



Influence of surfactant on the fast photodegradation of rhodamine B induced by TiO₂ dispersions in aqueous solution

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ABSTRACT

The photodegradation of dyes under visible light irradiation represents an important step in the study of advanced oxidation processes (AOP). The sensitization of dyes and surface modification of titanium dioxide with adsorption of dyes promote the electron transfer from excited dyes to the conduction band of semiconductor, optimizing and accelerating the dye degradation. In this direction, we report the use of an anionic surfactant (sodium dodecyl sulphate) which promotes the dimerization of rhodamine B and subsequent adsorption on the TiO₂ surface. As a result, it is verified that extremely reduced concentration of titanium dioxide (2×10^{-5} g/mL) is sufficient to provide the photodegradation of dye in scale of minutes.

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1. Introduction

The environmental remediation related with the treatment of high colored wastewater containing dyes represents an important field in applied science if considering the increase in the production of hazard materials as a consequence of industrial development [1–3].

Rhodamine B (Fig. 1), a xanthene cationic dye, is largely applied in industry as a dye for paper. However, it is considered toxic and carcinogenic [4,5], property that justifies the use of rhodamine B as a test pollutant. In this direction, the dye degradation has been studied from the use of procedures such as biological treatment, incineration and advanced oxidation processes (AOP) [6–8]. The last technique is based on the action of strong oxidants (elements with elevated reactivity) such as hydroxyl radicals (HO•) generated from the action of titanium dioxide and used for mineralizing substances such as chloroform and trichloroethylene as a consequence of strong oxidative power of photogenerated holes on the surface of titanium dioxide [9]. This property is associated with nontoxic, high chemical resistance and low cost of TiO₂ [4,10].

Rutile, anatase and brookite represent three possible crystalline structures of titanium dioxide. The most stable of them is the rutile if considering that other forms are converted to the former under heating. The band gap of rutile is 3.0 eV while for anatase its value is 3.2 eV (with a 388 nm cut-off wavelength).

The oxidative process is based on the excitation of TiO₂ by light in the ultraviolet region [11]. Upon excitation in the UV region, photons with energy superior to the bandgap of titanium dioxide are adsorbed and consequently promote the electron transference from valence band (VB) to conduction band (CB) and generate a hole (h⁺) in the valence band as described in Eq. (1):



However, the excitation in the UV region represents a strong limitation for heterogeneous photocatalysis if considering the complete spectrum of sun light. The typical procedure to circumvent this problem is to promote the surface modification of TiO₂ and the subsequent photosensitization in the visible region. This process is optimized with the adsorption of dye molecules on the surface of TiO₂, in an indication that electrostatic interaction between dye and semiconductor plays an important role in the definition of photodegradation efficiency [12].

The solubility of TiO₂ in aqueous media is increased with the acidification of solution, which introduces a serious problem related with low solubility of anionic dyes in acidic media and in other side from electrostatic repulsion between cationic dyes and positively charged semiconductor surface, minimizing consequently the photosensitization [13].

It is reported in the literature that introduction of anionic surfactant induces the adequate environment for aggregation of cationic dyes (at concentrations below the critical micelle concentration – CMC) being considered as a convenient solution for coverage of TiO₂ and allowing that dye can be adsorbed on the semiconductor surface at controlled distance. The use of surfactant as an interaction mediator of dye and TiO₂ assumes a fundamental role in the elec-

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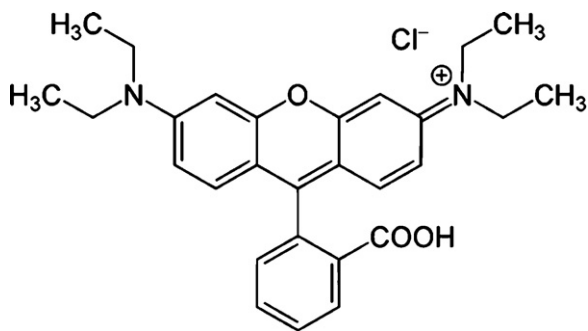


Fig. 1. Structure of rhodamine B.

tron injection from the excited dye to the conduction band of TiO_2 , promoting the subsequent photoconversion of light in the visible region [12–17].

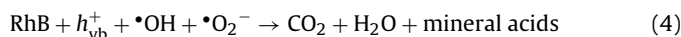
This process is established in the interface dye–semiconductor with the electronic injection occurring from the LUMO of dye to the conduction band of semiconductor (as schematically indicated in Fig. 2), optimizing the absorption of light in the visible region, and consequently a high proportion of incident solar light.

The photo-generated holes promote the oxidative reaction and are trapped by hydroxyl groups resulting in hydroxyl radicals while the electrons are trapped by oxygen providing oxygen species as summarized in Eqs. (2) and (3) [5]



The hole site that appears in the valence band of TiO_2 is thermodynamically favorable to oxidize water to $\bullet\text{OH}$ and the separated electron (in the conduction band) to reduce oxygen if considering that reduction potential of $\bullet\text{OH}$ is +2.85 V and oxygen is –0.13 V [18].

The action of holes, hydroxyl radicals and oxygen species degrades the rhodamine B, producing carbon dioxide, water and mineral acids, as described in the Eq. (4):



In spite of advantage, the promoted electrons in the CB of semiconductor can return to the VB of semiconductor or to the organic dye (processes indicated in Fig. 2 as steps 1 and 2) [14,15], representing a process that can be minimized from the modification of semiconductor surface. In the case of surfactant action, beyond the induced aggregation of dye, the coverage of semiconductor surface act as an additional impediment to the recombination of generated electrons and holes.

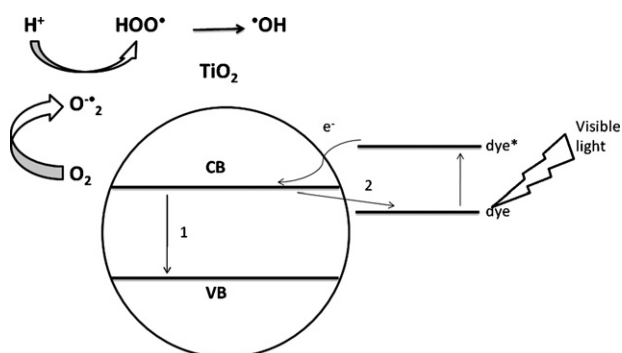


Fig. 2. Electron transfer process from the excitation of rhodamine B in the visible region.

With the aim of analyzing the effect of an anionic surfactant (SDS) on the rate of photodegradation of dye we have studied the effects of white light on the bleaching of rhodamine B characterizing the electrical response, ζ -potential, absorption of light and fluorescence induced by action of titanium dioxide dispersed in aqueous solution.

2. Materials and methods

2.1. Reagents

Rhodamine B (Vetec, Brazil), titanium dioxide (Aldrich, USA) in the form of anatase, and sodium dodecyl sulphate (Aldrich, USA) were used without further purification. A 60 W halogen lamp was used for illuminating the sample disposed in a distance of 30 cm from the light source, minimizing consequently the thermal effects.

2.2. Samples preparation

The samples were prepared using deionized water, in which the complete dispersion of rhodamine B in a concentration of 10^{-6} M was obtained after 10 min under intense stirring. After this step, a fixed amount of anatase (in a concentration of 2×10^{-5} g/mL) was dispersed in the solution in the absence/presence of surfactant (SDS) with varying concentration in the range from 0 to 18 mM. Each sample was intensely stirred during 30 min, a secure time in which adsorption/desorption equilibrium was established. This procedure was realized at dark condition, avoiding the previous photobleaching of samples.

2.3. Analytical methods

The ζ -potential of each sample was measured in a Zeta-sizer Nano ZS90 (Malvern Instruments, Malvern, UK) using folded capillary cells of 0.75 mL (Malvern Instruments). Dynamic light scattering was used to determine the electrophoretic mobility and conductivity while the ζ value was calculated using the Smoluchowski model. All experiments were conducted in triplicates, each one consisting of 20 individual measurements.

Photoluminescence properties were studied by the use of a PC1 spectrofluorimeter (ISS, USA) at 25.0 ± 0.1 °C. The samples were placed in a 5 mL quartz cuvette with a path length of 1.0 cm and excited at 310 nm, while the emission was recorded from 320 to 800 nm. All experiments were conducted in triplicates.

The impedance measurements [19,20] were performed using a SI 1260 (Solartron Instruments, UK) gain/phase impedance analyzer operating in the frequency range of 10^0 – 10^6 Hz. A 100 mV excitation, with no external polarization, was applied to each solution analyzed through a liquid sample holder SI 12962 (Solartron Instruments, UK). Five equally spaced points were obtained in logarithmic scale per decade, and the corresponding values of the real and imaginary parts of the impedance (Z' and Z'' , respectively) were processed through the Smart software (Solartron Instruments, UK), as discussed below. UV–vis spectra were obtained using a FEMTO 800XI spectrophotometer (FEMTO, Brazil).

3. Results and discussion

The interaction of SDS/ TiO_2 /rhodamine B plays a fundamental role in the photoexcitation process of samples [21] in the visible region. The understanding of a microscopic model relative to the disposition of dye molecules, surfactant and titanium dioxide represents the first step in the optimization of photocatalytic processes.

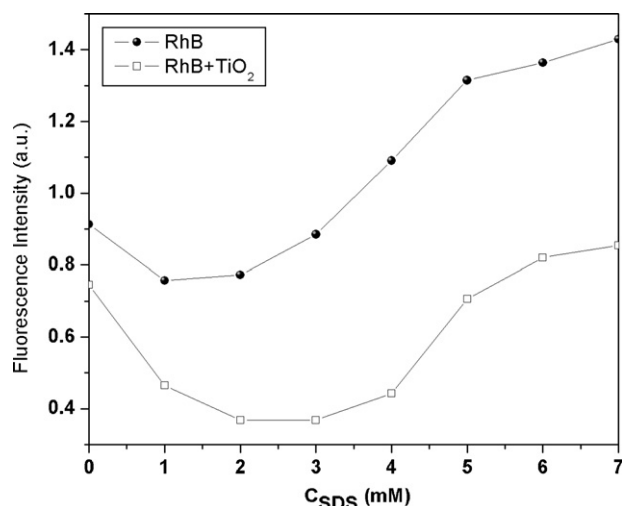


Fig. 3. Fluorescence intensity (measured at 578 nm) of aqueous solution of rhodamine B (10^{-6} M) in the presence (2×10^{-5} g/mL) and absence of TiO_2 as a function of surfactant concentration.

In this direction, we analyzed the fluorescence and ζ -potential of solutions as a function of surfactant and dye concentration. As we can see in Fig. 3, the fluorescence intensity (measured at 578 nm) of rhodamine B is quenched with the progressive insertion of surfactant, in an indication that dimerization is established in the presence of low concentration of SDS (it is known that dimers are typical quenchers [22]).

It is important to note that progressive inclusion of surfactant after the minimum in the fluorescence (Fig. 3) is accomplished by reduction in the dimer concentration since the emission (typical signature of monomers) return to increase. Another aspect to be considered is that inclusion of titanium dioxide act as an additional quencher of fluorescence (evidence of mutual interaction between dimers of rhodamine B and SDS pre-micelles – in the complete range of concentration of surfactant it is verified that fluorescence is enhanced in the absence of titanium dioxide).

The disposition of each component in the aggregate can be clarified from the measurement of ζ -potential of system with increasing concentration of rhodamine B [13,14,22]. As shown in Fig. 4 (as expected) the progressive inclusion of cationic dye induces the

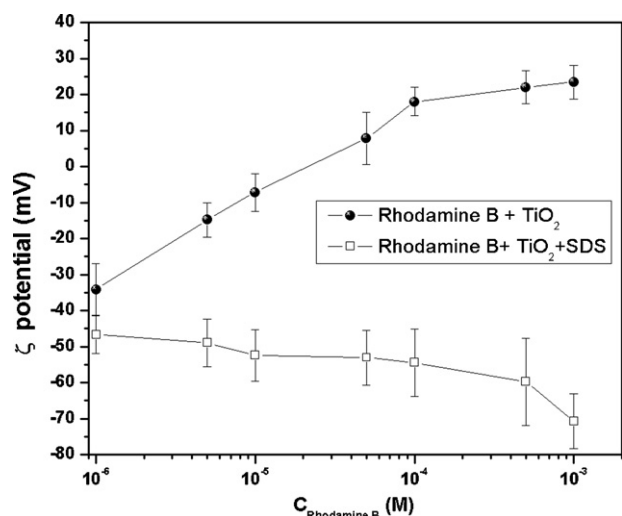


Fig. 4. ζ -Potential of rhodamine B+ TiO_2 (2×10^{-5} g/mL) and rhodamine B+ TiO_2 (2×10^{-5} g/mL)+SDS (5 mM) average and width of distribution in aqueous solution at different concentration of rhodamine B.

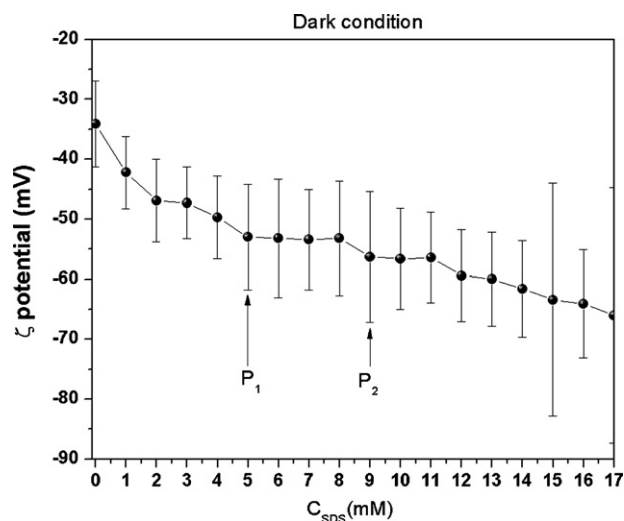


Fig. 5. ζ -Potential of RhB (10^{-6} M) and TiO_2 (2×10^{-5} g/mL) average and width of distribution in aqueous solution at different concentration of SDS.

elevation in the potential of particles (rhodamine B+ TiO_2) in the absence of surfactant. On the other side, the inclusion of SDS (an anionic surfactant) at 5 mM promotes a shift in the potential to a nearly constant negative value, as a consequence of coverage of positive particles, verified in the complete range of analyzed concentration of dye.

The measurement of ζ -potential of complete system as a function of surfactant concentration (Fig. 5) indicates that the increase in the concentration of SDS promotes a progressive elevation (in modulus) in the value of ζ -potential, a consequence of adsorption of components on the surface of TiO_2 .

The monotonic behavior is intercalary by two plateaus identified as P1 and P2, characterizing the saturation in the coverage process induced by inclusion of surfactant.

The former (P1) can be associated with the coverage of dioxido titanium, characterizing a range of surfactant concentration in which the electron transfer from the dye to semiconductor is maximized. The second plateau (P2) characterizes the self-aggregation of SDS (phase transition related with the critical micelle concentration (CMC) as confirmed from measurement of conductivity (see Fig. 6). Note that two linear regions are obtained with an abrupt change in the slope of curves at CMC (8.0 mM for SDS) (according

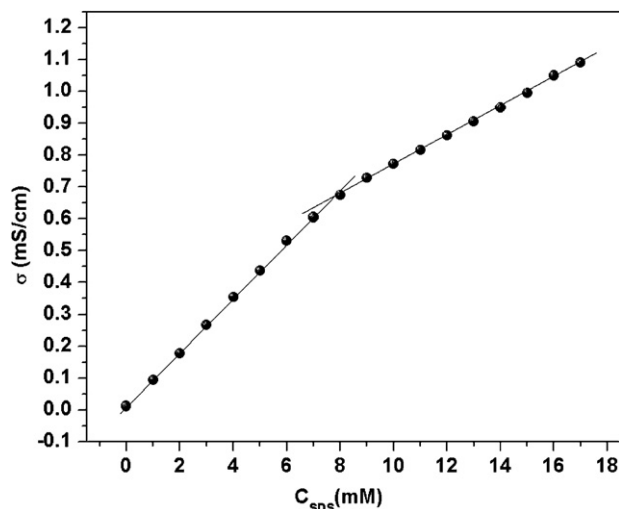


Fig. 6. DC electrical conductivity of RhB (10^{-6} M) and TiO_2 (2×10^{-5} g/mL) aqueous solution at different concentration of SDS.

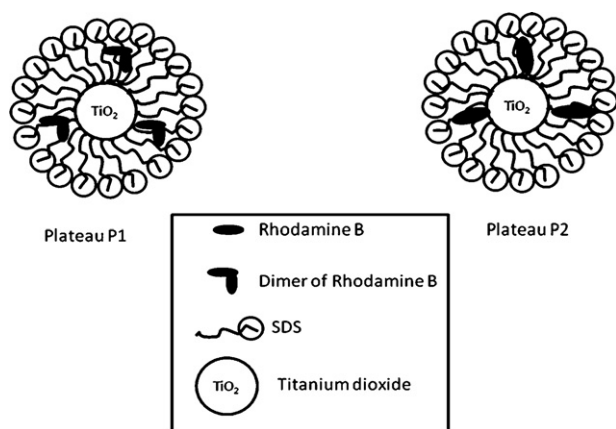


Fig. 7. Scheme of disposition of TiO_2 + rhodamine B + SDS at pre-micelle condition (P1) and above the CMC (P2).

to the Phillips criteria [23–25]) allowing the direct association of second plateau in Fig. 5 with the micellization of SDS. The progressive introduction of surfactant at concentration above the CMC is accomplished by monotonic variation in the ζ -potential, since this behavior characterizes the progressive formation of mixed aggregates (such as giant micelles). It is important to note that above the CMC, monomers are favored to be shielded at hydrophobic environment of micelles, minimizing the electron transfer and subsequent photodegradation.

The first plateau in Fig. 5 characterizes the condition of mutual coverage of dimers on titanium dioxide surface promoted by SDS aggregates, as indicated in the scheme at left side of Fig. 7 [26,27].

The second plateau in Fig. 5 characterizes the existence of micelles of SDS promoting the coverage of titanium dioxide and monomers of rhodamine B (scheme at right side of Fig. 7), since in its condition the emission of dye is maximized in an indication that dye aggregation is strongly reduced.

Based on these results we established in the following experiment a set of samples with a fixed amount of dye (10^{-6} M of rhodamine B) and titanium dioxide (2×10^{-5} g/mL) and different levels of surfactant (absence, 5 mM – typical concentration in the first plateau (P1), and 15 mM – above the CMC), characterizing the most important regions, as previously verified.

Using the procedure of exposing different samples for same irradiation conditions we promoted the incidence of white light, obtaining complete degradation in a few minutes (progressive bleaching of solution) for samples with 5 mM of SDS, as indicated in the images in Fig. 8. At right side we can see the samples before and after the illumination while at left side is shown the emission of samples excited at 365 nm.

It is important to note that analysis of photodegradation was expanded to the complete range of surfactant concentration similarly to the previously analyzed in Fig. 5 and the results indicate that photobleaching is observed only to samples with pre-aggregates of SDS micelles in the range of concentration from 5 mM to 6 mM, since in the absence of surfactant and in the presence of micelles the photobleaching is negligible, in an indication that induced dimerization and coverage of TiO_2 by SDS are sufficient conditions for enhancement of photodegradation rate of rhodamine B. These results are in agreement with those previously described to the ζ -potential data, since the photocatalysis is maximized in the system with optimized coverage of SDS (plateau P1 in Fig. 5). Based on this interesting result, we centered our analysis in the range of SDS

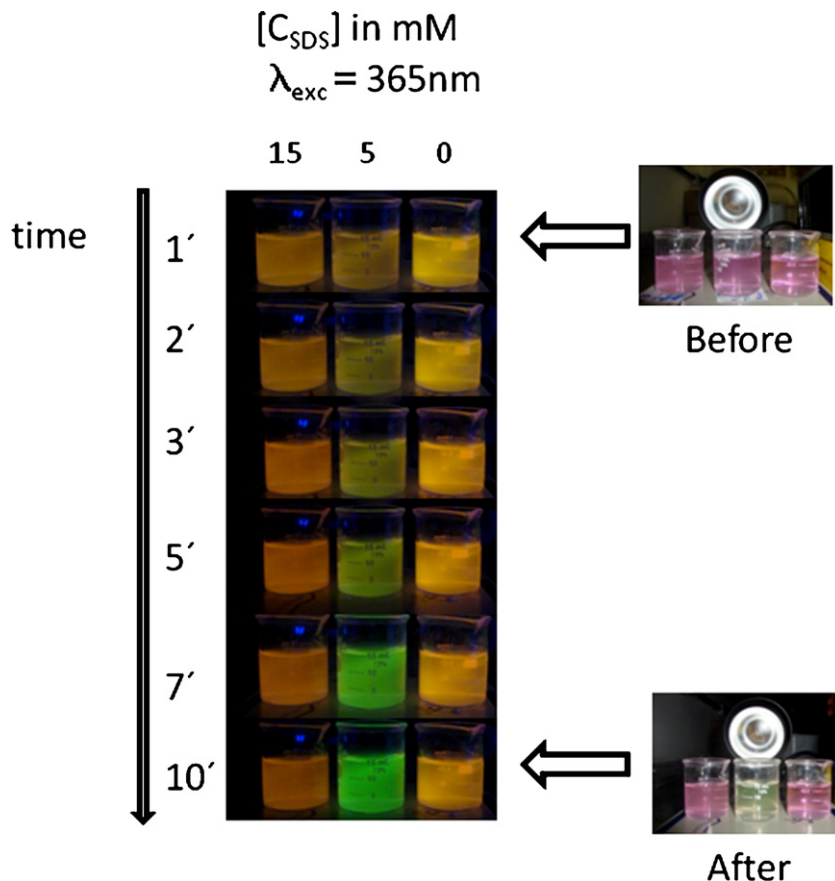


Fig. 8. Photodegradation process induced by white light in solutions of RhB (10^{-6} M) and TiO_2 (2×10^{-5} g/mL) containing 0 mM, 5 mM and 15 mM of SDS.

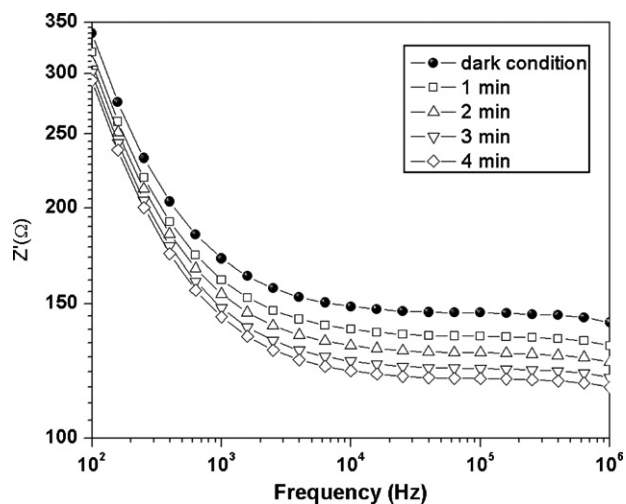


Fig. 9. Impedance spectrum of solutions containing RhB (10^{-6} M), TiO_2 (2×10^{-5} g/mL) and SDS (5 mM) as a function of irradiation time.

concentration that provides the fast photocatalysis of rhodamine B.

As we can see in Fig. 9, the incidence of light on the system promotes the reduction in the level of impedance in the range of frequencies from 100 Hz to 1 MHz, in an indication that electrical conduction increases from prolonged action of radiation, which induces the formation of mineral acids in solution.

The optical response of mixed system (rhodamine B + SDS + TiO_2 – R+S+T system) indicates that absorption in the UV–vis region is blue shifted after 2 min of incidence of white light (as indicated in Fig. 10). The continued incidence of light reduces the intensity of characteristic peak of rhodamine B, indicating that photobleaching is completed after 10 min of irradiation. The photodegradation of rhodamine B is accomplished by reduction in the intensity of absorption band centered at 552 nm and a subsequent hypsochromic shift (blue shift) as reported by Xu et al. [12]. The observed shift is a consequence of a multiple step process from which rhodamine B is de-ethylated and ethyl groups are removed one by one, promoting the shift in the peak from 552 nm to 498 nm as observed in Fig. 10. It is important to note that after 10 min of light incidence the peak at 498 nm disappears and the photodegradation can be considered as complete. In this case, the blue shift acts as a strong evidence of breakup of the chromophore [12] as a consequence of efficient surface modification provided by SDS on TiO_2 particles. The result is confirmed from measurement of fluorescence, as indicated in Fig. 11, where the typical signature

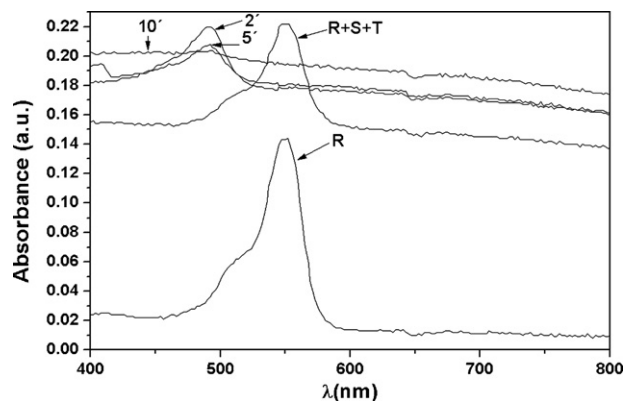


Fig. 10. Absorbance in the visible region for sample containing RhB (10^{-6} M), TiO_2 (2×10^{-5} g/mL) and SDS (5 mM) as a function of irradiation time.

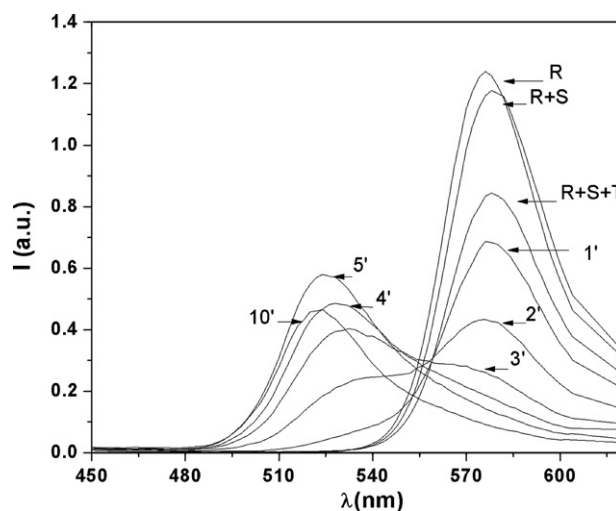


Fig. 11. Fluorescence of sample containing RhB (10^{-6} M), TiO_2 (2×10^{-5} g/mL) and SDS (5 mM) excited at 310 nm as a function of irradiation time.

of rhodamine B emission (peak at 578 nm) is strongly reduced with the incidence of light on the sample, inducing a progressive enhancement of other peak at 528 nm, characterizing the emission of photobleached products such as single aromatic rings obtained as products of photodegradation with strong absorption at 224 nm [22].

4. Conclusions

The coverage of TiO_2 and dimerization of dyes induced by surfactant action of pre-aggregates of SDS at 5 mM provide ideal condition for the fast degradation of rhodamine B, expanding the absorption of light from UV to visible region. The controlled distance from dimers to the surface of TiO_2 implies in the efficient energy transfer from excited dye molecules to the conduction band of TiO_2 , promoting the degradation of rhodamine B after few minutes of incidence of white light.

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