Article

Photocatalytic Degradation of Azo Dye Reactive Violet 5 on Fe-Doped Titania Catalysts under Visible Light Irradiation

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Abstract: The presence of azo dyes in textile effluents is an issue of major concern due to their potential impact on the environment and human health. In this study we investigate the photocatalytic degradation under visible light of Reactive Violet 5 (RV5), an azo dye widely used in the textile industry. A preliminary screening of different titania-based catalysts was carried out to identify the best candidate for RV5 removal. The selected catalyst was then tested in a stirred and aerated lab-scale reactor illuminated with a light LED source (λ_{max} = 460 nm). The effects of pH, catalyst load and hydrogen peroxide additions on the efficiency of dye removal were evaluated. Under the best conditions (pH 10, 3 g/L of catalyst and 60 mM hydrogen peroxide), the dye solution was completely decolorized in about 2 h. Overall, the results obtained suggest that the proposed process may represent a suitable method for the removal of RV5 from textile effluents.

Keywords: photocatalysis; visible light; titania catalysts; azo dye; reactive violet 5; textile wastewater

1. Introduction

Azo dyes are the largest class of dyes used in industry [1]. These compounds are characterized by the presence of one or more azo bonds (–N=N–) in their molecule in association with one or more aromatic structures [2]. In the textile industry, the use of azo dyes for coloring cellulosic fibers such as cotton and wool has increased significantly over the last decades due to their cost effectiveness, brightness of color and good resistance to washing and light exposure. A major drawback related to their application on textiles is the low fixation yield of the dye on the fiber caused by the hydrolysis of the reactive groups in the dye molecule [3]. As a result, up to about 30% of the initial amount of dye can be lost in water [4].

The presence of azo dyes in textile effluents makes them particularly harmful to the environment and to human health [5]. In fact, their release into aquatic ecosystems may lead to a reduction of sunlight penetration and dissolved oxygen concentration, with deleterious effects on local flora and fauna [6]. In addition, toxic and potentially carcinogenic compounds such as aromatic amines can be formed during dye degradation [7]. For these reasons, textile wastewater needs to be properly treated.

Since conventional water treatments are often ineffective in eliminating azo dyes from textile effluents, more efficient technologies, such as the advanced oxidation processes (AOPs), are used [8,9]. AOPs are based on the generation of highly reactive radical species, such as hydroxyl radicals

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(•OH), by solar, chemical or other forms of energy. These radicals can attack the target compounds through different reaction mechanisms leading to their degradation [10, 11].

In this paper we investigate the degradation of Reactive Violet 5 (RV5) by a photocatalytic treatment with Fe-doped TiO_2 photocatalysts exposed to visible light. RV5 is widely used in textile dyeing because of its brightness, ease of application and good fastness to washing. However, its complex aromatic structure (Figure 1) makes it highly resistant to degradation. A literature survey shows that very few studies have been performed on RV5 degradation, and none of them has investigated the photocatalytic removal of the dye under visible light [12–16]. Accordingly, a first aim of this study was to evaluate whether the use of the selected photocatalyst in the presence of visible light could be a suitable method to degrade RV5. Second, we were interested in assessing the effect of the main process parameters on the efficiency of dye removal and the possibility of enhancing it by addition of hydrogen peroxide.

The results obtained indicate that the proposed process may represent a viable and promising approach for the removal of RV5 from textile effluents.

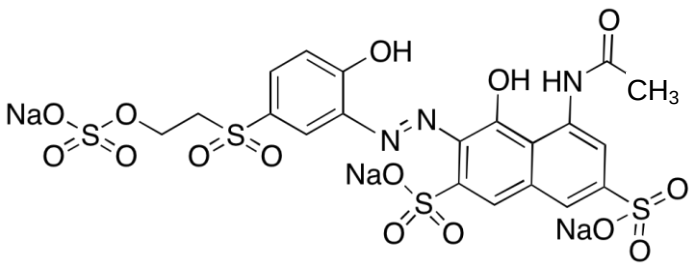

Figure 1. Chemical structure of azo dye Reactive Violet 5 (RV5).

2. Materials and Methods

2.1. Materials

Sodium hydroxide (NaOH, CAS 1310-73-2), sodium hydrogen carbonate ($NaHCO_3$, CAS 144-55-8), disodium hydrogen phosphate (Na_2HPO_4, CAS 7558-79-4), potassium dihydrogen phosphate (KH_2PO_4, CAS 7778-77-0), sodium acetate (CH_3COONa, CAS 127-09-3), acetic acid (CH_3COOH, CAS 64-19-7) and hydrogen peroxide (30 wt% in water, CAS 7722-84-1), iron acetylacetonate ($Fe(C_5H_7O_2)_3$, CAS 14024-18-1), titanium isopropoxide ($C_{12}H_{28}O_4Ti$, CAS 546-68-9) were purchased from Sigma-Aldrich Co. (St. Louis, Mo, USA). All chemicals were reagent grade and used as received.

RV5 of technical grade ($C_{20}H_{16}N_3Na_3O_{15}S_4$, MW 735.59 g mol^{-1}, color index number 18097) was provided by Gammacolor Srl (Seveso, Italy) and used as received. The natural pH of the dye solution was 7.2 ± 0.1. When needed, RV5 was dissolved in the following buffers: acetate buffer (0.1 M, pH 4), phosphate buffer (0.1 M, pH 6 and 8) and carbonate buffer (0.1 M, pH 10 and 12).

2.2. Catalysts Preparation and Characterization

P-25 Degussa was obtained from Sigma-Aldrich Co. (St. Louis, Mo, USA). Fe-TiO_2 photocatalysts were prepared by sol-gel method. In particular, 50 mg of iron acetylacetonate was dissolved in 25 mL of titanium isopropoxide. The obtained solution was sonicated in order to obtain the complete solubilization of iron acetylacetonate. Then, 100 mL of distilled water were added to obtain a precipitate which was separated from the liquid phase by centrifugation for 5 min at 5,000 rpm. The sample was washed with distilled water for three times to remove any impurities and it was calcined at 450 °C for 30 min [17]. The obtained samples were named x Fe-TiO_2 where x is the amount (in mg) of iron acetylacetonate used in the synthesis. The list of the prepared photocatalysts with the amount of chemicals used in the preparation procedure is reported in Table 1.

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All the photocatalysts were characterized using different techniques. The Raman spectra of the samples were recorded with a Dispersive MicroRaman system (Invia, Renishaw), equipped with 514 nm laser, in the range 100-2,000 cm^{-1} Raman shift. The crystal phases of photocatalysts were determined by XRD analysis carried out on Bruker D8 diffractometer, using Cu-Kα radiation. The surface area (SSA) of the catalysts was obtained from the dynamic N_2 adsorption measurement at −196 °C, using a Costech Sorptometer 1042 instrument, after a pre-treatment of the samples at 150 °C for 30 min in He flow. UV−vis reflectance spectra of powder catalysts were recorded by a Perkin Elmer spectrometer Lambda 35 using an RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). All spectra were obtained using an 8° sample positioning holder, giving total reflectance relative to a calibrated standard SRS-010-99 (Labsphere Inc., North Sut-ton, NH). Equivalent band gap determinations of the photocatalysts were obtained from Kubelka–Munk function $F(R_\infty)$ by plotting $[F(R_\infty) \times h\nu]^2$ vs. $h\nu$.

Table 1. List of the prepared photocatalyst, amount of chemicals used in the synthesis and Fe/Ti molar ratio.

Photocatalysts	$Fe(C_5H_7O_2)_3$ Amount [mg]	Titanium isopropoxide [mL]	Distilled water [mL]	Fe/Ti molar ratio [mol/mol]
TiO_2	0	25	100	0
10Fe-TiO_2	10	25	100	0.00033
50Fe-TiO_2	50	25	100	0.0017
100Fe-TiO_2	100	25	100	0.0033

2.3. Photocatalytic Apparatus

The experimental apparatus consisted of a borosilicate glass cylindrical photoreactor (ID = 3 cm, H = 18 cm) equipped with an air distributor and a magnetic bar. A flexible LED strip (SMD 5050, 60 LED/m, 0.24 W/LED) with an overall length of 1.5 m was wrapped around the reactor and used as light source. The emission wavelength of the LEDs was 460 nm. The air distributor provided a maximum flow rate of 300 NL/h and was placed at the bottom of the reactor, just above the stirring bar. Darkness conditions were achieved by covering the photocatalytic apparatus with an aluminum foil.

2.4. Photodegradation Experiments

Photodegradation experiments were carried out by putting 50 mL of the aqueous solution containing the dye and the catalyst in the reactor. The system was left in the dark under stirring for 1 h to allow the adsorption-desorption equilibrium of RV5 on photocatalyst surface. Then, the light source was switched on and the reactor was aerated. At the desired time, a small sample of liquid was taken, filtered at 0.45 μm and analysed spectrophotometrically. Measurements were made on a double-beam UV-Vis spectrophotometer (UV-2700, Shimadzu, Japan) at 560 nm, where the absorption spectrum of RV5 displays a maximum. The stirring rate was set at 400 rpm and the air flow rate at 200 NL/h. The initial dye concentration was varied between 20 and 100 ppm and the catalyst load between 0.5 and 6 g/L. When required, hydrogen peroxide was added in the appropriate amount to the reaction mixture.

3. Results and Discussion

3.1. Catalysts characterizations

The XRD results of undoped and doped TiO_2 with different Fe content are reported in Figure 2 It was possible to observe that the crystalline structure of the photocatalysts showed only patterns related to anatase TiO_2 for all the samples [18]. No signals due to iron oxides appear in the XRD patterns, suggesting insignificant iron segregation in Fe-doped TiO_2 samples [19].

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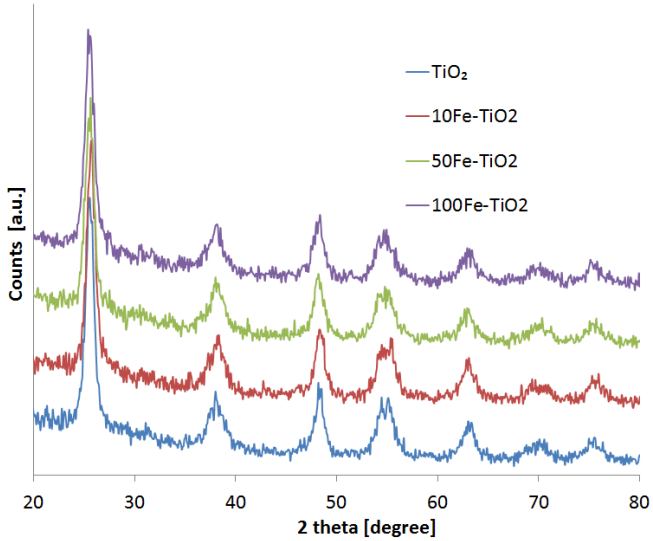

Figure 2. XRD spectra of the photocatalysts.

Since the ionic radius of the Fe^{3+} ion (0.064 nm) is smaller than that one of the Ti^{4+} ion (0.068 nm) [20], and considering that the Pauling electronegativities of Fe^{3+} (1.83) and Ti^{4+} (1.54) are similar [21], Fe^{3+} ions may enter the crystal cell of TiO_2 at substitutional sites [22]. To better investigate this aspect, the XRD spectra of the photocatalysts were more accurately analyzed in the range 20-30° (Figure 3).

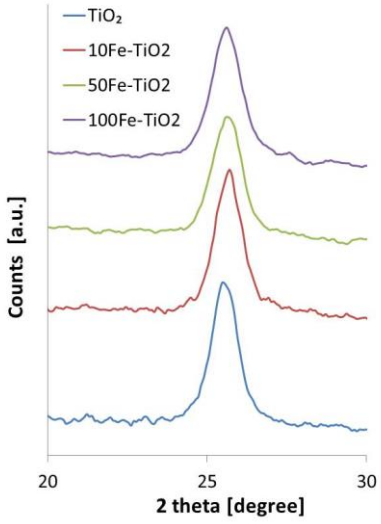

Figure 3. XRD spectra of the photocatalysts in the range 20–30°.

It is possible to observe that the diffraction peak of undoped TiO_2 at about 25.3 °shifted to higher angle for all the Fe-doped TiO_2 samples, indicating that doping of TiO_2 with iron led to a decrease of the lattice parameters. This phenomenon is a clear indication that our preparation method for the doped photocatalysts induced a replacement of the lattice Ti^{4+} ions by Fe^{3+} ions [22], evidencing, therefore, the successful doping of the TiO_2 crystalline structure with iron.

The crystalline size of the photocatalysts was calculated on the diffraction pattern visualized in Figure 3, using Scherrer's formula (Table 2).

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Table 2. List of the prepared photocatalyst and their characteristics.

Photocatalysts	Crystalline size [nm]	SSA [m²/g]	Band gap energy [eV]
TiO_2	8.4	169	3.20
10Fe-TiO_2	8.3	171	3.12
50Fe-TiO_2	7.9	179	2.90
100Fe-TiO_2	7.9	179	2.63

The calculated crystalline size for undoped TiO_2 was 8.4 nm and only a slight decrease for Fe doped TiO_2 samples was observed. Possibly, this phenomenon is due to the entrance of Fe^{3+} into the TiO_2 lattice [23], inducing also an increase of SSA values (Table 2) with respect to undoped TiO_2, as observed in literature [24].

Raman spectra in the range of 200-800 cm^{-1} of the doped catalysts and undoped TiO_2 are shown in Figure 4. In particular, only the TiO_2 common signals at 144, 396, 514, 637 cm^{-1} and a weak shoulder at 195 cm^{-1} due to the anatase crystalline phase of TiO_2 are evident [25]. Also in this case, no signals due to iron oxides are evident. These results confirm that TiO_2 doping process was correctly finalized.

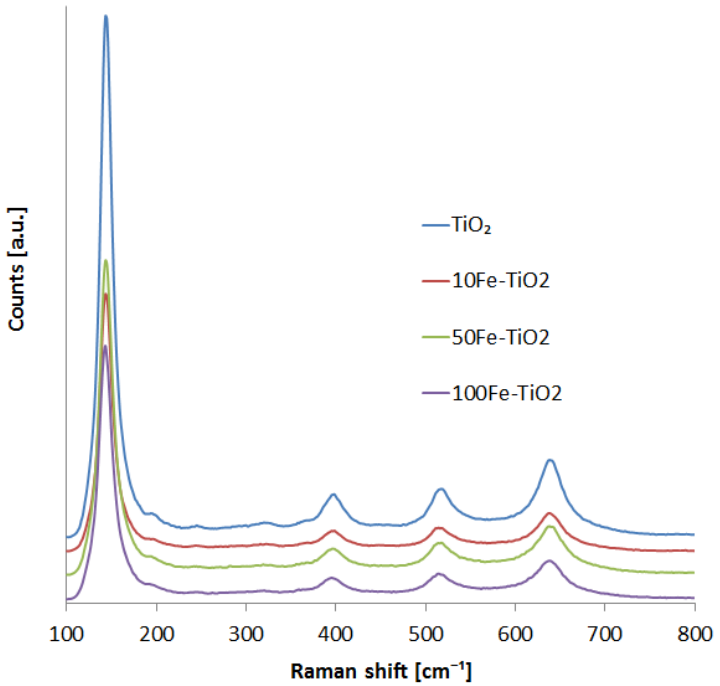

Figure 4. Raman spectra of undoped and Fe doped TiO_2 photocatalysts in the range 100–800 cm^{-1}.

Additionally, the intensity of the Raman bands for all the doped samples is lower than those ones of undoped TiO_2, supporting again the incorporation of Fe^{3+} into the substitution site of the TiO_2 lattice [26].

The data obtained from UV–Vis reflectance spectra were used for evaluating the band-gap energy of TiO_2 and of Fe-doped TiO_2 photocatalystsy (Figure 5). The doping of TiO_2 with iron significantly influenced the band-gap energy value. In fact, as the Fe amount was increased, a decrease of band-gap energy (from 3.20 for undoped TiO_2 to 2.63 eV for 100Fe-TiO_2) was observed.

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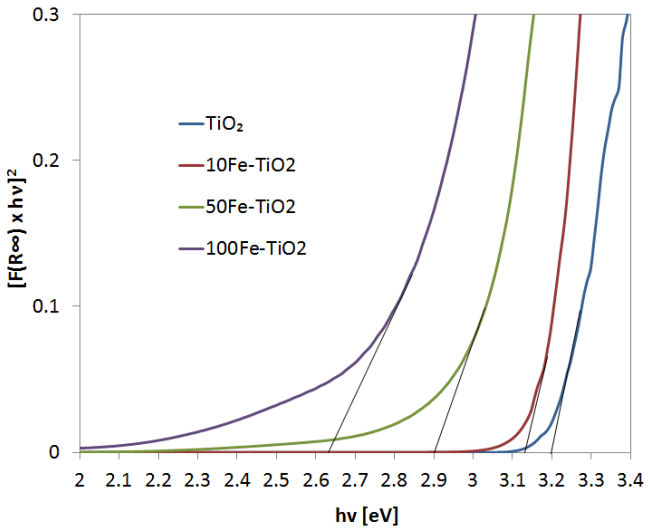

Figure 5. Band gap evaluation of for undoped and Fe-doped TiO_2 photocatalysts.

This decrease was due to the electronic transition from donor levels formed with dopants to the conduction band of the host photocatalyst [27]. The band-gap energy value of Fe-doped TiO_2 samples is an indication of their potential photoactivity under visible light irradiation.

3.2. Catalyst Screening and Selection

Preliminary experiments were performed to evaluate whether RV5 could be degraded by a photocatalytic treatment. In these experiments, the concentrations of the dye and the catalyst were held constant at 30 ppm and 3 g/L, respectively, so as to operate with a dye-to-catalyst weight ratio of 1:100. The photodegradation process was carried out at the spontaneous pH of the dye solution (pH 7.2) for an overall duration of 10 h (1-h darkness and 9-h irradiation). The following catalysts were tested: P-25 Degussa (P-25) and Fe-doped TiO_2 at three Fe levels: 10Fe-TiO_2, 50Fe-TiO_2 and 100Fe-TiO_2. The results are shown in Figure 6.

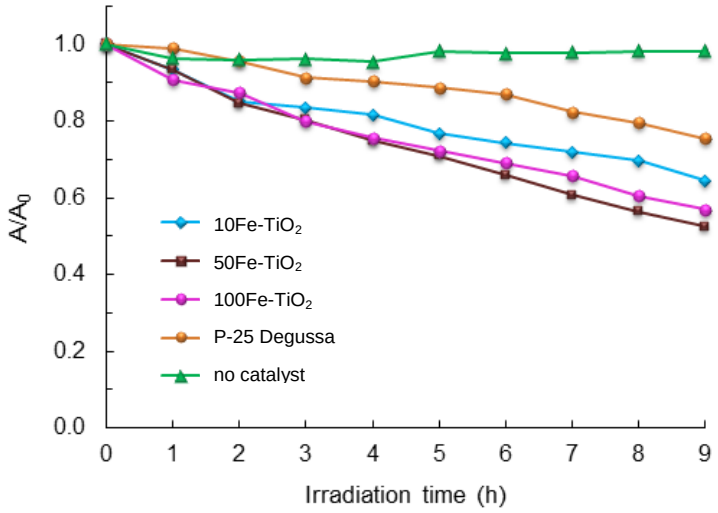

Figure 6. Photocatalytic degradation of Reactive Violet 5 (RV5) in the absence and presence of different catalysts (c^0_{RV5} = 30 ppm; pH = 7.2; catalyst load = 3 g/L). A is the absorbance of the dye solution at 560 nm.

The first point to note is that in the absence of catalyst no significant variations in dye concentration were observed, while all catalysts were able to degrade RV5. The removal efficiencies at the end of the treatment ranged from about 23% (P25) to 47.6% (50Fe-TiO_2). Furthermore, a closer analysis of the results in Figure 5 reveals that:

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- P-25 resulted in a color removal close to 23% at the end of the treatment;
- 100Fe-TiO_2 showed a final decolorization degree close to 42%;
- 10Fe-TiO_2 exhibited an intermediate behavior and decolorized the dye solution to about 35%;
- 50Fe-TiO_2 was the most effective catalyst, with a color removal efficiency of 47.6%.

It may be interesting to consider that, although the band-gap energy of 100Fe-TiO_2 is smaller than that of 50Fe-TiO_2 (2.63 and 2.90 eV, respectively), the first catalyst exhibited a lower photocatalytic activity. This could be due to the higher content of Fe(III) ions, which can act as recombination centers for the photogenerated hole-electron pairs [28,29].

Since 50Fe-TiO_2 was the most effective of the catalysts tested, it was selected as the best catalyst for RV5 degradation under visible light irradiation.

3.3. Analysis of the UV-vis Absorption Spectrum of RV5 During Degradation

Figure 7 shows the UV-Vis spectrum of RV5 and its changes during the photodegradation process. A prominent feature of the dye spectrum is the presence of two main bands centered around 220 and 560 nm. The broad band at 560 nm arises from the chromophoric group of the dye molecule, while that at 320 nm can be related to the aromatic groups in the molecule [30].

During photodegradation, the intensity of both bands decreased. The reduction in the intensity of the band at 560 nm indicates a decrease in the conjugation of the chromophore moiety, resulting in a progressive decolorization of the dye solution. The decrease of the band at 220 nm and the spectral changes at lower wavelengths suggest that also the aromatic part of the molecule was affected by the treatment.

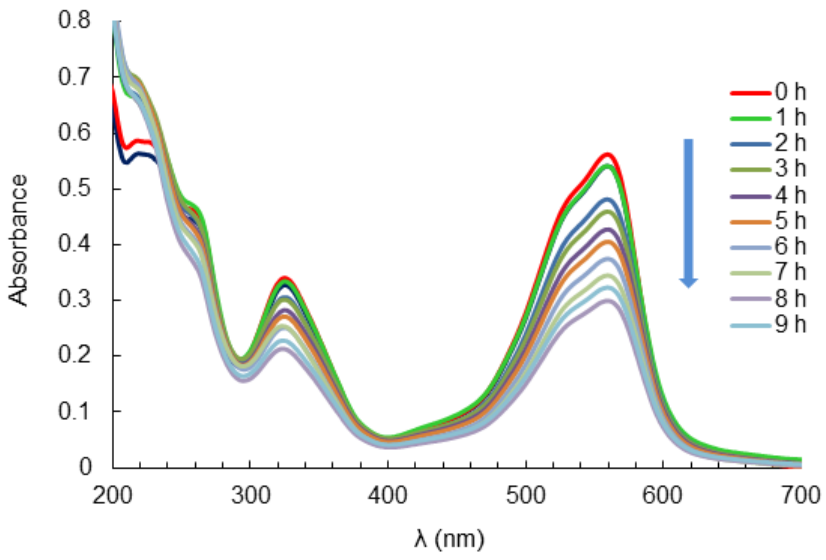

Figure 7. Absorption spectrum of Reactive Violet 5 (RV5) during the photocatalytic treatment.

Therefore, it can be concluded that the photocatalytic treatment of RV5 by the 50Fe-TiO_2 catalyst is effective not only for color removal but also for the degradation of the aromatic structures of the dye molecule and its cleavage into smaller fragments.

3.4. Effect of pH

As it is known, pH is one of the most important process parameters for the photocatalytic degradation of dyes [31]. In order to find the optimal pH for RV5 degradation, this parameter was varied from 4 to 12. The initial dye concentration was set at 30 ppm and the catalyst load was 3 g/L.

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The results obtained during a 10-h treatment period (1-h darkness and 9-h irradiation) are shown in Figure 8. It can be seen that at lower pH values ($4 \leq pH \leq 8$) the absorbance at 560 nm remained almost constant. By contrast, at pH 10 it decreased quickly, reaching a value close to zero after 2-h irradiation. At pH 12, an intermediate behavior was observed, with the initial absorbance being halved in about 6 h and reduced by around 80% at the end of the treatment. Thus, it can be concluded that, under the experimental conditions employed, the optimal pH for RV5 degradation was equal to 10. Accordingly, further experiments were carried out at this pH.

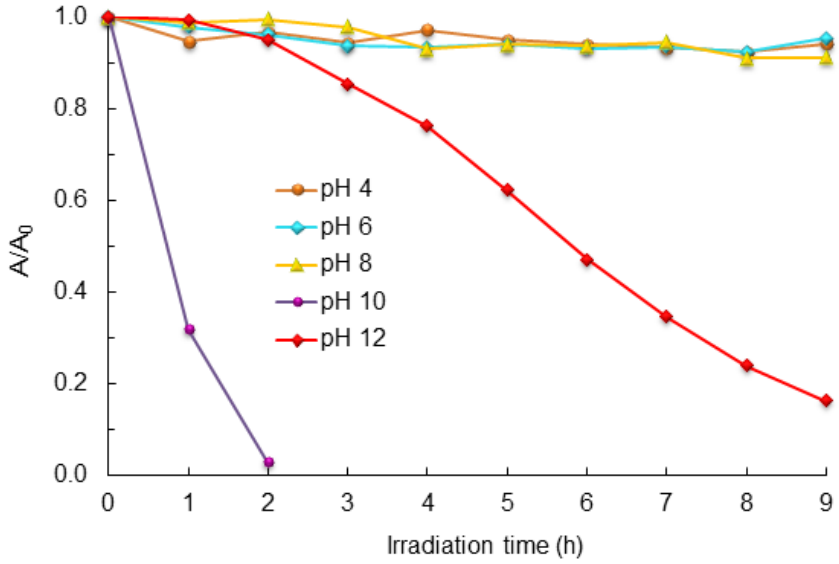

Figure 8. Photocatalytic degradation of Reactive Violet 5 (RV5) at different pH values (c^0_{RV5} = 30 ppm; catalyst load = 3 g/L). A is the absorbance of the dye solution at 560 nm.

The influence of pH on dye removal can be attributed to its effects on the generation of radical species, particularly hydroxyl radicals (•OH), during the photocatalytic process. These radicals are produced at the catalyst surface from the oxidation of OH^- or H_2O by the photogenerated holes (h^+):

$$OH^- + h^+ \rightarrow {}^\bullet OH \quad (1)$$

$$H_2O + h^+ \rightarrow {}^\bullet OH + H^+ \quad (2)$$

Hydroxyl radicals are powerful oxidizing agents and can easily attack the azo groups in the dye molecule, breaking the –N=N– bonds and causing a decolorization of the dye solution. They can also attack the aromatic structures of the dye, but these structures are more resistant than azo bonds, so that decolorization is achieved more easily than degradation [32].

From Equations (1) and (2) it can be seen that the production of •OH is favored under alkaline conditions, consistently with the results in Figure 8. The enhanced removal of azo dyes at alkaline pH was observed in several other studies. For example, after 40 min of the photocatalytic treatment with TiO_2 of a solution containing Reactive Orange 4, the color removal was 25.3% at pH 1 and 90.5% at pH 9 [33]. The degradation of the dye was less effective, as after 80-min irradiation it passed from 15.2%, at pH 1, to 87.2%, at pH 9. Similar results were obtained in a study on the photocatalytic degradation of Reactive Black 5 by TiO_2 [34].

In addition to the direct effect of pH on the production of •OH described by Equations (1) and (2), it should also be considered that [31,35]: (a) the extent of dye adsorption and photon absorption are also affected by pH; (b) at low pH, H^+ ions can interact with the azo bonds decreasing their electron density and their susceptibility to electrophilic attack by hydroxyl radicals; and (c) under acidic conditions, TiO_2 particles tend to agglomerate, reducing the surface area of the catalyst.

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The observed decrease in color removal at pH 12 could be due to a decreased adsorption of dye molecules on the catalyst surface. In fact, at this pH the catalyst surface is highly hydroxylated and hence negatively charged, repelling the RV5 molecules that have charges of the same sign.

3.5. Effect of Catalyst Load

The amount of catalyst to be used in the photocatalytic treatment is another important factor for the degradation of pollutants [31]. To evaluate the optimal catalyst load, this quantity was varied from 0 to 6 g/L, keeping the pH at 10 and the initial dye concentration at 30 ppm. The results of these experiments are shown in Figure 9. In the absence of catalyst, the decolorization of the dye solution proceeded quite slowly, with over 20% of the initial amount of RV5 still present at the end of the treatment. When the catalyst was added at 0.5 g/L, the decolorization was more rapid and completed in about 4 h. With a catalyst load of 1.5 g/L, this time was reduced to about 3 h. At higher catalyst loads (3 to 6 g/L), about 2 h were sufficient to achieve complete color removal. Furthermore, the observed decay curves were very similar to each other.

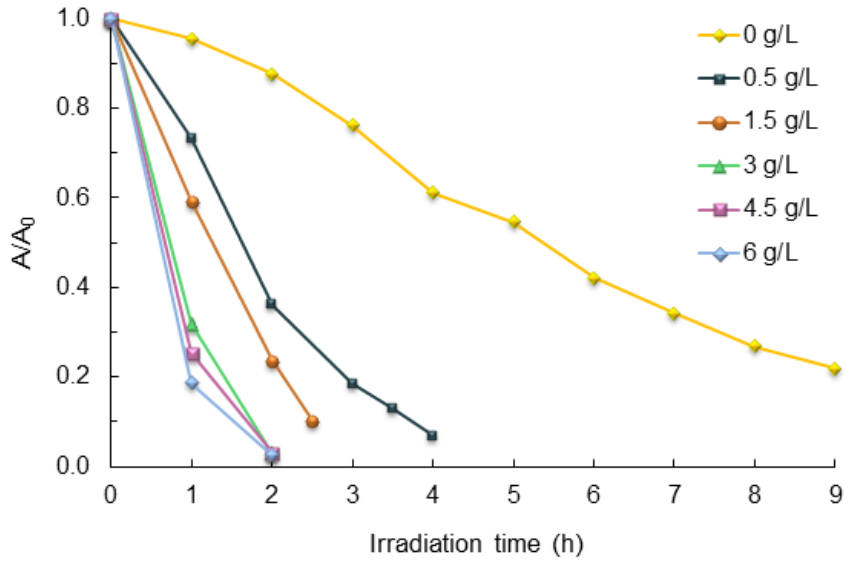

Figure 9. Photocatalytic degradation of Reactive Violet 5 (RV5) at different catalyst loads (c^0_{RV5} = 30 ppm; pH = 10). A is the absorbance the dye solution at 560 nm.

A simple kinetic analysis was used to provide a quantitative description of the effect of catalyst load on dye removal. In particular, the apparent rates of the photocatalytic process were determined by applying the initial rate method.

The initial rate of dye removal ($-r_0$), which is rigorously defined as:

$$-r_0 = -\frac{d(A/A_0)}{dt}\bigg|_{t=0} \quad (3)$$

was calculated as:

$$-r_0 = -\frac{(A/A_0)_{t_1} - (A/A_0)_{t_0}}{t_1 - t_0} \quad (4)$$

with $t_0 = 0$ and $t_1 = 1$ h. In the above equations, A_0 is the absorbance of the dye solution at 560 nm and at the beginning of irradiation ($t = 0$), while A is the absorbance at time t.

From the results in Figure 10 it can be seen that, at catalyst loads lower than 3 g/L, there was a nearly linear increase of the decolorization rate with the amount of catalyst, while above this value the effect was very small. Accordingly, a value of 3 g/L was selected as the optimal catalyst load.

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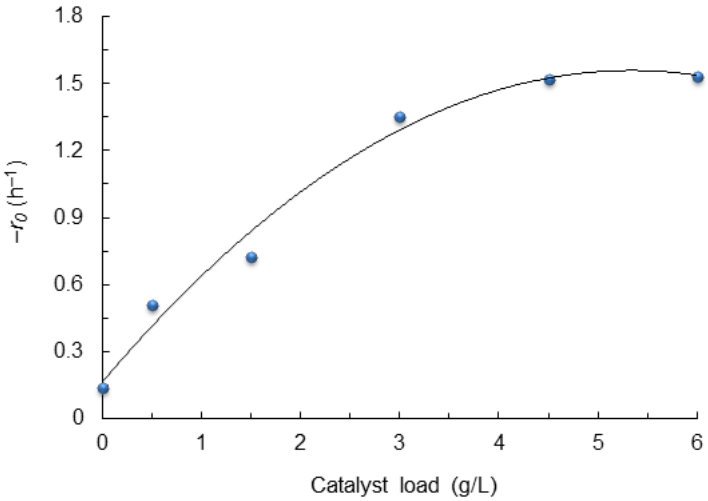

Figure 10. Initial rate of Reactive Violet 5 (RV5) removal as a function of catalyst load (c^0_{RV5} = 30 ppm; pH = 10).

The existence of a threshold value for catalyst load has been reported in many studies on the photocatalytic degradation of azo dyes including, for example, Reactive Black 5 [34], Reactive Blue 4 [36], Reactive Orange 4 [37], Reactive Red 120 [38], Reactive Blue 19 [39], Reactive Blue 198 and Reactive Yellow 145 [40]. This behavior is likely the result of multiple factors [30]. At low loadings, an increase in the amount of catalyst in the reaction mixture has a positive effect on the kinetics of dye removal due to the increased surface area available for dye adsorption and degradation. However, when all dye molecules are adsorbed on the catalyst surface, further additions of catalyst are no longer effective for decolorization of the dye solution. Moreover, an excessive amount of catalyst can reduce light penetration in the solution due to shielding and scattering effects resulting from aggregate formation. Finally, activated catalyst particles can interact with ground-state particles causing partial deactivation of the catalyst.

3.6. Effect of Hydrogen Peroxide

The presence of hydrogen peroxide in the reaction medium is known to enhance the rate of photocatalytic degradation of organic compounds [30]. To investigate the effect of hydrogen peroxide on the decolorization of RV5, experiments were performed by adding 10 to 100 mM hydrogen peroxide to a solution at pH 10 containing 30 ppm of dye and 3 g/L of catalyst. The results are presented in Figure 11. As it can be seen, the color removal efficiency increased upon addition of hydrogen peroxide, but the observed decolorization profiles varied not-monotonically with the amount of hydrogen peroxide present in the reaction medium. This can be better appreciated from Figure 12, where the initial rates of dye removal, calculated from Equation (4), are plotted against the initial hydrogen peroxide concentrations. These data reveal that an optimal hydrogen peroxide concentration of 60 mM exists. Similar results were found in other studies on the photocatalytic decolorization of azo dyes under visible light irradiation [34,37,39,41,42].

To provide an explanation to the above observation, it should be considered that hydrogen peroxide is an effective electron acceptor and can produce hydroxyl radicals through the following reaction:

$$H_2O_2 + e^- \rightarrow {}^\bullet OH + OH^- \quad (5)$$

Additional hydroxyl radicals can be formed from the reaction of hydrogen peroxide with the superoxide radical:

$$H_2O_2 + O_2^{\bullet-} \rightarrow O_2 + {}^\bullet OH + OH^- \quad (6)$$

However, at high concentrations, hydrogen peroxide can act as a scavenger of hydroxyl radicals, according to the following reactions [35]:

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$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2{}^{\bullet} + H_2O \quad (7)$$

$$HO_2{}^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (8)$$

$$2\ HO_2{}^{\bullet} \rightarrow H_2O_2 + O_2 \quad (9)$$

Furthermore, it can also react with TiO_2 to form peroxy compounds that are detrimental to the degradation process [43]. When the positive and negative effects balance each other, an optimum will be found for the amount of hydrogen peroxide in the reaction medium.

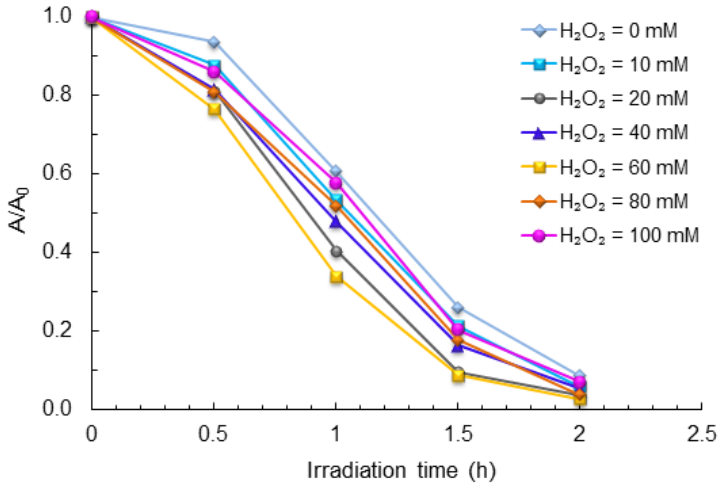

Figure 11. Photocatalytic degradation of Reactive Violet 5 (RV5) at different hydrogen peroxide concentrations (c^0_{RV5} = 30 ppm; pH = 10; catalyst load = 3 g/L). A is the absorbance the dye solution at 560 nm.

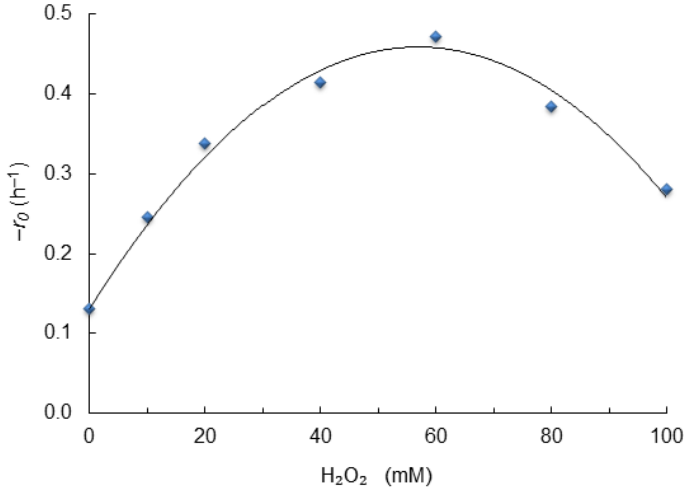

Figure 12. Initial rate of Reactive Violet 5 (RV5) removal as a function of hydrogen peroxide concentration (c^0_{RV5} = 30 ppm; pH = 10; catalyst load = 3 g/L).

3.7. Comparison with the Results of Other Published Studies

It may be interesting to compare the present results with those obtained in other studies on the degradation of RV5.

Chung et Chen [12] investigated the photocatalytic degradation of RV5 using TiO_2 nanoparticles under UV irradiation. Under optimized conditions, the photodegradation efficiency was 90% after 20 min of irradiation and reached nearly 100% after 80 min.

Cabansag et al. [13] studied the degradation of RV5 under UV light with bulk zinc oxide slurry as the photocatalyst. Under optimized conditions, the dye was degraded by 74% after 30 min of irradiation and almost completely after 90 min.

Kunal et al. [14] used an acclimatized indigenous bacterial mixed culture isolated from a dye contaminated soil to degrade RV5. The mixed culture was composed of six bacterial strains including *Bacillus*, *Lysinibacillus* and *Ochrobacterium* species and was grown in a minimal medium containing glucose and yeast extract. Under static growth conditions at 37 °C and pH 7, the dye solution was completely decolorized in about 18 h. However, in the absence of carbon and nitrogen sources only about 4% of the initial amount of dye was degraded after the same time, indicating that these sources are essential for the treatment.

Bheemaraddi et al. [15] investigated the ability of a bacterial strain of *Paracoccus* sp. isolated from a textile mill effluent to degrade RV5 as the sole source of carbon. Under static conditions and with minimal nutritional requirements this strain allowed complete decolorization of the dye solution within 16 h.

Finally, Ayed et al. [16] explored the feasibility of using a consortium of *Staphylococcus* species, two of which were isolated from a textile wastewater, to degrade RV5. Under optimal conditions, the dye solution was completely (>99%) decolorized within 8 h. The decolorization was also accompanied by a high COD removal (94.93%)

Therefore, the results obtained in the present study indicate that the degradation of RV5 by a Fe-doped titania catalyst under visible light irradiation can lead to dye removal efficiencies that are comparable with those reported for UV-photocatalytic or microbial treatments. Moreover, compared to microbial degradation processes, the investigated technology is simpler to implement and more flexible in operation.

4. Conclusions

The presence of dyes in industrial effluents is an issue of major concern due to the detrimental effects that these pollutants could have on the environment. In this study we have shown that RV5, an azo dye widely used in the textile industry, can be effectively degraded by a photocatalytic treatment using a Fe-doped TiO_2 catalyst under visible light irradiation. An analysis of the effects of the main process parameters (pH, catalyst load and hydrogen peroxide concentration) on the dye removal efficiency showed that the process can be optimized to provide rapid and complete degradation. The use of visible light and the relatively short treatment times support the suitability of the proposed process as a promising and cost-effective method for the removal of this or similar dyes from textile effluents.

Future studies should be directed at investigating the effects of the treatment on dye mineralization and evaluating the optimal conditions for mineralization. The identification of reaction products and intermediates formed during the treatment could be helpful to elucidate the mechanisms involved in RV5 degradation.

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