

## Research Article

# New Porphyrin/Fe-Loaded TiO<sub>2</sub> Composites as Heterogeneous Photo-Fenton Catalysts for the Efficient Degradation of 4-Nitrophenol

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Received 20 August 2012; Revised 14 November 2012; Accepted 15 November 2012

Academic Editor: Cláudia Gomes Silva

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A new class of porphyrin(Pp)/Fe co-loaded TiO<sub>2</sub> composites opportunely prepared by impregnation of [5,10,15,20-tetra(4-*tert*-butylphenyl)] porphyrin (H<sub>2</sub>Pp) or Cu(II)[5,10,15,20-tetra(4-*tert*-butylphenyl)] porphyrin (CuPp) onto Fe-loaded TiO<sub>2</sub> particles showed high activities by carrying out the degradation of 4-nitrophenol (4-NP) as probe reaction in aqueous suspension under heterogeneous photo-Fenton-like reactions by using UV-visible light. The combination of porphyrin-Fe-TiO<sub>2</sub> in the presence of H<sub>2</sub>O<sub>2</sub> showed to be more efficient than the simple bare TiO<sub>2</sub> or Fe-TiO<sub>2</sub>.

## 1. Introduction

Nowadays, due to the increasing presence of refractory molecules in the wastewater streams, it is important to develop new technologies to degrade such recalcitrant pollutant molecules into smaller innocuous ones. For this reason efficient oxidation processes operating under environmentally friendly conditions are needed [1]. As well known, Fenton chemistry encompasses reactions of hydrogen peroxide in the presence of iron to generate highly reactive species such as the hydroxyl radical and possibly others.

In the last few years, Fenton-like reactions, in combination with other advanced oxidation processes, are assuming fundamental and practical perspectives in water treatment processes [2, 3]. The combination of various technologies, in fact, is often effective to achieve a complete mineralization of the pollutant(s) present in the starting effluents because many stable products of environmental concern can be persistent after the treatment by Fenton reaction.

Recently, the utilization of TiO<sub>2</sub> as catalyst for the photooxidation of organic pollutants in water is becoming a relevant topic in view of a possible application in economically advantageous and environmentally friendly processes not only performed with the aim to abate pollutants but also for synthetic purposes [4–8].

Various advanced oxidation technologies have been used in the presence of TiO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and irradiation to enhance the efficiency of the overall photodegradation process [9–12]. Also, in the last years, dye-sensitized TiO<sub>2</sub>-based materials have been employed for improving the efficiency of energy light conversion towards photocatalytic processes [13–19].

In this work the design of novel composites metal free or Cu-porphyrin/Fe co-loaded TiO<sub>2</sub> as well as their application as catalytic systems for photoassisted heterogeneous Fenton-like reactions has been reported. In particular, we demonstrated that the presence of porphyrins and Fe species co-loaded onto the TiO<sub>2</sub> surface along with H<sub>2</sub>O<sub>2</sub> in the reacting

medium is beneficial for 4-nitrophenol (4-NP) photodegradation in aqueous medium.

## 2. Experimental

**2.1. Materials.** 4-Nitrophenol, used without further purification,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and hydrogen peroxide solution (30% wt.) were purchased from Aldrich. Solutions were prepared dissolving the required quantity of 4-NP in water obtained by a New Human Power I water purification system.

$\text{TiO}_2$  in the microcrystalline phase of anatase, specific surface area  $8 \text{ m}^2 \text{ g}^{-1}$ , was kindly provided by Tioxide Huntsman.

The synthesis of the [5,10,15,20-tetra(4-*tert*-butylphenyl)]porphyrin ( $\text{H}_2\text{Pp}$ ) and of the Cu(II) [5,10,15,20-tetra(4-*tert*-butylphenyl)]porphyrin ( $\text{CuPp}$ ) was carried out as reported previously [20].

**2.2. Preparation of the Hybrid  $\text{H}_2\text{Pp-Fe-TiO}_2$  and  $\text{CuPp-Fe-TiO}_2$  Catalysts.** The 1% wt  $\text{Fe-TiO}_2$  powder, successively indicated as  $\text{Fe-TiO}_2$ , was prepared by wet impregnation of  $\text{TiO}_2$  with aqueous solutions of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  by an incipient wetness impregnation followed by a drying process at 393 K and final calcination at 350 °C for 5 h as described in a previous work [21].

$\text{Fe}$ -loaded  $\text{TiO}_2$  powder impregnated with functionalized metal-free porphyrin and Cu(II)-porphyrin  $\text{Fe-TiO}_2$ , successively indicated as  $\text{H}_2\text{Pp-Fe-TiO}_2$  and  $\text{CuPp-Fe-TiO}_2$ , used as photocatalytic systems, were prepared by impregnation of  $\text{Fe-TiO}_2$  powders with  $6 \mu\text{mol/g}$  of sensitizer ( $\text{H}_2\text{Pp}$  or  $\text{CuPp}$ ) per gram of  $\text{TiO}_2$ . The opportune amount of sensitizers was dissolved in 15 ml of  $\text{CHCl}_3$  (or  $\text{CH}_2\text{Cl}_2$ ), and 2 g of finely ground  $\text{Fe-TiO}_2$  was added to this solution.

The mixture was stirred for 3-4 h, and the solvent was removed under vacuum.

**2.3. Characterizations.** The morphology of the  $\text{Fe-TiO}_2$  photocatalysts was studied by using a scanning electron microscopy (SEM) Zeiss Evo 40. X-ray diffraction patterns of all of the samples were performed by using a powder diffractometer (model Ultima<sup>+</sup> Rigaku) equipped with  $\text{CuK}\alpha$  radiation from 20° to 80°. The accelerating voltage and current used were 40 kV and 26 mA, respectively. The diffuse reflectance spectra (DRS) of photocatalysts were recorded in the range 200–800 nm by using a Varian CARY 100 Scan UV-vis spectrophotometer equipped with a diffuse reflectance integration sphere.

**2.4. Photocatalytic Measurements.** The set-up used for the photocatalytic experiments is reported in Figure 1 and consists of a 500 ml glass Pyrex reactor containing 4-NP solution/photocatalyst suspension placed in the center of a wood box and irradiated from the top with a 300 W UV-visible lamp (SANOLUX HRC) emitting in the wavelength range 300–900 nm. The lamp was housed in the upper window of the box at 14 cm distance from the reactor, and the radiant flux measured by a DELTA OHM Photo-Radiometer HD 9221, equipped with a sensor LP 9221 PHOT, was  $340 \text{ W/m}^2$  in the 200–950 nm range. The emission spectrum

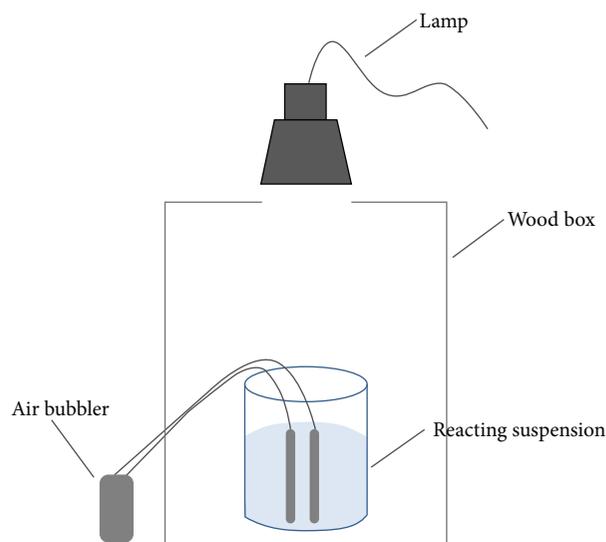


FIGURE 1: Set-up used for the photocatalytic experiments.

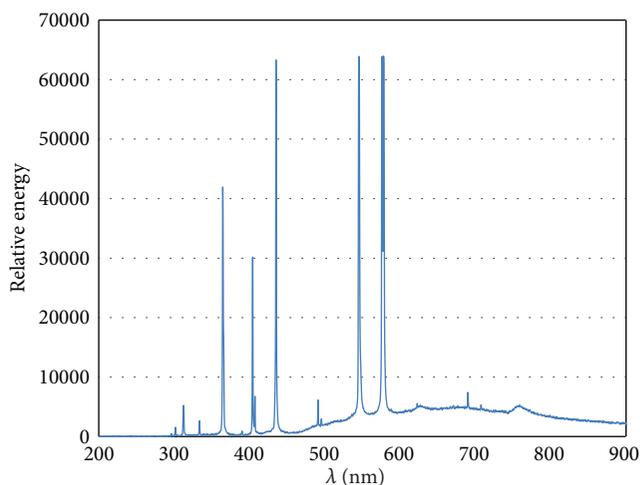


FIGURE 2: Emission spectrum of SANOLUX HRC UV-vis lamp.

of the lamp is reported in Figure 2. Oxygenation was ensured by bubbling air in the suspension during the experiments.

The novel hybrid composite photocatalysts based on the metal free and Cu porphyrins onto the  $\text{Fe}$ -loaded  $\text{TiO}_2$  have been used to test the degradation of 4-NP as a probe pollutant molecule.

The removal of 4-NP during the reaction processes has been evaluated as the ratio of the concentrations  $C_t/C_0$  versus time.  $C_t$  and  $C_0$  were calculated measuring the absorbance values  $A_t$  and  $A_0$  of 4-NP at 317 nm at time  $t$  and at the initial time  $t_0$ , respectively, by means of a UV-vis spectrophotometer (Cary 100 Scan, VARIAN).

The extent of mineralization of the 4-NP was determined on the basis of total organic carbon measurement using a TOC analyzer (IL550 TOC-TN, HACH-LANGE).

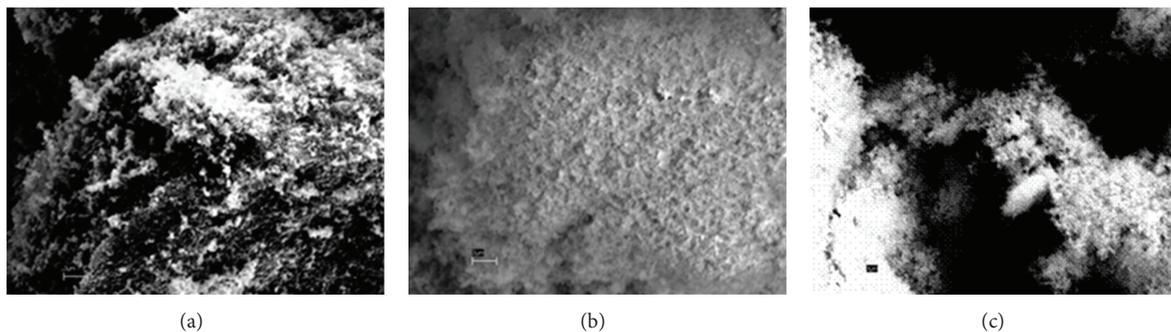


FIGURE 3: SEM micrographs of (a) BareTiO<sub>2</sub>, (b) Fe-TiO<sub>2</sub>, and (c) CuPp-Fe-TiO<sub>2</sub>.

The amount of Fe<sup>3+</sup> in solution was measured according to the UNI-EN-ISO 11885 method using an ICP spectrometer THERMO SCIENTIFIC iCAP 6000 SERIES.

### 3. Results and Discussion

**3.1. Synthesis and Characterization of the Photocatalysts.** Syntheses of the metal-free porphyrin [5,10,15,20-tetra(4-*tert*-butylphenyl)porphyrin], H<sub>2</sub>Pp, and its Cu(II) complex, CuPp, were performed according to a procedure already reported in the literature [20].

Also, the Fe-TiO<sub>2</sub> composite, used as the support for the sensitizers H<sub>2</sub>Pp and CuPp, was prepared by a wet impregnation process followed by dryness and calcination as described in a previous work [21].

Further, the novel composites used as the photocatalysts in this work were prepared by impregnation of the Fe-TiO<sub>2</sub> powder with 6 μmol/g of sensitizers (H<sub>2</sub>Pp or CuPp) *per* gram of Fe-TiO<sub>2</sub> as described in the experimental section, and they were indicated, respectively, as H<sub>2</sub>Pp-Fe-TiO<sub>2</sub> and CuPp-Fe-TiO<sub>2</sub>.

Analysis of SEM picture (Figure 3) shows that the Fe-TiO<sub>2</sub> (Figure 3(b)) and CuPp-Fe-TiO<sub>2</sub> (Figure 3(c)) samples have a higher number of irregular shaped particles than bare TiO<sub>2</sub> (Figure 3(a)). However, the sizes of the Fe-loaded particles, consisting of aggregates of tiny crystals, are smaller compared to that of the bare TiO<sub>2</sub> sample. The presence of Fe<sup>3+</sup> ions seems to hamper the growth of TiO<sub>2</sub> particles.

Figure 4 shows the X-ray diffractograms of selected samples. It can be noticed that no modification of the starting anatase phase of the bare TiO<sub>2</sub> supports occurred after the impregnation treatments as no additional lines attributable to the presence of other phases can be observed.

Figure 5 shows the diffuse reflectance spectra in air of the bare TiO<sub>2</sub>, Fe-TiO<sub>2</sub>, and CuPp-Fe-TiO<sub>2</sub> recorded in the range 200–800 nm.

The spectrum of bare TiO<sub>2</sub> clearly shows an absorption starting at about 380 nm which is typical of bare titania in the anatase phase.

An improvement of light absorption in the visible range can be observed for the Fe-TiO<sub>2</sub> and CuPp-Fe-TiO<sub>2</sub> metal loaded samples, due to the presence of both iron and porphyrin systems producing a modest shift of the band gap

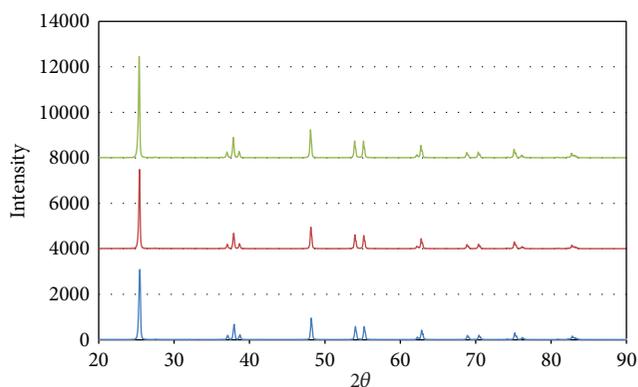


FIGURE 4: XRD patterns of TiO<sub>2</sub> powder samples compared with the bare sample.

edge in the case of CuPp-Fe-TiO<sub>2</sub> sample. Typical absorption bands centered at, respectively, 417 nm (Soret band) and 540 nm (Q band), due to the presence of the porphyrinic moiety, have been observed. Hence, the presence of iron onto the TiO<sub>2</sub> surface enhances the light absorption capability in the visible region which is a prerequisite for the better utilization of the visible light for the photocatalytic processes.

The band gap values ( $E_g$ ) of such unsupported materials were determined from their diffuse reflectance spectra by using the Kubelka-Munk equation [22]. This equation is based assuming that the reflectance  $F(R)$  at any wavelength is defined as  $F(R) = (1 - R)^2 / 2R$ , where  $R$  is the measured diffuse reflectance (%).

A plot of the modified Kubelka-Munk function  $[F(R)h\nu]^{1/2}$  versus the energy of absorbed light  $h\nu$  is shown in Figure 6. All materials are considered to be indirect semiconductors, as TiO<sub>2</sub>.

The results obtained afford band gap energies of 3.20, 3.09, and 3.05 eV for bare TiO<sub>2</sub>, Fe-TiO<sub>2</sub> and CuPp-Fe-TiO<sub>2</sub> samples, respectively. Iron-induced band gap narrowing of 0.11 eV was observed for Fe-loaded titania.

**3.2. Photoactivity of the Photocatalysts.** In this work, for the first time the synergistic effect of *t*-butyl-porphyrinic structures (H<sub>2</sub>Pp and Cu-Pp) supported onto the Fe-loaded TiO<sub>2</sub> surface powders was studied for the photodegradation

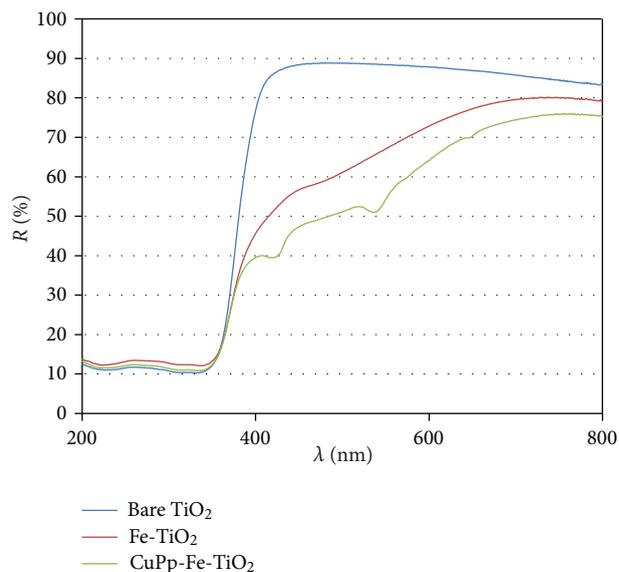


FIGURE 5: Diffuse reflectance spectra of bare  $\text{TiO}_2$  and samples obtained by impregnation of bare  $\text{TiO}_2$  with Fe or CuPp-Fe- $\text{TiO}_2$ .

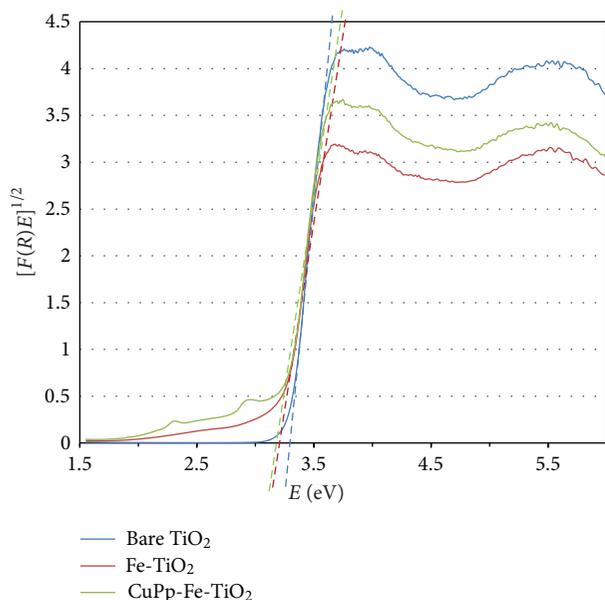


FIGURE 6: Modified Kubelka-Munk function versus energy of absorbed light of the bare  $\text{TiO}_2$  (blue line), Fe- $\text{TiO}_2$  (brown line), and CuPp-Fe- $\text{TiO}_2$  (green line).

of 4-nitrophenol (4-NP) in aqueous suspension under UV-visible light irradiation in the presence of  $\text{H}_2\text{O}_2$ . The amount of iron loaded onto the  $\text{TiO}_2$  surface during the first wet impregnation step followed by dryness at 393 K and final calcination at 350 °C used to prepare Fe- $\text{TiO}_2$  (1% wt) [21], support for  $\text{H}_2\text{Pp}$  and Cu-Pp porphyrins, as well as the amounts of porphyrins (6  $\mu\text{mol/g}$ ) [20] impregnated onto Fe- $\text{TiO}_2$  to prepare  $\text{H}_2\text{Pp-Fe-TiO}_2$  and  $\text{CuPp-Fe-TiO}_2$ , were chosen by taking into account our previous work [20, 21]. In a typical experiment the photodegradation of 20  $\text{mg}\cdot\text{L}^{-1}$

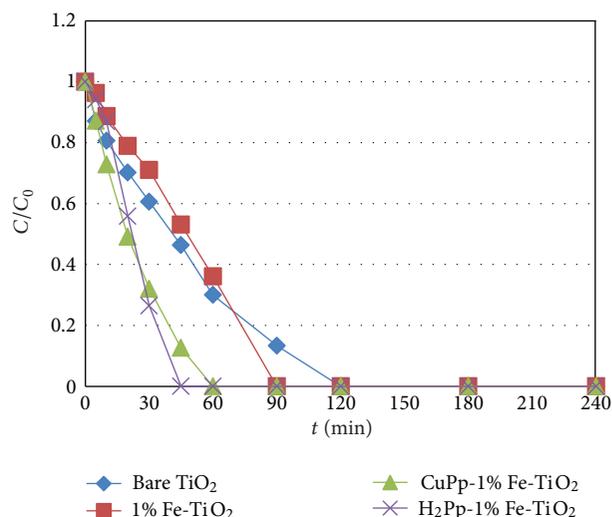


FIGURE 7: Degradation of 4-NP as a function of irradiation time in the presence of different photocatalysts,  $\text{H}_2\text{O}_2$  and air bubbling. Experimental conditions:  $[\text{4-NP}] = 20 \text{ mg}\cdot\text{L}^{-1}$ ;  $[\text{H}_2\text{O}_2] = 4.9 \text{ mM}$ ; catalyst amount =  $0.4 \text{ g}\cdot\text{L}^{-1}$ ; reaction volume = 300 mL; pH = 6.2; lamp: UV-vis lamp SANOLUX, 300 W.

solution of 4-NP was carried out at the initial value of pH = 6.2 in the presence of  $[\text{H}_2\text{O}_2] = 4.9 \text{ mM}$ , catalyst amount =  $0.4 \text{ g}\cdot\text{L}^{-1}$  and by bubbling air in a 300 mL batch photoreactor. A 300 W UV-visible lamp sketched in Figure 1 was used as irradiation system.

Figure 7 shows the changes in 4-NP concentrations occurring under these experimental conditions. The results obtained in the case of  $\text{H}_2\text{Pp-Fe-TiO}_2$  or  $\text{CuPp-Fe-TiO}_2$ —in the presence of hydrogen peroxide and under the experimental condition reported above—were more satisfactory than those performed by using bare  $\text{TiO}_2$  or Fe- $\text{TiO}_2$  under UV-visible light irradiation. The total organic carbon (TOC) analyses showed complete mineralization of 4-NP after ca. 60 min of irradiation for both samples loaded with porphyrins ( $\text{H}_2\text{Pp-Fe-TiO}_2$  and  $\text{CuPp-Fe-TiO}_2$ ). On the contrary residual amounts of TOC (40–50% of abatement) were found after the same irradiation time when bare  $\text{TiO}_2$  or Fe- $\text{TiO}_2$  samples were used.

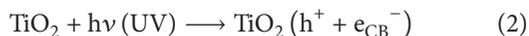
Interestingly, despite the fact that the observed initial photoreaction rate was higher when CuPp instead of  $\text{H}_2\text{Pp}$  was used as sensitizer, the maximum of degradation was obtained by using  $\text{H}_2\text{Pp-Fe-TiO}_2$  photocatalyst; in fact, 4-NP disappeared completely within 45 minutes of irradiation time.

Negligible photoactivity was observed for all of the samples when carried out under dark. This suggests that the photoexcitation, together with presence of  $\text{H}_2\text{O}_2$ , is essential for inducing the photodegradation of 4-NP processes.

The photostability and the reusability of the photocatalysts are important parameters for practical application. In this work we have observed that all the composites, freshly prepared, that is, Fe- $\text{TiO}_2$ ,  $\text{H}_2\text{Pp-Fe-TiO}_2$  and  $\text{CuPp-Fe-TiO}_2$ , can be recycled at least three times without any appreciable decrease of photoactivity.

In the light of the above results the beneficial effect of porphyrin-based sensitizers for the photodegradation of 4-NP has been confirmed [20, 23].

The porphyrins used as sensitizers (Sens) can be excited by visible light to produce electron-hole pairs (an electron in the excited singlet or triplet state of Pps and a hole in the ground state of Pps; see (1) and (3)):

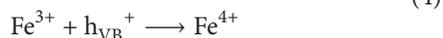
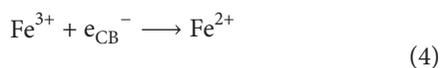


Photoexcitation with UV light of energy greater than the  $\text{TiO}_2$  band gap promotes an electron from the valence band to the conduction band and leaves an electronic vacancy or hole ( $h^+$ ) in the valence band (2).

As shown in Figure 6 the band gap energies for bare  $\text{TiO}_2$ ,  $\text{Fe-TiO}_2$ , and  $\text{CuPp-Fe-TiO}_2$  samples are, respectively, 3.20, 3.09, and 3.05 eV. Thus minor amount of energy is required for the generation of an electron-hole pair photoexcitation of the photocatalysts  $\text{Fe-TiO}_2$  and  $\text{CuPp-Fe-TiO}_2$ .

The Pp transfers electron into the conduction band of  $\text{TiO}_2$  according to (3).  $\text{TiO}_2$  works as an electron trapper and hinders the hole-electron recombination. In addition, Pp rapidly transfers excited electrons to  $\text{TiO}_2$  and enhances the separation of holes and electrons, significantly improving the photoefficiency.

In a cooperative manner, loading with  $\text{Fe}^{3+}$  ion can enhance the photocatalytic activity due to the charge trapping effect of  $\text{Fe}^{3+}$ , which prevents the recombination of  $e_{\text{CB}}^-$  and  $h_{\text{VB}}^+$  according to the following reactions:



In order to better establish the role of the iron ions to try the distinction between a heterogeneous or a homogeneous process we have measured the amount of  $\text{Fe}^{3+}$  in solution by ICP analyses. As result of these measurements, very low amounts of  $\text{Fe}^{3+}$  ions (1–3 ppb) were detected in solutions at the end of each experiment. These amounts can be considered negligible compared with 4 ppm of  $\text{Fe}^{3+}$  loaded onto  $\text{TiO}_2$  surface dispersed in the solution. Hence, although a possible contribution of the homogeneous Fenton reaction occurring in the process cannot be excluded, this contribution can be considered negligible compared with the contribution of the heterogeneous photo-Fenton process.

According to the crystal field theory,  $\text{Fe}^{2+}$  ( $d^6$ ) is relatively unstable compared to  $\text{Fe}^{3+}$  ( $d^5$ ). Therefore, a release of trapped electron becomes easy to return to  $\text{Fe}^{3+}$ . However, the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  energy level lies close to the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  level. As a result of this proximity, the trapped electron in  $\text{Fe}^{2+}$  can be easily transferred to a neighbouring superficial  $\text{Ti}^{4+}$  and combines with the oxygen molecule to form  $\text{O}_2^{\bullet-}$  and finally  $\bullet\text{OH}$  [24].

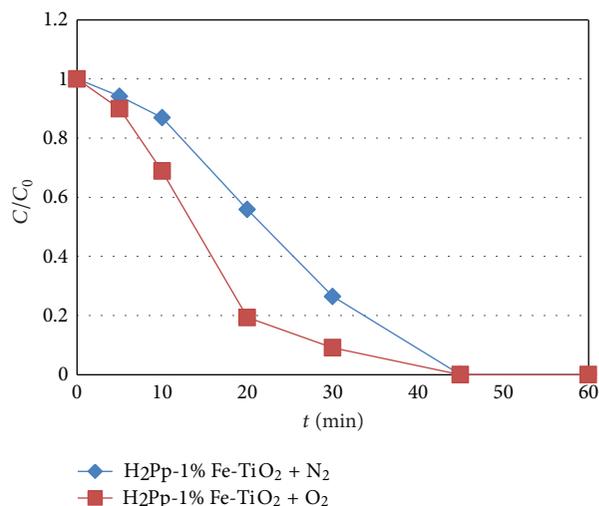
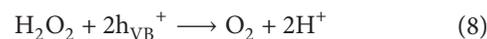
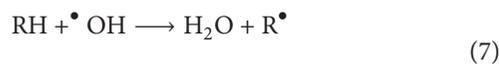


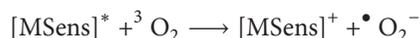
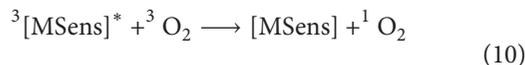
FIGURE 8: Degradation of 4-NP as a function of irradiation time in the presence of  $\text{H}_2\text{Pp-Fe-TiO}_2$  as photocatalyst and  $\text{H}_2\text{O}_2$ , under dinitrogen or pure dioxygen bubbling.

The heterogeneous photo-Fenton degradation of 4-NP occurring in the presence  $\text{H}_2\text{O}_2$  can be attributed to the increase of the concentration of hydroxyl radicals generated by photolytic peroxidation efficiently generated as shown in the following equation (5):



In order to assess the role of dissolved  $\text{O}_2$  during the photocatalytic degradation process,  $\text{N}_2$  was bubbled through the suspension to remove  $\text{O}_2$  from the solution. Figure 8 shows the photodegradation of 4-NP under  $\text{N}_2$ , air, or pure dioxygen bubbling. It is possible to observe that the degradation of 4-NP occurs also under dinitrogen atmosphere.

In addition to the role described previously [24], the presence of dioxygen could be also important during the process due to the possible generation of singlet oxygen ( ${}^1\text{O}_2$ ) or  $\bullet\text{O}_2^-$  species according to (10). The generation of  ${}^1\text{O}_2$  in a heterogeneous system, where porphyrins are present, has been highlighted by Zebger and coworkers [25]:



## 4. Conclusions

Novel porphyrin(Pp)/Fe co-loaded TiO<sub>2</sub> composites prepared by impregnation of [5,10,15,20-tetra(4-tert-butylphenyl)] porphyrin (H<sub>2</sub>Pp) or Cu(II)[5,10,15,20-tetra(4-tert-butylphenyl)] porphyrin (CuPp) onto Fe-loaded TiO<sub>2</sub> have been characterized.

The synergistic effect of these porphyrinic structures (H<sub>2</sub>Pp and Cu-Pp) and iron co-loaded onto TiO<sub>2</sub> powders has been studied for the photodegradation of 4-NP in aqueous suspension under UV-visible light irradiation in the presence of H<sub>2</sub>O<sub>2</sub>. To the best of our knowledge this complex system porphyrin-Fe-TiO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub>, that showed to be more performant than the simpler bare TiO<sub>2</sub>, Fe-TiO<sub>2</sub>, porphyrin-Fe-TiO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>-TiO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>-Fe-TiO<sub>2</sub> systems, has been studied for the first time.

## Acknowledgments

The authors wish to thank the University of Salento, Apulia Region: Progetto "Ritorno al Futuro" and the Interuniversity Consortium Chemistry for the Environment (INCA). Dr. Manuel Fernandez is acknowledged for helping the authors to measure the emission spectrum of UV-vis lamp used in this work.

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