were reported in table (1).

Table 1: Crystallinity rate and sizes of unmodified or iron-modified TiO₂ particles

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite size (Å)</th>
<th>Crystallinity rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ pur</td>
<td>176.7</td>
<td>80.6 %</td>
</tr>
<tr>
<td>2%Fe(III)-TiO₂</td>
<td>235.3</td>
<td>84.2 %</td>
</tr>
<tr>
<td>4%Fe(III)-TiO₂</td>
<td>221.8</td>
<td>83.2 %</td>
</tr>
<tr>
<td>5%Fe(III)-TiO₂</td>
<td>241.9</td>
<td>75.2 %</td>
</tr>
</tbody>
</table>

3.1.2. Optical studies using diffuse reflectance spectroscopy (DRS)

The UV-Vis absorption spectra of pure TiO₂ and TiO₂ modified with different mass percentages of Fe(III) are shown in Fig. 2. It is obvious that pure TiO₂ only absorbed UV light (about 400 nm wavelength). After the surface modification of TiO₂ with iron, a significant absorption shift of all samples (X%Fe(III)-TiO₂...
where X: 2, 4 and 5) was observed towards the visible regions. It is evident from Fig. 2 that the absorbance of 4%Fe-TiO$_2$ in the visible region was higher than that of pure TiO$_2$, 2%Fe(III)-TiO$_2$ and 5%Fe(III)-TiO$_2$. This displacement certainly depended on the iron quantity (an optimal number of iron atoms located on the surface). Therefore, 4%Fe-TiO$_2$ could be a promising photocatalyst for the efficient use of visible light, particularly solar radiation. Added to that, the presence of iron in a less deficient electronic state may be related to less interaction with oxygen atoms, thus reducing the band gap width of TiO$_2$. The band gap energy of the photocatalysts was determined through the Kubelka-Munk equation. The values of the band gap (E$_g$) were collected in Table 2. It is important to note that these values correspond to experimental results.

**Table 2**: Band gap and wavelength values from DRS of X%Fe-TiO$_2$ samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>E$_g$ (eV)</th>
<th>$\lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ pur</td>
<td>3.09</td>
<td>400</td>
</tr>
<tr>
<td>2%Fe(III)-TiO$_2$</td>
<td>2.97</td>
<td>417</td>
</tr>
<tr>
<td>4%Fe(III)-TiO$_2$</td>
<td>2.80</td>
<td>443</td>
</tr>
<tr>
<td>5% Fe(III)-TiO$_2$</td>
<td>2.95</td>
<td>420</td>
</tr>
</tbody>
</table>

### 3.1.3. Scanning electron microscopy-energy dispersion X-ray spectroscopy (SEM-EDS) microanalysis

SEM images were taken for pure TiO$_2$ and TiO$_2$ modified with X% Fe(III) to understand the influence of the mass percentage of iron on the surface morphology of TiO$_2$ (Fig.3). It is plain to see that the modified powder consists of black particles with almost uniform sizes and shapes (Fig.3.A). These black zones noticeably correspond to the iron covering the surface with TiO$_2$. Thus, unlike the XRD analysis, these results display the presence of iron on the surface of our photocatalysts by the SEM-EDS analysis. It is worth noting that the presence of Fe did not modify the spherical morphology of TiO$_2$ particles and had no major impact upon the particle size distribution (Fig.3.B). This phenomenon will mainly result in the following effects: reduction in the nanometric size, band gap shortening and thus displacement of the absorption band towards longer wavelengths. Modified TiO$_2$ is likely to enhance photosensitivity and photoresponse under solar irradiation.

**Table 3**: Atom and compound percent from EDS of 5%Fe-TiO$_2$ samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom (%)</th>
<th>Compnd(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>59.54</td>
<td>32.95</td>
</tr>
<tr>
<td>Ti</td>
<td>39.95</td>
<td>66.18</td>
</tr>
<tr>
<td>Fe</td>
<td>0.51</td>
<td>0.87</td>
</tr>
</tbody>
</table>
3.2. Photocatalytic performance of iron-modified TiO₂

In order to improve the photocatalytic performance of iron-modified TiO₂ and select the optimal conditions for the tryptophan oxidation to be carried out under solar irradiation, it is recommended to use an experiment design defined by:

3.2.1. Effect of mass percentage of Fe(III)

The effect of the percentage of Fe(III) on the photocatalytic activity of TiO₂ was examined by maintaining the same tryptophan concentration (20 ppm).

As regards adsorption, covering the catalyst surface with tryptophan was performed in the absence of irradiation during 60 min.

First, it is noticeable that the adsorbed quantities of tryptophan 1.01 and 1.35 mg.g⁻¹ were directly proportional to the percentage of Fe(III) ions in the presence of 2%Fe-TiO₂ and 4%Fe-TiO₂ respectively. Then, the amount decreased 0.77 mg.g⁻¹ with 5%Fe-TiO₂ as soon as the quantity of iron became more important (exceeding an optimum rate (4%)). This could be attributed to the decrease in the number of active sites on the catalyst surface. In Fig. 4, it is also observed that the tryptophan adsorption was mainly due to the particle size. A minimum size was expected to improve the contact surface between the organic contaminant (adsorbate) and the photocatalyst (adsorbent). Consequently, it was considered as a key to intensify the photocatalytic degradation.

As far as the kinetics of tryptophan degradation under solar lighting is concerned, it can be seen in Fig. 5 that for one hour of solar irradiation and in the presence of 4%Fe(III)-TiO₂, total degradation could be achieved. Thus, in the presence of 2%Fe(III)-TiO₂, 5%Fe(III)-TiO₂ and pure TiO₂, degradation rates of 83,77 and 72% were obtained after 60 min of natural irradiation respectively. It is worth mentioning here that the DRS analysis results in our work demonstrated that 4%Fe(III)-TiO₂ absorbed more visible light. This is why it was the most photoactive.

Hence, it is clear that an accurate and optimal amount of Fe(III) on the titanium oxide surface can greatly improve the photocatalytic efficiency. In addition to enhancing the ability to absorb sunlight, it is expected to improve the separation of photogenerated electrons and holes and to avoid their rapid recombination. Besides, it is important to note that an excess of Fe(III) (>4 wt% Fe) can decrease light penetration into the catalyst and can also behave as a recombination center, leading to a decline in the photocatalytic activity under solar irradiation.

Reducing the duration of the tryptophan treatment is a key objective which is achieved with the use of sunlight in the presence of the 4%Fe-TiO₂ catalyst when taking into consideration the cost of treatment. This performance was close to that achieved when using UV light directly emitted by an artificial lamp for the photocatalytic treatment of the same molecule under the same conditions in the presence of TiO₂-P25 (Elsellami et al. 2010).


3.2.2. Effect of iron oxidation state: Mechanism of photoactivity

The solid catalysts that were studied contained either Fe(III) or Fe(II). Therefore, this study examined the effect of the iron oxidation state in the same operating conditions. Fig. 6 illustrates the photocatalytic activity induced by solar radiation of virgin TiO$_2$ and modified with only 4% by mass of iron.

As can be seen, there was a difference in the photodegradation kinetics of tryptophan (faster with Fe(III)). The boost in the photocatalytic activity of modified TiO$_2$ is essentially attributed to the decrease in electron/hole recombination and the increase in the number of electrons injected into the conduction band compared with pure TiO$_2$. Thus, both Fe(III) and Fe(II) ions significantly influence and contribute to the photocatalytic activity. In this study, the photocatalyst containing 4%Fe(III)-TiO$_2$ always achieved the highest degradation rate in comparison with that of 4%Fe(II)-TiO$_2$ (degradation rate of 87%) after an irradiation period of 60 min. This demonstrates that the oxidation state plays a major part in the photodegradation of tryptophan. Consequently, a mechanism that could better explain these results was proposed. As for the beneficial effect of using Fe(II) or Fe(III), they have been described as electron and hole trapping agents (Eqs. (3)–(5)) where the excited electrons were held for a short time before being transferred once again (Garrido-Ramírez et al. 2010). The charge transfer steps can be described as follows:

\[
\begin{align*}
    \text{Fe}^{(\text{III})} + e^- & \rightarrow \text{Fe}^{(\text{II})} & (1) \\
    \text{Fe}^{(\text{II})} + h\nu & \rightarrow \text{Fe}^{(\text{III})} & (2) \\
    \text{Fe}^{(\text{III})} + h\nu & \rightarrow \text{Fe}^{(\text{IV})} + e^- & (3) \\
    \text{Fe}^{(\text{IV})} + e^- & \rightarrow \text{Fe}^{(\text{III})} & (4) \\
    \text{Fe}^{(\text{II})} & \rightarrow \text{Fe}^{(\text{III})} + e^- & (5)
\end{align*}
\]

As previously mentioned, the best photocatalytic activity was observed for 4%Fe(III)-TiO$_2$, which was very active under sunlight. This suggests that Fe(III) may act as a trap for electron/hole pairs forming Fe(II) or Fe(IV) (Eq 6-7), which can delay the recombination rate and enhance the photocatalytic activity. Therefore, Fe(II) and Fe(IV) are less stable than Fe(III). The latter could also react with water (Eq. 9) as well as with photo-generated electrons and holes in its excited state to produce hydroxyl radicals as shown in the mechanism below. As a result, the number of OH$^-$ radicals produced by 4%Fe(III)-TiO$_2$ was greater and, accordingly, its photocatalytic activity improved significantly.
3.2.3. Effect of pH during impregnation

Many works on the Fenton process (Fe with \( \text{H}_2\text{O}_2 \)) have shown that the pH must be acidic for optimal degradation of organic pollutants (Balasurya et al. 2023; De Laat et al. 1999). To evaluate the effect of pH in this study (Fe alone), 4%FeIII-TiO\(_2\) was also prepared by the impregnation process at acidic pH (equal to 1.5). The experimental results obtained by varying the pH during the impregnation (Fig. 7) indicate that there was a difference in efficiency between the two samples (at natural pH and acidic pH) during the tryptophan photodegradation under solar irradiation. The highest degradation rate was in the natural environment. In fact, 4%FeIII-TiO\(_2\) seemed promising in solar photocatalysis applications when the pH conditions were well adapted. Consequently, the Fe(III) reduction in Fe(II) essentially raised the problem (effect of oxidation state). The production of HO\(^•\) radicals, thus, became more restricted leading to a decline in the degradation rate. During impregnation, the acidification of the medium was detrimental to the degradation reaction. On the other hand, both the additional costs from the reagent consumption for acidification and the increase in the salt load of the treated water explained the normal pH traditionally recommended.

\[
\begin{align*}
\text{Fe}^{(\text{III})} + h^+ & \rightarrow \text{Fe}^{(\text{IV})} \\
\text{Fe}^{(\text{III})} + e^- & \rightarrow \text{Fe}^{(\text{II})} \\
\text{Fe}^{(\text{III})} + h\nu & \rightarrow \text{Fe}^{(\text{III})^*} \\
\text{Fe}^{(\text{III})^*} + \text{H}_2\text{O} & \rightarrow \text{Fe}^{(\text{II})} + \text{HO}^• + \text{H}^+ \\
\text{Fe}^{(\text{III})} + \text{H}_2 & \rightarrow \text{Fe}^{(\text{II})} + \text{OH}^• + \text{H}^+ \\
\text{Fe}^{(\text{IV})} + \text{OH}^- & \rightarrow \text{Fe}^{(\text{IV})} + \text{OH}^- \\
\text{Fe}^{(\text{II})} + \text{O}_2 & \rightarrow \text{Fe}^{(\text{III})} + \text{O}_2^• \\
\text{Fe}^{(\text{II})} + \text{OH}^- & \rightarrow \text{Fe}^{(\text{III})} + \text{OH}^- 
\end{align*}
\]

4. Conclusion

The photocatalyst (TiO\(_2\)) surface was successfully modified by a simple impregnation process. This photocatalyst was prepared with certain mass percentages of iron (2.4 and 5%) to extend its photoresponse to the visible region. The degradation of tryptophan was carried out in an aqueous solution under solar irradiation to evaluate the photocatalytic activity of the resulting materials. The experimental results show that each modification with iron had a positive effect and was greater than that of pure TiO\(_2\). In fact, 4%Fe(III)-TiO\(_2\) achieved the best performance. The optimal behavior of this sample can be explained by the optimal percentage of Fe(III) and the modification of the TiO\(_2\) surface at natural pH, which leads to the high production of hydroxyl radicals and the lower recombination rate of electron/hole pairs. The latter indicates a more efficient measure of charge separation. Furthermore, the high oxidation number (NO) (NO Fe(III) > NO Fe(II)) plays a key role in enhancing the tryptophan
photodegradation. All these factors make it possible to understand the good photocatalytic results of this most active sample.

The present study brings out the importance of the modification of the TiO\textsubscript{2} surface under controlled and precise conditions to significantly improve the catalytic efficiency of the material under solar irradiation.

This work demonstrates a new chemical strategy with a dual purpose (ecological and economical) that is acceptable and profitable for the degradation of organic contaminants in water treatment.

**Declarations**

**Author Contribution** All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Rania Amiri, Aymen Bourezgui, Wahid Djeridi, Frederic Dappozze, Ammar Houas, Chantal Guillard and Leila Elsellami. The first draft of the manuscript was written; review & editing; Supervision by Leila Elsellami. All authors read and approved the final manuscript.

**Data availability** Not applicable.

**Ethics approval** Not applicable.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

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**Competing interests** The authors declare no competing interests.

**References**


Figures
Figure 1

XRD diffractograms of pure and modified TiO$_2$ samples with various iron mass percentages

Figure 2

Diffuse reflectance spectra of pure TiO$_2$ and X%Fe-TiO$_2$. 
Figure 3

A: Transmission electron microscopy (TEM) images of virgin TiO$_2$ particles (a) and those modified with 5% of iron (b). B: EDS analysis of the sample 5%Fe-TiO$_2$. 
Figure 4

Amount of tryptophan adsorbed per gram of catalyst and its relationship with the average crystallite size of X%Fe-TiO$_2$ nanoparticles

Figure 5

Photocatalytic degradation process of tryptophan in the presence of X%Fe(III)-TiO$_2$ and pure TiO$_2$ samples under solar irradiation.
Figure 6

Influence of oxidation state on catalyst photocatalytic activity

Figure 7

Effect of pH during impregnation on the photodegradation activity of the 4%Fe(II)-TiO\textsubscript{2} sample under solar irradiation