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# Potential Applications for Solar Photocatalysis: From Environmental Remediation to Energy Conversion

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## 1. Introduction

Taking into consideration the impacts of increasing concern as a result of human activity on the environment in recent decades, different approaches have been developed and proposed to minimize the persistence of organic and inorganic pollutants, not only the dangerous or biorecalcitrant. Industrial waste discharges, those from domestic sewage, and so-called emerging contaminants (pesticides, hormones and drugs), among others, have caused numerous problems for the sustainability of ecosystems (Amat et al., 2011).

In general, environmental problems are largely associated with the disposal of waste into sewers, rivers and eventually into the ocean. The damage caused to biota by these discharges is incalculable (Hermann & Guillard, 2002; Corcoran et al., 2010).

New and effective forms of wastewater treatment are essential to enable a responsible economic development of the planet ensuring its sustainability for future generations (Amat et al., 2011). These processes need to be environmentally safe, providing the elimination of contaminants and not just promoting a phase transfer, ensuring the reuse of water (Hermann & Guillard, 2002; Machado et al., 2003a; Sattler et al., 2004; Wojnárovits et al., 2007).

Besides the application in order to minimize the environmental impacts of human action, via photocatalytic processes, semiconductor oxides have also been employed in producing chemical raw materials through specific chemical reactions (Kanai et al., 2001; Murata et al., 2003; Amano et al., 2006; Denmark & Venkatraman, 2006; Hakki et al., 2009; Swaminathan & Selvam, 2011; Swaminathan & Krishnakumar, 2011), in the conversion of solar energy into electricity (Prashant, 2007; Patrocínio et al., 2010; Huang et al., 2011; Zhou et al., 2011) and

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production of hydrogen for subsequent generation of energy (Jing et al., 2010; Kim & Choi, 2010; Melo & Silva, 2011).

## 2. Advanced Oxidation Processes (AOP)

Advanced Oxidation Processes (or Advanced Oxidative Technologies) stand out among the new technologies potentially useful for the minimization of environmental impacts to biota (Ismail et al., 2009), and, among these technologies, are the photocatalytic degradation of contaminants in the environment, especially using solar radiation (Martin et al., 1995; Zioli & Jardim, 1998; Machado et al., 2003a; Duarte et al., 2005; Augugliaro et al., 2007; Machado et al., 2008). They are characterized by being able to degrade a wide range of organic contaminants into carbon dioxide, water and inorganic anions through reactions involving oxidizing species, particularly hydroxyl radicals which have a high oxidizing power ( $E^\circ=2.8$  V) (Nogueira & Jardim, 1998; Machado et al., 2003a; Machado et al., 2008; Kumar & Devi, 2011).

Among the AOP can be cited processes involving the use of ozone, hydrogen peroxide, catalytic decomposition of hydrogen peroxide in acid medium (Fenton or/and photo-Fenton reactions), and semiconductors such as titanium dioxide (heterogeneous photocatalysis) (Nogueira & Jardim, 1998; Kumar & Devi, 2011). The heterogeneous photocatalysis is considered one of the most promising advanced oxidation technologies. In heterogeneous photocatalytic processes, highly oxidizing reactive oxygen species (ie hydroxyl radicals, superoxide radical-ions, etc.) are generated from interaction between the semiconductor electronically excited, oxygenated species and other substrates (Andreozzi et al., 1999; Fujishima et al., 2007; Machado et al., 2008; Kumar & Devi, 2011).

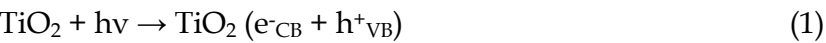
The solar photocatalysis deserves special attention, since the sun is a virtually inexhaustible source of energy at no cost (Machado et al., 2008; Amat et al., 2011).

### 2.1 Heterogeneous photocatalysis

The great potential of heterogeneous photocatalysis has been demonstrated mainly in the treatment of industrial effluents and wastewater through the degradation of contaminants (Malato et al., 1997; Andreozzi et al., 1999; Malato et al., 2002; Sattler et al., 2004a, 2004b; Duarte et al., 2005; Pons et al., 2007; Palmisano et al., 2007a; Machado et al., 2008). A significant number of these studies have focused on the photocatalytic properties of  $\text{TiO}_2$ , suggesting a promising use of this material in heterogeneous photocatalysis (Mills & Hunte, 1997; Malato et al., 2002; Mills et al., 2002; Machado et al., 2003a; Machado et al., 2003b; Sattler et al., 2004a, 2004b; Duarte et al., 2005; Palmisano et al., 2007a; Pons et al., 2007; Machado et al., 2008; Oliveira et al., 2012).

The potential of heterogeneous photocatalysis has been demonstrated in studies originally reported by Fujishima and Honda (Fujishima & Honda, 1971, 1972). The photoactivation of a semiconductor is based on its electronic excitation by photons with energy greater than the band gap energy. This tends to generate vacancies in the valence band – VB (holes,  $h^+$ ) and regions with high electron density ( $e^-$ ) in the conduction band – CB (Hoffmann et al., 1995; Nogueira & Jardim, 1998; Kumar & Devi, 2011). These holes have pH dependent and strongly positive electrochemical potentials, in the range between +2.0 and +3.5 V, measured against a saturated calomel electrode (Khataee et al., 2011). This potential is sufficiently positive to generate hydroxyl radicals ( $\text{HO}^\cdot$ ) from water molecules adsorbed on the surface of the

semiconductor (eqs. 1-3). The photocatalytic efficiency depends on the competition between the formation of pairs of electrons and holes in semiconductor surface and the recombination of these pairs (eq.4) (Nogueira & Jardim, 1998; Ziolli & Jardim, 1998; Ni et al., 2011).



The electrons transferred to the conduction band are responsible for reducing reactions, such as the formation of gaseous hydrogen and the generation of other important oxidizing species such as superoxide anion radical. In the case of TiO<sub>2</sub>, the band gap energy, E<sub>g</sub>, is between 3.00 and 3.20 eV (Hoffmann et al., 1995; Palmisano et al., 2007a; Jin et al., 2010; Kumar & Devi, 2011). This process can be viewed schematically in Fig. 1.

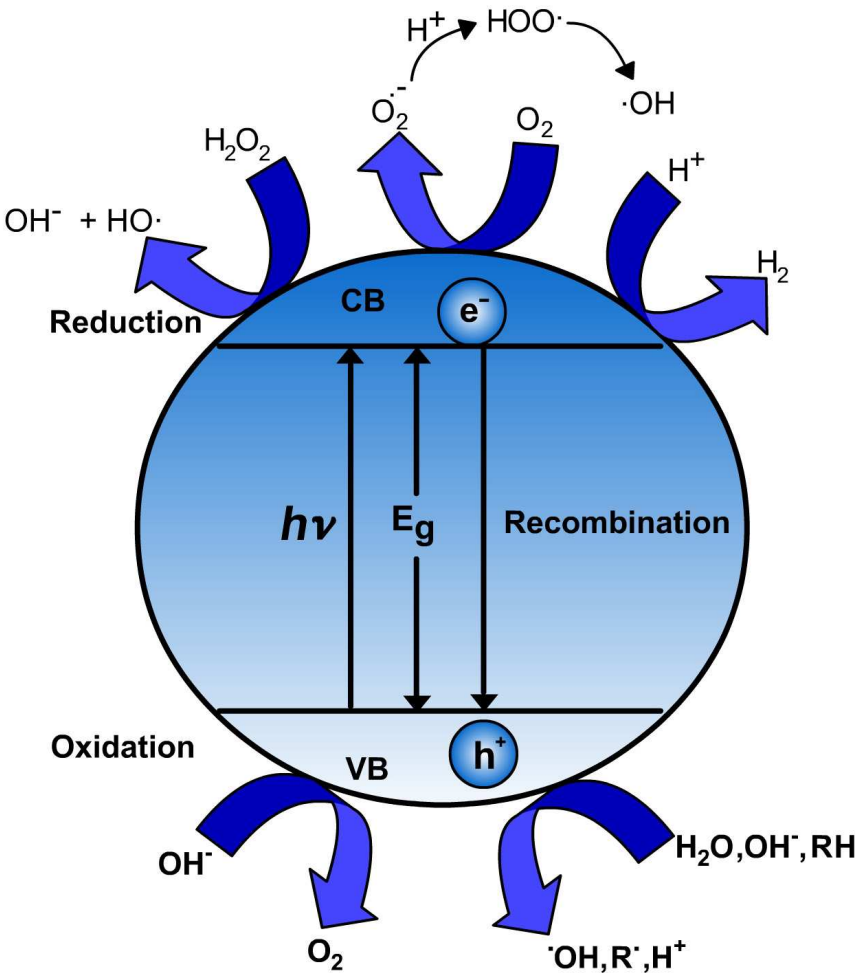


Fig. 1. General scheme for some primary processes that occur after photoactivation of a semiconductor and for photocatalytical production of gaseous hydrogen by decomposition of water.

The production of reactive species by a  $\text{TiO}_2$  photocatalyst is influenced by a series of factors, such as surface acidity and pH of the reaction medium, control of the kinetic of recombination of charge carriers, interfacial electron-transfer rate, optical absorption of the semiconductor, phase distribution, morphology, specific surface area and porosity (Hoffmann et al., 1995; Furube et al., 2001; Diebold, 2003; Carp et al., 2004; Kumar & Devi (2011).

The reactions (1) to (4) combined with other (Hoffmann et al., 1995; Machado et al., 2008; Kumar & Devi, 2011) give an approximate view of the chain reactions that compose a heterogeneous photocatalytic process.

Different semiconductors are able to trigger the heterogeneous photocatalytic processes. Other in addition to  $\text{TiO}_2$  are: CdS, ZnO, ZnS, and  $\text{Fe}_2\text{O}_3$  (Nogueira & Jardim, 1998).

$\text{TiO}_2$  stands in front of others for its abundance, low toxicity, good chemical stability over a wide pH range, photosensitivity, photostability, insolubility in water, low cost, chemical inertness, biological and chemical inertness, and stability to corrosion and photocorrosion (Martin et al., 1995; Augugliaro et al., 2007). However, its band gap energy limits, in principle, its application in photocatalytic processes induced by solar radiation, since the radiation incident on the biosphere consists of approximately 5 % UV, 43 % visible and 52 %, harvesting infrared (Kumar & Devi, 2011).

The introduction of changes in the crystalline structure of  $\text{TiO}_2$  through the introduction of dopant ions and/or modifying ions and associations between  $\text{TiO}_2$  and other semiconductor oxides in order to expand the use of incident radiation, is particularly important if the aim is to use solar radiation in photocatalytic processes. The synthesis of new materials based on  $\text{TiO}_2$  has resulted in substantial progress towards the improvement of the photocatalytic activity of this semiconductor (Imhof & Pine, 1997; Cavalcheiro et al., 2008; Eguchi et al., 2001; Agostiano et al., 2004; Machado et al., 2008; Zaleska et al., 2010; Batista, 2010; Machado et al., 2011b).

Titanium dioxide can be found in nature in the form of three different polymorphs: Anatase, Rutile and Brookite (Hanaor & Sorrell, 2011; Khataee et al., 2011; Kumar & Devi, 2011). Among these polymorphs, the thermodynamically more stable is the rutile, which can be obtained from the conversion of anatase, which in turn is the most photoactive polymorph (Hoffmann et al., 1995; Khataee et al., 2011).

Technological applications of titanium oxide are quite large. In addition to the previously described,  $\text{TiO}_2$  has been used in filters to absorb ultraviolet radiation (sunscreens, for example), pigments, in chemical sensors for gases (Pichat et al., 2000), as constituents of ceramic materials for bone and dental implants (Chen et al., 2008), among others.

## 2.2 Changes in the structure and surface of titanium dioxide

Strong light absorption and suitable redox potential are prerequisites for photocatalytic reactions. Growing interest has focused on doped  $\text{TiO}_2$  catalysts (Ohno et al., 2003; Luo et al., 2004; Li et al., 2005; Labat et al., 2008; Yang et al., 2008; Long et al., 2009; Zhang et al., 2010; Zaleska et al., 2010; Iwaszuk & Nolan, 2011; Long & English, 2011; Spadavecchia et al., 2011; Kumar & Devi, 2011;), however current achievements are still far from the ideal goal.



In order to extend the photocatalytic activity in the region of visible light, and in order to achieve a better use of solar radiation, several approaches have been proposed for tuning the band gap response of titania to the visible region. Doping or incorporate trace impurities in the structure of  $\text{TiO}_2$  in order to obtain materials with photocatalytic activity maximized in the visible region are strategies widely used (Ohno et al., 2003; Li et al., 2005; Zaleska et al., 2010). These strategies include doping with transition metals (Nogueira & Jardim, 1998; Yamashita et al., 2001; Cavaleiro et al., 2008; Zaleska et al., 2010), nonmetals (Ohno et al., 2003; Li et al., 2005), and the inclusion of low-valence ions on the surface of the semiconductor (for example,  $\text{Ag}^+$ ,  $\text{Ni}^{3+}$ ,  $\text{V}^{3+}$  e  $\text{Sc}^{3+}$ ). Certain metals, when incorporated to titanium dioxide, are able to decrease the band gap, making possible in some cases its application in solar photocatalysis. Furthermore, they can contribute to minimize the electron-hole recombination, increasing the photocatalytic efficiency of the semiconductor (Zaleska et al., 2010).

Coupling of two photocatalysts has also been considered effective for improvement of photocatalytic efficiency. As example, nitrogen doped  $\text{TiO}_2$  coupled with  $\text{WO}_3$  and after loaded with noble metal, resulted in a material with improved photocatalytic efficiency (Yang et al., 2006).

### 2.2.1 Synthesis of $\text{TiO}_2$

We have performed the synthesis of titanium dioxide using different methodologies (Batista, 2010; Oliveira, 2011). A modification was introduced in the methodology of the synthesis by precipitation of  $\text{TiO}_2$  using titanium tetraisopropoxide as precursor suggested by Batista (Batista, 2010). It consists in making the whole process, since the solubilization of the precursor in 2-propanol, always under the action of ultrasound. The solid obtained was dried at  $60^\circ\text{C}$  and subjected to heat treatment at  $400^\circ\text{C}$ . This new photocatalyst has been adopted in our most recent studies since it has shown impressive photocatalytic activity in the mineralization of different organic substrates (Machado et al., 2011b). As a result, we have studied the introduction of modifications in order to enlarge it, especially expanding it to the visible.

After annealing, the semiconductor was highly crystalline, being only anatase with average crystallite size around 12 nm, estimated from the line width obtained for the peak of greatest intensity in XRD (**Fig.2**). For a semiconductor synthesized according to a similar methodology adopted by Batista, the minimum crystallite size obtained was equal to 22 nm (Batista, 2010).

From the curves of diffuse reflectance, the band gap of the synthesized  $\text{TiO}_2$  and  $\text{TiO}_2$  P25 Degussa were estimated. For this, we used Tauc's method (Wood & Tauc, 1972). For the synthesized  $\text{TiO}_2$  was obtained a value equal to 3.18 eV while for  $\text{TiO}_2$  P25 Degussa the estimated band gap was equal to 3.20 eV, in agreement with the value described by many authors (Hoffmann et al., 1995; Machado et al., 2008; Batista, 2010). The earlier versions obtained by precipitation, reported by Batista in his DSc Thesis (Batista, 2010) showed no photocatalytic activity due to its proper degree of aggregation and in some cases limited surface area. Most likely, due to the significant aggregation observed in semiconductor synthesized by Batista (2010), the recombination of charge carriers was more favored at the expense of photocatalytic reactions. It is very likely that the introduction of ultrasound in

the synthesis process resulted in significant increase in the dispersion of the particles formed during the formation of critical nuclei, resulting in the precipitation of particles with minimal or no aggregation. Morphological characterization of this new photocatalyst is ongoing.

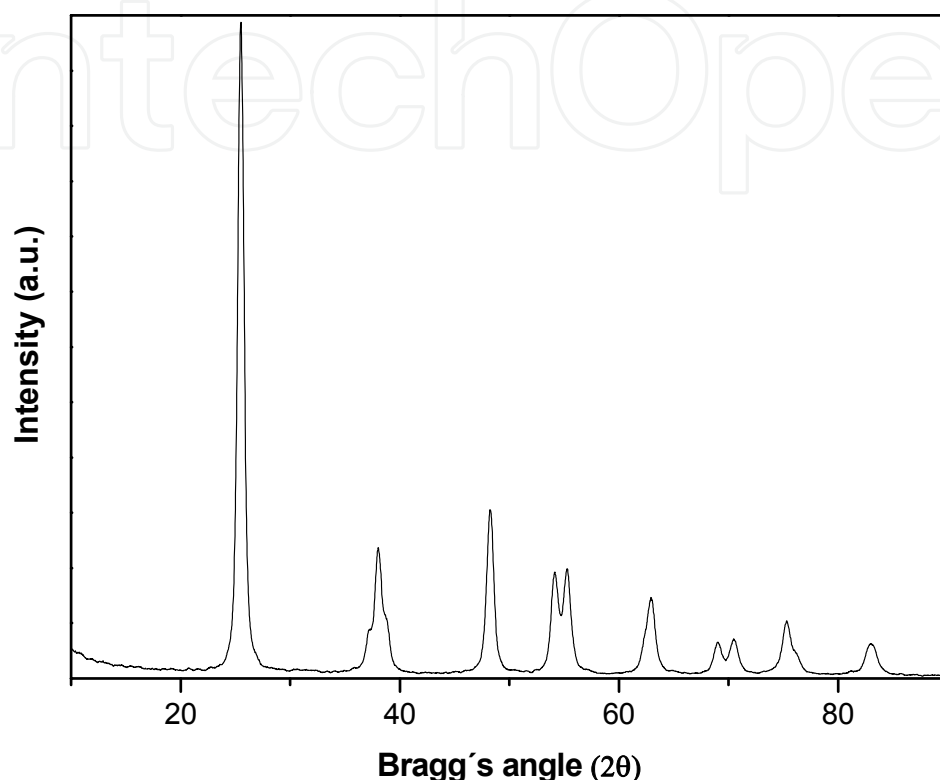


Fig. 2. X-ray diffraction patterns of  $\text{TiO}_2$  synthesized by solubilization of titanium tetraisopropoxide in 2-propanol and subsequent hydrolysis and precipitation by slow addition of ultrapure water.

The mineralization of food dye tartrazine, C.I. 19140, mediated by this new photocatalyst is presented as an example. It was promoted at pH 3, using 100 mg/L of photocatalyst, in experiments on laboratory scale, using as radiation source a 400 W high pressure mercury vapor lamp. 4 L of the model effluent were used per experiment. Hydrogen peroxide (166 mg/L) was added as an extra font of radicals (Machado et al., 2003a). The results were compared to the obtained under the same conditions using  $\text{TiO}_2$  P25 Degussa as photocatalyst. Additionally, all photolysed samples underwent the following tests: pH monitoring, spectrophotometric measurements through the use of a UV/VIS dual beam Shimadzu UV-1650PC spectrophotometer. The aliquots collected in the experiments in the presence of the photocatalyst were filtered using Millipore filters (0.45  $\mu\text{m}$  of mean pore size) to remove suspended  $\text{TiO}_2$  before the measurements. The experimental setup is similar to that described in previous studies (Machado, 2003; Oliveira, 2012).

After 120 minutes of reaction, 52% of mineralization was reached with the use of the synthesized  $\text{TiO}_2$ . For  $\text{TiO}_2$  P25-mediated degradation, the mineralization was 84% under

the same conditions. In the absence of  $\text{H}_2\text{O}_2$ , the levels of mineralization were respectively 24 and 38% for the synthesized  $\text{TiO}_2$  and  $\text{TiO}_2$  P25 (**Fig. 3**). The mineralization was estimated from measurements of dissolved organic carbon using a Shimadzu TOC-VCPH Total Organic Carbon Analyzer.

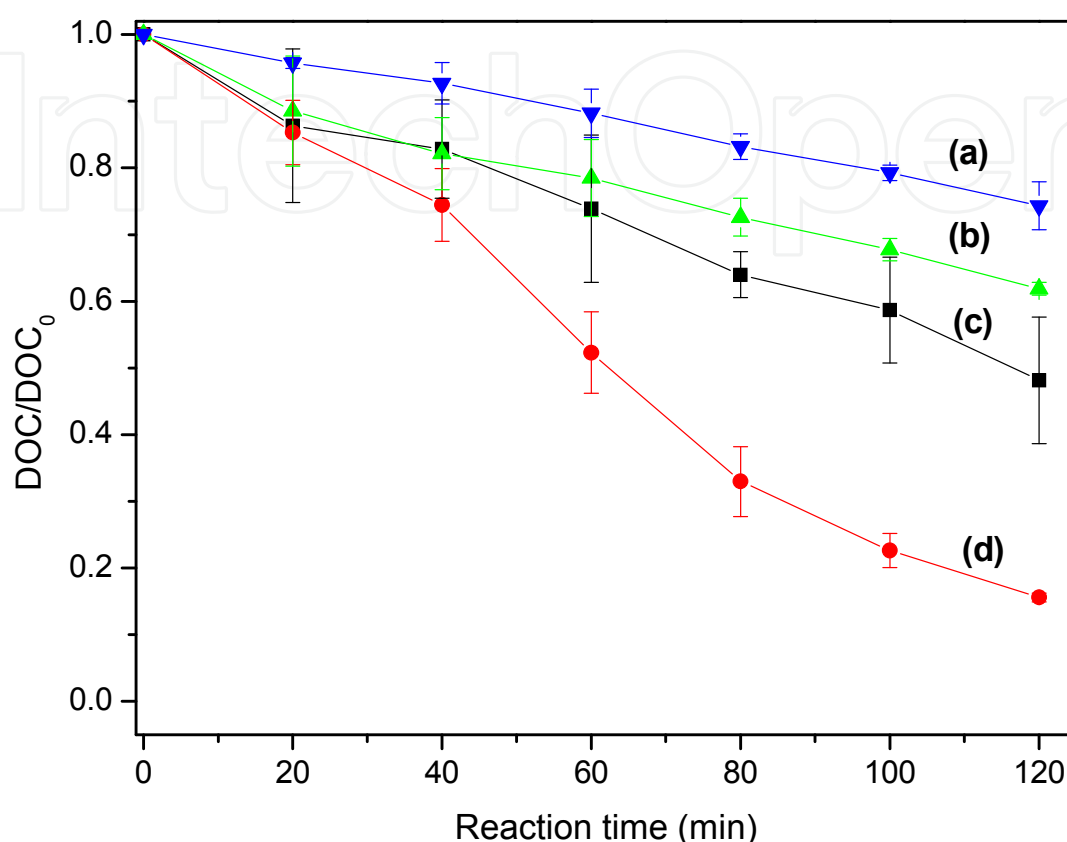


Fig. 3. Mineralization of tartrazine by heterogeneous photocatalysis using: (a)  $\text{TiO}_2$  synthesized in reaction in the absence of  $\text{H}_2\text{O}_2$ ; (b)  $\text{TiO}_2$  P25 in reaction in the absence of  $\text{H}_2\text{O}_2$ ; (c)  $\text{TiO}_2$  synthesized, in reaction in the presence of  $\text{H}_2\text{O}_2$ , and (d)  $\text{TiO}_2$  P25 reaction in the presence of  $\text{H}_2\text{O}_2$ .

The changes introduced during the solubilization and synthesis process itself should have been enough to guarantee a level of ordering of the particles formed. The final product after thermal treatment of the oxide formed proved to be 100% anatase.

### 2.2.2 Photocatalysts based on the association between a photosensitizing dye and a semiconductor oxide

Electron transfer at the interface between a photoactive species and the semiconductor surface is a fundamental aspect for organic semiconductor devices (Grätzel, 2001; Ino et al., 2005). Certain photoactive compounds has proven to be able, when electronically excited, to inject electrons in the conduction band of semiconductors (Grätzel, 2001; Ino et al., 2005; Rehm et al., 1996; Nazeeruddin et al., 1993; Asbury et al., 2001; Krüger et al., 2001; Argazzi et al., 1998; Xargas et al., 2000; Tennakone et al., 1997; Sharma et al., 1991; Hao et al., 1998; Chen et al., 1997; Wu et al., 2000), increasing the performance of dye-sensitized solar cells. In



particular, ultrafast charge separation led by electron injection from electronically excited photoactive molecules to the conduction band of a wide-gap metal oxide, and a good electronic coupling between dye molecules and surface of the substrate are key steps for improving the performance of these materials (Rehm et al., 1996; Nazeeruddin et al., 1993; Asbury et al., 2001). In the dye sensitization process, dye gets excited rather than the  $\text{TiO}_2$  particles to appropriate singlet and triplet states, being subsequently converted to cationic dye radicals after electron injection to  $\text{TiO}_2$  CB (Benko et al., 2002). The electrons injected to  $\text{TiO}_2$  CB react with the preadsorbed  $\text{O}_2$  to form oxidizing species (superoxide, hydroperoxyl and hydroxyl radicals) which combined to the species produced from photoexcited  $\text{TiO}_2$ , induce oxidative reactions (Wu et al., 1998). Thus  $\text{TiO}_2$  plays an important role in electron-transfer mediation, even though  $\text{TiO}_2$  itself is not excited. A photodegradation mechanism of dyes under visible irradiation without  $\text{TiO}_2$  photoexcitation was recently presented by Kumar & Devi (2011). The formation of singlet oxygen has been reported in some cases (Stylidi et al., 2004).

The association between photosensitizing dyes and oxides semiconductors with photocatalytic activity constitutes a strategy for obtaining more efficient photocatalysts for a wider range of applications. These photosensitizing dyes, when excited by photons of lower energy, allow the injection of electrons from these species to the conduction band of the semiconductor increasing the concentration of charge carriers (Benkő et al., 2002; Sharma et al., 2006; Machado et al., 2008; Shang et al., 2011; Kumar & Devi, 2011). The electrons, in turn, can be transferred to reduce organic acceptors adsorbed on the catalyst surface (Machado et al., 2008). Thus, the photocatalyst composites containing a photosensitizing dye associated with the photoactive semiconductor have, in general, improved photocatalytic activity. The possibility of utilization of solar radiation, because they have the range of absorption expanded to the visible, makes it possible achieve important contributions in solving problems concerning effluent treatment (Machado et al., 2008). Machado and coworkers (2003b; 2008; 2011; Duarte et al., 2005) have studied composites prepared by the association between zinc phthalocyanine (ZnPc) and titanium dioxide, obtained by coating  $\text{TiO}_2$  particles using a solution of zinc phthalocyanine followed by controlled drying of the organic suspension (Machado et al., 2008). These materials have been intensively characterized (Machado et al., 2008; Batista et al., 2011). A decrease between 20 and 30% in the specific surface area (SSA) is verified for the composites when compared to the  $\text{TiO}_2$  P25 (Machado et al., 2008; Oliveira et al., 2011; Batista et al., 2011). This difference should be as a result of the incorporation of ZnPc aggregates on the surface of the semiconductor. The changes in the specific area caused by the incorporation of zinc phthalocyanine do not imply distortions in the crystal structure (Machado et al., 2008). Scanning tunneling microscopy of different metal phthalocyanines confirm that the above mentioned aggregates are adsorbed onto the semiconductor surface (Qiu et al., 2004).

For these composites, the surface sensitization by electron transfer via physisorbed ZnPc should compensate the decrease in surface area, increasing the efficiency of the photocatalytic process. It should be emphasized that the extended range of wavelengths shifted to the visible region of the electromagnetic spectrum, which is capable of positively influencing the electron transfer between the excited dye and the semiconductor conduction band tends to improve electron-hole separation (Machado et al., 2008; Carp et al., 2004;

Wang et al., 1997; Shourong et al., 1997; Zhang et al., 1997; Zhang et al., 1998). These composites have shown to be better photocatalysts for wastewater decontamination, mainly mediated by visible light, than pure  $\text{TiO}_2$  (Machado et al., 2003b; Duarte et al., 2005; Machado et al., 2008; França, 2011; Oliveira et al., 2012), performance that remains even when reused (Machado et al., 2008).

The zero point charge pH ( $\text{pH}_{\text{ZPC}}$ ) was estimated for  $\text{TiO}_2$  P25 and a composite containing 1.6% m/m of ZnPc by zeta potential measurements, carried out in a disperse suspension using a Zetasizer Nano ZS90. The estimated value for the composite,  $\text{pH}_{\text{ZPC}} = 5.50$ , lower than the one for P25 ( $\text{pH}_{\text{ZPC}} = 6.25$ ) suggests a differentiated behavior for the composite since its surface is negatively charged in a pH range in which P25 is still with the surface positively charged. The value measured for  $\text{TiO}_2$  P25 agrees with the reported in the literature (Hoffmann et al., 1995). The morphological characteristics of both samples were investigated by SEM, carried out in a Philips XL-30 microscope coupled to a field emission gun and a EDX analytical setup. The micrographs show the occurrence of macro-aggregates in the composite and spherical particles around 25 nm in P25. The estimated concentration of ZnPc on P25 surface is around 1.6%, confirmed by EDX measurements (Batista et al., 2011). Also, the thickness of ZnPc coating, homogeneity, and aggregation on the  $\text{TiO}_2$  composite surface were evaluated by TEM using a Philips CM-120 microscope. The improvement of visible light absorption in  $\text{TiO}_2/\text{ZnPc}$  and electronic surface properties of this composite (Machado et al., 2008) are responsible for an almost three times faster mineralization of Ponceau 4R (C.I. 16255), an azo dye employed in the food industry, when compared with the result obtained using only  $\text{TiO}_2$  P25, and still much higher than the presented by the other  $\text{TiO}_2$ -based photocatalysts (Oliveira et al., 2012). This dye is classified as a carcinogen in some countries and is currently listed as a banned substance by U.S. Food and Drug Administration (FDA).

The highest photocatalytic activity of  $\text{TiO}_2/\text{ZnPc}$  1.6% seems to be the result of synergism between the photocatalytic characteristics inherent to  $\text{TiO}_2$  P25 with the redox properties and charge transport of ZnPc Frenkel's "J" aggregates on the semiconductor surface (Fidder et al., 1991; Kim et al., 2006; Machado et al., 2008; Machado et al., 2011a). The sensitization of  $\text{TiO}_2$  P25, induced by zinc phthalocyanine aggregates was effective in producing more active photocatalysts.

**Fig. 4** presents the diffuse reflectance spectra (DRS) of ZnPc,  $\text{TiO}_2$  and some of the studied  $\text{TiO}_2/\text{ZnPc}$  composites.

Unlike what occurs with  $\text{TiO}_2$  (**Fig. 4a**), for composite materials obtained by the association between  $\text{TiO}_2$  and ZnPc there is a significant electronic absorption for wavelengths above 390 nm. Comparison between the graphs presented in As can be seen in **Fig. 4 (a to e)**, the UV-Vis absorption spectrum (DRS) of these composites is not the result of an additive effect between the absorption spectra of the precursors. The absorption spectra of the composites are quite different from the typical absorption profiles of  $\text{TiO}_2$  (**Fig. 4a**) and pure ZnPc in the solid state (**Fig. 4f**) or even in very dilute liquid solutions (Miranda et al., 2002).

The absorption spectrum of these composites is characterized by an intense absorption band below 460 nm, and a large, intense and non structured absorption band above 475 nm. Both bands are most probably the result of superposition of electronic states of  $\text{TiO}_2$  and ZnPc aggregates.

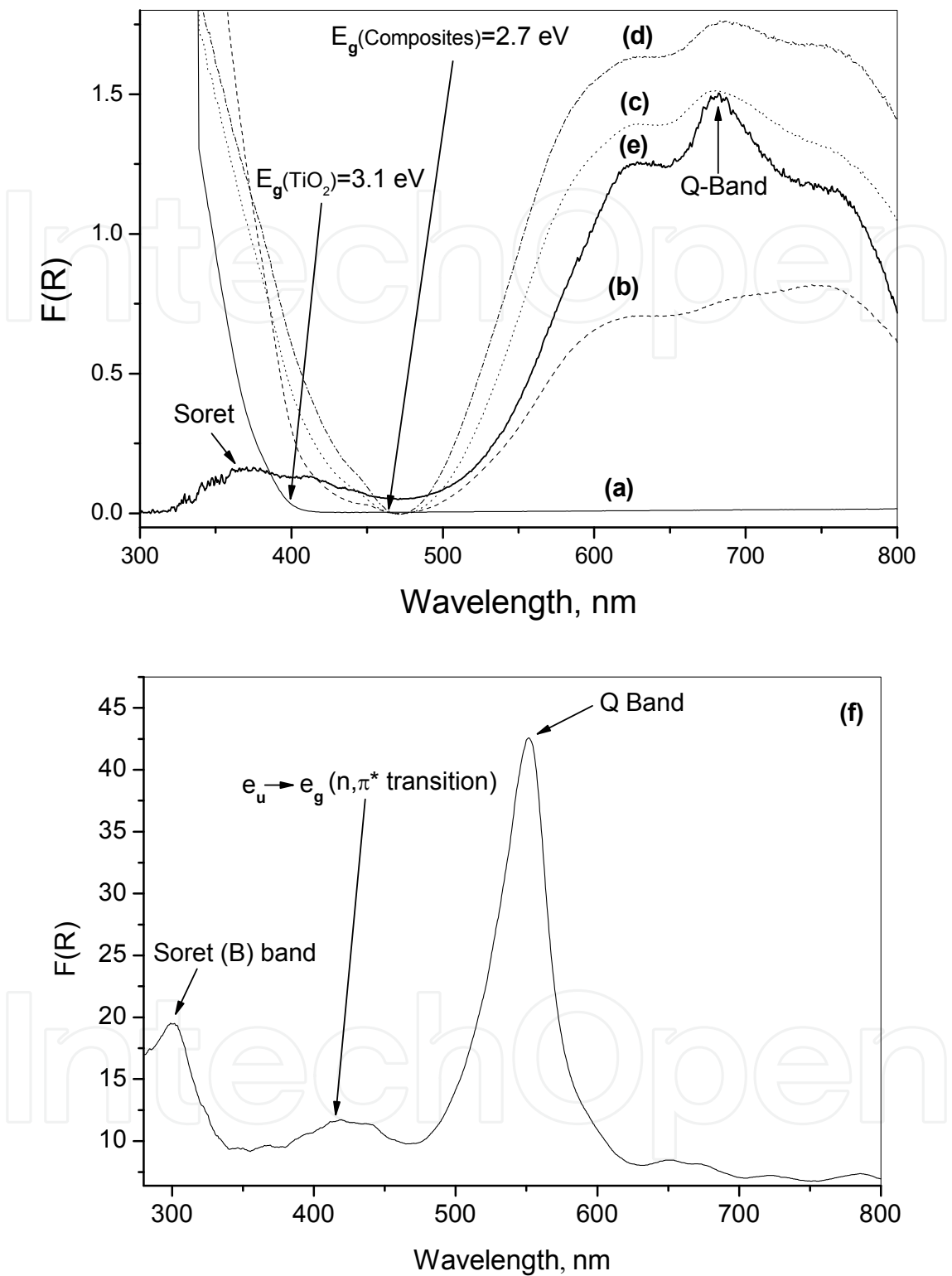


Fig. 4. Diffuse reflectance spectra (DRS) of TiO<sub>2</sub> and TiO<sub>2</sub>/ZnPc composites, prepared with different percent in mass of ZnPc. TiO<sub>2</sub> P25 (a) and composite containing: 1.0% of ZnPc (b); 2.5% of ZnPc (c); 5.0% of ZnPc (d); composite containing 2.5% of ZnPc, using TiO<sub>2</sub> P25 as reference (e) and DRS of pure ZnPc (f). Barium sulphate was used as reference for (a) to (d) (Machado et al., 2008).

In **Fig. 4e** the shape of the bands in the ultraviolet and visible portions of the electronic spectrum of the composite containing 2.5% m/m of ZnPc, obtained using  $\text{TiO}_2$  as reference, is very different from that observed for pure ZnPc in the solid state, **Fig. 4f**. In the visible, it presents a large and intense three peak band centered by a red shifted Q band, with maximum at 683 nm. The bathochromic shift of the absorption maximum associated to Q band, suggests the occurrence of Frenkel's J aggregates of ZnPc (**Fig. 5**) in the composites (Köhler & Schmid, 1996; Einfeld & Briggs, 2006; Chen, Z. et al., 2008), which agrees with results of a theoretical study employing methods of Density Functional Theory on the formation of aggregates of zinc phthalocyanine (Machado et al., 2011a). The bathochromic shift of the absorption maximum of the Q band highlights the differentiated nature of these compounds against pure  $\text{TiO}_2$  and ZnPc. The Soret (B) band also presents a different shape compared to its equivalent in pure ZnPc in the solid state (**Fig. 4f**), and is red shifted. The spectrum of **Fig. 4e** is very similar to the absorption spectrum for a flash-evaporated ZnPc thin film deposited on a glass substrate (Senthilarasu et al., 2003), in which the two energy bands characteristic of phthalocyanines are evident, one in the region between 500 and 900 nm, with an absorption peak at 690 nm, related to the Q band, and the other, very intense, at 330 nm, attributed to Soret (B) band (Meissner & Rostalski, 2001), similar to that reported for the absorption spectrum for thin films of Magnesium Phthalocyanine (Mi et al., 2003). The unstructured band in the visible and the red shifted Q band of these composites can be attributed to the strong intermolecular interactions due to ZnPc aggregation ( $\text{ZnPc}_{\text{agg}}$ ), resulting in coupling effects of excitons on the allowed transitions, with significant effects on the mobility of charge carriers (Hoffmann, 2000).

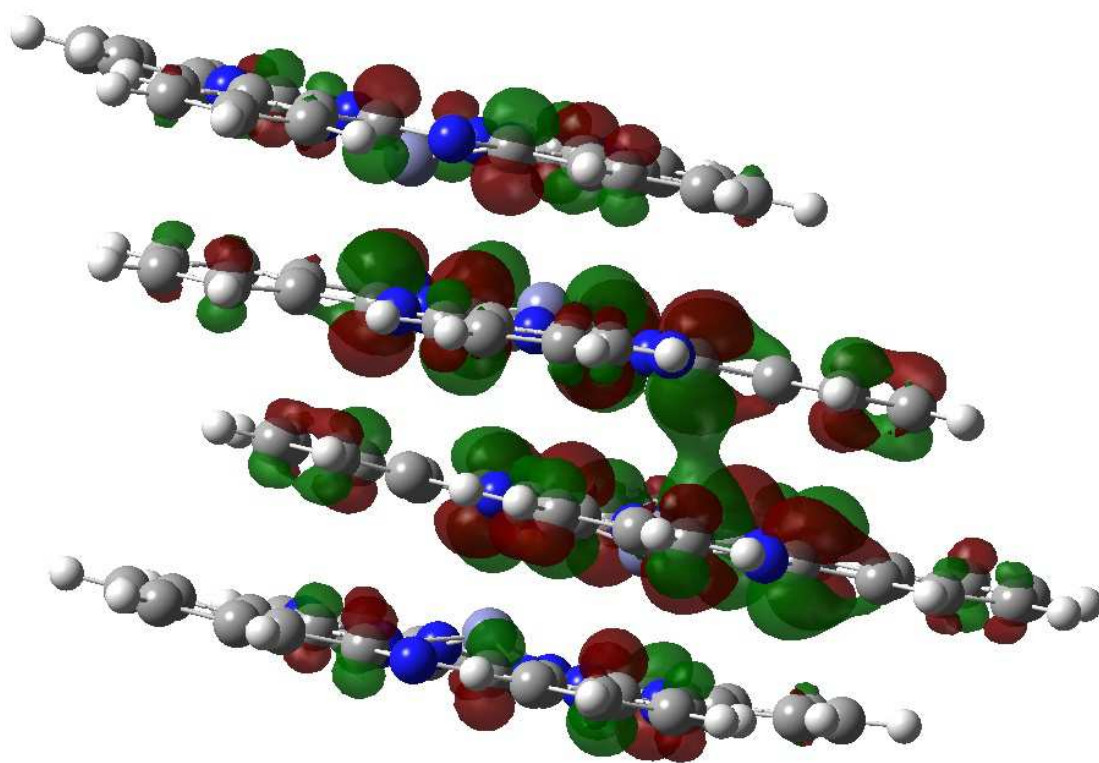


Fig. 5. Representation of the molecular structure of a Frenkel's J aggregate of ZnPc formed by four grouped individual molecules, indicating the sharing the same ligand MO between the ZnPc 2 and 3, in the HOMO (Machado et al., 2011a).



**Fig. 4f** presents the diffuse reflectance spectrum of pure ZnPc. The intense absorption peak at 552 nm, is related to the Q band and is attributed to very intense  $\pi \rightarrow \pi^*$  transitions (Leznoff & Lever, 1990). The Soret band presents an absorption maximum at 301 nm. A low intensity and non structured absorption band with the absorption peak centered at 416 nm, is related to an  $n \rightarrow \pi^*$  transition involving the  $e_u$  azanitrogen lone pair orbital with the  $e_g$  LUMO (Ricciardi et al., 2001). A set of three very small intensity low energy bands, above the Q band, can also be observed.

The  $E_g$  value for the  $\text{TiO}_2/\text{ZnPc}$  composites, 2.7 eV, lower than the estimated for pure  $\text{TiO}_2$  (Hoffmann et al., 1995), has a value similar to the estimated for iron (II) phthalocyanine excitons (2.6 eV) in  $\text{TiO}_2/\text{FePc}$  blends (Sharma et al., 2006) and other metal phthalocyanine associated to semiconductor oxides (Iliev et al., 2003). For ZnPc thin films, Senthilarasu et al. assigned an  $E_g$  of 1.97 eV (Senthilarasu et al., 2003) with a directly allowed optical transition, near the value estimated for the peak absorption Q-band (2.25 eV) of pure ZnPc in the solid state (**Fig. 4f**). The  $E_g$  for the composites might be related to the coupling between  $\text{TiO}_2$  and ZnPc electronic states and their positive implications. Similar to  $\text{TiO}_2/\text{FePc}$  blends (Sharma et al., 2006) and ZnPc thin films (Ino et al., 2005; Senthilarasu et al., 2003), the photoexcitation of ZnPc aggregates should result in the formation of  $e^-/\text{ZnPc}^+$  pairs, followed by electron transfer from ZnPc excitons to the conduction band of bulk  $\text{TiO}_2$ , which explains at least in part the improved photocatalytic activity observed for some of the  $\text{ZnPc}/\text{TiO}_2$  composites (Machado et al., 2008; Oliveira et al., 2012). Sharma et al. reported charge separation after photo-excitation of  $\text{TiO}_2/\text{FePc}$  composite film due to charge transfer from FePc to  $\text{TiO}_2$  resulting in  $\text{FePc}(h^+)$  and  $\text{TiO}_2(e^-)$  (Sharma et al., 2006). Additionally, they reported that the charge transport and the current leakage through FePc films and the photo-generation are due to the efficient dissociation of exciton at the donor-acceptor interface of the bulk, and that the higher holes mobility in the organic material layer, combined with lower conductance leakage, leads to the more efficient collection of photo-generated carriers. Thus, the electronic coupling strength between donor and acceptor is one of the critical conditions to ensure the occurrence of such electron transfer (Ino et al., 2005; Rehm et al., 1996; Senthilarasu et al., 2003; Meissner & Rostalski, 2001).

The spectrum presented in **Fig. 4e** is very similar to the absorption spectrum for a flash-evaporated ZnPc thin film deposited on a glass substrate (Senthilarasu et al., 2003), in which the two energy bands characteristic of phthalocyanines are evident, one in the region between 500 and 900 nm, with an absorption peak at 690 nm, related to the Q band, and the other, very intense, at 330 nm, attributed to Soret (B) band (Meissner & Rostalski, 2001), similar to that reported for the absorption spectrum for thin films of Magnesium Phthalocyanine (Mi et al., 2003).

## 2.3 Solar photocatalysis using a compound parabolic concentrator (CPC) reactor

### 2.3.1 Design and construction of a CPC reactor

The study of new technologies has now focused on decontamination methods feasible alternatives that are environmentally friendly, and allow its application in large scale, with easy operation and low cost.

The economic use of AOPs based on the use of solar radiation in the treatment of wastewater has been proposed for their low cost, especially in regions with high insolation

(Malato et al., 2002; Machado et al., 2003; Sattler et al., 2004a, 2004b; Machado et al., 2004; Palmisano et al., 2007; Machado et al., 2008; Torres et al., 2008; Li et al., 2009). Literature reports suggest that the reactors most suitable for application in solar photocatalysis are CPC type (Malato et al., 1997; Malato et al., 2002; Sattler et al., 2003a, 2003b; Machado et al., 2004; Duarte et al., 2005; Machado et al., 2008).

CPC reactors are static collectors of solar radiation with reflective surfaces in the form of involute positioned around cylindrical tubes, **Fig. 6**. Reflectors with this geometry allows the pock up of solar radiation, either by direct incidence, as the diffuse radiation, directing it to a glass tube through which circulates the effluent to be treated (Duarte et al., 2005).

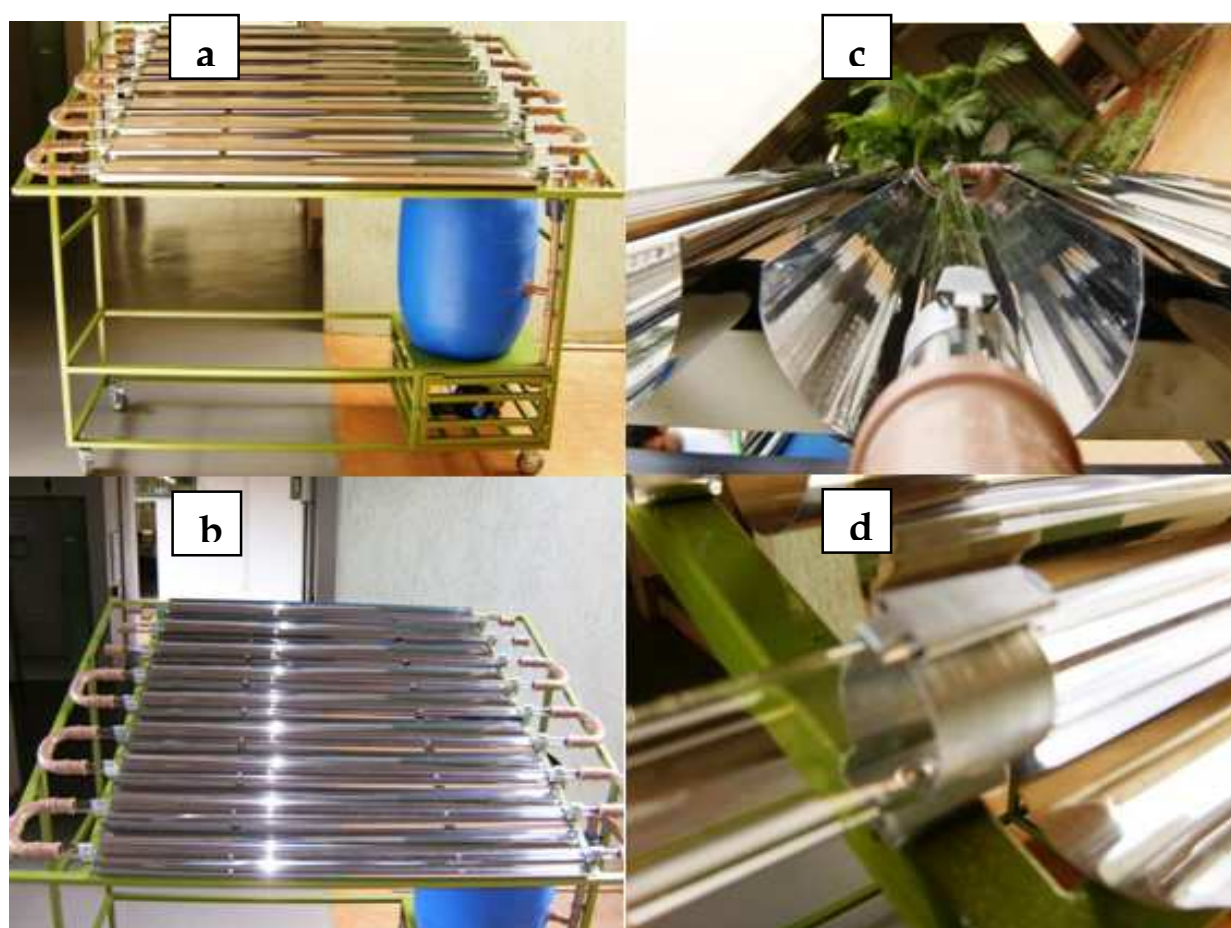


Fig. 6. Representation in two angles (a and b) of a CPC reactor, detailing one of the reflectors in the form of involute (c), and pipes the fixed to the body of the reactor (d).

Our CPC reactor was designed to process up to 150 L of effluent, This reactor consists in a module with an aperture of about 1.62 m<sup>2</sup>, elevation angle adjusted to the latitude of Uberlândia, Brazil (19° S), ensuring a better use of incident radiation. The reflecting surface contains 10 borosilicate glass tubes (external diameter 32 mm, wall thickness of 1.4 mm, and length of 1500 mm), mounted in parallel and connected in series, each on double parabolic shaped inox steel reflector surfaces (Duarte et al., 2005). A centrifugal pump of 0.50 HP with rotor and housing made in inert material has been used to ensure a flow of 2 m<sup>3</sup>/h.



The flow of effluent in tubular reactors is usually turbulent, which may cause loss of efficiency in the capture of solar radiation. However, this difficulty can be minimized during the design of the reactor, and the use of balanced amounts of the catalyst, in the case of heterogeneous photocatalysis, so as to guarantee a uniform flow and a good dispersion of the photocatalyst in the effluent to be treated, minimizing possible effects of co-absorption of the incident radiation (Duarte et al., 2005). Non-uniform flows implies in non uniform residence times that can lower efficiency compared to the ideal conditions (Koca & Sahin, 2002). In the case of the heterogeneous processes with photocatalyst powder in suspension, sedimentation and depositing of the catalyst along the hydraulic circuit should be avoided and turbulent flow in the reactor needs be guaranteed. Reynolds's number varying between 10 000–50 000 ensures fully turbulent flow and avoids the settlement of the photocatalyst particles in the tubes (Malato et al., 2002). In our project, the Reynolds' number were defined as being  $Re_{\text{glass}} = 34,855.4$  and  $Re_{\text{PVC}} = 40,070.0$ , for glass and PVC, the materials where the effluent with the photocatalyst in suspension circulate.

Details of the project of a CPC reactor similar to the built in our laboratory are available in Duarte et al., 2005.

## 2.3.2 Photocatalytic degradation of organic substrates using solar radiation

### 2.3.2.1 Degradation of organic matter present in a model-effluent simulating the wastewater produced by a pulp and paper industry, using $\text{TiO}_2$ P25 and the composite $\text{TiO}_2/\text{ZnPc}$ 2.5% m/m

The performance of the studied composites to degrade organic matter present in wastewaters, in reactions mediated by solar irradiation, and the possibility of reuse of such photocatalysts, was evaluated monitoring the consumption of the organic matter content during the treatment of three 50 L batches of a model effluent (an aqueous solutions containing  $160 \text{ mg L}^{-1}$  of a sodium salt of lignosulphonic acid (Sigma-Aldrich), possessing a mean molecular mass of 52,000 D. The reactions were done at pH 3, with the addition of hydrogen peroxide ( $30 \text{ mg L}^{-1}$ ), used as additional source of reactive species (Machado et al., 2003a), and monitored by chemical oxygen demand (COD) analysis of aliquots of effluent samples collected at different accumulated doses of UV-A radiation (this option was due to operational limitations. However, the spectral pattern of the visible light does not change significantly during the execution of the experiments). To evaluate the observed (global) reaction kinetics, the temporal variations were substituted by the UVA accumulated dose, which warrants the reproducibility of these experiments under different latitude and weather conditions. The incident UV-A radiation was monitored using a Solar Light PMA-2100 radiometer. All reactions were stopped when the accumulated dose of UVA reached  $900 \text{ kJ m}^{-2}$  (Machado et al., 2008). This corresponds to about 3 hours of sunlight on a sunny day, or 5 to 6 hours during a cloudy day with moderate to high nebulosity in Uberlândia, MG, Brasil (Duarte et al., 2005).

The COD measurements considered the Environmental Protection Agency (EPA) recommended method (Jirka & Carter, 1975).

A same sample of the photocatalyst (100 mg per liter of effluent), containing initially 2.5% of ZnPc, was used to treat the three effluent batches. The treatment of each batch was performed using a CPC (Compound Parabolic Concentrator) reactor (Duarte et al., 2005).

As reference, an additional effluent batch was treated under similar conditions using pure  $\text{TiO}_2$  P25 as photocatalyst.

The degradation of the sodium salt of lignosulphonic acid (LSA) suggests higher photocatalytic efficiency for the  $\text{TiO}_2/\text{ZnPc}$  composite. **Fig. 7** shows a more effective LSA degradation under the action of  $\text{TiO}_2/\text{ZnPc}$ , which increases with reuse, with significant changes in the degradation profile due to the use of the recovered composite. While under the action of  $\text{TiO}_2$  P25 was reached 60% degradation, under the same conditions, with the unused composite, the degradation reached 96%. For the composite in both the first and second reuse, the degradation of the LSA was about 90%. The change in profile suggests that other processes, less likely to occur before, became important for the overall reaction (Machado et al., 2008). The production of singlet oxygen by photosensitization from  $^3\text{ZnPc}^*$ , for example, is an event plausible if the level of aggregation of  $\text{ZnPc}$  is reduced. The formation of singlet oxygen has been reported in some cases (Stylidi et al., 2004).

On the other hand, the better hydration of the surface of the composite due to the increasing number of cycles of use, should favor reactions from the valence band.

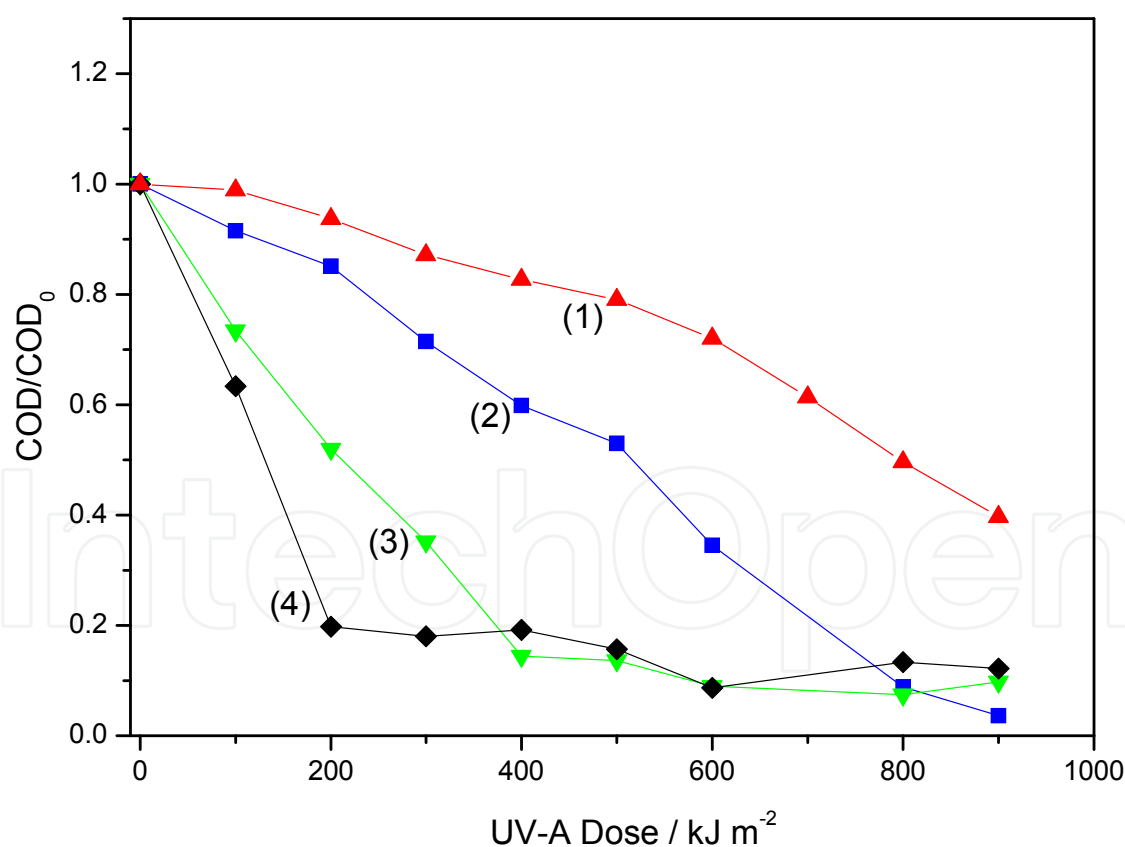


Fig. 7. Degradation of the organic load present in 50 L of a model waste water containing LSA monitored in terms of relative chemical oxygen demand ( $\text{COD}/\text{COD}_0$ ), induced by: (1)  $\text{TiO}_2$  P25; (2)  $\text{TiO}_2/\text{ZnPc}$  2.5%; (3)  $\text{TiO}_2/\text{ZnPc}$  2.5% in the first recycling; (4)  $\text{TiO}_2/\text{ZnPc}$  2.5% in the second recycling.

Despite the fact that part of ZnPc adsorbed to the surface of TiO<sub>2</sub> P25 may have been degraded during the photocatalytic process, surprisingly, the photocatalytic efficiency of the composite did not decrease when reused. Results suggest that the composite can be reused at least five times before making any significant loss of photocatalytic efficiency.

### 2.3.2.2 Photocatalytic degradation of paracetamol using solar photocatalysis

Conditions were evaluated to promote the mineralization of paracetamol (or acetaminophen), a known emerging contaminant (Daughton, C. G. & Ternes, T. A., 1999; Bound, J. P. & Voulvoulis, N., 2004; Jones, O. A. H., Voulvoulis, N. et al., 2007; Nikolaou, A., Meric, S. et al., 2007; Zhang, X. et al., 2008; Bartha, B. et al., 2010), employing heterogeneous photocatalysis mediated by TiO<sub>2</sub>/ZnPc 2.5% m/m, under the action of solar radiation. The results were compared with process under similar conditions, using TiO<sub>2</sub> P25 as photocatalyst.

Firstly, to find the best experimental conditions, the influence of hydrogen peroxide concentration and pH was evaluated in the photocatalytic reactions mediated by 100 mg L<sup>-1</sup> of photocatalyst, on a laboratory scale using an experimental setup already described (Machado et al., 2003a; Oliveira et al., 2012). The best conditions for the reactions in laboratory scale were obtained at pH 6.80 using 33.00 mg L<sup>-1</sup> of hydrogen peroxide for the degradation and mineralization of aqueous solutions containing 10 mg L<sup>-1</sup> of paracetamol (França, 2011). Under these conditions, the substrate was completely oxidized after 40 minutes of reaction using TiO<sub>2</sub> P25, while 78% of mineralization with this same photocatalyst was reached after 120 minutes of reaction. Using the TiO<sub>2</sub>/ZnPc composite, the substrate was completely oxidized after 60 minutes of reaction, and 63% was mineralized after 2 hours of reaction.

In the photocatalytic tests using a CPC reactor and solar radiation (**Fig. 8**), the experiments were done preferentially at pH 3.00 (França, 2011), using 50 L of an aqueous solution containing 10 mg L<sup>-1</sup> of paracetamol and 100 mg L<sup>-1</sup> of photocatalyst. Hydrogen peroxide, used as additional radical source (Machado et al., 2003a), was employed at the same concentration as defined in studies on laboratory scale.

Although the mineralization of paracetamol under the action of solar radiation has been equivalent in both cases (56%), after the accumulation of an UVA dose equal to 700 kJ m<sup>-2</sup>, comparing the results obtained on laboratory scale and induced by solar radiation, it was observed that the increase in mineralization obtained with the use of the composite, 33%, was higher than that obtained using the commercial photocatalyst, equal to 25%, suggesting a better utilization of solar radiation by TiO<sub>2</sub>/ZnPc composite.

In terms of degradation, monitored by high performance liquid chromatography (HPLC), the commercial photocatalyst required the accumulation of less UVA radiation (200 kJ m<sup>-2</sup>) to oxidize 96% of paracetamol, whereas for the composite this level of degradation was achieved when the dose reached 350 kJ m<sup>-2</sup> (**Fig. 9**).

The results obtained by Zhang et al (2010) indicated that TiO<sub>2</sub> photocatalytic degradation is an effective way to remove paracetamol from wastewater and drinking water without any generation of more toxic products. Although we have not analyzed the intermediates and products obtained, our results also point to the efficiency of heterogeneous photocatalysis in the treatment of acetaminophen, even if present in high concentrations in wastewater and drinking water.

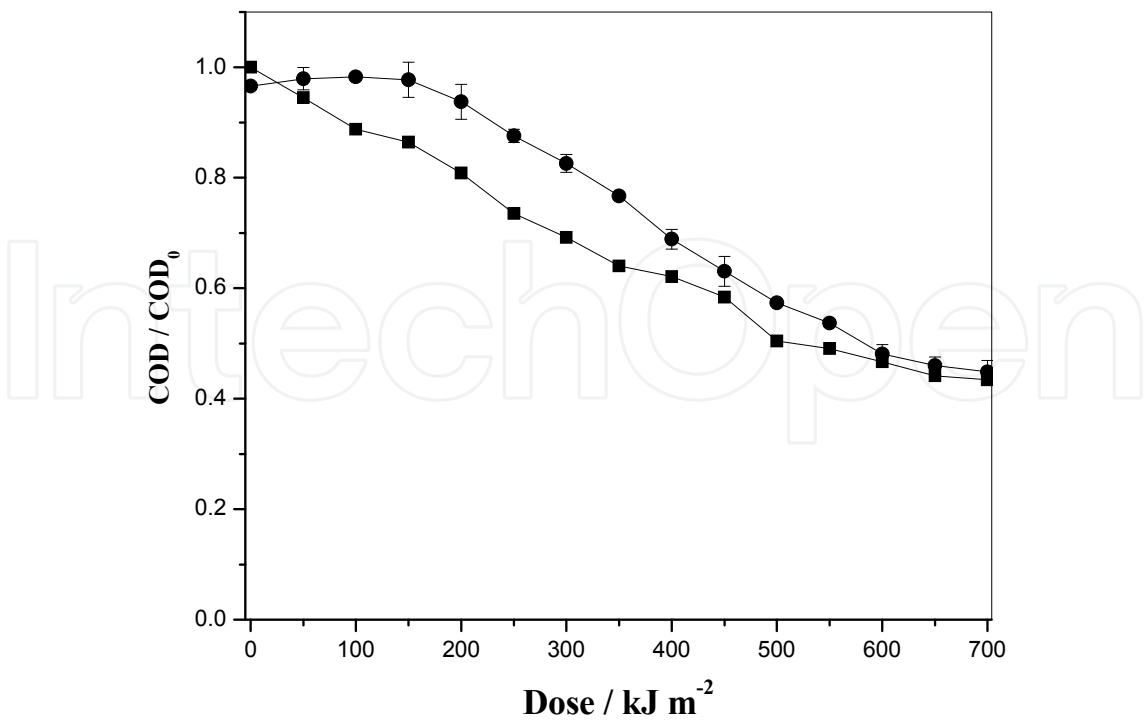


Fig. 8. Variation of dissolved organic carbon (DOC) as a function of cumulative dose of UVA, during the photocatalytic degradation of paracetamol mediated by solar radiation: TiO<sub>2</sub>/ZnPc 2.5% m/m (●);TiO<sub>2</sub> P25 (■).

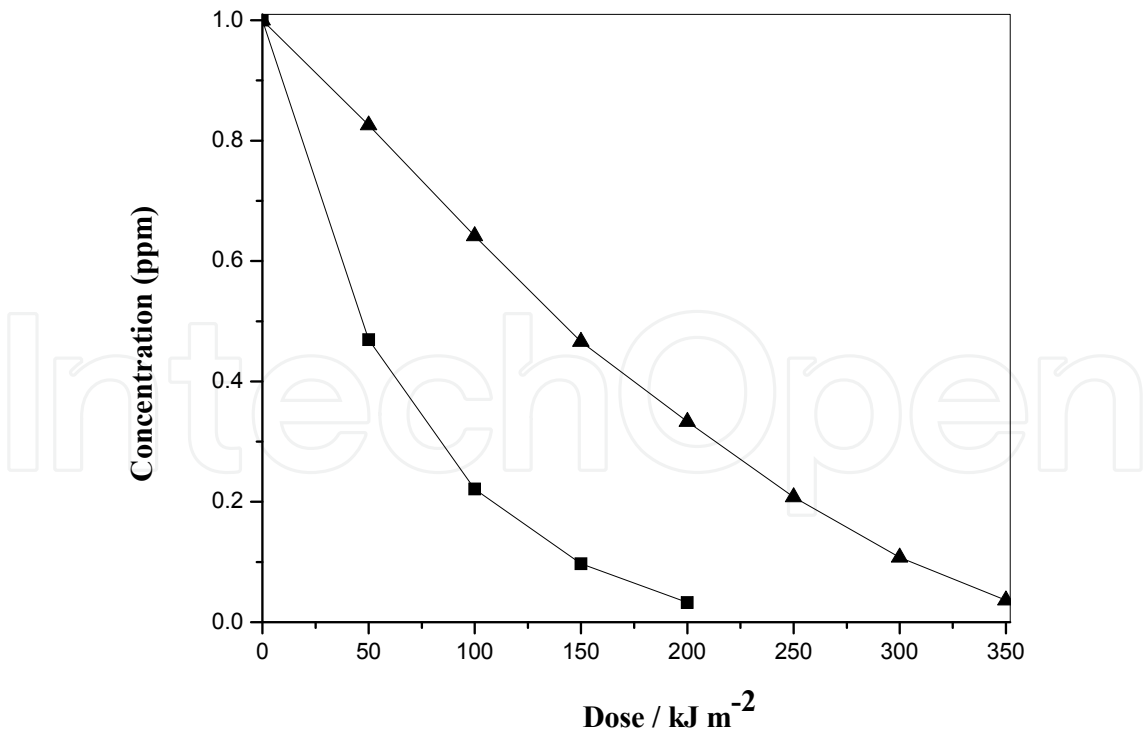


Fig. 9. Variation in the concentration of paracetamol measured by HPLC during photodegradation experiments mediated by TiO<sub>2</sub> P25 (■) and TiO<sub>2</sub>/ZnPc 2.5% m/m (▲) and induced by solar radiation.

### 3. Obtention of gaseous hydrogen for energy production

The International Energy Agency (IEA) estimates that world demand for energy should suffer an increase of 45% by 2030 (Biroi, 2008). Based on the projections presented, one can expect a worsening of global warming, if no measures are taken that result in significant reduction of CO<sub>2</sub> emissions. In addition, we expect a worrying shortage of fossil fuels, if alternative sources of energy are not being widely used.

Among the alternative energy sources, H<sub>2</sub> is a very attractive option, as it concentrates high energy per unit mass – 1.0 kg of hydrogen contains approximately the same energy furnished by 2.7 kg of gasoline, which facilitates the portability of energy (Smith & Shantha, 2007). Besides, its combustion generates no contaminants.

Experts have pointed out three major obstacles to the expansion of consumption of hydrogen taking into consideration the technology available at the moment: clean production, low cost, storage and transportation. As a result, most efforts to expand the use of hydrogen as a source of cheap energy has been based on the development of new materials and processes of production.

Among the technologies for hydrogen production, biomass gasification (Albertazzi et al., 2005; Smith & Shantha, 2007), photocatalysis (Ni et al. 2007; Patsoura et al., 2007; Jing et al., 2010), and biological processes (Peixoto, 2008), have been focus of many studies for being routes clean and renewable. The heterogeneous photocatalysis and hydrogen generation by decomposition of water using concentrated solar radiation as primary source energy are between the most promising having gain attention due to their potential.

The great expectation of the global market for the use of hydrogen gas as an important input in the production of energy has been driven by the sectors of energy generation and distribution, which moves large numbers of capital around the world, and is in frank expansion, due to the enormous demand for energy by all sectors (Steinfeld, 2005; Preguer et al., 2009; Pagliaro et al., 2010). Most efforts to expand the use of hydrogen as a renewable energy source has been based on the development of fuel cell technology, both for expansion of its service life, by minimizing costs. Volumes of hydrogen gas have already been produced, both in EU-funded projects, such as the United States.

#### 3.1 Hydrogen production using heterogeneous photocatalysis

In recent decades, research has been conducted on the possibility of using hydrogen as energy vector with low carbon emissions. The policy guidance for reducing the emission of greenhouse gases, and the prospect of decline in oil and other fossil fuels, has brought to light again the discussion about the use of hydrogen and technologies related to it. However, it is clear that large-scale use of hydrogen will only be possible if renewable sources are used in its production (Preguer et al., 2009). Currently, renewables contribute only about 5% of the commercial production of hydrogen, while the remaining 95% are derived from fossil fuels, given the still high cost of production from renewable sources.

The photocatalytic degradation of water to produce hydrogen, under the action of solar energy, offers a promising way to produce hydrogen cleanly, inexpensive and environmentally friendly. While great progress in photocatalysis using radiation in the ultraviolet region has occurred in recent decades, it has been extended with some difficulty,



considering the use of visible radiation as a trigger for photocatalytic processes. Particularly, we have achieved some progress in this direction, involving the association between a photosensitizer dye and a semiconductor oxide.

The development of semiconductor oxides capable to be excited by radiation in the visible region became one of the most important topics in photocatalysis research, since the visible light represents a significant fraction of solar energy usable (Hwang et al., 2004). However, finding another photocatalyst than  $\text{TiO}_2$ , which has good chemical stability, corrosion resistance, be able to efficiently absorb radiation in the visible, and is environmentally friendly, has proved an arduous task. However, no semiconductor material capable of catalyzing the overall water splitting under action of visible radiation around 600 nm, with a quantum efficiency high enough to make possible the commercial application (Maeda & Domen, 2007; Jing et al., 2010). Besides, many of the photocatalysts capable to induce hydrogen production with commercially acceptable quantum efficiency, with excitation between 300 and 450 nm, are expensive and inadequate from the environmental point of view (Zeug et al., 1985; Maeda et al., 2006; Bao et al., 2008).

The low efficiency for the hydrogen production by semiconductor photocatalysis already with appropriate band gap should be due to the following reasons: 1) quick electron/hole recombination in the bulk or on the surface of semiconductor particles; 2) quick back reaction of oxygen and hydrogen to form water on the surface of catalyst; and 3) inability to promote efficient use of visible radiation. It is known that photogenerated electrons easily recombine with holes in the semiconductor (Hoffmann et al., 1995; Li et al., 2010; Kumar & Devi, 2011), compromising the quantum efficiency of the photocatalytic process (Kudo, 2006). Noble metal loading can suppress to some extent the charge recombination by forming a Schottky barrier (Chand & Bala, 2007; Fu et al., 2008). Often, sacrificial reagents has been added to the reaction media for the elimination of photo-generated holes, minimizing the electron/hole recombination, improving the quantum efficiency (Liu et al., 2006; Zaleska, 2008a; Jing et al., 2010). Methanol, ethanol and acetic acid have usually been employed as agents of sacrifice. Toxic organic substrates can also be a good option of sacrificial reagent (Jing et al., 2010).

Much progress has been made in photocatalytic water splitting since the Fujishima-Honda effect was reported (Fujishima & Honda, 1971, 1972). Thermodynamically, water splitting into  $\text{H}_2$  and  $\text{O}_2$  can be seen as an unfavorable reaction ( $\Delta G = +238 \text{ kJ/mol}$ ) (Jing et al., 2010; Melo & Silva, 2011). However, the efficiency of water splitting is determined by the band gap, band structure of the semiconductor and the electron transfer process (Linsebigler et al., 1995; Hagfeldt & Grätzel, 1995; Melo & Silva, 2011).

Generally for efficient  $\text{H}_2$  production using visible light-driven semiconductor the band gap should be less than 3.00 eV (ca. 420 nm) and higher than 1.23 eV (ca. 1000 nm), corresponding to the water splitting potential (Jing et al., 2010; Melo & Silva, 2011). Moreover CB and VB levels should satisfy the energy requirements set by the reduction and oxidation potentials for  $\text{H}_2\text{O}$ , respectively: the bottom of the conduction band must be located at a more negative potential than the  $\text{H}^+/\text{H}_2$  reduction potential ( $E_0 = 0 \text{ V vs. NHE}$  at pH 0), while the top of the valence band must be more positively positioned than the  $\text{H}_2\text{O}/\text{O}_2$  oxidation potential ( $E_0 = 1.23 \text{ V vs. NHE}$ ) (Melo & Silva, 2011). Band engineering is thus necessary for the design of new semiconductors with the combined properties (Jing et al., 2010).



Oxides as  $\text{HPb}_2\text{Nb}_3\text{O}_{10}$ ,  $\text{MgWO}_x$  and  $\text{NiInTaO}_4$  among others, active under the action of ultraviolet radiation, were also active in the visible region after doping using C, N and S ( $\text{TiO}_2\text{N}_x$ ,  $\text{TiO}_2\text{C}_x$ ,  $\text{TaON}$  and  $\text{Sm}_2\text{Ti}_2\text{O}_5\text{S}$ ) (Hwang et al., 2004), as well as certain perovskite-type photocatalysts, with significant absorption in the visible. Zhang & Zhang (2009) reported the synthesis of a photocatalyst based on  $\text{BiVO}_4$  which showed high photocatalytic activity in the visible region. However, most of these catalysts are not environmentally friendly as  $\text{TiO}_2$ .

Photocatalytic induced water-splitting technology involving nanosized  $\text{TiO}_2$ , despite the considerable variety of semiconductor photocatalysts capable to split water using solar energy and other photocatalytic processes has great potential to support an economy based on low-cost and environmentally friendly hydrogen production using solar radiation (Ashokkumar, 1998; Ni et al., 2007).

The photocatalytic hydrogen production using  $\text{TiO}_2$  as photocatalyst can be schematized through **Figs. 1 and 10**.

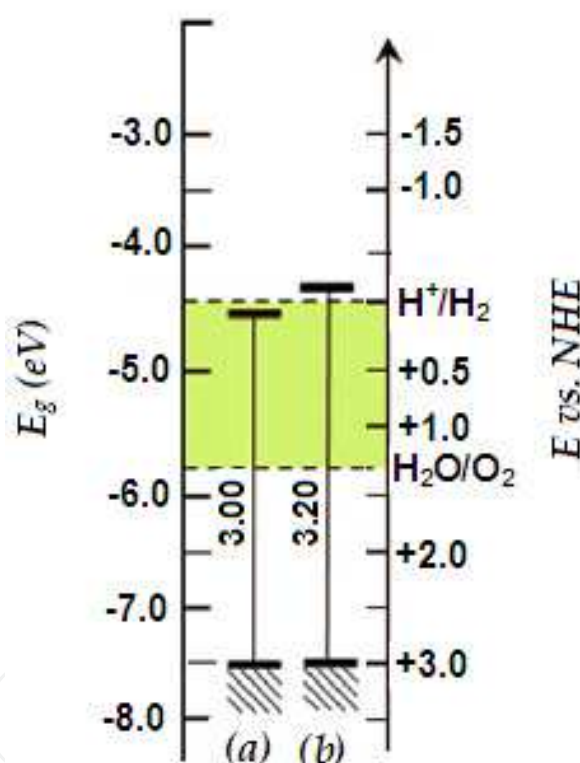
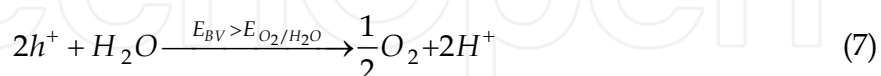
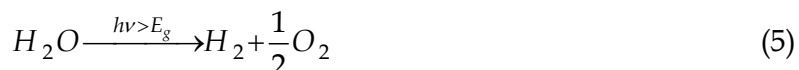


Fig. 10. Band gap of (a) Rutile and (b) Anatase compared to the redox potential of water at pH 1.

For an efficient production of  $\text{H}_2$ , the energy level of the CB should be more negative than the energy level of the reduction of hydrogen, while the energy level of VB should be more positive than the energy level of the oxidation of water to formation of  $\text{O}_2$  (**Fig.10**) (Ashokkumar, 1998; Ni et al., 2007), eqs 5 to 7. As outlined in **Fig. 1**, the vacancies photogenerated in the VB oxidize water into oxygen and hydrogen cations. These cations are reduced to molecular hydrogen in the conduction band. In other words, the separated electrons and holes act as reducer and oxidizer, respectively, in the water splitting reaction to produce hydrogen and oxygen. However, for this to happen effectively, it is necessary to

ensure the fast transportation of the photogenerated carriers, avoiding bulk electron/hole recombination. Separation of hydrogen gas is also required as oxygen and hydrogen are produced simultaneously.



Having the adequate semiconductor, capable to induce water splitting when photoexcited by solar radiation, a key issue concerns the efficient utilization of the solar energy itself. Two major drawbacks of solar energy must be considered: (1) the intermittent and variable manner in which it arrives at the earth's surface (2) efficient collection of solar light on a useful scale. The first drawback can be solved by converting solar energy into storable hydrogen energy. For the second, the solution could be the use of solar concentrators (Jing et al., 2010).

For photocatalytic hydrogen production, it is imperative the use of visible radiation, especially if the goal is the storage of the energy supplied by the sun. Thus, photocatalysts able to mediate reactions through the use of visible radiation are more than desirable. Amplify the sensitivity of photocatalysts through the introduction of dopants, impurities and / or association between semiconductor and photosensitizers capable of shifting the absorption of the resulting composite to visible, are alternatives to a more efficient water photolysis (Hwang et al., 2004; Machado et al., 2008; Zaleska, 2008a, 2008b; Zhang & Zhang, 2009).

When a metal (eg platinum) is deposited on a semiconductor, the excited electrons migrate from the semiconductor to the metal until the Fermi levels of both species are aligned. The Schottky's barrier (Chand & Bala, 2007; Fu et al., 2008) formed at the metal/semiconductor interface can serve as a trap for electrons, efficient enough to minimize electron-hole recombination, increasing the efficiency of the photocatalytic process. At the same time, the metal is important for its own catalytic activity. Metals deposited on a semiconductor serve as active sites for the production of  $H_2$ , in which the trapped electrons are transferred to photogenerated protons to produce  $H_2$  (**Fig. 11**) (Melo & Silva, 2011).

Research on photocatalytic hydrogen production in our laboratory is very recent. Our primary aim is the development of highly efficient, stable and low-cost visible-light-driven photocatalyst using different modification methods, such as doping, sensitization, supporting and coupling methods to extend the light response and performance of the photocatalyst aiming its application in environmental photocatalysis and photocatalytic hydrogen production. Despite a considerable variety of semiconductor photocatalysts capable to split water using solar energy and mediate other photocatalytic processes (Ashokkumar, 1998; Kim et al., 2010; Jing et al., 2010; Kumar & Devi, 2011), our studies have focused on improving the photocatalytic activity of  $TiO_2$  through its synthesis by different procedures, their use and of hybrid variants, doped or not, and composites involving  $TiO_2$  and photosensitizing dyes, especially considering issues related to the environment. In particular, we have studied photocatalytic reactions using solar radiation, with the photocatalyst in aqueous suspensions, with methodologies based on CPC reactor.

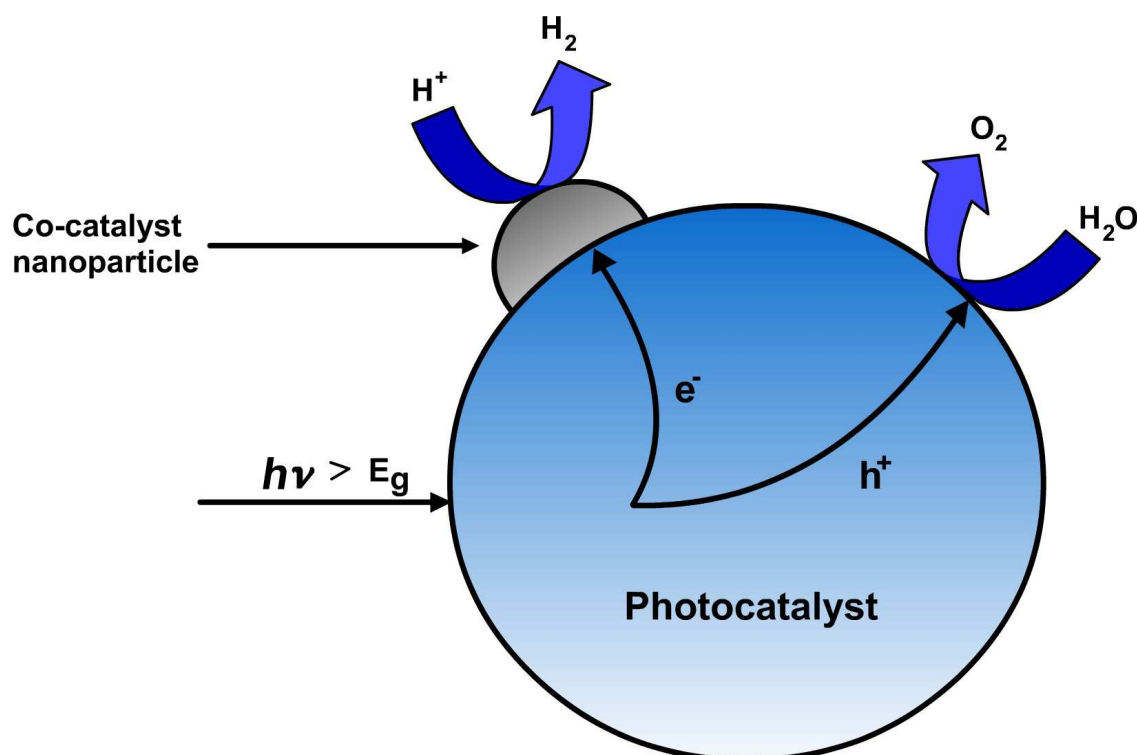


Fig. 11. Schematic representation of the photocatalytic water splitting on a platinized semiconductor powder particle.

We have developed small closed circulation reactor for bench-scale tests. These reactors ensure the evaluation of the developed photocatalyst from lab scale to out-door scale, in a batch mode.

The object of these studies is to improve hydrogen production and its storage under low pressure.

#### 4. Solar cells

Photovoltaic cells are a good example of an alternative energy source, converting sunlight into electricity. Research in this field is quite intense given the importance of solar cells as sources of sustainable energy, as well as due to their reduced cost, low environmental impact, and fair efficiency for conversion of solar energy into electricity (O'Regan & Grätzel, 1991; Grätzel, 2003; Brennaman et al., 2011).

The efficiencies obtained for a silicon solar cell is about 24%, although at a very high manufacturing cost. Therefore, other materials have been studied in order to facilitate the conversion of solar energy into electrical energy (Zhao et al, 1998; Jayaweera et al., 2008; Cao et al., 2009; Patrocinio et al., 2010; Brennaman et al., 2011).

New developed devices such as dye solar cells, capable of converting solar energy into electrical (dye solar cells – DSCs), have been presented as alternatives for power generation (Hagfeldt & Gratzel, 1995; Gratzel & Hagfeld, 2000; Jayaweera et al., 2008). Despite its efficiency is still lower than that of silicon cells, the DSCs have been particularly interesting

because they have a much lower production cost than devices based on silicon. In addition, the resulting material can be extremely thin as well as flexible and can be applied to almost any surface (Brabec et al., 2001; Kippelen & Bredas, 2009). Technically they are known as dye-sensitized solar cells, or DSSCs.

#### 4.1 Dye-sensitized solar cells (DSSCs)

The use of solar cells based on a combination of dyes and photosensitizers oxide semiconductor (DSCs) have attracted great attention since the pioneering work of Grätzel and collaborators (O'Regan & Gratzel, 1991; Grätzel, 2005). The most efficient sensitizers for wide band gap semiconductors are the well-known metallo-organic ruthenium complexes (Grätzel & O'Regan, 1991). Certain Ru(II) complexes have shown to be excellent photosensitizers for TiO<sub>2</sub> in DSSCs, having gained the attention because of the high efficiencies achieved ( $\eta \approx 11\%$ ) in converting sunlight into electricity (Nazeeruddin et al., 2005; Gao et al., 2008a, 2008b; Cao et al., 2009). In dye-sensitized solar cells, the conversion of visible light to electricity is achieved through the spectral sensitization of wide band gap semiconductors. Light is absorbed by the dye molecules, which are adsorbed on the surface of the semiconductor, thus inducing charge separation. Excitation of the dye molecules results in electron injection into the conduction band of the semiconductor. For electron injection to occur, the excited electrons must be at higher energy level than the semiconductor conduction band. An electrolyte of high ionic strength is also used in dye-sensitized solar cells to facilitate charge transfer across the device.

DSSCs have emerged as one of the most promising devices for sustainable photovoltaics due to their usually reduced cost, low environmental impact, and fair efficiency of conversion of solar energy into electricity (Grätzel, 2003; Polo et al., 2004; Brennaman et al., 2011).

Research in this field has been intense, given the growing worldwide demand for new energy sources (Kamat, 2007; Jacobson, 2009), either with focus on new materials and components or on cell assemblies for development of more efficient and environmentally friendly devices (Garcia et al., 2003; Prochazka et al., 2009; Zakeeruddin & Grätzel, 2009; Snaith, 2010). It is increasingly urgent the need to diversify energy matrices in order to rely on truly renewable energy sources, cleaner and environmentally friendly, if the goal is to build an ecologically sustainable society (Kamat, 2007; Herrero et al., 2011).

However, the high cost of dyes based on Ru (II), due to the low abundance of this metal and use restrictions from the environmental point of view are aspects that restricts its application on a large scale, which has stimulated efforts to use photosensitizing dyes with good features, safe and low cost (Hamann et al., 2008; Mishra et al 2009; Imahori et al., 2009).

Several simple organic dyes, and especially xanthene dyes (Eosin Y, Rose Bengal, etc.), yield efficiencies comparable to those achieved with ruthenium complexes, especially when used to sensitize ZnO films (Guillén et al., 2008; Plank et al., 2009; Pradhan et al., 2007). Organic dyes such as these are inexpensive (Kroon et al., 2007), can be easily recycled (Lee et al., 2006) and do not rely on the availability of precious metals such as ruthenium. They also have high extinction coefficients and their molecular structures contain adequate anchoring groups to be adsorbed onto the oxide surface. However, solar cells sensitized with such dyes tend to have low stability. The development and optimization of solar cells is of great interest, both commercially and scientifically. However, dye sensitized devices are still not

commercially available in large volumes. Disadvantages such as the low efficiency and stability of these cells pose a hindrance to their commercialization.

A considerable increase in conversion efficiency of components of solar radiation into electrical energy by other photosensitizing dyes has been achieved in recent years. Macrocyclic systems such as porphyrins, phthalocyanines and derivatives have been shown to be capable of application in solar cells (Lu et al., 2009a).

Special attention has been given to the electron recombination processes that limit the DSC efficiency (Wang et al., 2006; Peter, 2007a; Zhao et al., 2008). Experimental and theoretical studies have been carried out in order to better understand and control these processes (Kruger et al., 2003; Cameron & Peter, 2005; Peter, 2007b; Xia et al., 2007a), typical interface phenomena. Strategies have been proposed to prepare efficient blocking layers in DSCs by using different techniques, such as spray pyrolysis, sputtering or by immersion in oxide precursor solutions (Xia et al., 2007a; Xia et al., 2007b; Wang et al., 2003; Handa et al., 2007). For example, the application of a compact layer onto the FTO glass before the mesoporous oxide film can prevent electron recombination at the FTO/TiO<sub>2</sub> interface. This blocking layer physically avoids the contact between the electrolyte and the FTO surface, decreasing the occurrence of triiodine reduction by photoinjected electrons (Patrocinio et al., 2010; Lei et al., 2010). Efficient layer-by-layer (LbL) TiO<sub>2</sub> compact films is considered one of the most effective blocking layers to avoid recombination processes at FTO surface in DSCs (Patrocinio et al., 2009). Although not previously reported as blocking layers, LbL metal oxide films have been applied in several devices (Krogman et al., 2008; Srivastava & Kotov, 2008; Jia et al., 2008; Lu et al., 2009b), including DSCs (Tsuge et al., 2006; Agrios et al., 2006). Iha and coworkers have shown that an LbL film based on TiO<sub>2</sub> nanoparticles and sodium sulphonated polystyrene, PSS, applied onto the FTO substrate before the mesoporous TiO<sub>2</sub> layer improved the overall conversion efficiency of DSCs by 28% (Patrocinio et al., 2009). Other complementary effects of the compact LbL TiO<sub>2</sub> layer in DSCs and the role of the polyelectrolyte itself were still under investigation.

LbL films using polyelectrolytes with good thermal stability at the electrode sintering temperature (450° C), such as sodium sulphonated polystyrene and sulphonated lignin, SL, maintain the compact morphology, and act as effective contact and blocking layers in DSCs. TiO<sub>2</sub> LbL films with poly(acrylic acid) as a polyanion presented similar morphology to that exhibited by TiO<sub>2</sub>/PSS and TiO<sub>2</sub>/SL films before sintering (Patrocinio et al., 2010). The best performance so far achieved is through the use of the TiO<sub>2</sub>/PSS compact layer that increases the overall efficiency of DSCs to 30%, from 5.6 to 7.3%. The LbL TiO<sub>2</sub>/PSS film imposes a longer time for a charge exchange at the electrode surface decreasing the electron recombination. The TiO<sub>2</sub>/SL films (23% improvement) can be a cost effective option if a commercial application is considered.

## 5. Organic synthesis mediated by heterogeneous photocatalysis

Despite the widespread use of titanium dioxide, modified or not, or even other semiconductors with photocatalytic activity in photodegradation and mineralization of organic matter (Agostiano et al., 2003; Mrowetz et al., 2004; Machado et al., 2008; Hoffmann et al., 2010; Gupta et al., 2011), and its other capabilities (Mrowetz et al., 2004; Zaleska, 2008a, 2008b), these semiconductors have been little explored in the synthesis of compounds of interest, although it is recognized that the photocatalytic synthesis should enable the



efficient production of chemicals through combined fotoredox reactions with significant advantages compared to other methods (Swaminathan & Krishnakumar, 2011).

Synthetic methods based on photocatalytic processes have been reported for the preparation of different organic substrates (Amano et al., 2006; Palmisano et al., 2007b; Denmark & Venkatraman, 2006; Hakki et al., 2009; Swaminathan & Selvam, 2011; Swaminathan & Krishnakumar, 2011). Although the production of chemicals of industrial interest using heterogeneous photocatalysis has been shown to be a viable process, there is still little research on the use of photocatalysis for this purpose, and about the performance of these photocatalytic processes (Kanai et al., 2001; Murata et al., 2003; Amano et al., 2006; Denmark & Venkatraman, 2006; Hakki et al., 2009; Swaminathan & Selvam, 2011; Swaminathan & Krishnakumar, 2011). Apparently, the reason for this is that, in general, these methods are not yet fully satisfactory with regard to operational simplicity, cost of reagents and performance.

The stimulus for research in this field is necessary so that new and viable methodologies can be established.

## 6. Conclusion

In this chapter we combined a fast literature review about the different applications of heterogeneous photocatalysis, involving environmental photocatalysis, Hydrogen production for power generation, solar energy conversion into electricity using dye/semiconductor oxide cells and organic synthesis, with some experimental results obtained in our research group.

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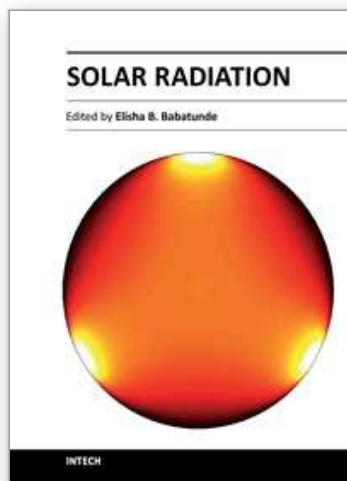
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