

Photosensitised Degradation of Organic Dyes by Visible Light Using Riboflavin Adsorbed on the Surface of TiO₂ Nanotubes

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A degradação de soluções aquosas de índigo carmim (IC), azul de metileno (MB) e laranja de metilo (MO) assistida pela luz visível foi conseguida sobre a superfície de nanotubos (NTs) de TiO₂ impregnados com riboflavina (RF). Soluções aquosas diluídas de RF na presença de RF-NTs TiO₂ irradiados com luz UV produziram O₂, CO e CO₂ como principais produtos gasosos. As mesmas soluções quando irradiadas com luz visível mostraram que o O₂ foi o produto principal obtido. Esta geração de O₂ *in situ* com luz visível permite a degradação dos corantes, sem a necessidade de borbulhar ar ou oxigênio no sistema de reação. A degradação fotocatalítica de MO, MB e IC pode ser descrita por um modelo de cinética de pseudo-primeira ordem obtendo ca. 100% de degradação de MB, MO e IC em menos de 3 h de iluminação de luz visível. Os resultados aqui apresentados são altamente promissores em vista da potencial aplicação dos catalisadores RF-TiO₂ NTs preparados com dois compostos ambientalmente corretos na degradação de poluentes utilizando radiação solar.

Visible light-assisted degradation of indigo carmine (IC), methylene blue (MB) and methyl orange (MO) aqueous solutions has been achieved on the surface of TiO₂ nanotube (NT) arrays impregnated with riboflavin (RF). Diluted RF water solutions in the presence of RF-TiO₂ NTs irradiated with UV light produced O₂, CO and CO₂ as main gas products. On the contrary, the same solutions irradiated with visible light evolved O₂ as a main product. This *in situ* O₂ generation under visible light absorption allows the degradation of the dyes without the necessity to bubble air or oxygen in the reaction system. The photocatalytic degradation of MO, MB and IC can be described by a pseudo-first-order kinetic model obtaining ca. 100% degradation of MB, MO and IC in less than 3 h of visible light illumination. The results provided here are highly promising in view of various photocatalytic applications of the prepared RF-TiO₂ NTs catalysts by two environmentally friendly compounds in the degradation of pollutants using solar radiation.

Keywords: sensitiser, titanium dioxide, riboflavin, nanotubes, visible light

Introduction

Organic pollutants are a particular type of mankind compound whose concentrations continue to increase each year. As a consequence, their degradation has become a central issue of research efforts in today's scientific community. The bio-degradation of pollutants emitted from various sources is often very slow and conventional treatment is mostly ineffective and not environmentally compatible. In this sense, the application of photocatalysis using semiconductor nanostructured systems appears to

be more efficient than conventional chemical oxidation methods for the transformation of toxic compounds to a non-hazardous product which reaches the complete mineralisation of the pollutant.¹⁻³

Titanium dioxide nanoparticles (TiO₂ NPs), particularly in their usual commercial form known as P25, have been extensively used to oxidise organic pollutants of water using ultraviolet (UV) light.^{2,4-8} Despite TiO₂ presenting high photocatalytic activity in its anatase form, the charge separation of this semiconductor is only possible by absorption of UV solar photons which represent less than 5% of the solar energy that reaches the Earth's surface. In this sense, sensitisation processes resulting

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from photoexcitation of dye molecules (sensitisers) bound to semiconductor NPs are of great importance for photochemical solar energy conversion.⁹ Sensitisation requires that the distance between the sensitiser and the semiconductor's surface be as small as possible. This can be achieved by adsorption of the sensitiser to the semiconductor's surface by an electrostatic, hydrophobic, hydrophilic, or chemical interaction. Thus, after absorption of the photon and electronic excitation, the injection of an electron into the conduction band of the semiconductor is possible, leading to the formation of radical species with high oxidant power. The sensitisation of semiconductors has been widely studied in the past in the development of photoelectrochemical solar cells,^{10,11} electronic devices,^{12,13} heterogeneous photocatalysis,^{3,14-16} and recently many efforts have been made in the production of a visible light photocatalyst to produce hydrogen through water splitting using sensitiser dyes.¹⁷⁻²² The efficiency of those processes depends on the properties of the sensitisers, semiconductor and their interaction under photoexcitation.

Colloidal TiO₂ can be sensitised with different dyes and organic molecules, such as arylimidazole derivatives,²³ hypocrellin B,²⁴ cyanine dyes,²⁵ chlorophyll,²⁶ riboflavin²⁷ and also by the use of metal NPs.^{16,28} In particular riboflavin (RF) photochemistry, the precursor of all the biologically important flavins and recognised as a constituent of the vitamin B complex, has been extensively investigated.^{27,29-35} It was even hypothesised that water can be split photochemically with RF.³⁴ The photochemistry of RF involves two major reactions: (i) normal photolysis (intramolecular photoreduction) and (ii) photoaddition (intramolecular photoaddition).³⁶ Both reactions may occur separately or concomitantly; the extent of each reaction depends on the conditions employed, such as the anion concentration, pH and radiation source. Very low concentrations of sensitisers are usually present in water courses, lakes and seas.^{37,38} Among them, the RF pigment is relevant in the sensitised photooxidation of contaminants and the kinetic mechanisms, which were recently the object of studies on O₂(¹Δ_g) generation under concentrations similar to those frequently found in nature.^{29,39}

Among the various methods available for the preparation of TiO₂ nanomaterials,⁴⁰ the syntheses of TiO₂ nanotubes (NTs) through the anodisation of metallic Ti surfaces has several advantages.⁴¹ The main benefits are a simple synthetic procedure, enhanced charge transport properties, and a cost-effective scale-up process.⁴² In addition, self-organised TiO₂ NT arrays grown with anodisation processes present enhanced photocatalytic activity when compared with randomly-oriented NPs or NTs prepared with other methods, such as the sol-gel (hydrothermal) process.^{42,43} In

the drive to obtain a suitable photocatalyst for harvesting solar energy and converting it to chemical energy, such as hydrogen or hydrocarbons, nanotubes are one of the main choices for the research groups.⁴⁴⁻⁴⁶ This tendency is not generally found in the field of degradation of pollutants, where more traditional synthetic methods or commercial P25 TiO₂ are employed to prepare the photocatalyst. The adsorption of RF on the surface of TiO₂ colloidal particles has already been studied by Kathiravan *et al.*²⁷ The electron transfer process from its singlet excited state to the conduction band of TiO₂ was examined with absorption and fluorescence quenching measurements. The authors suggested a mechanism where there is an electron injection from its singlet excited state into the conduction band of TiO₂.

The main aim of the present work was to examine the experimental conditions that show the existence of an efficient sensitisation process of highly ordered TiO₂ NTs arrays impregnated with a natural pigment, RF, using visible light irradiation. The study was carried out under dye-sensitised photooxidation conditions similar to those frequently found in nature, i.e., in the presence of the natural dye sensitiser RF. We describe the photodegradation by visible light irradiation of three organic dyes (methylene blue, methylene orange, and indigo carmine) using a photocatalyst prepared with two environmentally friendly compounds, RF and TiO₂. The results show the potential of the prepared photocatalyst for cleaning waste water using solar light.

Experimental

Materials and methods

All chemicals were purchased from commercial sources: NH₄F (98%), ethylene glycol (99%) (ETG) and Ti foil (99.6%) from Synth. Solvents and reagents were used as received. RF (98%) and methylene blue (MB) (100%) were obtained from Vetec, Brazil. Methyl orange (MO) (100%) and indigo carmine (IC) (100%) were obtained from Merck, Brazil.

TiO₂ NTs were prepared by anodisation of a Ti foil with a constant applied voltage at room temperature, using an electrolyte containing ethylene glycol + 0.25 wt.% NH₄F + 10 wt.% H₂O with an ultrasonic bath following a methodology already described.⁴⁷⁻⁴⁹ After anodisation, the TiO₂ NTs were annealed at 400 °C for 3 h in air atmosphere in order to crystallise the oxide nanotubes layer. The nanotube structures were characterised by scanning electron microscopy (SEM) obtained with EVO50-Carl Zeiss equipment. Diffuse reflectance UV-Vis spectra

were recorded on a CARY 5000 spectrophotometer with an integrated sphere. UV-Vis absorption spectra were measured with a Varian 50 UV-Visible spectrophotometer. The gaseous products of the photocatalytic reaction were quantified by gas chromatography at room temperature on an Agilent 6820 GC chromatograph. Gases H₂, O₂ and CO, CO₂, CH₄ were analysed simultaneously with a thermal conductivity detector (TCD) and a flame ionisation detector (FID), respectively.⁵⁰

Sensitisation of TiO₂ NTs has been done by impregnation method. The NTs were immersed in an RF solution of about 40 ppm and left in contact in dark ambient conditions for 24 h under continuous stirring. Then the catalysts with adsorbed RF were washed thoroughly with water and finally dried in an oven at 350 K for 2 h.

Photocatalytic activity measurements

Photocatalysis experiments under UV and visible light irradiation were carried out in two different systems. Gas phase product measurements were carried out in a calibrated, gas-closed photochemical reactor made of polytetrafluoroethylene (PTFE) under continuous magnetic stirring.^{49,51} A quartz window allowed irradiation of the aqueous mixture under a wide incident spectral range, including UV and visible light. A 150 W mercury-xenon lamp (Sciencetech Inc.) operating at about 90% power was used as an excitation source. The light beam was focused to homogeneously cover the whole photocatalyst surface (1.23 cm²). TiO₂ NTs were placed in a special PTFE support to avoid photocatalytic activity in regions other than the NTs. The reactor was deaerated with argon by using custom-made PTFE valves prior to irradiation. A maximum volume of 500 µL of the gas contained in the closed reactor was collected with a gas-tight syringe, and the amount of gases produced was measured at hourly intervals. When visible light was used, wavelengths higher or equal to 400 nm were allowed to enter the reactor by using a proper cut-off filter (Newport 10LWF-400-B).

An aqueous solution of the dyes was used to investigate the adsorption performance and photocatalytic activities of the prepared materials. A quartz photochemical reactor was used for the degradation experiments. The same TiO₂ NTs used in the Teflon close reactor were placed in a special PTFE support set in the centre of the reactor and illuminated with the same UV-Vis excitation source. The change in concentration of the dyes was monitored regularly by measuring the absorbance at the correspondent wavelengths: 465 nm (MO), 660 nm (MB), and 610 nm (IC). Most of the time, a 35 mL solution of a dye was irradiated during several hours with a typical concentration

of dyes of 4 ppm (MB), 12 ppm (MO) and 75 ppm (IC), depending on the solubility of the dye. Desorption of RF was observed during the experiments and for this reason the photodegradation of the dyes was carried out with RF dissolved in the water solution at a concentration between 5 and 15 ppm. No decomposition of RF was observed under dark conditions. This was confirmed by UV-Vis spectroscopy analysis.

Results and Discussion

SEM images of the TiO₂ NTs with a roughly 100 nm diameter can be seen in Figure 1-top. TiO₂ NTs were annealed at 400 °C for 3 h in air atmosphere to obtain the anatase phase.^{47,49,51} Finally, TiO₂ NTs were impregnated with RF. The inset of Figure 1-top shows that after RF impregnation, the SEM image of the NTs is blurred and the visualisation of the NTs structure is not clear. This may indicate the presence of RF on the NTs' surface. The impregnation of the TiO₂ NTs with RF was checked after several cycles of washing in ultrasound with diffuse reflectance UV-Vis spectroscopy. The optical properties of the synthesised TiO₂ NTs and RF-TiO₂ NTs were investigated using the Kubelka-Munk model⁵² and, assuming that the sample scattering coefficient was constant for the UV-Vis wavelength range, the absorption behaviour of the samples was determined with the following expression:

$$\frac{\alpha}{s} = \frac{(1 - R)^2}{2R} \quad (1)$$

where α and s are the absorption and scattering coefficients and R is the diffuse reflectance of the samples.

Figure 1-bottom shows the corresponding spectra of crystallised pure and RF-impregnated TiO₂ NTs after 3 h of annealing. From the figure, an intense absorption band can be observed between ca. 275 nm (3.5 eV) and 400 nm (3.1 eV), which is indicative of crystalline semiconducting TiO₂ with a typical band gap of the anatase phase.⁵³ The NTs impregnated with RF show an absorption component between 380 and 540 nm (see Figure 1-bottom), which indicates the presence of RF adsorbed on the TiO₂ NT arrays. Previous studies on absorption and fluorescence spectroscopy showed that RF adsorbs on the surface of colloidal TiO₂ through its phenolic group.²⁷

The general properties of flavins in a free solution have been extensively studied in the past³⁶ and their photochemistry has also been the subject of intense research.^{30,32,54,55} However, a few studies have addressed the photocatalytic properties of RF^{27,56,57} despite there being

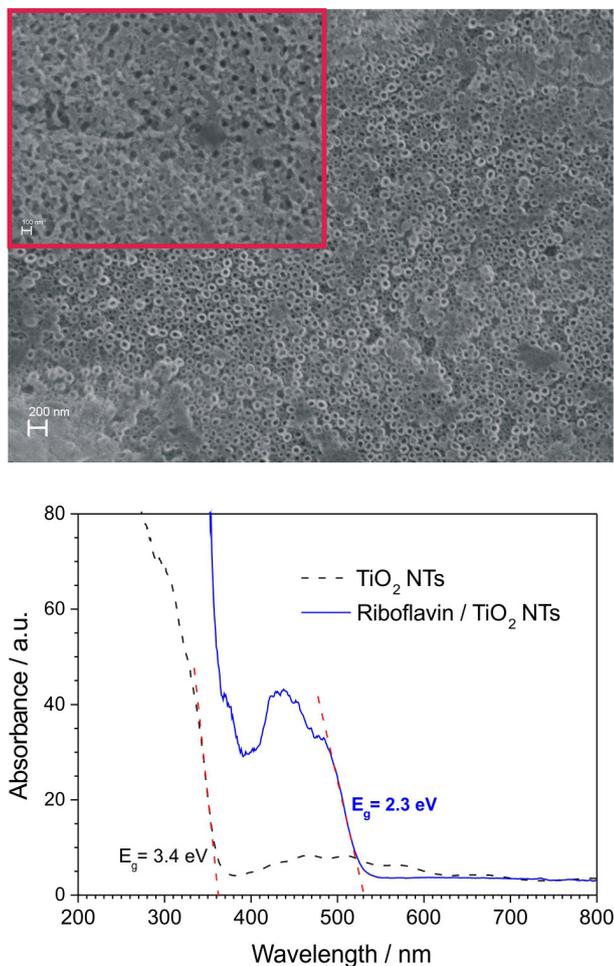


Figure 1. Top view SEM images of a typical TiO_2 nanotube (NT) array grown in an ETG/ammonium fluoride solution (top) and TiO_2 NTs impregnated with RF (inset, error bar: 100 nm). UV-Vis absorption coefficient spectra calculated from diffuse reflectance measurements corresponding to anodic pure TiO_2 NTs and with the impregnation of RF (bottom).

reports in the past proposing a reaction scheme that postulates the splitting of water.³⁴ Therefore, the prepared RF- TiO_2 NT arrays were first tested to know the photocatalytic activity when their water solutions were irradiated with UV-Vis or with only visible light. A common practice in the study of hydrogen generation by water splitting is the addition of sacrificial species, such as methanol, as an electron donor in deaerated solutions.⁵¹ Other alcohols, such as benzyl alcohol, were also used to study the photooxidation reactions under natural weather conditions during the sensitisation of anatase titanium dioxide (Degussa P25) with the impregnation of several dyes (RF, safranin O, methyl red, eosin B and MB).³² Figure 2 shows the evolution of the amounts of gas products for RF impregnated with TiO_2 NTs under UV-Vis or visible ($\lambda \geq 400$ nm) light irradiation. Under dark or illumination conditions without the presence of the TiO_2 NTs, no formation of gases was detected.

Furthermore, Figure 2 also shows that the main gaseous products detected, O_2 , CO and CO_2 , have a strong dependence on the excitation wavelength. Under our experimental illumination conditions, hydrogen was a minority product, with its amount more than 1000 times lower than the main gaseous products detected. When the photocatalysis was carried out with visible light irradiation ($\lambda \geq 400$ nm), the main product obtained was oxygen. CO and CO_2 were detected as minor contributions of the reaction (Figure 2-top). Additionally, the oxygen concentration increased as the illumination time increased, showing it to be an actual sensitised photocatalytic reaction. Under these visible irradiation conditions, TiO_2 NTs are not able to absorb photons (see Figure 1-bottom) and therefore oxygen has to be produced due to an efficient sensitisation process. Electron injection from the RF singlet excited state into the conduction band of TiO_2 was already suggested by fluorescence quenching experiments on colloidal TiO_2 .²⁷ The authors calculated the free energy (ΔG_{et}) of the electron transfer process as -3.1 eV. This high negative ΔG_{et} value indicates that the electron transfer process is thermodynamically favourable.

When UV-Vis irradiation is allowed to reach the system, the amounts of CO_2 detected is comparable with O_2 and in less extension CO (see Figure 2-bottom). This result shows that the TiO_2 NTs are now participating directly in the photodegradation process of RF. In previous studies of photo-induced reforming of alcohols on TiO_2 NTs^{49,51} the mineralisation of the alcohols was not observed, probably due to their high concentration in the water solution. In the present study, CO and CO_2 may certainly be mineralisation products of the RF photocatalysis.

Figure 2 also shows that after RF visible light excitation, an efficient electron transfer from the singlet state of the RF to the conduction band of the TiO_2 NTs takes place. Additionally, those results indicate a very interesting property of the RF- TiO_2 NTs system under visible light illumination: the generation of oxygen *in situ*. This is very relevant, since the degradation of organic pollutants [advanced oxidation processes (AOP)] takes place under aerated conditions with the participation of photogenerated holes. These holes act either directly or indirectly in the degradation process via the generation of hydroxide radicals (OH^\cdot), superoxide ($\text{O}_2^{\cdot-}$) or hydroperoxide (HO_2^\cdot) radicals produced on the surface of TiO_2 by the reduction of atmospheric oxygen.⁵³ These powerful oxidising agents attack on pollutant molecules, ultimately leading to the production of mineralisation products. RF- TiO_2 NTs under visible light illumination produce oxygen *in situ* without the necessity to bubble air or oxygen in the reaction system, which is the standard procedure in photodegradation studies

of aqueous contaminants, and therefore it seems to be a very suitable photocatalyst for pollutant degradation.

Anaerobic and aerobic photobleaching of RF solutions was studied in the past, showing very interesting properties in its photochemical degradation mechanism.^{30,35} It was observed that the concentration of RF decreased with the increase of irradiation time, producing a series of products that were carefully identified.^{30,31,54,55} In particular, when anaerobic conditions were used and air was admitted to the partially bleached solution, reoxidation of the isoalloxazine ring occurred as was indicated by the important recovery of the original absorption at 445 nm and the return of the yellow colour. It was shown that when samples were removed after 17 and 24 h of irradiation, the colour was restored upon admission of air in 89% and 84%, respectively.³⁵ The same mechanism may work in our experimental conditions to keep a high level of RF concentration in the solution. Simultaneously, a small decrease in the pH of the irradiated solutions with the increase in the irradiation time was observed. This could suggest that the oxidation of the water can lead to oxygen evolution, but the study of the actual mechanism is part of further work.

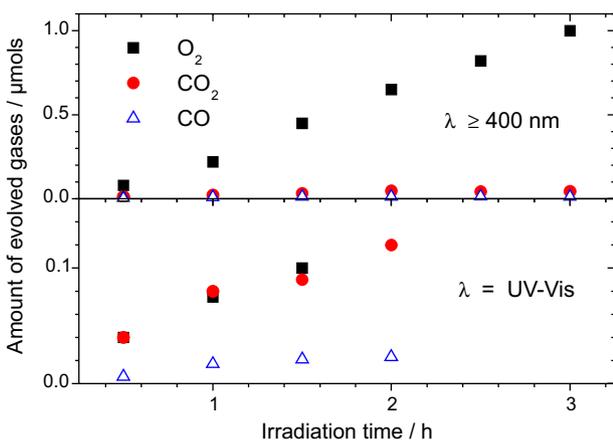


Figure 2. Photocatalytic gas evolution from water solutions containing methanol as an electron donor on RF-impregnated TiO₂ nanotubes. Water:methanol ratio: 8:1, v/v.

Visible light illumination ($\lambda \geq 400$ nm) of the MO solutions in the presence of RF-TiO₂ NTs shows that the decolourisation of MO is proportional to the increase in the irradiation time (Figure 3). As can be seen in Figure 3, the absorption spectra of the MO and RF overlap; nevertheless the main features of the MO, with its characteristic absorption maxima located at 445 and 372.5 nm, remained for up to approximately 2 h of irradiation. After this period of visible light irradiation, the degradation of the remaining RF solution is observed and typical products of RF degradation,^{54,55} such as lumiflavin (LF), lumichrome

(LC) and probably minor products formylmethylflavin (FMF) and cyclodehydroriboflavin (CDRF), still remained in the UV spectra (Figure 3). The photolysis of RF in an aqueous solution occurs through 7,8-dimethyl-10-(formylmethyl) isoalloxazine (formylmethylflavin) as an intermediate, which is hydrolysed to LC and LF as the major photoproducts.⁵⁵ A general scheme of the chemical reactions that occur in RF photolysis is the following:³⁰



Depending on the reaction conditions, the photodegradation reactions of RF can lead to the formation of CDRF by photoaddition and FMF by photoreduction, subsequently leading to LC and LF by hydrolysis.^{54,55} CDRF and LC are the two major final products obtained and FMF is an intermediate in the photoreduction reaction. Comparison of the final UV spectra shown in Figure 3, after 5 h of visible irradiation, with typical UV spectra obtained after photodegradation of RF in water solution^{30,54,55} may indicate that LF [main molar absorption coefficients (ϵ_{max} at 445 and 356 nm)] and LC (ϵ_{max} at 356 nm) may remain as the main RF photocatalytic products. CDRF may also be present in lower concentrations (ϵ_{max} at 410 nm). It is important to point out that an aqueous solution of MO in the presence of pure TiO₂ NTs irradiated with a cut of filter of $\lambda \geq 400$ nm did not produce any decolouration of the solution after 6 h of irradiation.

To avoid overlapping of the UV-Vis absorption of the dye with the RF, a different dye was photodegraded under the same illumination conditions used for MO. The inset

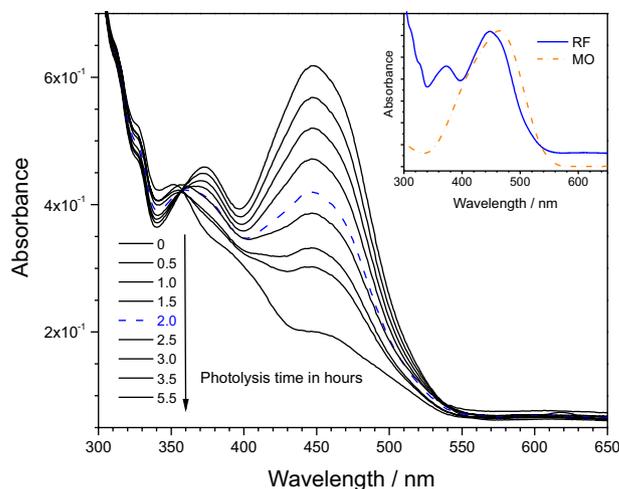


Figure 3. Decolourisation of a methyl orange (MO) solution vs. time in typical photocatalytic experiments performed using RF-TiO₂ NTs under visible light illumination (cut of filter ≥ 400 nm). Initial MO concentration was 6 ppm. Normalised spectra of pure aqueous solutions of RF and MO are also shown in the inset figure.

of Figure 4 shows the UV-Vis spectrum of IC, where it is possible to see a large shift to longer wavelengths in the absorption maximum of the IC compared to the RF (Figure 3). In this case, there is not interference in the absorption spectra of both dyes. When an IC aqueous solution of 75 ppm is illuminated with visible light in the presence of pure TiO₂ NTs (without RF impregnation), no change in the IC UV-Vis spectrum is observed (see inset of Figure 4). It means that the presence of IC did not sensitise the TiO₂ NTs and there was not any electron transfer process after photon excitation of the IC dye to the semiconductor. The lack of a photocatalytic reaction of IC in the presence of pure TiO₂ NTs contrasted when the NTs were impregnated with RF and irradiated with $\lambda \geq 400$ nm (see Figure 4). Figure 4 shows a fast photocatalytic reaction that totally degrades the dye (IC) in less than 3 h of irradiation with visible light. The results presented in Figure 4 show the potential of the impregnated photocatalyst prepared where a complete decolouration of the solution can be obtained only with visible light by using a RF-TiO₂ NTs photocatalyst.

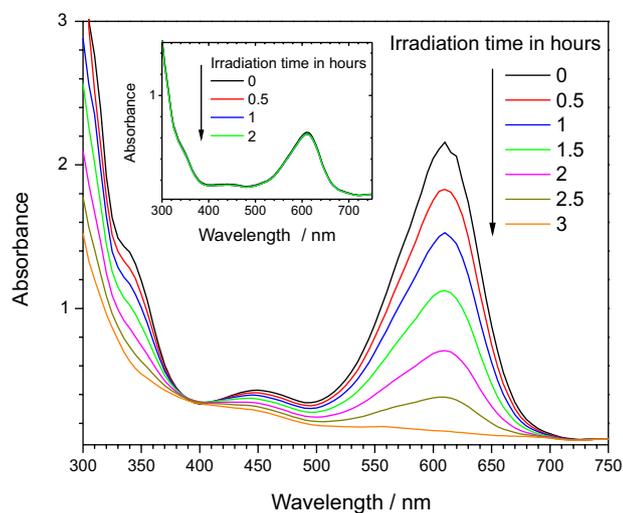


Figure 4. Photodegradation of an indigo carmine (IC) solution vs. time in typical photocatalytic experiments performed using RF-TiO₂ NTs under visible light illumination (cut of filter ≥ 400 nm). Initial IC concentration was 75 ppm. Inset: 75 ppm IC solution irradiated with visible light ($\lambda \geq 400$ nm) in the presence of pure TiO₂ NTs without RF impregnation.

The rate of the heterogeneous photocatalytic degradation of a dye has been described with the Langmuir-Hinshelwood mechanism,⁵⁸ which can be expressed with the following mathematical equation:

$$r = -\frac{dC}{dt} = \frac{kK_{ad}C}{1 + K_{ad}C} \quad (4)$$

where r represents the initial rate of photooxidation, C is the variable concentration at any time t , k is the reaction

rate constant, and K_{ad} is the adsorption coefficient of dye on photocatalyst. If the concentration of the dye is low enough, pseudo-first-order reaction conditions apply and the product $K_{ad} \times C$ is very small compared with 1 in the denominator of equation 4. Integrating equation 4, after the above simplification, the following is obtained:

$$\ln \frac{C_0}{C} = kK_{ad}C = k_{app}t \quad (5)$$

where $k_{app} = kK_{ad}$ is the apparent pseudo-first-order reaction rate constant and C_0 is the initial concentration of the dye.

In order to evaluate qualitatively the rate of photodegradation of different dyes under visible light illumination using a RF-TiO₂ NT photocatalyst, the linear relationship of the natural logarithm of the ratio between the initial concentration of the dye and the concentration after photocatalytic degradation [$\ln(C_0/C)$] versus the corresponding irradiation time is plotted in Figure 5. The results indicate that the photocatalytic degradation of MO, MB (without UV-Vis absorption overlapping with the RF spectrum) and IC can be described by the first-order kinetic model. The value of k_{app} obtained from the slopes of the linear curves shown in Figure 5 gives a qualitative indication for the activity of the photocatalyst because the concentrations of the dyes used were different and the amount of dyes adsorbed in each case may also be different. Nevertheless, the apparent pseudo-first-order reaction rates obtained from Figure 5 show that the ratio of the degradation rates for the dyes follow the order 3.6, 1.4, and 1 for IC, MO, and MB, respectively. Additionally, as in the case of MO, the irradiation of IC and MB under visible light in the presence of TiO₂ NTs without impregnation

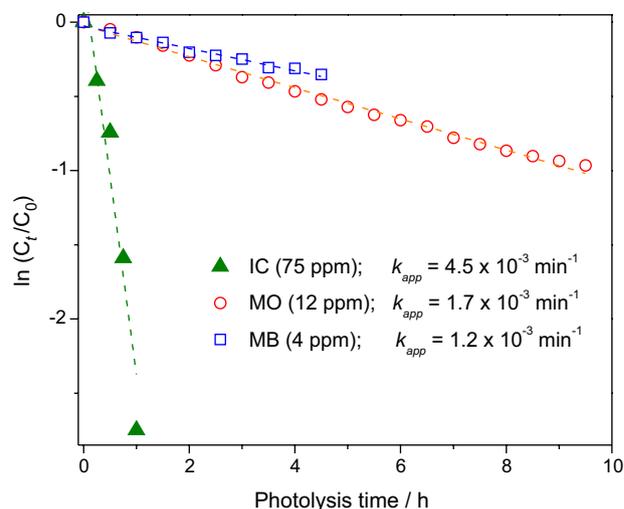


Figure 5. Apparent first-order linear plot of $\ln(C_t/C_0)$ versus the irradiation time of indigo carmine (IC), methylene blue (MB) and methyl orange (MO) degradation kinetics for RF-TiO₂ NTs photocatalyst under visible light illumination (cut of filter ≥ 400 nm).

of RF, did not produce any decolouration of the dyes (see Figure S1 in the Supporting Information section).

On the surface of unmodified crystal TiO₂, oxygen atoms with a high electron density (negative centres) are mainly present. Thus, the TiO₂ NTs may have a negative charge and adsorption and higher values of the photocatalytic degradation rate constant for cationic dyes should be expected.⁵⁹ Although the literature survey has revealed many examples of degradation studies, there is no example of any correlation which might exist between degradation percent and structure or class of dyes.⁵⁹⁻⁶¹ Our own studies on three different classes of dyes, where MB is a cationic dye and IC and MO are anionic types, have established a relative rank order of ease of dye degradation as follows: IC > MO > MB. Various operational parameters affect the activities of TiO₂-based photocatalysts. Some dyes are degraded at lower pH, while others at higher pH; hence in photocatalytic degradation of dyes in wastewaters, the reaction depends on the proper pH. Oxidising agents, calcination temperature, type of TiO₂ catalyst and catalyst loadings are found to exert their individual influence on the photocatalytic degradation of any dye. In the present work, a decrease in pH was observed during irradiation with visible light (oxygen was potentially generated by water splitting). Therefore, for the effective study of the photocatalytic degradation of different dyes, all the aforementioned parameters must be given full consideration. This kind of detailed investigation is out of the scope of the present work focused on the photosensitised degradation of organic dyes by visible light using a RF-TiO₂ NTs photocatalyst.

Conclusions

An efficient photocatalyst for oxidation of water-dissolved dyes by visible light irradiation was prepared with RF anchored on the surface of TiO₂ NTs. RF water solutions irradiated in the presence of RF-TiO₂ NTs with UV or visible light led to different gaseous products. RF degradation was observed by UV irradiation producing O₂, CO and CO₂ as the main gaseous products. On the other hand, visible light irradiation mainly evolved O₂ with CO and CO₂ as minor products. The fact that oxygen gas was generated *in situ* during irradiation with no mineralisation of RF allows the use of the prepared photocatalyst for the degradation of dyes with visible light as excitation source. The results obtained in the present study on photocatalytic degradation of three prototype dyes using a RF-TiO₂ NT photocatalyst demonstrated that in the presence of visible light, surface adsorbed RF can efficiently sensitise a TiO₂ NT semiconductor. Water solutions of IC, MB and MO were

irradiated with $\lambda \geq 400$ nm and their degradation kinetics were measured. The apparent pseudo-first-order reaction rate constants have been determined from absorption changes, showing that the photocatalytic degradation of MO, MB and IC can be described by a pseudo-first-order kinetic model. The results provided here are highly promising in view of various photocatalytic applications of the prepared RF-TiO₂ NT catalysts in the degradation of water dissolved pollutants using solar radiation, taking into account that RF is frequently found dissolved in water in nature.

Supplementary Information

Supplementary data are available free of charge at <http://jbcbs.sbgq.org.br> as PDF file.

Acknowledgments

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References

1. Malato, S.; Fernandez-Ibanez, P.; Maldonado, M. I.; Blanco, J.; Gernjak, W.; *Catal. Today* **2009**, *147*, 1.
2. Gaya, U. I.; Abdullah, A. H.; *J. Photochem. Photobiol., C* **2008**, *9*, 1.
3. Chatterjee, D.; Dasgupta, S.; *J. Photochem. Photobiol., C* **2005**, *6*, 186.
4. Chen, D.; Ray, A. K.; *Water Res.* **1998**, *32*, 3223.
5. Acosta, D. R.; Martinez, A. I.; Lopez, A. A.; Magana, C. R.; *J. Mol. Catal. A: Chem.* **2005**, *228*, 183.
6. Reyes, C.; Fernández, J.; Freer, J.; Mondaca, M. A.; Zaror, C.; Malato, S.; Mansilla, H. D.; *J. Photochem. Photobiol., A* **2006**, *184*, 141.
7. Patsoura, A.; Kondarides, D. I.; Verykios, X. E.; *Catal. Today* **2007**, *124*, 94.
8. Mai, J.; Sun, W.; Xiong, L.; Liu, Y.; Ni, J.; *Chemosphere* **2008**, *73*, 600.
9. Oregan, B.; Gratzel, M.; *Nature* **1991**, *353*, 737.
10. Tulloch, G. E.; *J. Photochem. Photobiol., A* **2004**, *164*, 209.
11. Nazeeruddin, M. K.; Baranoff, E.; Graetzel, M.; *Sol. Energy* **2011**, *85*, 1172.
12. Krebs, F. C.; *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 394.
13. Chen, X.; Li, C.; Graetzel, M.; Kostecki, R.; Mao, S. S.; *Chem. Soc. Rev.* **2012**, *41*, 7909.

14. Wang, Z. P.; Jun, X.; Cai, W. M.; Zhou, B. X.; He, Z. G.; Cai, C. G.; Hong, X. T.; *J. Environ. Sci.* **2005**, *17*, 76.
15. Kuznetsov, V. N.; Serpone, N.; *J. Phys. Chem. B* **2006**, *110*, 25203.
16. Li, W.; Cui, X.; Wang, P.; Shao, Y.; Li, D.; Teng, F.; *Mater. Res. Bull.* **2013**, *48*, 3025.
17. Jiang, L.; Wang, Q. Z.; Li, C. L.; Yuan, J. A.; Shangguan, W. F.; *Int. J. Hydrogen Energy* **2010**, *35*, 7043.
18. Tachan, Z.; Hod, I.; Zaban, A.; *Adv. Energy Mater.* **2014**, *4*, DOI: 10.1002/aenm.201301249.
19. Maitani, M. M.; Zhan, C.; Mochizuki, D.; Suzuki, E.; Wada, Y.; *Appl. Catal., B* **2014**, *147*, 770.
20. Antoniadou, M.; Sfaelou, S.; Dracopoulos, V.; Lianos, P.; *Catal. Commun.* **2014**, *43*, 72.
21. Waskasi, M. M.; Hashemianzadeh, S. M.; Sarhangi, O. M.; Harzandi, A. P.; *Energy Convers. Manage.* **2012**, *62*, 154.
22. McCormick, T. M.; Calitree, B. D.; Orchard, A.; Kraut, N. D.; Bright, F. V.; Detty, M. R.; Eisenberg, R.; *J. Am. Chem. Soc.* **2010**, *132*, 15480.
23. Karunakaran, C.; Jayabharathi, J.; Jayamoorthy, K.; Devi, K. B.; *Spectrochim. Acta, Part A* **2012**, *89*, 187.
24. Wu, T.; Xu, S.-J.; Shen, J.-Q.; Chen, S.; Zhang, M.-H.; Shen, T.; *J. Photochem. Photobiol., A* **2000**, *137*, 191.
25. Chen, C.; Qi, X.; Zhou, B.; *J. Photochem. Photobiol., A* **1997**, *109*, 155.
26. Kathiravan, A.; Chandramohan, M.; Renganathan, R.; Sekar, S.; *Spectrochim. Acta, Part A* **2009**, *71*, 1783.
27. Kathiravan, A.; Renganathan, R.; *Spectrochim. Acta, Part A* **2008**, *71*, 1080.
28. Zhang, D.; Wen, M.; Zhang, S.; Liu, P.; Zhu, W.; Li, G.; Li, H.; *Appl. Catal., B* **2014**, *147*, 610.
29. Escalada, J. P.; Pajares, A.; Gianotti, J.; Biasutti, A.; Criado, S.; Molina, P.; Massad, W.; Amat-Guerri, F.; Garcia, N. A.; *J. Hazard. Mater.* **2011**, *186*, 466.
30. Ahmad, I.; Ahmed, S.; Sheraz, M. A.; Vaid, F. H. M.; Ansari, I. A.; *Int. J. Pharm.* **2010**, *390*, 174.
31. Ahmad, I.; Ahmed, S.; Sheraz, M. A.; Vaid, F. H. M.; *J. Photochem. Photobiol., B* **2008**, *93*, 82.
32. Hussein, F. H.; Alkhateeb, A. N.; *Desalination* **2007**, *209*, 350.
33. Melo, T. B.; Ionescu, M. A.; Haggquist, G. W.; Naqvi, K. R.; *Spectrochim. Acta, Part A* **1999**, *55*, 2299.
34. Enns, K.; Burgess, W. H.; *J. Am. Chem. Soc.* **1965**, *87*, 1822.
35. Smith, E. C.; Metzler, D. E.; *J. Am. Chem. Soc.* **1963**, *85*, 3285.
36. Silva, E.; Edwards, A. M.; *Flavins: Photochemistry and Photobiology*; The Royal Society of Chemistry: Cambridge, 2006.
37. Chacon, J. N.; McLearnie, J.; Sinclair, R. S.; *Photochem. Photobiol.* **1988**, *47*, 647.
38. Benassi, C. A.; Scoffone, E.; Galiazzo, G.; Iori, G.; *Photochem. Photobiol.* **1967**, *6*, 857.
39. Escalada, J. P.; Pajares, A.; Gianotti, J.; Massad, W. A.; Bertolotti, S.; Amat-Guerri, F.; Garcia, N. A.; *Chemosphere* **2006**, *65*, 237.
40. Chen, X.; Mao, S. S.; *Chem. Rev.* **2007**, *107*, 2891.
41. Mor, G. K.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A.; *Nano Lett.* **2005**, *5*, 191.
42. Zhu, K.; Neale, N. R.; Miedaner, A.; Frank, A. J.; *Nano Lett.* **2007**, *7*, 69.
43. Jitputti, J.; Pavasupree, S.; Suzuki, Y.; Yoshikawa, S.; *Jpn. J. Appl. Phys.* **2008**, *47*, 751.
44. Liu, G.; Wang, K.; Hoivik, N.; Jakobsen, H.; *Sol. Energy Mater. Sol. Cells* **2012**, *98*, 24.
45. Rajeshwar, K.; *J. Appl. Electrochem.* **2007**, *37*, 765.
46. Bavykin, D. V.; Friedrich, J. M.; Walsh, F. C.; *Adv. Mater.* **2006**, *18*, 2807.
47. Wender, H.; Feil, A. F.; Diaz, L. B.; Ribeiro, C. S.; Machado, G. J.; Migowski, P.; Weibel, D. E.; Dupont, J.; Teixeira, S. R.; *ACS Appl. Mater. Interfaces* **2011**, *3*, 1359.
48. Feil, A. F.; Weibel, D. E.; Corsetti, R. R.; Pierozan, M. D.; Michels, A. F.; Horowitz, F.; Amaral, L.; Teixeira, S. R. R.; *ACS Appl. Mater. Interfaces* **2011**, *3*, 3981.
49. Feil, A. F.; Migowski, P.; Pierozan, M. D.; Corsetti, R. R.; Scheffer, F. R.; Rodrigues, M.; Pezzi, R. P.; Machado, G.; Amaral, L.; Teixeira, S. R.; Weibel, D. E.; Dupont, J.; *J. Braz. Chem. Soc.* **2010**, *21*, 1359.
50. Gonçalves, R. V.; Migowski, P.; Wender, H.; Eberhardt, D.; Weibel, D. E.; Sonaglio, F. V. C.; Zapata, M. J. M.; Dupont, J.; Feil, A. F.; Teixeira, S. R.; *J. Phys. Chem. C* **2012**, *116*, 14022.
51. Languer, M. P.; Scheffer, F. R.; Feil, A. F.; Baptista, D. L.; Migowski, P.; Machado, G. J.; de Moraes, D. P.; Dupont, J.; Teixeira, S. R. R.; Weibel, D. E.; *Int. J. Hydrogen Energy* **2013**, *38*, 14440.
52. Murphy, A. B.; *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1326.
53. Fujishima, A.; Zhang, X.; Tryk, D. A.; *Surf. Sci. Rep.* **2008**, *63*, 515.
54. Ahmad, I.; Fasiliullah, Q.; Vaid, F. H. M.; *J. Photochem. Photobiol., B* **2004**, *75*, 13.
55. Ahmad, I.; Fasihullah, Q.; Noor, A.; Ansari, I. A.; Ali, Q. N. M.; *Int. J. Pharm.* **2004**, *280*, 199.
56. Li, Y.; Hsu, P.-C.; Chen, S.-M.; *Sensor. Actuat. B-Chem.* **2012**, *174*, 427.
57. Yamashita, M.; Rosatto, S. S.; Kubota, L. T.; *J. Braz. Chem. Soc.* **2002**, *13*, 635.
58. Houas, A.; Lachheb, H.; Ksibi, M.; Elaloui, E.; Guillard, C.; Herrmann, J.-M.; *Appl. Catal., B* **2001**, *31*, 145.
59. Rauf, M. A.; Ashraf, S. S.; *Chem. Eng. J.* **2009**, *151*, 10.
60. Devi, L. G.; Murthy, B. N.; Kumar, S. G.; *Chemosphere* **2009**, *76*, 1163.
61. Akpan, U. G.; Hameed, B. H.; *J. Hazard. Mater.* **2009**, *170*, 520.

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