Photocatalytic degradation of a model textile dye using Carbon-doped titanium dioxide and visible light

Giuseppe Cinelli[a§], *Francesca Cuomo*[a§], *Luigi Ambrosone*[b], *Matilde Colella*[c], *Andrea Ceglie*[a], *Francesco Venditti*[a]*, *Francesco Lopez*[a]*

[a]Department of Agricultural, Environmental and Food Sciences (DiAAA) and Center for Colloid and Surface Science (CSGI), Università degli Studi del Molise, Via De Sanctis, I-86100 Campobasso, Italy.

[b]Department of Medicine and Health Sciences "Vincenzo Tiberio", Università degli Studi del Molise, Via De Sanctis, I-86100 Campobasso, Italy.

[c]Dipartimento di Bioscienze, Biotecnologie e Biofarmaceutica, Università degli Studi di Bari "Aldo Moro", Bari, Italy.

§ These two authors contributed equally to this work.

*Corresponding authors:
Francesco Lopez, Department of Agricultural, Environmental and Food Sciences and Center for Colloid and Surface Science (CSGI), Università degli Studi del Molise, via De Sanctis, I-86100 Campobasso, Italy. Phone: +39 0874404632; fax: +39 0874404652; mail: lopez@unimol.it.
Francesco Venditti, Department of Agricultural, Environmental and Food Sciences and Center for Colloid and Surface Science (CSGI), Università degli Studi del Molise, via De Sanctis, I-86100 Campobasso, Italy. Phone: +39 0874404633; fax: +39 0874404652; mail: francesco.venditti@gmail.com.

Abstract

Rhodamine B (RhB), a dye widely used in the textile manufacturing, contributes with other dyes to harm the environment. Here, with the final goal to provide new tools for the removal of dyes from water, a visible light activated carbon-doped titanium dioxide was used to investigate on the decolourization and the photocatalytic degradation of RhB dye from water solutions. The photodegradation activity was tested varying the initial concentration of RhB and the amount of carbon-doped titanium dioxide, taking into account the ratio between the amount of catalyst and the amount of RhB (TiO_2/RhB), thus obtaining a parameter that allows the method to be scaled up without losing its effectiveness. Values of k_2 and $t_{0.5}$ were obtained by fitting kinetics data to a second-order kinetic adsorption model. The important role played by doped TiO_2 particles is demonstrated by the highly efficient color removal obtained during the visible light-induced photocatalysis. The presence of different degradation intermediates was demonstrated by means of UV-Visible Absorption and Fluorescence spectroscopy. Such results underline that the whole photodegradation process does not end with the decolourization occurrence.

Keywords: Water treatment, TiO_2, Photocatalysis, Dye, Kinetics, Fluorescence.

1. Introduction

Dye pollutants produced from the textile manufacturing are becoming a serious source of environmental contamination [1, 2]. It is estimated that thousands of different dyes and pigments are used industrially and an enormous number of synthetic dyes are yearly produced worldwide. Textile factories are second only to agriculture in the amount of pollution they create and the large amounts of water they use. Pollutants released by the global textile industry are continuously doing incredible harm to the environment, polluting lands and making them useless and unproductive [3].

Dyes are substances widely used in textile, as well as in pharmaceutical, food, plastics, paper manufacturing [4-8]. The chromophores, responsible for the specific dye color, are classified according to their chemical structure and their application field. The chromophore-containing centers are based on various functional groups, among these the main are azo, anthraquinone, methine, nitro, arylmethane, carbonyl groups. Donating substituents able to generate color amplification of the chromophores are denominated auxochromes (amine, carboxyl, sulfonate and hydroxyl).

Among these molecules Rhodamine B (RhB) is a fluorescent cationic dye widely used in textile dyeing because of its more rigid structure than other organic dyes, and is also a well-known fluorescent water tracer [9]. Due to its cationic structure, it can be used for anionic fabrics that contain negative charges such as polyester fibers. RhB results harmful to human and animals: it causes irritation of the skin, eyes and respiratory tract. Also, Rhodamine dyes are highly toxic to reproductive and nervous systems and it has been proven that drinking water contaminated with Rhodamine could lead to subcutaneous tissue borne sarcoma [10].

Worldwide regulations for industrial wastewater require significant elimination of the dyestuff amount from the effluent [11]. Nevertheless, it has been evaluated that a considerable part of the dyestuff is still being released to the ecosystem. Several approaches have been developed for the effluent treatment but none of them is still sufficiently effective and a combination approach seems to be so far the most efficient.

Generally, dyestuff is faced with chemical and physical methods, such as adsorption and bio-treatment, co-precipitation, coagulation, filtration, activated carbon, ozonation, and photochemical decolourization [12, 13]. These methods frequently share the inconvenience of incomplete degradation of the dye molecule, which leads to the formation of toxic by-products. These limits of conventional water treatment methods can be overcome by the use of advanced oxidation processes, which has the ability to completely mineralize the dyes, including the opening of the aryl ring. Usually, advanced oxidation processes consist of procedures in which active hydroxyl radicals act as strong oxidants for degradation of polluting materials. Most of these processes are based on the high oxidation capacity of hydroxyl radicals (2.8 V). One of the most effective methods among the advanced oxidation route is the use of UV rays combined with oxidant such as titanium dioxide.

Titanium dioxide (TiO_2) is well recognized as a low cost and efficient catalyst for degradation of organic matters [14]. The application of titanium dioxide as heterogeneous photocatalyst is well established for the remediation of water and air purification [15, 16]. For instance, the photocatalytic degradation of azo dyes in aqueous solution is based on photo activation of TiO_2 with UV light, which leads to a sequence of reactions resulting in the production of oxidants. The so formed compounds (hydroxyl radicals) can easily react with organic compounds on the TiO_2 surface.[17] However, since titanium dioxide has a band gap of 3.2 eV, which can be activated only under UV-light irradiation, efforts have been made to discover methods providing the photoactivation of this photocatalyst under visible light. Doping of TiO_2 represents a widely used approach for developing TiO_2 based materials useful for environmental applications [18]. Different methods for the synthesis of carbon doped TiO_2 particles have been proposed to improve the photocatalytic activity [16, 19]. Recently different research groups highlighted the efficiency of a visible-light-active TiO_2 photocatalyst prepared through carbon doping using glucose as the carbon source towards organic compounds [20-22].

RhB is largely used to prove the efficiency of catalysts in general and for TiO_2 in particular, towards organic matter [23-27]. Nerveless, as stated above due to the possibility of incomplete

degradation of the dye molecule, to some extent, would be useful to clarify the difference between decolourization and degradation. In fact, a decolourization processes does not necessarily correspond to a complete degradation of the dye [28]. Furthermore, the presence of different photocatalytic degradation processes, such as chromophore cleavage, opening-ring, N-de-ethylation, and mineralization have also to be taken into account [29, 30].

The aim of this investigation is the study of the photodegradation process of the dye, RhB, induced by a carbon doped visible light-active TiO_2 photocatalyst. Furthermore, an accurate investigation of the decolourization and the photocatalytic activity of carbon doped TiO_2 toward RhB was accomplished. The final goal is to provide new tools for the challenging removal of dyes from water.

2. Materials and Methods

2.1. Materials. Glucose, titanium isopropoxide (97%), ethanol absolute, potassium chloride, sodium carbonate and Rhodamine B (RhB) were purchased from Sigma-Aldrich.

2.2. Carbon-Doped Titanium. Carbon-doped TiO_2 (CDT) was synthesized following the method reported by Ren et al.[21]. TiO_2 particles were prepared by the hydrolysis of titanium isopropoxide in ethanol performed in the presence of potassium chloride. The sample was continuously stirred to produce a white precipitate, and the obtained suspension was aged for 24 hours. The suspension after filtration was overdried to yield amorphous TiO_2 particles. Carbon-doped TiO_2 was synthesized by supplying a glucose solution to amorphous TiO_2 powder (0.25 g of TiO_2 and 0.018 g of glucose). The suspension was treated at 160 °C for 12 h and washed several times with water and ethanol before use.

2.3. Rhodamine photodegradation. Photocatalytic degradation of RhB was carried out by using CDT activated under visible light irradiation. Photocatalysis were performed by placing the samples in a homemade reactor. The photocatalytic activity was activated with lamps providing visible light (6500 K). The photoemission spectrum of the fluorescence lamps provides visible light in the range

of 400−800 nm. The distance between the light source and the bottom of the solution was ∼15 cm. 10 mg of CDT were added to 10 mL of RhB solutions at different concentrations (6 - 60 mgL^{-1}) and mechanically stirred. The temperature was kept constant at 25 °C. Samples were air-equilibrated and placed in the reactor and treated with visible light. Aliquots of the sample were withdrawn, diluted 1:10 with water, centrifuged at 10000 rpm for 10 minutes and analyzed. Changes in RhB concentrations due to water evaporation were taken into account and corrected. Experiments were performed in duplicate, and results were the mean values. The initial RhB concentration was obtained by means of a calibration curve performed at 25 °C.

2.4. Spectroscopic characterization. The RhB decolourization was determined spectrophotometrically by means of a double-beam thermostated spectrometer (Cary 100-Varian) in the 200−800 nm region. The decolourization extent was followed at 554 nm, and its decrease was determined as the difference between initial and final solution concentrations with appropriate corrections based on blanks. The percentage of RhB decolourization was calculated as normalized absorbance (C/C_0, where C_0 is the initial concentration of RhB and C is the concentration of RhB at time t). Fluorescence measurements were performed using a Varian Eclipse spectrofluorimeter in a 1 cm quartz fluorescence cuvette, at 25 °C. The excitation and the emission slits width were 5 mm. The excitation wavelengths utilized for this study were 495, 510, 530 and 554 nm.

2.5. ζ potential. ζ potential measurements were performed by laser Doppler velocimetry using a Zetasizer-Nano ZS90 Malvern UK instrument operating with a 4 mW He−Ne laser (633 nm wavelength).

2.6. Scanning electron microscopy (SEM). Images were obtained with a Zeiss DSM 940 instrument. Samples were deposited onto glass plates, left for 5 h at room temperature and sputtered with gold.

3. Results and Discussion

3.1. RhB decolourization. The photocatalytic activity of carbon-doped TiO_2 (CDT) was tested for the degradation of RhB (whose structure is reported in Fig.1) by lighting aqueous suspensions containing RhB and CDT particles with visible light radiations.

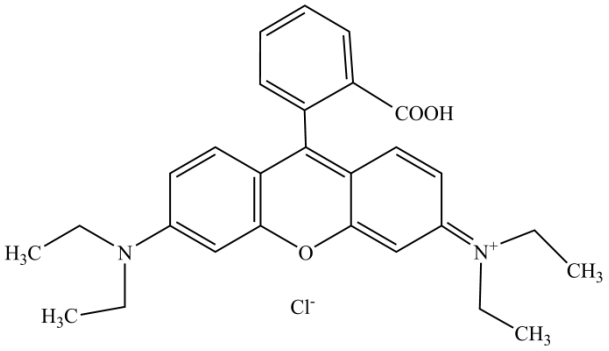

Fig. 1. Rhodamine B chemical structure.

CDT is made of a mesoporous material obtained by the substitution of carbon atoms in the TiO_2 with values of the band gap energy, micropore size and surface area are 3.01 eV, 8 nm and 126.5m^2 g^{-1} respectively [21]. SEM images, shows that freshly prepared CDT particles are monodisperse in agreement with the method introduced by Ren and coworkers (see SI1) [21]. A significant aspect of the whole photodegradation process is related to the surface charge of CDT particles [22]. Value of ζ-potential in aqueous solution was ∼18 mV (data not shown).

The first objective was an inspection on the decolourization ability of carbon doped TiO_2 towards RhB at fixed appropriate amounts of CDT particles and RhB. Fig. 2 shows the RhB adsorption spectra at different irradiation times. At a first sight it can be easily appreciated that: i) the characteristic absorption band of RhB at 554 rapidly decreases upon irradiation and completely disappears in about 60 min; ii) a progressive hypsochromic shift from 554 nm to 495 nm takes place. Fig. 2 also reports the pictures of the sample during the photoreaction at different time points. From a visual inspection of the sample it appears obvious that the characteristic brilliant pink color of RhB rapidly disappears, turning first into orange followed by yellow and white in agreement with the displayed spectra. Both blue shift and color variations suggest the existence of different intermediates produced in the presence of CDT under visible irradiation. Such intermediates share

an irradiation time dependent transient change of λ_{max} starting from the initial RhB species at 554 nm (inset of Fig. 2). From these results, it is evident that bleaching of the pink color (554 nm) does not correspond to the whole RhB degradation process. The maximum absorption shift from 554 to 495 nm with the increased illumination time has been correlated in earlier studies performed in the presence of TiO_2 and O_2 with products coming from RhB N-de-ethylation [31].

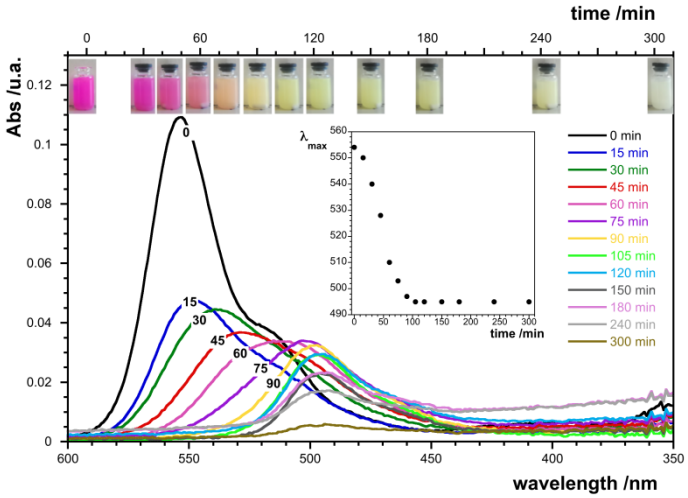

Fig. 2. RhB UV-visible adsorption spectra and sample decolourization pictures as function of time exposure to visible light irradiation. Inset λ_{max} shift. Ti/RhB: 150.

The effect of the amount of substrate on the decolourization process was tested by focusing only on changes in absorbance at 554 nm. From an applicative point of view it may be advantageous to combine both TiO_2 and RhB in a unique parameter, namely the ratio between the catalysts particle (mg of TiO_2) and the amount of dye (mg of RhB) [20].

Fig. 3A shows the decolourization ability of carbon doped titanium for samples with different values of the ratio TiO_2/RhB (20, 80 and 150) during exposure to visible light irradiation. The experimental data, expressed with normalized concentration (C/C_0) of RhB as a function of time at 25 °C, indicate that the RhB decolourization rate increases with increasing TiO_2/RhB ratios. The results are in agreement with a degradation process strictly related to the amounts of catalyst and

substrate, respectively as well as the ability of the substrate to be adsorbed on the surface of the catalyst and other parameters such as pH and O_2 concentration [22, 31, 32].

As shown, the kinetics becomes slower with time, reaching the equilibrium after different time intervals depending on the TiO_2/RhB ratio. From the kinetics data, a dependence of the RhB decolourization process on the TiO_2/RhB ratio, typical of an adsorption process, was demonstrated, foretelling a pivotal function of the adsorption event on the photoreaction in agreement with a recent study performed on caffeic acid degradation in the presence of carbon doped TiO_2 [22].

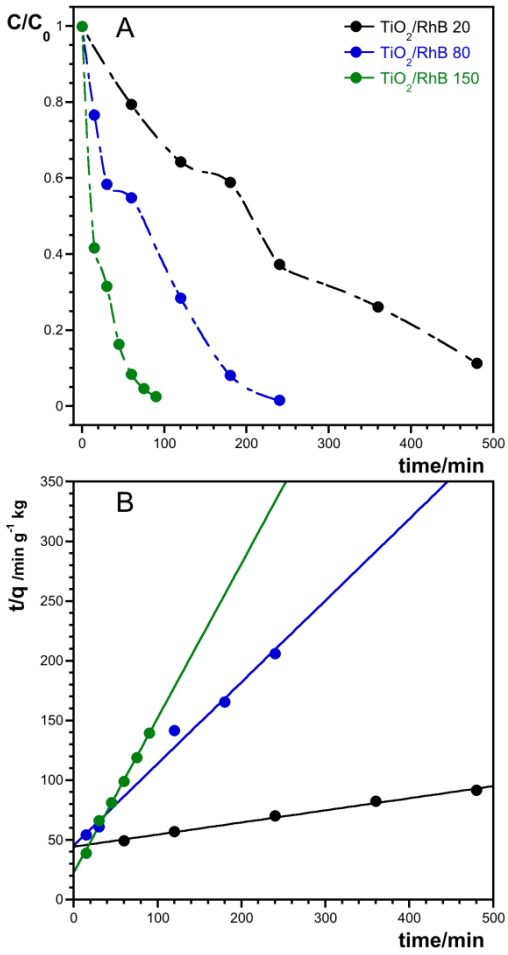

Fig. 3. (A) RhB decolourization profiles as function of time. RhB under light irradiation with different amounts of carbon doped TiO_2. TiO_2/RhB ratios 20, 80 and 150. (B) Fitting of the decolourization profiles to Eq. 1.

The decolourization profiles determined at different TiO_2/RhB were fitted to a second-order kinetics model by means of Eq. 1.

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (1)$$

where k_2 (kg/g per min) is the rate constant of second-order adsorption, q and q_e are the amounts of RhB adsorbed on CDT at time t and at equilibrium, respectively (g/kg). The linear relationship, as reported in Fig. 3B, indicates that a second-order kinetics is applicable. From Eq. 2 the half-life of the process can be calculated as:

$$t_{0.5} = \frac{1}{k_2 q_e} \qquad (2)$$

The k_2, q_e and $t_{0.5}$ parameters at each TiO_2/RhB ratio are presented in Table 1. From these data, it emerges that the values of k_2 increase with the increase of TiO_2/RhB ratio (thus, with the decrease of RhB concentration) while, the q_e values, as expected, decrease with increasing TiO_2/RhB ratios. The $t_{0.5}$ values represent suitable parameters that underline the high decolourization rate attainable at high values of TiO_2/RhB ratios.

Table 1. Values of k_2 , q_e , and $t_{0.5}$ at different TiO_2/RhB ratio obtained by fitting the experimental data to Eqs. 1 and 2.

	k_2 (kg/g min)	q_e (g/kg)	$t_{0.5}$ (min)
TiO_2/RhB 20	2.31×10^{-4} (± 1.32×10^{-5})	9.87 (± 0.46)	438 (± 32)
TiO_2/RhB 80	0.01 (± 0.002)	1.46 (± 0.11)	68 (± 12)
TiO_2/RhB 150	7.35 (± 0.93)	0.77 (± 0.03)	0.17(± 0.022)

The low $t_{0.5}$ value for the TiO_2/RhB 150 should not surprise due to the large extent (excess) of the adsorption particles in the earlier stages of the reaction [22].

3.2 RhB degradation.

So far, we showed that CDT particles activated by visible light can quickly decolorize RhB. Furthermore, as inferred from Fig. 2, the presence of different peaks detectable during the photodegradation process suggests the presence of different photoprocesses. To further investigate this item we performed fluorescence measurements setting the excitation wavelength in correspondence of some of the species identified through the adsorption maxima spectra of the UV-

Visible spectroscopy (see Fig. 2), namely at 554 nm, 530 nm, 510 nm and 495 nm. Fluorescence spectroscopy has been shown to be a valuable procedure to monitor wastewater as well as an investigating tool on biological macromolecules [33-37]. Fig. 4 shows fluorescence spectra during the CDT mediated visible light RhB degradation carried out at the specified excitation wavelengths. With this approach the identification of at least 4 different intermediates is ascertained. In fact, by focusing one by one on the different excitation wavelength, the presence and the evolutions of transient species is well deductible.

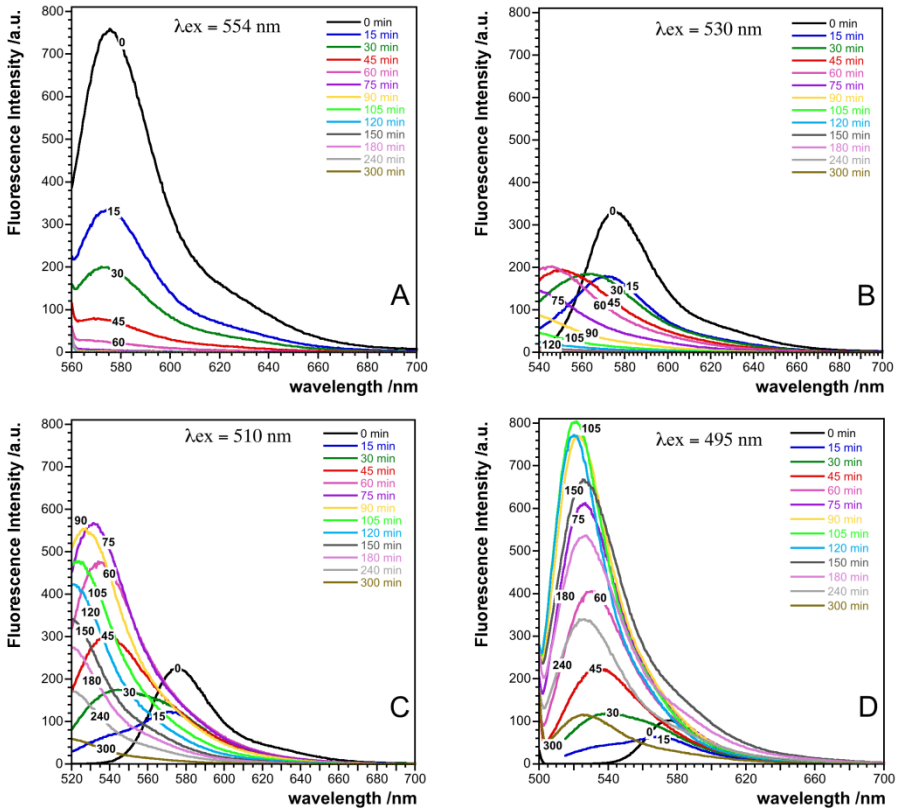

Fig. 4. RhB fluorescence spectra at different excitation wavelengths as function of visible light irradiation time. A: $??_{ex}$ = 554 nm, B: $??_{ex}$ = 530 nm; C: $??_{ex}$ = 510 nm; D: $??_{ex}$ = 495 nm. Ti/RhB: 150.

By exciting the RhB at 554 nm the only species that can be identified is the one that emits at 574 nm. This species completely disappears within 60 minutes of light exposure in the presence of CDT (Fig. 4A). Exciting the Rhodamine at lower wavelengths revealed the existence of other degradation intermediates. The excitation at 530 nm, indeed, allowed the detection of a first N-de-ethylation product already after 30 minutes of light exposure, corresponding to the blue shifted emission maximum. Some species, however, were not well identified because with the progress of the

reaction other intermediates emitting at even lower wavelengths were produced. As apparent in Fig. 4B, the spectra collected starting from the 75 min time point cropped and are better identified at $??_{ex}$ = 510 nm until the 90 min time point. This inconvenience is overcome by exciting the sample at 495 nm. In this condition, it is clear that after 105 minutes no more intermediates are formed and, during the residual time, the degradation of the last intermediate occurs. Such results underline that the whole photodegradation process does not end with the decolourization occurrence.

Furthermore by paying attention at the single emission peaks obtained with the different excitation wavelengths both extents of intermediate lifetimes and the coexistence of intermediates can be identified as a function of the irradiation times (Fig. 5). The main information of Fig. 5 other than the emission wavelength shift is the fact that, after 15 minutes there are 3 or 4 different degradation intermediates of RhB, other 4 species (at least) are detectable at 30 and 45 minutes. After 1 hour there are 3 species and after 105 minute only one intermediate is detectable.

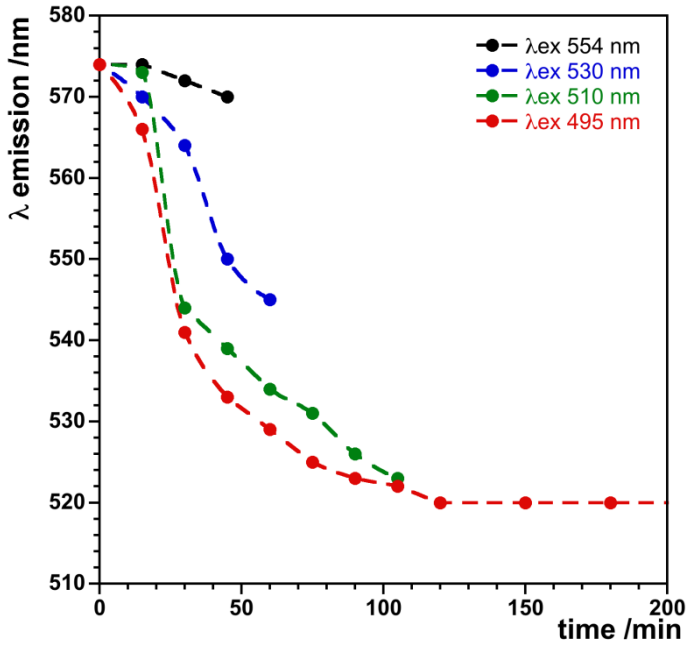

Fig. 5. RhB fluorescence. Emission wavelength shift according to the different excitation wavelength (554, 530, 510 and 495 nm) as function of irradiation time.

Evolutions of the combined fluorescence transient peaks at different reaction times reveal and confirm that all the photoprocesses are connected each other (Fig. 6). In particular, by focusing on

the black and the red spectra of Fig. 6, referring to $??_{ex}$ of 554 and 495 nm, respectively, it is easy to identify the two main species, the first RhB that decomposes and the last intermediate that first increases in intensity, than decomposes, decreasing in emission intensity. The correlation between different fluorescence signals and intermediate evolutions is well highlighted. This evidence should be seen, therefore, as a very important step forward in demonstrating that fluorescence spectroscopy is a suitable tool concerning the subject-matter addressed.

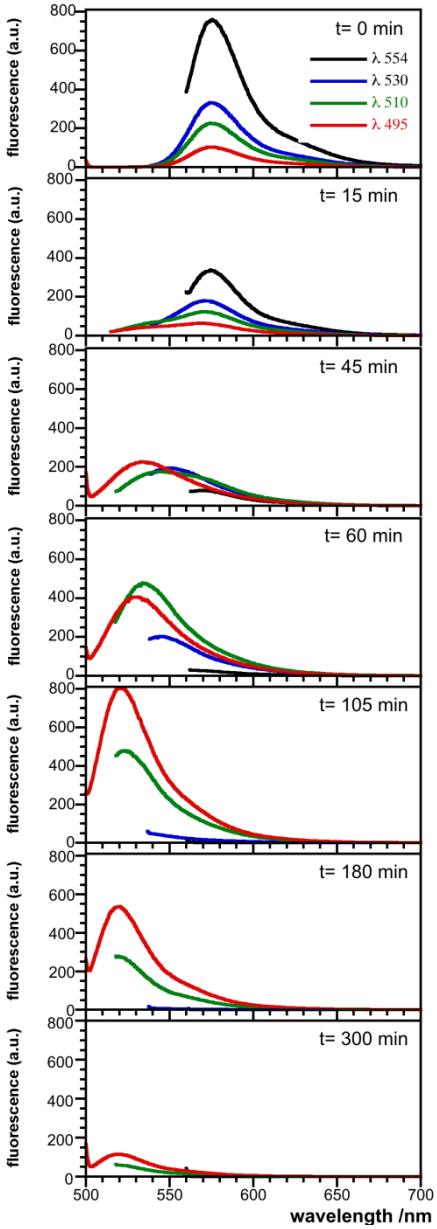

Fig 6. Evolutions of the combined fluorescence transient peaks (554, 530, 510 495 nm) at different reaction times (0, 15, 45, 60, 105, 180, 300 min).

Our results, based on the presence of different intermediates during RhB degradation in the presence of carbon-doped titanium dioxide are in agreement with literature data [29, 30, 38]. In these studies the evidence of such intermediates were identified by means of HPLC where it was reported that intermediates were produced one by one and every intermediates were transformed from the one just before itself.

Moreover, the role of both the catalyst and the dye properties is well established by the presence of two different photoprocesses, photobleaching and N-de-ethylation, that compete each other in the primary steps of the photoreaction [31]. Specifically, it has been shown that the formation of RhB^+ is a prerequisite for photobleaching, while •OH is responsible for the N-de-ethylation step. According to the oxidation potential of RhB and the band edges of TiO_2 the excited dye can inject electrons into the conduction band of TiO_2, which become themselves cationic radicals and undergo further transformation to products [39]. The photosensitization reaction possibly includes the following reactions $RhB + h\nu \rightarrow RhB^* + TiO_2 \rightarrow RhB^+ + TiO_2$ (e).

Alternatively, in the presence of O_2 upon visible light irradiation, electrons can be excited directly into the TiO_2 conduction band and transferred to the adsorbed oxygen molecule to produce O_2^- and then •OH with a strong oxidation power. Carbon doped titanium (CDT) used in this study is characterized by the substitution of carbon atoms in the TiO_2 photocatalyst that adds new states close to the valence band edge of TiO_2 (band gap energy of 3.01 eV) [20, 21]. Hereafter, the conduction band edge shifts to narrow the band gap. The arrangement of carbon into TiO_2 leads to the formation of carbonaceous species, which promotes light absorption in the presence of visible light [18, 32]. Meanwhile, the photogenerated hole oxidizes the adsorbed water molecule (OH^-) to produce •OH radical. The adsorbed dye can thus react with •OH radical and be mineralized into CO_2 and H_2O after a series of reactions [40]. Accordingly, it appears clear that to perform the whole RhB degradation all the criteria such as the presence of O_2 and visible light must met. Therefore with this study carbon doped titanium dioxide in the presence of visible light fulfils the condition to

avoid eventual competitive reaction that do not allow the whole RhB degradation process consisting in N-de-ethylation, chromophore cleavage, opening-ring, mineralization [29].

4. Conclusions

The present study, centered on the removal of Rhodamine B from aqueous solutions, highlights the potential application of this technology for the elimination of dyes from wastewater, a fundamental goal in both the environmental and agronomical fields. Rhodamine B was degraded in the presence of carbon-doped TiO_2 through a photocatalytic process activated by visible light. Kinetics data obtained by means of UV−Vis spectroscopy revealed high degradation rate and substrate concentration dependence. The importance of adsorption process and visible light for such kind of catalyst is confirmed [22]. Fluorescence Spectroscopy allowed understanding that the degradation process of RhB was more than a simple adsorption based decolourization process, but passes through the formation of a series of intermediates generated from the N-de-ethylation reaction and gave information on the formation and co-existence of different intermediates. Such kind of evidence in agreement with previously study obtained by means of HPLC and LC-MS for Rhodamine B degraded in the presence of TiO_2/SiO_2 the presence of Bi_2WO_6 [28,29]. Furthermore, the synergic presence of carbon-doped titanium dioxide and visible light is an important condition to avoid the occurrence of competitive reactions that affect the whole RhB degradation process [29].

Figure legends

Fig. 1. Rhodamine B chemical structure.

Fig. 2. RhB UV-visible adsorption spectra and sample decolourization pictures as function of time exposure to visible light irradiation. Inset λ_{max} shift. Ti/RhB: 150.

Fig. 3. (A) RhB decolourization profiles as function of time. RhB under light irradiation with different amounts of carbon doped TiO_2. TiO_2/RhB ratios 20, 80 and 150. (B) Fitting of the decolourization profiles to Eq. 1.

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Fig 6. Evolutions of the combined fluorescence transient peaks (554, 530, 510 495 nm) at different reaction times (0, 15, 45, 60, 105, 180, 300 min).

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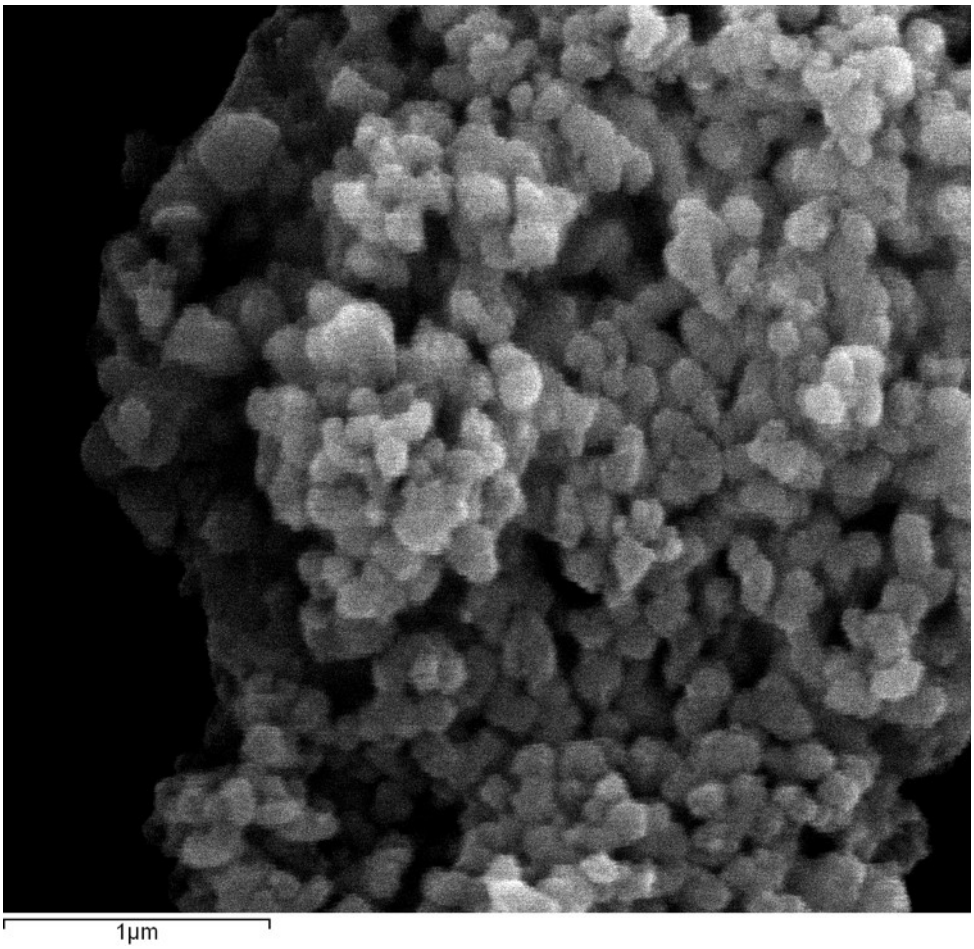

SI1. Freshly prepared Carbon doped titanium particles.