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Synergy Effect in the Combined Photodegradation of an Azo Dye by Titanium dioxide Photocatalysis and Photo-Fenton Oxidation

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Abstract Decolorization of the azo dye Basic Blue 41 was studied separately by photocatalysis in the presence of nanocrystalline Titania films or oxidation by Photo Fenton. Optimization procedures helped to determine the optimal quantity of TiO_2 photocatalyst, hydrogen peroxide and Fe^{+2} ions. By simultaneous treatment of an aqueous solution of the dye with TiO_2 and Photo Fenton, a synergy effect demonstrated itself giving an extensive acceleration of the decolorization of the dye and a large increase of the apparent first-order rate constant. This synergy is most probably related with the interaction of H_2O_2 with Titania and the interference of iron ions in this interaction.

Keywords Titanium dioxide films · Photodegradation · Photo Fenton · Basic Blue 41 · Azo dyes

1 Introduction

Heterogeneous photocatalysis using Titania photocatalyst has been established as a principal Advanced Oxidation Process (AOP) for waste-water treatment [1, 2]. Combination of heterogeneous photocatalysis with another AOP is considered to be cost-effective [2] as long as this combination produces a synergistic effect. In the present work we have investigated the combination of Titania photocatalysis with Photo-Fenton oxidation and we have searched for conditions of synergy by developing a process protocol. We have used as target pollutant an azo dye, Basic Blue 41 (BB, see Fig. 1 for chemical structure). Treatment of dye-polluted water, in particular of azo dyes, is interesting from many points of view: Azo dyes are pollutants with serious environmental hazards, since their photodegradation products involve carcinogenic aromatic amines [3]. From the pure research point of view, photodegradation of dyes is easy to monitor, at least during the decolorization stage, by using absorption spectrophotometry.

The principles of Titania heterogeneous photocatalysis as well as of Photo-Fenton oxidation have been well established and presented in a multitude of publications [1–5]. We have adopted all these principles and we proceeded with the investigation of their proper combination conditions. UVA radiation has been used as excitation source by employing low energy (4 W nominal electric power) fluorescent Black-light tubes. The light from such sources peaks around 360 nm, as can be seen in Fig. 1. The intensity of radiation reaching the photocatalyst, as will be seen below, was very low, comparable or even lower than UVA of Solar noon [6, 7]. Therefore, it is viable to use Solar Radiation for carrying out the same processes.

2 Experimental

All reagents used were from Aldrich, they were of the best quality available and were used as received. Water was purified by using a Millipore installation.

2.1 Synthesis and Deposition of Nanocrystalline Titania Films

Films were made by observing previously published sol–gel procedures [8–10]. Briefly, 1.4 g of the non-ionic surfactant Triton X-100 [polyoxyethylene-(10) isooctylphenyl ether] was mixed with 7.6 mL of ethanol, followed by

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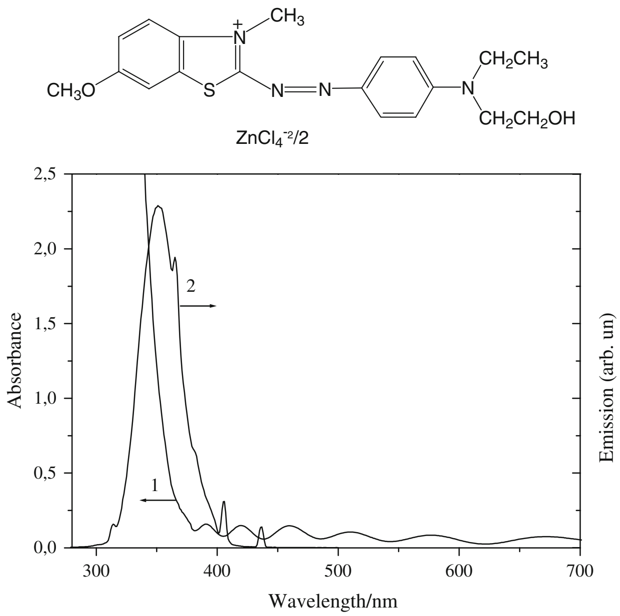

Fig. 1 Chemical structure of BB, absorption spectrum of a typical nanocrystalline Titania film (1) and emission profile of a Black Light tube (2). The periodic ripples in the absorption of Titania at wavelengths >375 nm are due to interference fridges

addition of 1.36 mL of glacial acetic acid and 0.72 mL of Titanium isopropoxide under vigorous stirring. Self organization of the surfactant in this original sol creates organized assemblies that act as templates defining nanoparticle size. The surfactant is burned out during calcination. After a few minutes stirring, a glass (pyrex) ring, especially cut for the purposes of the present work, was dipped in the above sol and was withdrawn at a speed of 40 mm/min. Prior to dipping, the glass ring was thoroughly washed, sonicated in ethanol and dried in an oven. All glass rings used had a height of 15 mm and a diameter of 35 mm. The nanocomposite film formed by dipping was left to dry in air for a few minutes and then it was calcined in an oven. The temperature was raised at a heating rate of 20 °C/min up to 550 °C and left at that temperature for about 10 min. When the film was taken out of the oven it was transparent and optically uniform. The above procedure was repeated three more times. The mass of titania deposited on each ring after four dipping and calcination steps was approximately 3.8–4.2 mg, of course, deposited on both the external and internal surface of the ring. Six such rings were used to equip the reactor, as will be described below.

2.2 Description of the Reactor and the Experimental Procedure

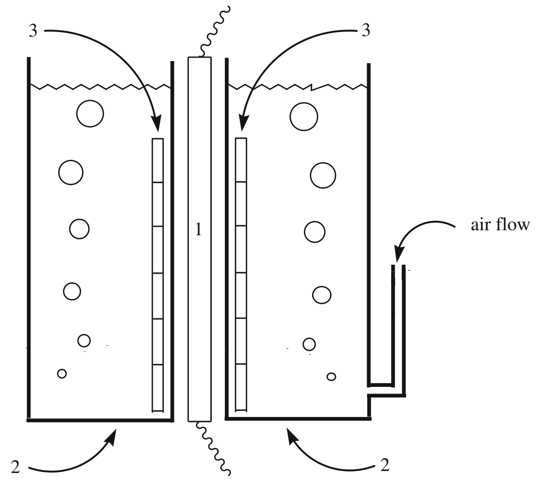

Fig. 2 Cross-sectional view of the reactor: (1) Black-light lamp; (2) Reactor walls; (3) Stack of rings supporting Titania

We used the batch reactor which is schematically shown in Fig. 2. The whole system is built of pyrex glass. The lamp was a 4 W commercial Black-light tube. In the case of Titania photocatalysis six glass cylinders (rings) covered with Titania were coaxially stacked in the reactor. The intensity of radiation at the position of the catalyst was around 0.7 mW cm^{-2} as measured by an Oriel Radiant Power Meter. A constant air flow produced by a small pump ensured agitation and oxygenation of the solution. The volume of the solution, which covered all stacked rings was 150 mL. In the case of treatment with UV/H_2O_2 and UV/H_2O_2/Fe^{+2} (Photo-Fenton), either in the absence or in the presence of Titania, the concentration range of the oxidants was the following: H_2O_2: 0–100 mmol L^{-1}; and Fe^{+2} ($FeCl_2 \cdot 4H_2O$): 0–0.15 mmol L^{-1} (0–30 mg L^{-1}). The concentration of BB in water was always 0.01 mmol L^{-1}. The concentration of the non-degraded dye in solution was monitored by absorption spectrophotometry by measuring the absorbance at 606 nm (cf. Fig. 3). Three milliliters aliquots were periodically collected and after measurement were poured back into the reactor, in order to keep the volume of the solution constant. UV-vis absorption measurements were made with a Varian Cary 1E spectrophotometer.

3 Results and Discussion

As it has been reported in previous publications [8–11], films made by the sol–gel procedure described in the Sect. 2 consist of anatase nanocrystals of about 15 nm average size. Size polydispersity is limited and the active surface area is around 110 m^2/g, as measured by Nitrogen adsorption using the BET model. These films have been proven to be very efficient in dye photodegradation experiments [8, 9], Dye-sensitized Solar Cells [10] and photocatalytic H_2 production [11]. The absorption

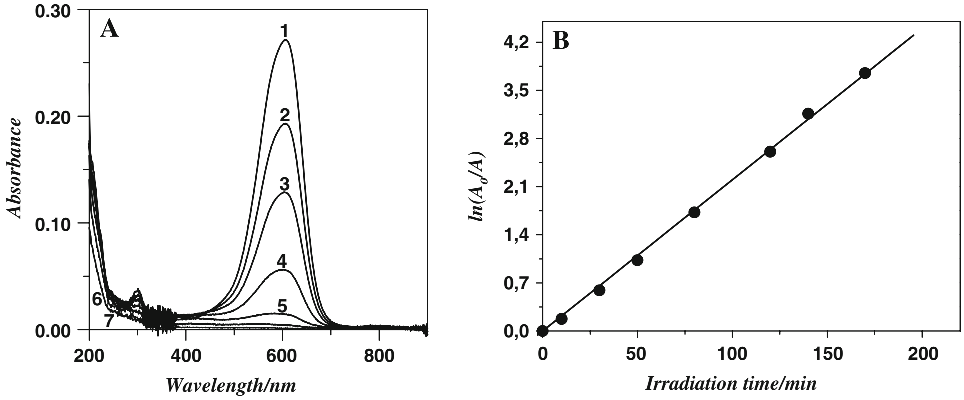

Fig. 3 (**a**) Absorbance of the aqueous solution of BB at various irradiation times in the presence of Titania photocatalyst, after: (1) 0 min; (2) 10 min; (3) 30 min; (4) 50 min; (5) 80 min; (6) 120 min; and (7) 170 min. Original BB concentration 0.01 mmol L^{-1}. (**b**) Plot of $\ln(A_0/A)$ values versus irradiation time for the data of Fig. 3a. The quantity of Titania was 154 mg L^{-1}

spectrum of a similar film deposited on a glass slide is shown in Fig. 1. Figure 1 also shows the emission profile of the Black Light tube employed in the presence work as excitation source. It is obvious that the proposed combination provides Band-gap excitation of Titania and thus secures optimized excitation conditions without internal energy losses.

3.1 Decolorization Studies with Titania Photocatalyst

3.1.1 Parameter Optimization

Figure 3 shows the decolorization of BB solutions by photocatalytic treatment in the presence of Titania alone. When the Titania films were immersed in the dye solution, a percentage of the dye was adsorbed on the film. As a matter of fact, a substantial amount of BB is always adsorbed by these Titania films at the dye's natural pH [12]. Adsorption of BB on the present Titania films was studied by drawing a Langmuir adsorption isotherm, similarly to [13]. The maximum quantity of adsorbed BB per gram of Titania was 0.09 mmol g^{-1}. As a consequence, while the original absorbance of the present solution was 0.31 after the introduction of Titania it decreased and became 0.27. About 1 h in the dark was judged necessary for equilibrium since beyond this time no more adsorption could be detected. The dye absorbance during photodegradation is shown in Fig. 3a as a function of irradiation time. The absorbance data fit Langmuir-Hinshelwood kinetics [14, 15] as seen by the straight line plot of Fig. 3b, which obeys the following equation:

$$\mathrm{In}(A_0/A) = K_{\mathrm{app}}t \quad (1)$$

The apparent first-order reaction rate K_{app} can be calculated from Eq. 1, under the assumption that the absorbance and the concentration are proportional. To verify this proportionality we have plotted a calibration curve (not shown) of absorbance versus concentration of BB in water and we found that this proportionality (i.e. the Beer-Lambert Law) holds up to 0.1 mmol L^{-1}, which includes the present concentration range. The calculated values corresponding to Fig. 3 were $K_{\mathrm{app}} = 2.15 \times 10^{-2}$ min^{-1} (with correlation coefficient $R^2 = 0.999$). The effect of the quantity of photocatalyst on the decolorization rate can be seen in Fig. 4 and Table 1. These experiments allowed us to define the optimal quantity of catalyst for maximum decolorization

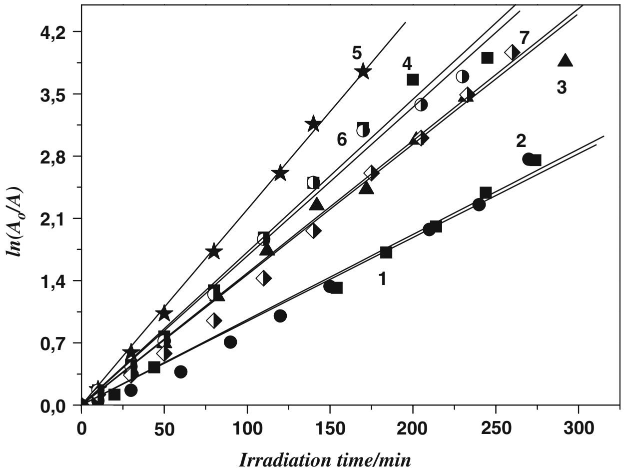

Fig. 4 Plot of $\ln(A_0/A)$ values versus irradiation time for the photodegradation of 0.01 mmol L^{-1} aqueous BB solutions in the presence of various quantities of Titania photocatalyst (mg L^{-1}): (1) 40.6; (2) 60.0; (3) 75.3; (4) 120.6; (5) 154.0, (6) 196.0; and (7) 240.0

Table 1 Values of the pseudo first-order decolorization rate constant K_{app} and correlation coefficient R^2 for various photocatalyst loads

C (mg L^{-1}) TiO_2	K_{app} (min^{-1})	R^2
40.6	0.96×10^{-2}	0.996
60.0	0.96×10^{-2}	0.997
75.3	1.43×10^{-2}	0.994
120.6	1.72×10^{-2}	0.945
154.0	2.15×10^{-2}	0.999
196.0	1.68×10^{-2}	0.996
240.0	1.47×10^{-2}	0.998

rate. It is seen that the optimal value was 154 mg L^{-1}, while at larger quantities the rate decreased, obviously due to screening effects. The data of Fig. 3 correspond to the optimal amount of photocatalyst.

3.2 Decolorization Studies with Photo-Fenton

3.2.1 Parameter Optimization

Oxidation of BB leading to decolorization was also obtained in the presence of various quantities of hydrogen peroxide. As it is well known [1], hydrogen peroxide is dissociated in water under UV irradiation producing hydroxyl radicals [1, 3, 4] according to the following reaction:

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \qquad (2)$$

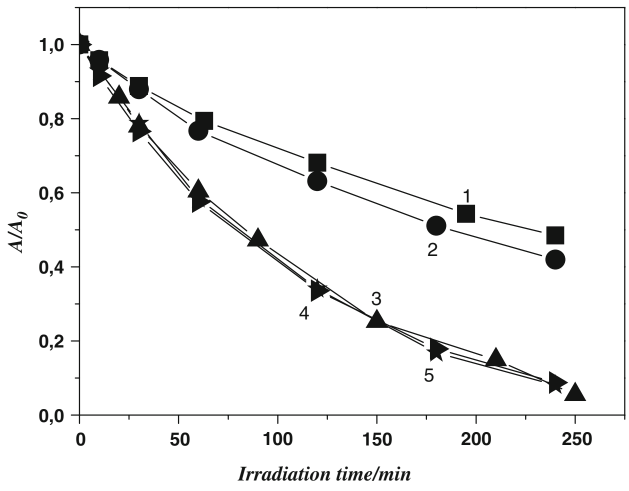

Fig. 5 Variation of A/A_0 versus UVA irradiation time for the decolorization of 0.01 mmol L^{-1} BB aqueous solution in the presence of various concentrations of H_2O_2 (in mmol L^{-1}): (1) 10; (2) 25; (3) 50; (4) 75; and (5) 100

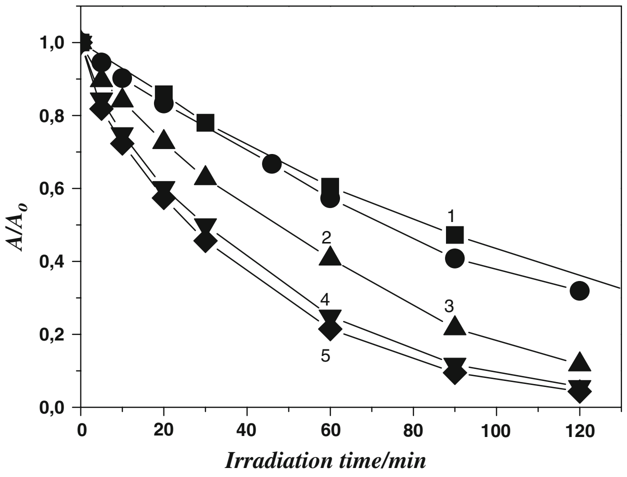

Fig. 6 Variation of A/A_0 versus irradiation time for the decolorization of 0.01 mmol L^{-1} BB aqueous solution in the presence of 50 mmol L^{-1} H_2O_2 and various concentrations of Fe^{+2} (in mmol L^{-1}): (1) 0; (2) 0.025; (3) 0.075; (4) 0.100; and (5) 0.150

Oxidation occurs by interaction with these strongly oxidant agents. Figure 5 presents related data. The decolorization rate increased with the concentration of hydrogen peroxide up to 50 mmol L^{-1}, reaching saturation. The decolorization rate did not further increase for higher H_2O_2 concentrations. This is expected, since at excessively high H_2O_2 concentrations adverse effects have been observed [1, 3]. We have then adopted 50 mmol L^{-1} H_2O_2 concentration as the optimal concentration of this oxidant for the present experimental setup. Then we added Fe^{+2} to monitor decolorization as a result of Photo-Fenton under UVA (Black Light) irradiation. At the moment of Fe^{2+} addition (in the dark), the Fenton reaction started (Reactions 3–6) [1, 4, 16], which led to rapid decolorization of an important percentage of the solution. Thus the original absorbance of 0.31 dropped to 0.22. This value was taken as the starting value for the subsequent Photo-Fenton treatment (Reaction 7). The related data are presented in Fig. 6.

$$Fe^{+2}_{aq} + H_2O_2 \rightarrow Fe^{+3}_{aq} + OH^{\bullet} + OH^{-} \qquad (3)$$

$$Fe^{+3}_{aq} + H_2O_2 \rightarrow Fe^{+2}_{aq} + OH_2^{\bullet} + H^{+} \qquad (4)$$

$$Fe^{+3}_{aq} + HO_2^{\bullet} \rightarrow Fe^{+2}_{aq} + O_2 + H^{+} \qquad (5)$$

$$Fe^{+3}_{aq} + OH^{-} \rightarrow Fe(OH)^{2+} \leftrightarrow +Fe^{2+}_{aq} + OH^{\bullet} \qquad (6)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+}_{aq} + OH^{\bullet} \qquad (7)$$

Again, the optimal concentration of added Fe^{+2}_{aq} was determined and it was 0.1 mmol L^{-1}. These data allowed us to determine the optimal conditions for achieving highest decolorization rates with Photo-Fenton oxidation. As seen in Fig. 7 (Curve #3) and Table 2, K_{app} in that case was equal to 2.38×10^{-2} min^{-1}. It is interesting that this value is very close to the one determined in the case of optimized Titania photocatalysis, i.e. 2.15×10^{-2} min^{-1}. This matching of values determined by independent optimization procedures demonstrates the efficiency of the optimization process.

3.3 Synergy Between Titania Photocatalysis and Photo-Fenton

Finally, we have studied the combination of Photo-Fenton and Titania photocatalysis. The procedure was the following. First, we introduced into the reactor the optimal quantity of Titania photocatalyst, i.e 154 mg L^{-1}. We waited for an hour to obtain adsorption equilibrium. Then

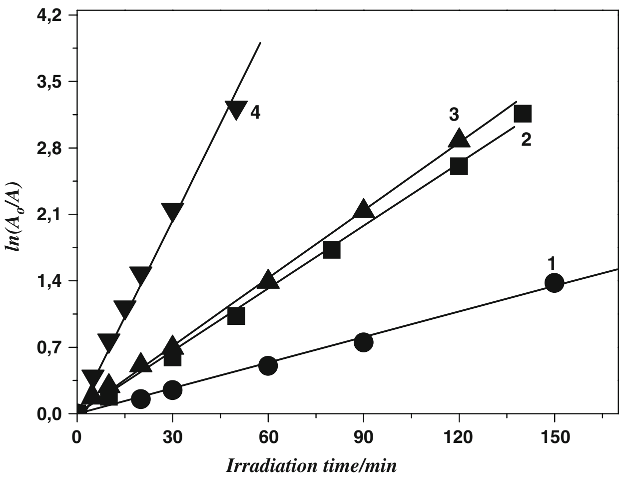

Fig. 7 Plot of $\ln(A_0/A)$ values versus irradiation time for the decolorization of 0.01 mmol L^{-1} BB aqueous solutions by different AOPs alone or in combination: (1) UVA/H_2O_2; (2) UVA/TiO_2; (3) UVA/Fe^{+2}/ H_2O_2; and (4) UVA/Fe^{+2}/ H_2O_2/TiO_2

Table 2 Values of the maximum apparent first-order decolorization rate constant K_{app} and correlation coefficient R^2 for the different AOPs

Advanced Oxidation Process	K_{app} (min^{-1})	R^2
UVA/H_2O_2	0.90×10^{-2}	0.999
UVA/TiO_2	2.15×10^{-2}	0.999
UVA/Fe^{+2}/H_2O_2	2.38×10^{-2}	0.999
UVA/Fe^{+2}/H_2O_2/TiO_2	6.79×10^{-2}	0.996

we added the optimal quantity of H_2O_2, i.e. 50 mmol L^{-1}. Finally, we added the optimal quantity of Fe^{2+}, i.e. 0.1 mmol L^{-1}. All this was done in the dark. At the moment of Fe^{2+} addition, the Fenton reaction started as above and decreased the original absorbance of the dye solution. That value was considered the starting absorbance (irradiation time 0 min). Then we turned Black light on. The obtained $\ln(A_0/A)$ vs. time plot is shown in Fig. 7 (Curve #4), while the corresponding K_{app} value was 6.79×10^{-2} min^{-1} as seen in Table 2. This last value is larger than just the addition of the separate values obtained for Titania-photocatalysis and Photo-Fenton. Since it is a logarithmic value, it corresponds to more than two orders of magnitude higher A_0/A ratio. Therefore, there is no additive effect but a clear synergy of the two processes that increases oxidation rate. The explanation of this synergy is not clear and more work needs to be first done before a clear model could be proposed. In previous publications [4, 5], it was supported that the presence of hydrogen peroxide in a reactor containing Titania photocatalyst leads to the following interactions (8, 9, 17):

$$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+) \tag{8}$$

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \tag{9}$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^\bullet + OH^- + O_2 \tag{10}$$

which produce additional $OH^\bullet$ oxidative agents. Our own data pointed to the same direction. Indeed, a 20% increase in the value of K_{app} has been measured when photocatalysis was performed in the presence of H_2O_2. This limited increase of K_{app} cannot, of course, explain the impressive increase observed with the UVA/Fe^{+2}/H_2O_2/TiO_2 system (Table 2). Furthermore, combination of Titania with Fe^{+2} alone has also been studied and proved to have detrimental effects on the value of K_{app}, which in that case was ten times lower than when pure Titania was employed. Additional and more drastic effects could then justify the increase of K_{app} in the case of the UVA/Fe^{+2}/H_2O_2/TiO_2 system. It is necessary to consider the adsorption of iron ions on Titania and the possible role the semiconductor might play on the Fe^{2+}/Fe^{3+} redox interaction. Furthermore, one should take into account the effect that iron ions would have on the adsorption of hydrogen peroxide on Titania films. Adsorbed H_2O_2 would act as hole scavenger, which would lead to the reaction (11) [5] that creates the less oxidant $HO_2^\bullet$ radical species:

$$H_2O_2 + h^+ \rightarrow HO_2^\bullet + H^+ \tag{11}$$

which would act in the opposite direction. This was indeed observed in [17], where combination of photocatalysis and H_2O_2 alone was studied and it is in line with our own above data. Thus it is possible that adsorption of iron ions prevents adsorption of hydrogen peroxide and enhances the quantity of $OH^\bullet$ oxidant species in solution with beneficial consequences for the decolorization rate.

As already stated in the Sect. 2, the intensity of radiation incident on the solution was less than 1 mW/cm^2. This intensity is much lower than the UVA portion of the Solar noon [6, 7]. Potentially, solar radiation could then be employed to degrade a pollutant like the one treated in this work, achieving interesting photodegradation rates by exploiting this Titania-Fenton synergy in photodegradation.

4 Conclusion

Combination of Titania photocatalyst with Photo Fenton produces a synergy effect that increases photodegradation rate of an azo dye to a value that is larger than just the addition of the optimized values of these AOPs when performed separately. Synergy can be due to both interaction of excited Titania with H_2O_2 and to the consequences of adsorption of iron ions on the surface of Titania.

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