Photocatalytic Degradation of Estriol Using Iron-Doped TiO$_2$ under High and Low UV Irradiation

Irving M. Ramírez-Sánchez 1 and Erick R. Bandala 2,3,*

1 Department of Civil, Architectural and Environmental Engineering, The University of Texas at Austin, Austin, TX 78712, USA; irwingmoises@gmail.com
2 Desert Research Institute (DRI), 755 E. Flamingo Road, Las Vegas, NV 89119-7363, USA
3 Graduate Program Hydrologic Sciences, University of Nevada, Reno, NV 89557, USA
* Correspondence: erick.bandala@dri.edu; Tel.: +1-(702)-862-5395

Received: 29 September 2018; Accepted: 28 November 2018; Published: 5 December 2018

Abstract: Iron-doped TiO$_2$ nanoparticles (Fe-TiO$_2$) were synthesized and photocatalitically investigated under high and low fluence values of UV radiation. The Fe-TiO$_2$ physical characterization was performed using X-ray Powder Diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Diffuse Reflectance Spectroscopy (DRS), and X-ray Photoelectron Spectroscopy (XPS). The XPS evidenced that the ferric ion (Fe$^{3+}$) was in the TiO$_2$ lattice and unintentionally added co-dopants were also present because of the precursors of the synthetic method. The Fe$^{3+}$ concentration played a key role in the photocatalytic generation of hydroxyl radicals (•OH) and estriol (E3) degradation. Fe-TiO$_2$ accomplished E3 degradation, and it was found that the catalyst with 0.3 at.% content of Fe (0.3 Fe-TiO$_2$) enhanced the photocatalytic activity under low UV irradiation compared with TiO$_2$ without intentionally added Fe (zero-iron TiO$_2$) and Aeroxide® TiO$_2$ P25. Furthermore, the enhanced photocatalytic activity of 0.3 Fe-TiO$_2$ under low UV irradiation may have applications when radiation intensity must be controlled, as in medical applications, or when strong UV absorbing species are present in water.

Keywords: iron-doped TiO$_2$; photocatalytic activity; low UV irradiation; hydroxyl radical; estriol

1. Introduction

In recent years, society and the scientific community have concerned of Emerging Contaminants (ECs, also called Contaminants of Emerging Concern), which are chemicals that threaten the environment, human health, and water safety and are not currently covered by existing local or international water quality regulations [1]. ECs include chemical species such as algae toxins, illegal drugs, industrial compounds, flame retardants, food additives, nanoparticles, pharmaceuticals (human and veterinary), personal care products, pesticides, biocides, steroids, synthetic and natural hormones, and surfactants [2].

Natural hormones (e.g., estrone (E1), 17β-estradiol (E2), and estriol (E3)) as ECs are susceptible of persisting and bioaccumulating in the environment, and could induce endocrine disruption in humans and wildlife (vertebrates [3–5] and invertebrates [6,7]). Natural attenuation, drinking water purification, and conventional municipal wastewater treatment processes are either incapable or only partially capable of removing estrogens from water [8]. As result, water treatment techniques are being developed to manage, reduce, degrade, and mineralize low-concentrated ECs (including natural estrogen) in drinking and wastewater [9]. Advanced Oxidation Processes (AOPs) are promising techniques to treat ECs in aqueous phase, which include well-known processes such as Fenton and Fenton-like processes, UV/H$_2$O$_2$, ozonation, and photocatalysis using semiconductors, perozone...
which prevents increases in estrogenic activity in water [14,15] and partially or completely mineralizing processes (H₂O₂/O₃), and cavitation [10,11]. Although there are many known AOPs, since Coleman’s work [12], photocatalysis using titanium dioxide (TiO₂) has been identified as one of the most effective methods to degrade estrogens in water [13]. Several reports recognized that TiO₂ can degrade estrogens, which prevents increases in estrogenic activity in water [14,15] and partially or completely mineralizing estrogens [14,16].

Titanium dioxide is the most commonly used photocatalyst because of its reasonable optical and electronic properties, good photocatalytic activity, insolubility in water, chemical and photochemical stability, nontoxicity, low cost, and high efficiency in pollutant mineralization [17–20]. However, the band gap energy (Eg) of TiO₂, frequently reported as 3.2 eV [21], restrains the photocatalytic activation to energy sources with a portion of spectrum emission below 387.5 nm [22].

In general the photocatalytic mechanism is as shown in Figure 1. According to Density Functional Theory (DFT) computations, the valence band (VB) and conduction band (CB) of pure TiO₂ are mainly composed of O2p orbitals and Ti3d orbitals, respectively. Hence, the Fermi level (EF) is located in the middle of the band gap (BG), indicating that VB is full filled while CB is empty [23]. When using photons with energy higher than 3.2 eV, photoexcitation of the semiconductor promotes electrons from VB to CB creating a charge vacancy or hole (h⁺) in the VB. The h⁺ in the VB can react with hydroxide ion to form hydroxyl radical (•OH) or can also be filled by donor absorbed organic molecule (OM_ads). Photogenerated electrons in the CB can be transferred to acceptor of electrons and bring about •OH.

![Figure 1. Photocatalytic mechanism of TiO₂ for •OH generation. Where E_g: Band gap energy; E: photon energy; OM_ads: adsorbed organic molecule; and OM_oxi: oxidized organic molecule.](image)

Consequently, reducing the photon energy needed for TiO₂ photoactivation has been the focus of the scientific community until now. Doping is one of the techniques that has been tested to control or modify the surface properties or internal structure of TiO₂. Doping introduces a foreign element into TiO₂ to cause an impurity state in the band gap. The most frequently used doping materials are transition-metal cations (e.g., Cr, V, Fe, and Ni) at Ti sites, and anions (e.g., N, S, and C) at O sites [24]. Among anion- and cation-dopants, the ferric ion (Fe³⁺) is one of the most often used because the ionic radius of Fe³⁺ (0.69 Å) is similar to Ti⁴⁺ (0.745 Å) [25]. Therefore, Fe³⁺ can be easily incorporated into the TiO₂ crystal lattice.

The main reported effects of iron-doped TiO₂ is a rapid increase in photocatalytic activity that increases with increased Fe doping, which then reaches a maximum value, and finally decreases with
further increased Fe content [23,26–37]. However, detrimental effects have been also reported because of high Fe content [38,39] or agglomerated Fe-TiO$_2$ nanoparticles [40,41].

Although several theoretical and experimental Fe-TiO$_2$ studies have been developed, the trade-off between doping ratio and radiation intensity is scarcely mentioned. Furthermore, Fe-TiO$_2$ photocatalyst has rarely been considered to be a useful technique for the degradation of E3 [42].

In this work, Fe-TiO$_2$ nanoparticles were synthesized to increase the understanding of the relationship between doping ratio and radiation intensity for hydroxyl radical (•OH) generation and E3 degradation. Therefore, we investigated the photocatalytic degradation of E3 using Fe-TiO$_2$ under high and low UV irradiation. We highlight the term low UV irradiation to avoid confusion with the term “photocatalytic processes under visible light” because we did not intentionally use UV cutoff filters for the experiments.

2. Results and Discussion

2.1. Characterization of Iron-Doped TiO$_2$

Figure 2 shows X-ray Photoelectron Spectroscopy (XPS) general spectra of TiO$_2$ without added Fe (zero-iron TiO$_2$) and Fe-TiO$_2$ materials (b, c, and d). For the experimental condition used, Fe did not affect the bonding structure between titanium and oxygen because the main peaks for all samples were Ti2p and O1s with the proportion 1:2.2, which is in agreement with the atomic formula of TiO$_2$.

XPS detected unintentionally added elements such as carbon, sulfur, and nitrogen (Table 1) as co-dopants of zero-iron TiO$_2$ and Fe-TiO$_2$, which were introduced into TiO$_2$ via precursors of the synthesis. Carbon and sulfur could come from sodium dodecyl sulfate (SDS), and nitrogen could come from iron (III) nitrate (Fe(NO$_3$)$_3$·9H$_2$O) and HNO$_3$, all of them used in the synthesis process.
Table 1. Surface elemental composition determined by XPS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic % of Elements (at.%)</th>
<th>Ti2p</th>
<th>O1s</th>
<th>C1s</th>
<th>Fe2p</th>
<th>S2p</th>
<th>N1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero-iron TiO₂</td>
<td></td>
<td>24.4</td>
<td>52.9</td>
<td>21.3</td>
<td>0</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>0.3 Fe-TiO₂</td>
<td></td>
<td>23.8</td>
<td>51.1</td>
<td>22.9</td>
<td>0.3</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td>0.6 Fe-TiO₂</td>
<td></td>
<td>23.9</td>
<td>53.1</td>
<td>22.5</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0 Fe-TiO₂</td>
<td></td>
<td>23.5</td>
<td>52.5</td>
<td>20.6</td>
<td>1</td>
<td>1.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

High-resolution XPS spectra for the iron region (Figure 3) was studied only for 1.0 Fe-TiO₂ because no Fe2p signals were detected for zero-iron TiO₂, 0.3 Fe-TiO₂, or 0.6 Fe-TiO₂. The deconvolution of high-resolution XPS spectra (Figure 3) was developed for previously reported peaks of Fe²⁺ and Fe³⁺ [43]. Shirley baseline was subtracted before peak fitting. The Gaussian–Lorentzian mix function was used with a 40% factor. Charge compensation was set by the O1s peak charge with $-E$. The XPS technique detected Fe²⁺ because Fe³⁺ underwent reduction to Fe²⁺ during XPS measurement because the ionic radius of Fe³⁺ (0.69 Å) is similar to the ionic radius of Ti⁴⁺ (0.745 Å) [25].

According to the theoretical model (sum of fitting peaks), both Fe³⁺ and Fe²⁺ were present in the lattice of 1.0 Fe-TiO₂. We suggest that Fe³⁺ was incorporated into the lattice of TiO₂ to form Ti–O–Fe bonds, because the ionic radius of Fe³⁺ (0.69 Å) is similar to the ionic radius of Ti⁴⁺ (0.745 Å) [25]. The XPS technique detected Fe²⁺ because Fe³⁺ underwent reduction to Fe²⁺ during XPS measurement in vacuum [44].

The band gap energy ($E_g$) obtained with the Kubelka–Monk method (Figure 4) for Aeroxide® TiO₂ P25 was 3.2 eV, which is consistent with the value reported previously [45]. For Aeroxide® TiO₂ P25 $E_g$, red-shifts were detected as 0.22, 0.24, 0.25, and 0.3 eV for zero-iron TiO₂, 0.3 Fe-TiO₂, 0.6 Fe-TiO₂, and 1.0 Fe-TiO₂, respectively, which is consistent with values reported by Shi et al. of 0.25 eV [46] and with density functional theory calculations that suggested the hybridized band of Ti3d and Fe3d reduces $E_g$ approximately 0.3–0.5 eV [44], or 0.2–0.34 eV [47].
For zero-iron TiO$_2$, $E_g$ for Fe-TiO$_2$ materials (Table 2) decreased as long as the Fe content increased, so the Fe content generated red-shift. For Aeroxide® TiO$_2$ P25, the red-shift of Fe-TiO$_2$ agreed with previously reported values, but it agreed less for zero-iron TiO$_2$. Therefore, red-shift was not only related to Fe content, but also to the synthesis method and unintentionally co-doped TiO$_2$.

XRD patterns in Figure 5 revealed zero-iron TiO$_2$ and Fe-TiO$_2$ materials had both anatase and rutile phases. No XRD Fe$_2$O$_3$ peaks ($2\theta$ equal to 33.0°, 35.4°, 40.7°, 43.4°, and 49.2°) were observed, concluding that Fe$^{3+}$ replaced Ti$^{4+}$ in the TiO$_2$ crystal framework [48,49]. The synthesis method allowed uniform distribution of Fe within TiO$_2$. The anatase:rutile phase ratio calculated by Spurr and Myers’ method showed that zero-iron TiO$_2$ and Fe-TiO$_2$ materials were a mixture of anatase and rutile phases (Table 2). The amount of anatase was less in Fe-TiO$_2$ materials than in Aeroxide® TiO$_2$ P25. The smaller proportion of anatase could lead to a reduction of photocatalytic activity because the anatase phase has higher photocatalytic activity than rutile TiO$_2$ [50,51]. However, it is accepted that the optimal photocatalytic activity of TiO$_2$ is reached with an optimal mixture of anatase and rutile phases [52]. Moreover, the increased anatase proportion in 0.3 Fe-TiO$_2$ and 0.6 Fe-TiO$_2$ compared

![Figure 4. Band gap energy ($E_g$) by the Kubelka–Monk method. Zero-iron TiO$_2$ (a), 0.3 Fe-TiO$_2$ (b), 0.6 Fe-TiO$_2$ (c), and 1.0 Fe-TiO$_2$ (d).](image)
with zero-iron TiO$_2$ could improve photocatalytic activity. The increased anatase proportion was attributable to Fe doping disturbing the arrangements of TiO$_2$ phases [53]. This trend has also been observed when Fe-doped TiO$_2$ was synthesized using sol-gel [54] or co-precipitation methods [32].

The average particle size of Fe-TiO$_2$ materials obtained by Scherrer’s formula was 6.9 nm, which is less than the particle size of Aeroxide® TiO$_2$ P25 (Table 2). Fe-TiO$_2$ materials should increase photocatalytic activity because of their higher surface area and the short migration distance of the photogenerated charge carriers (electron/hole ($e^-/h^+$)) from the bulk material to the surface.

Further BET analysis (Figure 6) confirmed that average surface area of Fe-TiO$_2$ materials was 77.9 m$^2$ g$^{-1}$, higher than zero-iron TiO$_2$ and Aeroxide® TiO$_2$ P25. BET isotherms followed a type IV shape according to the Langmuir classification, which is associated with the characteristics of mesoporous material [55]. The observed hysteresis is probably due to gas cooperative adsorption or condensation inside the pores of material [56]. BET analysis showed pore sizes (Table 2) were in the mesoporous range (2–50 nm, according to IUPAC classification) for zero-iron TiO$_2$ and 0.6 Fe-TiO$_2$, and the microporous range (0.2–2 nm, according to IUPAC classification) for 0.3 Fe-TiO$_2$ and 0.6 Fe-TiO$_2$. Mesoporous pore size should facilitate the mass transfer of reactants and products in the reaction system, so photocatalytic improvement based on this property could improve zero-iron TiO$_2$ and Fe-TiO$_2$ materials with respect to Aeroxide® TiO$_2$ P25 [31].

Patra et al. [49] developed a similar nanoparticle synthesis procedure, which generated surface area values ranging from 126 to 385 m$^2$ g$^{-1}$ and mesoporous size distribution values ranging from 3.1 to 3.4 nm. Particles obtained in our work were different, probably because of the application of a mild thermal treatment and the use of SDS at critical micelle concentration as a template.

Figure 7 shows SEM images of agglomerated and assembled nanoparticles of zero-iron TiO$_2$. The different amounts of Fe in the TiO$_2$ lattice changed neither the particle size nor the morphology of the zero-iron TiO$_2$. Although the average pore size allowed an increase of the superficial area, agglomeration could lead to lower photocatalytic activity.
Patra et al. [49] developed a similar nanoparticle synthesis procedure, which generated surface area values ranging from 126 to 385 m$^2$ g$^{-1}$ and mesoporous size distribution values ranging from 3.1 to 3.4 nm. Particles obtained in our work were different, probably because of the application of a mild thermal treatment and the use of SDS at critical micelle concentration as a template.

Figure 7 shows SEM images of agglomerated and assembled nanoparticles of zero-iron TiO$_2$. The different amounts of Fe in the TiO$_2$ lattice changed neither the particle size nor the morphology of the zero-iron TiO$_2$. Although the average pore size allowed an increase of the superficial area, agglomeration could lead to lower photocatalytic activity.

Transmission electron microscopy (TEM) images confirmed nanoparticle clusters and particle sizes of zero-iron TiO$_2$ (Figure 8b) and 0.3 Fe-TiO$_2$ (Figure 8a) between 5 and 10 nm (between 1.2 and 9.4 nm according to Scherrer’s formula). The lattice fringe spacing was 0.35 nm, as shown in Figure 8b, which was consistent with the d-spacing (101) of anatase [25]. The lattice fingers of the nanoparticles showed that Fe-TiO$_2$ materials were highly crystallized.
2.2. Characterization of Irradiation Source

Figure 9 shows the emission spectra of irradiation sources used in this study. Using the main peaks reported for a fluorescent lamp (Figure 9a), the calibration of the spectrometer generated an R² value equal to 0.999. The emission spectrum of the GE F15T8 BLB lamp (Figure 9b) was in the 356–410 nm range. However, the emission spectrum of the GE F15T8 D lamp (Figure 9c) was continuous broadband between 380 and 750 nm. The light intensity of the GE F15T8 lamp was reported to be between 3440 µW cm⁻² [58], from which 6% was UV radiation [59]. The intensity of the GE F15T8 lamp was 1500 µW cm⁻². This lamp has an internal coating that absorbs 78% of visible light (as specified by the manufacturer) in the spectrum below 400 nm, as shown in Figure 9b. Therefore, the GE F15T8 BLB and GE F15T8 D lamps were designated as high and low UV irradiation sources, respectively.

Figure 8. Transmission electron microscopy (TEM) image of 0.3 Fe-TiO₂ (a) and zero-iron TiO₂ (b).

Figure 9. Emission spectrum and intensity graph of the irradiation source of Tecnolite fluorescent lamp (a), GE F15T8 BLB lamp (b), and GE F15T8 D lamp (c).
Because $E_g$ of Aeroxide® TiO$_2$ P25 is 3.2 eV (387.5 nm), see Figure 9, both the GE F15T8 BLB and GE F15T8 D lamps emitted photons that could photoactivate Aeroxide® TiO$_2$ P25. However, the proportion of the emission spectrum that Aeroxide® TiO$_2$ P25 could use for photocatalytic activity was different. An approximation of the amount of radiative intensity used for photocatalytic activity was obtained with the area under the curve-spectrum below the $E_g$ value. Consequently, Aeroxide® TiO$_2$ P25 could take advantage of 36.4% of the emission spectrum of the GE F15T8 BLB lamp and 0.8% of the emission spectrum of the GE F15T8 D lamp. Table 2 lists amount of radiative spectrum used by zero-iron TiO$_2$ and Fe-TiO$_2$ materials according to each $E_g$.

Based on morphological and crystalline structure analysis, the favorable characteristics to enhance photocatalytic activity of Fe-TiO$_2$ material are effective insertion of the Fe$^{3+}$ ion into the TiO$_2$ lattice, red-shift (2.90–2.96 eV), nanoparticle size (6.9–7.1 nm), specific surface area (73.0–83.1 nm), pore size (1.2–9.4 nm), and radiation absorbance below the equivalent $E_g$ wavelength (8.21–10.63% of daylight lamp spectrum). Its main disadvantageous characteristics are expected to be high particle agglomeration and lower anatase phase compared with zero-iron TiO$_2$. Further, photocatalytic activity is very sensitive to crystalline array and particle size and shape; differences in the density of hydroxyl groups on the particle surface and the number of water molecules hydrating the surface; the surface area and surface charge; differences in the number and nature of trap sites; the dopant concentration, localization, and chemical state of the dopant ions; radiation intensity; particle aggregation and superficial charge; and scavenger species in media [39,60]. Consequently, material characterization alone could not predict photocatalytic activity [28]. Therefore, in this research, we used the $N,N$-dimethyl-p-nitrosoaniline (pNDA) probe and E3 to evaluate the photocatalytic activity by following $^•$OH production, which is one of the most significant reactive oxygen species (ROS), and E3, which is an EC.

2.3. Hydroxyl Radical Generation under High and Low UV Irradiation

The generation of $^•$OH was measured using pNDA, which is a well-characterized $^•$OH scavenger as mentioned in Section 3.5. In brief, pNDA undergoes bleaching when reacting with $^•$OH according to Muff et al. mechanism of the oxidation of pNDA by $^•$OH [61].

In this work, pNDA bleaching followed a pseudo-first-order equation, so the apparent rate constant was calculated by $\ln(C/C_0) = k_1t$, where $C_0$ is the initial concentration, $C$ is the reaction concentration at a given time, and $k_1$ is the pseudo-first-order reaction rate constant. The slope of the plot after applying a linear fit represents the rate constant, $k_1$.

Because the relationship between pNDA bleaching and $^•$OH production follows a 1:1 stoichiometry [61], the steady-state of $^•$OH generation ($[^•$OH]$_{ss}$) can be considered equal to the initial velocity ($r_0$) according to Equation (1) and reported in Table 3:

$$\frac{[\text{pNDA}]}{dt} = r_0 = [^•\text{OH}]_{ss}$$  \(1\)

Fe-TiO$_2$ materials showed a similar anatase:rutile phase ratio, particle size, and specific surface area, and therefore the variation in $r_0$ values was due to the difference of Fe content inside TiO$_2$. The generation of $^•$OH radicals ($r_0$) was feasible using zero-iron TiO$_2$, Fe-TiO$_2$ materials, and Aeroxide® TiO$_2$ P25 under both high (Figure 10a) and low UV irradiation (Figure 10b).
react with hydroxide ions to form \( \text{Fe}^{3+} \), the \( \text{Fe}\) orbitals split into two bands, one is a hybrid band (A\( _{2g} \)) and one is midgap band (T\( _{2g} \)), are shown in Equations (2)–(5) [62].

Following a dark redox reaction at the interface, as suggested by Neubert et al. [63] and consequently bring about •OH.

When high UV irradiation was used, the maximum \( r_0 \) was 0.58 \( \mu \text{M}_{•\text{OH}} \text{min}^{-1} \) for 0.3 Fe-TiO\(_2\). The enhancement in photocatalytic activity of 0.3 at.% Fe-TiO\(_2\), compared with zero-iron TiO\(_2\) was by the extended lifetime values of the photogenerated charge carriers (\( e^- \) and \( h^+ \)) produced by \( \text{Fe}^{3+} \) ions, which played a role as charge carriers trapped at or near the particle surface. The trapping mechanisms are shown in Equations (2)–(5) [62].

\[
\begin{align*}
\text{Fe}^{3+} + e_{el}^- & \rightarrow \text{Fe}^{2+} & \text{electron trap} \\
\text{Fe}^{2+} + \text{Ti}^{4+} & \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+} & \text{migration} \\
\text{Fe}^{3+} + h_{vb}^+ & \rightarrow \text{Fe}^{4+} & \text{hole trap} \\
\text{Fe}^{4+} + \text{OH}^- & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} & \text{migration}
\end{align*}
\]

The mechanism suggested for •\OH generation is shown in Figure 11. When TiO\(_2\) contains a \Fe^{3+} ion, the \Fe3d orbitals split into two bands, one is a hybrid band (A\( _{2g} \)) and one is midgap band (T\( _{2g} \)), which induce a new localized BG state [23]. Therefore, when TiO\(_2\) absorbs photons with energy less than 3.2 eV, photoexcitation of the semiconductor promotes an electron from the VB to the midgap band (T\( _{2g} \)), also called a shallow trap, creating an electron-hole pair. The hole in the valence band (VB) can react with hydroxide ions to form •\OH, absorbed organic molecules, or trap \Fe^{3+} following Equations (4) and (5). Additionally, photogenerated electrons in the midgap band (T\( _{2g} \)) can be transferred to \Fe^{3+} following a dark redox reaction at the interface, as suggested by Neubert et al. [63] and consequently bring about •\OH.
Figure 11. Photocatalytic mechanism of Fe-TiO$_2$ and •OH generation. $E_g$ is band gap energy, $E$ is photon energy, OM$_{ads}$ is adsorbed organic molecule, OM$_{oxi}$ is oxidized organic molecule.

Increasing the Fe$^{3+}$ doping content of Fe-TiO$_2$ to 0.6 and 1.0 at.%, Fe-TiO$_2$ was unfavorable to the photocatalytic activity because the additional Fe$^{3+}$ doping in the TiO$_2$ sample inhibited the extended lifetime of charge carriers, acted as recombination sites and consequently decreased the photocatalytic efficiency [29], as proposed in Equations (6)–(9) [39].

$$\text{Fe}^{2+} + h_{vb}^+ \rightarrow \text{Fe}^{3+} \quad \text{recombination} \quad (6)$$

$$\text{Fe}^{4+} + e_{cd}^- \rightarrow \text{Fe}^{3+} \quad \text{recombination} \quad (7)$$

$$\text{Fe}^{4+} + \text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} \quad \text{recombination} \quad (8)$$

$$\text{Fe}^{4+} + \text{Ti}^{3+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{4+} \quad \text{recombination} \quad (9)$$

When low UV irradiation conditions were used, the $r_0$ values for zero-iron TiO$_2$ and Fe-TiO$_2$ materials were lower than the value estimated for Aeroxide® TiO$_2$ P25. Compared with the effects of high UV irradiation, the reduction in $r_0$ value observed was related both to pNDA adsorption of UV-visible radiation (lowered the number of photons available to activate the photocatalyst), and the augmented Fe content, which increased the recombination rate.

2.4. Photocatalytic Degradation of Estriol under High and Low UV Irradiation

E3 photocatalytic degradation curves are shown in Figure 12a,b using both high and low UV irradiation, respectively. In both cases, E3 photocatalytic degradation followed a pseudo-first-order model and the rate constant, $k_1$ (Table 4), was obtained by fitting experimental data to $\ln ([E3]/[E3_0]) = k_1 t$. Fe content influenced $k_1$ for both high and low UV irradiation.
Figure 12. Photocatalytic degradation of E3 under high UV irradiation (a), and low UV irradiation (b); where □ zero-iron TiO$_2$, ○ 0.3 Fe-TiO$_2$, △ 0.6 Fe-TiO$_2$, ▽ 1.0 Fe-TiO$_2$, and ♦ Aerosol® TiO$_2$ P25; at pH 6 ± 0.1, and 20 °C.

Table 4. Kinetic values of E3 degradation using zero-iron TiO$_2$ and Fe-TiO$_2$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Load</th>
<th>High UV Irradiation</th>
<th>Low UV Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg L$^{-1}$</td>
<td>k$_1$</td>
<td>R$^2$</td>
</tr>
<tr>
<td>TiO$_2$ Aerosol® P25</td>
<td>20</td>
<td>0.021</td>
<td>0.996</td>
</tr>
<tr>
<td>Zero-iron TiO$_2$</td>
<td>320</td>
<td>0.007</td>
<td>0.997</td>
</tr>
<tr>
<td>0.3 Fe-TiO$_2$</td>
<td>320</td>
<td>0.009</td>
<td>0.994</td>
</tr>
<tr>
<td>0.6 Fe-TiO$_2$</td>
<td>320</td>
<td>0.011</td>
<td>0.997</td>
</tr>
<tr>
<td>1.0 Fe-TiO$_2$</td>
<td>320</td>
<td>0.003</td>
<td>0.979</td>
</tr>
</tbody>
</table>

Figure 13 shows the pseudo-first-order rate constant (k$_1$) of E3 photocatalytic degradation. In general, the photocatalytic activity first increased and then decreased as the Fe concentration increased, which is similar to the behavior found with the •OH probe in Section 2.3 and has been previously reported using other organic molecules [23,29,64].

Figure 13. Photocatalytic reaction rate (k$_1$) for degradation of E3 under high UV irradiation (a), and low UV irradiation (b); where □ zero-iron TiO$_2$, ○ 0.3 Fe-TiO$_2$, △ 0.6 Fe-TiO$_2$, and ▽ 1.0 Fe-TiO$_2$; at pH 6 ± 0.1, and 20 °C.

Under high UV irradiation (Figure 13a), 0.6 Fe-TiO$_2$ k$_1$ was higher than for zero-iron TiO$_2$, 0.3 Fe-TiO$_2$, and 1.0 Fe-TiO$_2$. The increase in photocatalytic performance of 0.6 Fe-TiO$_2$ was related with the increase in the lifetime of electron-hole pairs because Fe created additional energy levels near the conduction band of TiO$_2$, as the mechanism suggests in Figure 11.
Under low UV irradiation (Figure 13b), zero-iron TiO\textsubscript{2}, 0.3 Fe-TiO\textsubscript{2}, and 0.6 Fe-TiO\textsubscript{2} showed more photocatalytic activity than Aeroxide\textsuperscript{®} TiO\textsubscript{2} P25 because those materials had enhanced superficial properties, such as particle size, and superficial area, as mentioned in Section 2.1. Furthermore, 0.3 Fe-TiO\textsubscript{2} enhanced photocatalytic activities with \( k_1 \) values as high as 0.005 min\textsuperscript{-1}. The high photocatalytic activity of 0.3 Fe-TiO\textsubscript{2} was due to the synergistic effect of unintentionally added co-dopants, superficial properties, and Fe content that increased the lifetime of photogenerated charge carriers and the efficiency of electron transfer.

The photocatalytic degradation rate of E3 using Aeroxide\textsuperscript{®} TiO\textsubscript{2} P25 was reported to be 0.25 min\textsuperscript{-1} [65], 0.134 min\textsuperscript{-1} [66], and 0.12 min\textsuperscript{-1} [67]. However, the experimental setups and catalyst loads were different. Besides these few studies, E3 degradation using Fe-TiO\textsubscript{2} nanoparticles is scarcely reported. Only comparing magnitudes of \( k_1 \), the first-order rates to degrade pharmaceuticals using Fe-TiO\textsubscript{2} nanoparticles were 0.001 min\textsuperscript{-1} for ibuprofen, 0.0015 min\textsuperscript{-1} for carbamazepine, and 0.0014 min\textsuperscript{-1} for sulfamethoxazole [68], which are in the order of magnitude obtained in this work (see Table 4).

Regarding unintentionally added co-dopants, Fe-TiO\textsubscript{2} co-doping demonstrated a synergistic effect to increase photocatalytic activity under visible light for sulfur [69], nitrogen [44], and Fe\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{2-y}N\textsubscript{y} co-doping [70]. Surface properties of the material, such as a particle size (6.9 nm) and surface area (77.6 m\textsuperscript{2} g\textsuperscript{-1}), also facilitated the mass transfer between interface, E3, and sub-products.

The relationship between \(^{•}\text{OH}\) radical system and E3 kinetic degradation was determined via linear fit between \(^{•}\text{OH}\) initial rate generation (\( r_{0,\text{OH}} \)) and initial E3 degradation (\( r_{0,E3} \)). In general, the procedure to correlate \( r_{0,\text{OH}} \) and \( r_{0,E3} \) was first to sort pair values (\( r_{0,\text{OH}}, r_{0,E3} \)), and then fit the data to linear regression, as shown Figure 14a,b.

![Figure 14](image)

**Figure 14.** Correlation between \(^{•}\text{OH}\) initial rate generation (\( r_{0,\text{OH}} \)) and initial E3 degradation (\( r_{0,E3} \)) under high UV irradiation (a), and low UV irradiation (b); where □ zero-iron TiO\textsubscript{2}, ○ 0.3 Fe-TiO\textsubscript{2}, △ 0.6 Fe-TiO\textsubscript{2}, and ▼ 1.0 Fe-TiO\textsubscript{2}; at pH 6 ± 0.1, and 20 °C.

Under high UV irradiation, the linear fit correlation was \( r_{0,E3} = 0.091 r_{0,\text{OH}} + 0.040 \) with \( R^2 = 0.197 \). Under low UV irradiation, the linear fit correlation was \( r_{0,E3} = 0.066 r_{0,\text{OH}} + 0.012 \) with \( R^2 = 0.975 \). The correlation between the pair (\( r_{0,\text{OH}}, r_{0,E3} \)) under high UV irradiation was too low to be considered a linear relationship. We suggest the low correlation was because not only \(^{•}\text{OH}\) caused E3 degradation, but holes (h\textsuperscript{+}) or other reactive oxygen species also caused E3 degradation.

However, a linear relationship under low UV irradiation was attributable to \(^{•}\text{OH}\) being the main reactive oxygen species responsible for photocatalytic activity. Therefore, the contribution of h\textsuperscript{+} to photocatalytic activity was lower because oxidation power was lower due to reduced \( E_g \). This suggestion supports the mechanisms proposed in Figure 11, in which adding Fe into the lattice of TiO\textsubscript{2} reduced the \( E_g \) with a consistent reduction of redox potential, as mentioned by others [28].

The main mechanism of E3 degradation under low UV irradiation was via electron (e\textsuperscript{-}) transfer to give rise \(^{•}\text{OH}\). Additionally, the enhanced photocatalytic activity of 0.3 Fe-TiO\textsubscript{2} under low UV
irradiation provides evidence that the trapping-recombination mechanism of Fe-TiO$_2$ can be controlled by irradiation intensity. Therefore, we suggest that there is a trade-off between irradiation intensity, the trapping-recombination rate, and *OH production that is worthy of further research.

The efficiency resource of the Fe-TiO$_2$/Low UV system was obtained through dimensional analysis of the slope of the linear fit of data shown in Figure 14b. The units of slope are E3 moles degraded per *OH mol generated at initial time, so 0.662 E3 molecules underwent degradation when one *OH was generated for the photocatalytic system independent of Fe doping content in TiO$_2$. A sustainable process was also achieved, for which 0.3 Fe-TiO$_2$ since absorbed 8.21% of emission spectra of the lamp below the equivalent $E_g$ wavelength over 0.8% or 7.64% of Aeroxide® TiO$_2$ P25 and zero-iron TiO$_2$, respectively.

2.5. Relationship between Fe Content and Kinetic Constant

Photonic efficiency has been suggested to increase linearly with the doping ratio due to the formation of the charge carrier trapping centers, while it concurrently decreases quadratically with the doping ratio because to the creation of recombination centers [71]. Alternatively, we suggest an empirical relationship between the E3 degradation pseudo-first-order rate constant ($k_1$) and Fe content (at.%) in TiO$_2$, as described in Equation (10):

$$k_1(\delta) = c\left[e^{-k_e(\delta+\alpha)} - e^{-k_a(\delta+\alpha)}\right]$$  \hspace{1cm} (10)

where $k_1$ is the pseudo-first-order constant, $k_e$ is the electron trap constant, $k_a$ is the electron recombination constant, $\delta$ at.% is the Fe doping amount in TiO$_2$, and $c$ and $\alpha$ are system constants. To solve the model described in Equation (10), a numerical approximation by root-mean-square error minimization method was used according to Equation (11):

$$\varepsilon = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left|\frac{k_{1,i}}{k_{1,i}}\right|}$$  \hspace{1cm} (11)

where $\frac{k_{1,i}}{k_{1,i}}$ is the theoretical $k_1$ value, $\frac{k_{1,i}}{k_{1,i}}$ is the experimental $k_1$ value, $n$ is the number of data, and $\varepsilon$ is the root-mean-square error. The solution of Equation (10) was performed by simultaneously solving $k_e$, $k_a$, $c$, and $\alpha$ using Excel Solver® (Frontline Systems, NV, US). As an example, photocatalytic degradation of E3 under low UV irradiation was fitted to Equation (10), as shown in Figure 15.

The empirical model solved in Equation (12) shows that electron trap constant ($k_e$) overcome electron recombination ($k_a$) before optimal catalyst load. This model could lead to experimental work using iron-doped TiO$_2$ in which the optimal content of Fe gives rise to the maximum E3 degradation.

$$k_1(\delta) = -1.99\left[e^{-2.81(\delta+0.197)} - e^{-2.78(\delta+0.197)}\right]$$  \hspace{1cm} (12)
Figure 12. Photocatalytic degradation of E3 under high UV irradiation (Figure 13a), 0.6 Fe-TiO$_2$ k 1 \leq 0.009, 0.994 \leq 0.090, 0.005 \leq 0.992, 0.042 \leq 0.030; at pH 6 ± 0.1, and 20 °C.

Table 4. Kinetic values of E3 degradation using zero-iron TiO$_2$, 0.3 Fe-TiO$_2$, 0.6 Fe-TiO$_2$, and 1.0 Fe-TiO$_2$; at pH 6 ± 0.1, and 20 °C.

<table>
<thead>
<tr>
<th>Catalyst Load</th>
<th>High UV Irradiation</th>
<th>Low UV Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>zero-iron TiO$_2$</td>
<td>k$_1$ R $\propto$ r$_0$,E3 k$_1$ R $\propto$ r$_0$,E3</td>
<td>k$_1$ R $\propto$ r$_0$,E3 k$_1$ R $\propto$ r$_0$,E3</td>
</tr>
<tr>
<td>0.3 Fe-TiO$_2$</td>
<td>320 μM</td>
<td>0.003</td>
</tr>
<tr>
<td>0.6 Fe-TiO$_2$</td>
<td>320 μM</td>
<td>0.011</td>
</tr>
<tr>
<td>1.0 Fe-TiO$_2$</td>
<td>320 μM</td>
<td>0.009</td>
</tr>
<tr>
<td>Aeroxide® TiO$_2$</td>
<td>320 μM</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Figure 15. Experimental relationship between pseudo first order constant and at.% content; where □ zero-iron TiO$_2$, ○ 0.3 Fe-TiO$_2$, ▲ 0.6 Fe-TiO$_2$, and ▼ 1.0 Fe-TiO$_2$; at pH 6 ± 0.1; and 20 °C.

3. Materials and Methods

3.1. Reagents

Sigma-Aldrich (St. Louis, MO, USA) supplied estriol (E3, C$_{18}$H$_{24}$O$_3$, ≥97%), titanium isopropoxide (TTIP, Ti[OCH(CH$_3$)$_2$]$_4$, 97%), N,N-Dimethyl-4-nitrosoaniline (pNDA, also called RNO, C$_8$H$_{10}$N$_2$O, 97%), sodium dodecyl sulfate (SDS), and iron (III) nitrate (Fe(NO$_3$)$_3$·9H$_2$O, >99.99%). Aeroxide® TiO$_2$ P25 (formerly Degussa P25 with 50 ± 15 m$^2$ g$^{-1}$ of the specific surface area, 21 nm of average particle size, 80:20 of anatase:rutile ratio according to the manufacturer) granted by Evonik Industries (Essen, Germany) was the photocatalytic standard. Fremont (CA, USA) supplied HNO$_3$, H$_2$SO$_4$, absolute ethanol, HPLC-grade methanol, and HPLC-grade water. All chemicals were used as received.

3.2. Photoreactor Setup

Figure 16 depicts the photoreactor, which was a cylindrical water-jacketed glass vessel (318 mL) with 102 mm and 63 mm of interior height and diameter, respectively. The horizontal and vertical position of the photoreactor was constant for all experiments. Lamps were set horizontally and centered above the photoreactor. Two 15 W GE F15T8 BLB lamps (also called black-light lamps, Boston, MA, USA) supplied high UV irradiation, and two 15 W GE F15T8 D lamps (also called daylight lamps) provided low UV irradiation. The overall system was in a closed box to avoid the effects of sunlight or any artificial radiation sources. Lamp emission spectra were measured using a lab-made spectrophotometer using a CMOS webcam with a diffraction grating of 1000 lines mm$^{-1}$ [72,73]. Emission spectra calibration of the spectrophotometer was developed using a 9 W fluorescent lamp (Tecnolite, Jalisco, Mexico). The temperature of all experiments was set at 20 °C using a thermostatic bath with recirculation (Polystat, Cole-Palmer, Vernon Hills, IL, USA). An optical filter was not used in the experiments, so visible light condition was not simulated.
A was continuously stirred and solution B was slowly dropped into solution A. The pH of the resulting mixture was adjusted to 1 using concentrated HNO₃ and stirred for 3 h. The mixture was kept at 3 °C for 36 h. The precipitated solid was collected by filtration using Whatman Quantitative Filter Paper Grade 42. The materials were simultaneously dried and calcinated with a programmed thermal treatment [49]. Our synthesis method used iron (III) nitrate instead of FeCl₃ and absolute ethanol instead of isopropyl alcohol. The thermal treatment was a programmed cycle of 31 h (increasing ramp-drying-increasing ramp-calcination-decreasing ramp) instead of direct calcination for 6 h. First, solution A was prepared by dissolving 1.44 g of SDS in 10 mL of deionized water. Then, four different solutions B were prepared to dissolve iron (III) nitrate in 2 mL of absolute ethanol (≥99.8 %) and 3 mL of TTIP was added slowly. The amounts of iron (III) nitrate were 0, 0.4, 4.3, and 42.6 mg of Fe(NO₃)₃·9H₂O identified as zero-iron TiO₂, 0.3 Fe-TiO₂, 0.6 Fe-TiO₂, and 1.0 Fe-TiO₂, respectively. Once ready, solution A was continuously stirred and solution B was slowly dropped into solution A. The pH of the resulting mixture was adjusted to 1 using concentrated HNO₃ and stirred for 3 h. The mixture was kept at 3 °C for 36 h. The precipitated solid was collected by filtration using Whatman Quantitative Filter Paper Grade 42. The materials were simultaneously dried and calcinated with a programmed thermal treatment (Isotemp® Programmable Muffle Furnace, Fisher Scientific, Dubuque, IA, USA) following first the temperature increase from ambient temperature to 353 K, with a temperature ramp of 1 K min⁻¹ that was held for 720 min. The temperature was then increased from 353 K to 773 K with a temperature ramp of 1 K min⁻¹ that was held for 360 min. Finally, the temperature was decreased from 773 K to 353 K with a temperature ramp of −1 K min⁻¹, and then the furnace was turned off. The materials were washed with 50:50 methanol-water and dried to 377 K overnight.

3.3. Synthesis of Materials

The synthesis method of iron-doped TiO₂ (Fe-TiO₂) materials followed the hydrothermal sol-gel synthetic approach proposed by Patra et al. with some differences in precursor and thermal treatment [49]. Our synthesis method used iron (III) nitrate instead of FeCl₃ and absolute ethanol instead of isopropyl alcohol. The thermal treatment was a programmed cycle of 31 h (increasing ramp-drying-increasing ramp-calcination-decreasing ramp) instead of direct calcination for 6 h. First, solution A was prepared by dissolving 1.44 g of SDS in 10 mL of deionized water. Then, four different solutions B were prepared to dissolve iron (III) nitrate in 2 mL of absolute ethanol (≥99.8 %) and 3 mL of TTIP was added slowly. The amounts of iron (III) nitrate were 0, 0.4, 4.3, and 42.6 mg of Fe(NO₃)₃·9H₂O identified as zero-iron TiO₂, 0.3 Fe-TiO₂, 0.6 Fe-TiO₂, and 1.0 Fe-TiO₂, respectively. Once ready, solution A was continuously stirred and solution B was slowly dropped into solution A. The pH of the resulting mixture was adjusted to 1 using concentrated HNO₃ and stirred for 3 h. The mixture was kept at 3 °C for 36 h. The precipitated solid was collected by filtration using Whatman Quantitative Filter Paper Grade 42. The materials were simultaneously dried and calcinated with a programmed thermal treatment (Isotemp® Programmable Muffle Furnace, Fisher Scientific, Dubuque, IA, USA) following first the temperature increase from ambient temperature to 353 K, with a temperature ramp of 1 K min⁻¹ that was held for 720 min. The temperature was then increased from 353 K to 773 K with a temperature ramp of 1 K min⁻¹ that was held for 360 min. Finally, the temperature was decreased from 773 K to 353 K with a temperature ramp of −1 K min⁻¹, and then the furnace was turned off. The materials were washed with 50:50 methanol-water and dried to 377 K overnight.

3.4. Materials Characterization

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectrometer (Waltham, MA, USA) with a monochromatized Al Kα X-ray source (1487 V). The deconvolution of high-resolution XPS spectra was developed using the software XPSpeak 4.1. (Raymund W.M. Kwok, Shatin, Hong Kong).
UV-visible reflectance spectroscopy was obtained with Video–Barrelino integrating sphere coupled to Cary 50 spectrophotometer (Varian Inc, Palo Alto, CA, USA). Diffuse reflectance spectra were transformed using the Kubelka–Munk method to obtain $E_g$ of zero-iron TiO$_2$ and Fe-TiO$_2$ materials. Kubelka–Munk method plots $(F(R)hv)^{1/2}$ versus $hv$, draws a tangent at the inflection point on the curve and estimates $E_g$ with the $hv$ value at the intersection with abscissa. In this case, $F(R)$ is a reflectance function equal to $(1 - R)^2/2R$, $R$ is the reflectance percentage, $h$ is the Planck’s constant, and $v$ is frequency.

XRD patterns were recorded in a Siemens D-5000 diffractometer (Munich, Germany) using Cu K$_\alpha$ radiation ($\lambda = 1.54060$ Å) from $10^\circ$ to $85^\circ$. The procedure for phase identification used the QualX2.0 software with database developed by Altomare et al. [74]. The cards used for identification were 00-901-5929, 00-900-1681, and 00-900-4140 for anatase, rutile, and brookite, respectively. The quantification phases followed the method proposed by Spurr and Myers according to Equation (13):

$$f = \frac{1}{1 + 1.26 \frac{I_R}{I_A}}$$

where $f$ is the anatase percentage, $I_A$ is intensity at a diffraction angle $2\theta$ of 25.36$^\circ$, and $I_R$ is intensity at a diffraction angle $2\theta$ of 27.46$^\circ$ [75].

The particle size was estimated by Scherrer’s formula described in Equation (14), where $\beta$ is the full width at half of the maximum of the diffraction peaks (radians), $k$ is the shape constant, $\lambda$ is the wavelength of the incident Cu K$_\alpha$ radiation ($\lambda = 1.54060$ Å), $\theta$ is the Bragg’s angle (radians), and $D$ is the particle size (Å).

$$D = \frac{k \lambda}{\beta \cos \theta}$$

Brunauer–Emmett–Teller (BET) isotherms were obtained in Nova Station A equipment (Quantachrome Instruments, Boynton Beach, FL, USA). The surface morphology was observed by SEM in a JEOL ultrahigh resolution field emission electron microscope JSM-7800 F (JEOL, Tokyo, Japan) with 20 kV accelerating voltage, and 3 mm WD. Transmission electron microscopy (TEM) images were obtained in a JEM-2100 LaB6 electron microscope (JEOL, Tokyo, Japan).

3.5. Hydroxyl Radical Generation

In this study, pNDA bleaching was selected as an •OH probe because pNDA was useful for measuring the photocatalytic performance of TiO$_2$ [51,76,77] because of the following advantages: (1) it is selective of the reaction of pNDA with •OH [78]; (2) its high reaction rate with •OH on the order of $10^{10}$ M$^{-1}$ s$^{-1}$ [51,79]; (3) its easy application through observable bleaching at 440 nm following Beer’s Law, in which pNDA bleaching a yellowish solution to transparent; and (4) its 1:1 stoichiometry, meaning that one •OH can bleach one pNDA molecule [51,80–82].

The pNDA absorption (Figure 17) measurements were obtained using a UV-visible spectrophotometer (Hatch DR/4000U, Loveland, CO, USA) at 440 nm following Beer-Lambert law. The pNDA test solution was 10 µM initial concentration and pH 6.0 ± 0.1 adjusted using NaOH or HCl when needed. No buffer solutions were used because they can compete for •OH. Final pH was verified at the end of tests to discharge pH-pNDA bleaching.
The adsorption of pNDA was detected near the detection limit of UV-visible spectrophotometer. Once the catalyst load was used and after the dark phase, no adsorption of pNDA was detected. Aliquots were withdrawn after specific periods. Each sample was centrifuged at 6000 rpm for 15 min (Biofuge Primo, Sorvall, Hanau, Germany) and measured in the UV-visible spectrophotometer. The system was fully illuminated, and aliquots were withdrawn after specific periods. To evaluate the adsorption of pNDA on TiO\textsubscript{2}, an aliquot was withdrawn and centrifuged. Then, the system was fully illuminated, and aliquots were withdrawn after specific periods. Each sample was centrifuged at 6000 rpm for 15 min (Biofuge Primo, Sorvall, Hanau, Germany) and measured in the UV-visible spectrophotometer.

The photocatalytic experiments were conducted as follows. First, a pNDA test solution was set at 20 °C, the catalyst was added, and the suspension was mixed for 20 min without radiation. To evaluate the adsorption of pNDA on TiO\textsubscript{2}, an aliquot was withdrawn and centrifuged. Then, the system was fully illuminated, and aliquots were withdrawn after specific periods. Each sample was centrifuged at 6000 rpm for 15 min (Biofuge Primo, Sorvall, Hanau, Germany) and measured in the UV-visible spectrophotometer. Once the catalyst load was used and after the dark phase, no adsorption of pNDA was detected near the detection limit of UV-visible spectrophotometer.

Figure 17. Structural formula and absorbance spectrum of N,N-dimethyl-p-nitrosoaniline (pNDA).

The photocatalytic standard was Aeroxide\textsuperscript{®} TiO\textsubscript{2} P25, and the load was 20 mg L\textsuperscript{-1}. The choice of catalyst load was based on our previous work on \textsuperscript{•}OH generation of Aeroxide\textsuperscript{®} TiO\textsubscript{2} P25 [16]. For zero-iron TiO\textsubscript{2} and Fe-TiO\textsubscript{2} materials, the catalyst load used was 320 mg L\textsuperscript{-1}, which produced a \textsuperscript{•}OH generation rate under high UV irradiation to set a baseline. Catalyst load differences were attributable to the aggregation of lab-made TiO\textsubscript{2}, superficial properties, and optical properties of suspensions, as shown in Figure 18.

Figure 18. Suspension transmittance of Fe-TiO\textsubscript{2} material and Aeroxide TiO\textsubscript{2} P25; where zero-iron TiO\textsubscript{2} (a), 0.3 Fe-TiO\textsubscript{2} (b), 0.6 Fe-TiO\textsubscript{2} (c), and 1.0 Fe-TiO\textsubscript{2} (d).


3.6. Photolysis and Photocatalytic Degradation of E3

The initial E3 concentration was 10 µM because (1) this research was part of a project focused on the removal of E3 in water using sequentially coupled membrane filtration; (2) the solubility limit of E3 in water was previously reported to be 11.1 µM [83], and 45.1 µM [8,84], and (3) the sensitivity of the analytical techniques used in this work. The E3 solution was prepared to dissolve 2.88 mg of E3 in 1 L of deionized water by stirring at room conditions in the dark for six hours. Working solutions were stored in an amber flask.

Each photocatalytic experiment used 100 mL of E3 working solution. Initial pH was adjusted to obtain a similar surface charge of TiO$_2$ [85]. Depending on the initial water conditions, the initial pH value was adjusted to 6.0 ± 0.1 using NaOH or HCl when needed. A dark period (no radiation) was allowed for 20 min. Then, similar experimental conditions were carried out as described in Section 3.5. Additionally, the aliquots withdrawn from suspension were filtered using a 0.1 µm syringe filter (MillexVV, Millipore, Billerica, MA, USA). A blank experiment without irradiation and TiO$_2$ photocatalyst was conducted for comparison. The blank experiment showed that E3 cannot be degraded in the absence of either TiO$_2$ or UV light. Once the catalyst was loaded and after the dark phase, no adsorption of E3 was detected near the detection limit of HPLC.

3.7. Analytical Methods

The E3 concentration was monitored using an HPLC system (Waters 1515; Milford, MA, USA) equipped with a UV detector (Waters 2787) that has an injection volume of 20 µL. The analytical method was performed in isocratic analytical mode using an Inertsil® ODS-3 column (GL Science, Tokyo, Japan; 150 mm × 4.6 mm, 5 µm) thermostated at 25 °C. The wavelength was at 280 nm according to E3 maximum absorbance. The mobile phase was methanol (49%) and deionized water (51%) at a flow rate of 1 mL min$^{-1}$. The retention time of E3 was 10 min, and the limit of E3 detection was 0.1 µM (0.029 mg L$^{-1}$). The detection limit was obtained by developing two calibration curves: the first between 10 and 0.1 and second between 1 and 0.01. Both calibration curves followed area = 2928[E3] with R$^2$ = 0.9899, but areas below 0.1 were not detected.

4. Conclusions

This study provided an understanding of the relationship between the Fe doping ratio and radiation intensity for •OH generation and estriol (E3) degradation. The main results were that:

- E3 degradation using 0.3 Fe-TiO$_2$ was feasible and can be improved by controlling radiation intensity which was found closely related with light absorption and the catalytic reaction rate;
- the synthesis method and thermal treatment allowed nanoparticles with large superficial areas and the incorporation of iron ions into the TiO$_2$ lattice.; and
- changes in trapping recombination centers could be controlled with irradiation intensity to enhance the photocatalytic activity.

Therefore, our findings provide the opportunity to reconsider studies in which iron-doped TiO$_2$ impaired photocatalytic activity and to improve an application in which irradiation should be controlled. For example, Fe-TiO$_2$ can potentially be applied to medical uses in which low irradiation intensity should be used to avoid adverse effects in humans or wildlife, which has also been suggested by others [86]. In the field of water treatment, we propose that Fe-TiO$_2$ is an efficient material that could harvest low-energy photons to degrade and mineralize dyes [87], biocides [88], pharmaceuticals [89], industrial chemicals [90], and estrogens—as shown in this study—to create an energetically green water treatment process.

Author Contributions: Funding acquisition, E.R.B.; Investigation, I.M.R.-S.; Project administration, E.R.B.; Supervision, E.R.B.; Writing—original draft, I.M.R.-S.; Writing—review & editing, E.R.B.
**Funding:** This manuscript is based on work supported in part by ConTex postdoctoral program, which is an initiative of the University of Texas System and Mexico’s National Council of Science and Technology (CONACYT). The research was partially funded by CONACYT under Project CB-2011/168285. The APC was funded by the Institutional Open Access Program (IAOP) between The University of Texas at Austin and Desert Research Institute (DRI) at Nevada.

**Acknowledgments:** The Aeroxide® P25 Evonik catalyst used for this work was provided by Intertrade S.A. de C.V., the supplier of Evonik Industries in Mexico. The authors thank L. Lartundo-Rojas, Raul Borja Urbi, Hugo Martinez Gutierrez, and Joao Jairzinho Salinas Camargo for assistance in XPS spectroscopy, TEM images, SEM images, and absorption isotherms, respectively, all of whom are from Centro de Nanociencias y Micro y Nanotecnologia (CNMN) of IPN, Mexico. The authors thank M.A. Quiroz Alfaro for his excellent technical help and for his permission to use materials and equipment at the UDLAP’s electrochemical lab. The authors also thank Nicole Damon (DRI) for her editorial review.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**


40. Seabra, M.P.; Salvado, I.M.M.; Labrincha, J.A. Pure and (zinc or iron) doped titania powders prepared by sol-gel and used as photocatalyst. *Ceram. Int.* 2011, 37, 3317–3322. [CrossRef]


90. Hemmati Borji, S.; Nasseri, S.; Mahvi, A.; Nabizadeh, R.; Javadi, A. Investigation of photocatalytic degradation of phenol by Fe(III)-doped TiO₂ and TiO₂ nanoparticles. *J. Environ. Health Sci. Eng.* **2014**, *12*, 101. [CrossRef] [PubMed] © 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).