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Research Article

New Porphyrin/Fe-Loaded TiO_2 Composites as Heterogeneous Photo-Fenton Catalysts for the Efficient Degradation of 4-Nitrophenol

Giuseppe Mele,[1] Iolanda Pio,[1] Anna Scarlino,[1] Ermelinda Bloise,[1] Roberta Del Sole,[1] Leonardo Palmisano,[2] and Giuseppe Vasapollo[1]

[1] *Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via Arnesano, 73100 Lecce, Italy*
[2] *Dipartimento di Ingegneria Elettrica, Elettronica e delle Telecomunicazioni, di tecnologie Chimiche, Automatica e modelli Matematici (DIEETCAM) Università di Palermo, Viale delle Scienze, Edificio 6, 90128 Palermo, Italy*

Correspondence should be addressed to Giuseppe Mele; giuseppe.mele@unisalento.it

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A new class of porphyrin(Pp)/Fe co-loaded TiO_2 composites opportunely prepared by impregnation of [5,10,15,20-tetra(4-*tert*-butylphenyl)] porphyrin (H_2Pp) or Cu(II)[5,10,15,20-tetra(4-*tert*-butylphenyl)] porphyrin (CuPp) onto Fe-loaded TiO_2 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_2 in the presence of H_2O_2 showed to be more efficient than the simple bare TiO_2 or Fe-TiO_2.

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_2 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_2, H_2O_2, and irradiation to enhance the efficiency of the overall photodegradation process [9–12]. Also, in the last years, dye-sensitized TiO_2-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_2 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_2 surface along with H_2O_2 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, $Fe(NO_3)_3 \cdot 9H_2O$, 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.

TiO_2 in the microcrystalline phase of anatase, specific surface area 8 $m^2 g^{-1}$, was kindly provided by Tioxide Huntsman.

The synthesis of the [5,10,15,20-tetra(4-*tert*-butylphenyl)]porphyrin (H_2Pp) and of the Cu(II) [5,10,15,20-tetra(4-tert-butylphenyl)]porphyrin (CuPp) was carried out as reported previously [20].

2.2. Preparation of the Hybrid H_2Pp-Fe-TiO_2 and CuPp-Fe-TiO_2 Catalysts. The 1% wt Fe-TiO_2 powder, successively indicated as Fe-TiO_2, was prepared by wet impregnation of TiO_2 with aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$ 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].

Fe-loaded TiO_2 powder impregnated with functionalized metal-free porphyrin and Cu(II)-porphyrin Fe-TiO_2, successively indicated as H_2Pp-Fe-TiO_2 and CuPp-Fe-TiO_2, used as photocatalytic systems, were prepared by impregnation of Fe-TiO_2 powders with 6 μmol/g of sensitizer (H_2Pp or CuPp) *per* gram of TiO_2. The opportune amount of sensitizers was dissolved in 15 ml of $CHCl_3$ (or CH_2Cl_2), and 2 g of finely ground 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 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$^+$ Rigaku) equipped with CuKα 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 W/m^2 in the 200–950 nm range. The emission spectrum of the lamp is reported in Figure 2. Oxygenation was ensured by bubbling air in the suspension during the experiments.

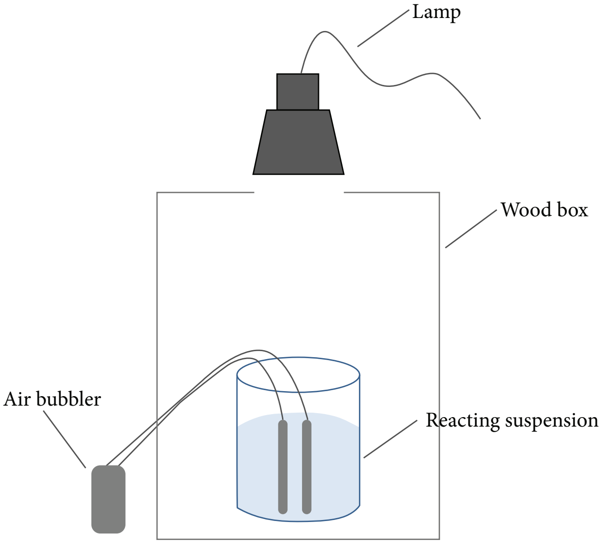

Figure 1: Set-up used for the photocatalytic experiments.

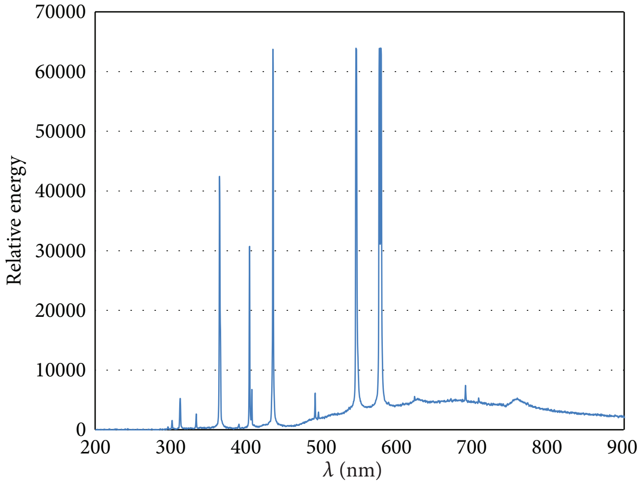

Figure 2: Emission spectrum of SANOLUX HRC UV-vis lamp.

The novel hybrid composite photocatalysts based on the metal free and Cu porphyrins onto the Fe-loaded 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).

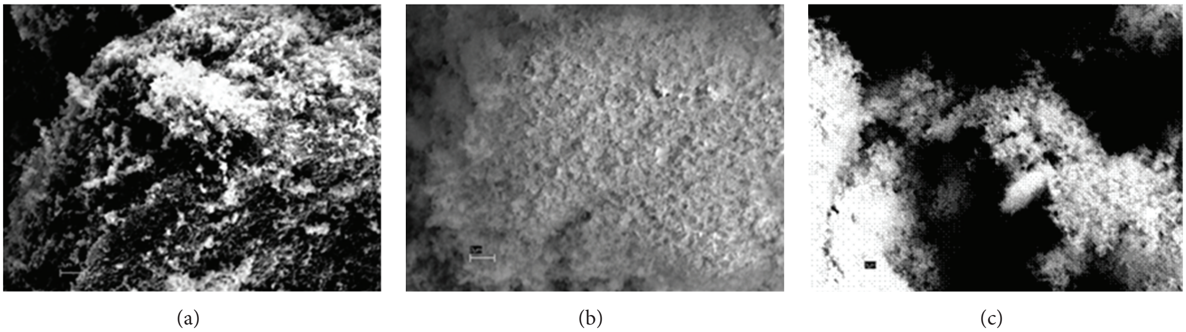

Figure 3: SEM micrographs of (a) BareTiO_2, (b) Fe-TiO_2, and (c) CuPp-Fe-TiO_2.

The amount of Fe^{3+} 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_2Pp, and its Cu(II) complex, CuPp, were performed according to a procedure already reported in the literature [20].

Also, the Fe-TiO_2 composite, used as the support for the sensitizers H_2Pp 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_2 powder with 6 μmol/g of sensitizers (H_2Pp or CuPp) *per* gram of Fe-TiO_2 as described in the experimental section, and they were indicated, respectively, as H_2Pp-Fe-TiO_2 and CuPp-Fe-TiO_2.

Analysis of SEM picture (Figure 3) shows that the Fe-TiO_2 (Figure 3(b)) and CuPp-Fe-TiO_2(Figure 3(c)) samples have a higher number of irregular shaped particles than bare TiO_2 (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_2 sample. The presence of Fe^{3+} ions seems to hamper the growth of TiO_2 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_2 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_2, Fe-TiO_2, and CuPp-Fe-TiO_2 recorded in the range 200–800 nm.

The spectrum of bare TiO_2 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_2 and CuPp-Fe-TiO_2 metal loaded samples, due to the presence of both iron and porphyrin systems producing a modest shift of the band gap edge in the case of CuPp-Fe-TiO_2 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_2 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.

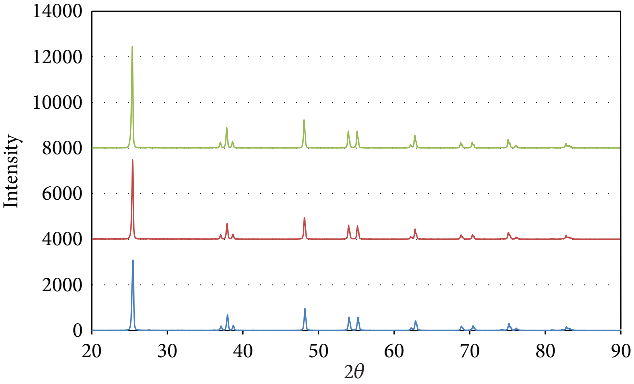

Figure 4: XRD patterns of TiO_2 powder samples compared with the bare sample.

The band gap values (*Eg*) 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_2.

The results obtained afford band gap energies of 3.20, 3.09, and 3.05 eV for bare TiO_2, Fe-TiO_2 and CuPp-Fe-TiO_2 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_2Pp and Cu-Pp) supported onto the Fe-loaded TiO_2 surface powders was studied for the photodegradation

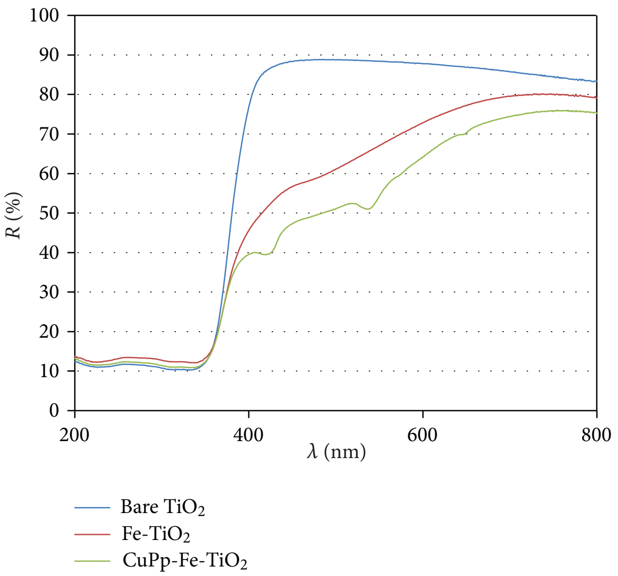

Figure 5: Diffuse reflectance spectra of bare TiO_2 and samples obtained by impregnation of bareTiO_2 with Fe or CuPp-Fe-TiO_2.

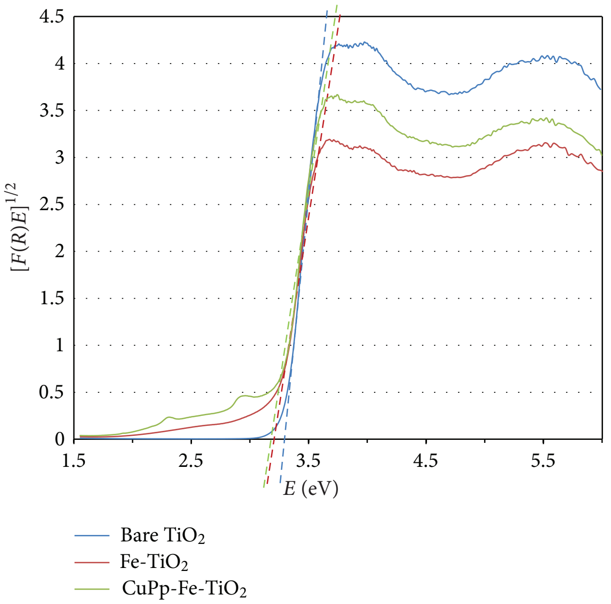

Figure 6: Modified Kubelka-Munk function versus energy of absorbed light of the bare TiO_2 (blue line), Fe-TiO_2 (brown line), and CuPp-Fe-TiO_2 (green line).

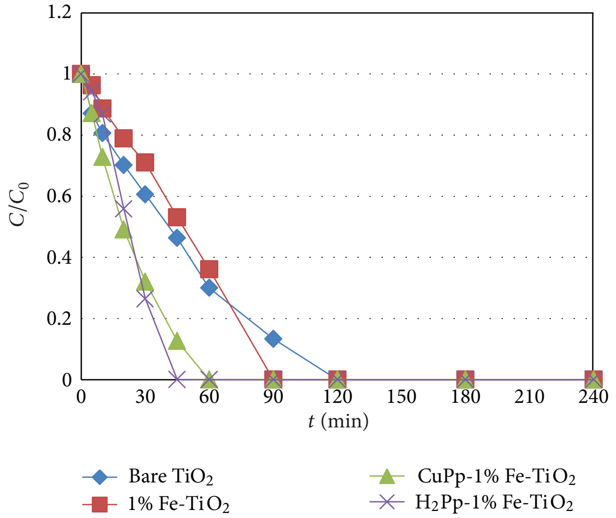

Figure 7: Degradation of 4-NP as a function of irradiation time in the presence of different photocatalysts, H_2O_2 and air bubbling. Experimental conditions: [4-NP] = 20 mgL^{-1}; [H_2O_2] = 4.9 mM; catalyst amount = 0.4 gL^{-1}; reaction volume = 300 mL; pH = 6.2; lamp: UV-vis lamp SANOLUX, 300 W.

of 4-nitrophenol (4-NP) in aqueous suspension under UV-visible light irradiation in the presence of H_2O_2. The amount of iron loaded onto the 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-TiO_2 (1% wt) [21], support for H_2Pp and Cu-Pp porphyrins, as well as the amounts of porphyrins (6 μmol/g) [20] impregnated onto Fe-TiO_2 to prepare H_2Pp-Fe-TiO_2 and CuPp-Fe-TiO_2, were chosen by taking into account our previous work [20, 21]. In a typical experiment the photodegradation of 20 mg·L^{-1} solution of 4-NP was carried out at the initial value of pH = 6.2 in the presence of [H_2O_2] = 4.9 mM, catalyst amount = 0.4 g·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 H_2Pp-Fe-TiO_2 or 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 TiO_2 or Fe-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 (H_2Pp-Fe-TiO_2 and CuPp-Fe-TiO_2). On the contrary residual amounts of TOC (40–50% of abatement) were found after the same irradiation time when bare TiO_2 or Fe-TiO_2 samples were used.

Interestingly, despite the fact that the observed initial photoreaction rate was higher when CuPp instead of H_2Pp was used as sensitizer, the maximum of degradation was obtained by using H_2Pp-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 H_2O_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-TiO_2, H_2Pp-Fe-TiO_2 and 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)):

$$[\text{Sens}] + h\nu\,(\text{Vis}) \xrightarrow{1} [\text{Sens}]^* \xrightarrow{3} [\text{Sens}]^* \quad (1)$$

$$\text{TiO}_2 + h\nu\,(\text{UV}) \longrightarrow \text{TiO}_2\left(\text{h}^+ + \text{e}_{\text{CB}}{}^-\right) \quad (2)$$

$$\text{TiO}_2[\text{Sens}]^* \longrightarrow \text{TiO}_2[\text{Sens}]^+ + \text{e}_{\text{CB}}{}^- \quad (3)$$

Photoexcitation with UV light of energy greater than the 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 TiO_2, Fe-TiO_2, and 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 Fe-TiO_2 and CuPp-Fe-TiO_2.

The Pp transfers electron into the conduction band of TiO_2 according to (3). TiO_2 works as an electron trapper and hinders the hole-electron recombination. In addition, Pp rapidly transfers excited electrons to TiO_2 and enhances the separation of holes and electrons, significantly improving the photoefficiency.

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

$$\begin{aligned} \text{Fe}^{3+} + \text{e}_{\text{CB}}{}^- &\longrightarrow \text{Fe}^{2+} \\ \text{Fe}^{3+} + \text{h}_{\text{VB}}{}^+ &\longrightarrow \text{Fe}^{4+} \end{aligned} \quad (4)$$

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 Fe^{3+} in solution by ICP analyses. As result of these measurements, very low amounts of 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 Fe^{3+} loaded onto 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, Fe^{2+} (d^6) is relatively unstable compared to Fe^{3+} (d^5). Therefore, a release of trapped electron becomes easy to return to Fe^{3+}. However, the Fe^{2+}/Fe^{3+} energy level lies close to the Ti^{3+}/Ti^{4+} level. As a result of this proximity, the trapped electron in Fe^{2+} can be easily transferred to a neighbouring superficial Ti^{4+} and combines with the oxygen molecule to form $O_2{}^{\bullet-}$ and finally ${}^\bullet OH$ [24].

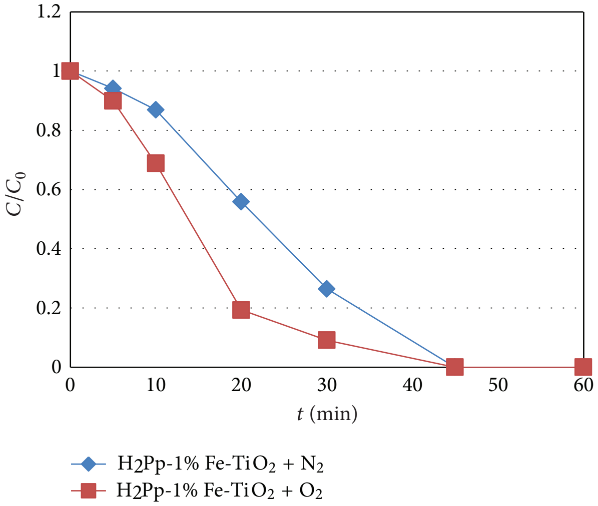

Figure 8: Degradation of 4-NP as a function of irradiation time in the presence of H_2Pp-Fe-TiO_2 as photocatalyst and H_2O_2, under dinitrogen or pure dioxygen bubbling.

The heterogeneous photo-Fenton degradation of 4-NP occurring in the presence H_2O_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):

$$\text{H}_2\text{O}_2 + \text{e}_{\text{CB}}{}^- \longrightarrow {}^\bullet\text{OH} + \text{OH}^- \quad (5)$$

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + {}^\bullet\text{OH} + \text{OH}^- \quad (6)$$

$$\begin{aligned} \text{RH} + {}^\bullet\text{OH} &\longrightarrow \text{H}_2\text{O} + \text{R}^\bullet \\ &\longrightarrow \text{furtheroxidation} \end{aligned} \quad (7)$$

$$\text{H}_2\text{O}_2 + 2\text{h}_{\text{VB}}{}^+ \longrightarrow \text{O}_2 + 2\text{H}^+ \quad (8)$$

$$\text{H}_2\text{O}_2 + {}^\bullet\text{OH} \longrightarrow \text{HO}_2{}^\bullet + \text{H}_2\text{O}. \quad (9)$$

In order to assess the role of dissolved O_2 during the photocatalytic degradation process, N_2 was bubbled through the suspension to remove O_2 from the solution. Figure 8 shows the photodegradation of 4-NP under 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 (${}^1O_2$) or ${}^\bullet O_2{}^-$ species according to (10). The generation of ${}^1O_2$ in a heterogeneous system, where porphyrins are present, has been highlighted by Zebger and coworkers [25]:

$$\begin{aligned} {}^3[\text{MSens}]^* + {}^3\text{O}_2 &\longrightarrow [\text{MSens}] + {}^1\text{O}_2 \\ [\text{MSens}]^* + {}^3\text{O}_2 &\longrightarrow [\text{MSens}]^+ + {}^\bullet\text{O}_2{}^- \end{aligned} \quad (10)$$

4. Conclusions

Novel porphyrin(Pp)/Fe co-loaded TiO_2 composites prepared by impregnation of [5,10,15,20-tetra(4-tert-butylphenyl)] porphyrin (H_2Pp) or Cu(II)[5,10,15,20-tetra(4-tert-butylphenyl)] porphyrin (CuPp) onto Fe-loaded TiO_2 have been characterized.

The synergistic effect of these porphyrinic structures (H_2Pp and Cu-Pp) and iron co-loaded onto TiO_2 powders has been studied for the photodegradation of 4-NP in aqueous suspension under UV-visible light irradiation in the presence of H_2O_2. To the best of our knowledge this complex system porphyrin-Fe-TiO_2 + H_2O_2, that showed to be more performant than the simpler bare TiO_2, Fe-TiO_2, porphyrin-Fe-TiO_2, H_2O_2-TiO_2, H_2O_2-Fe-TiO_2 systems, has been studied for the first time.

Acknowledgments

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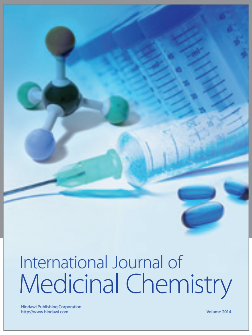
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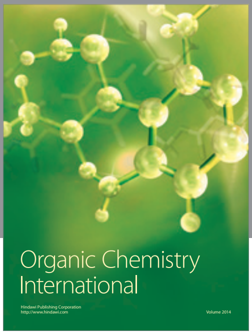
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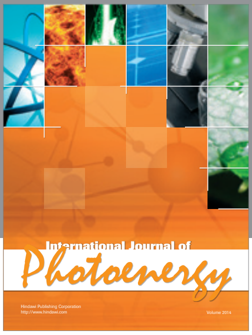
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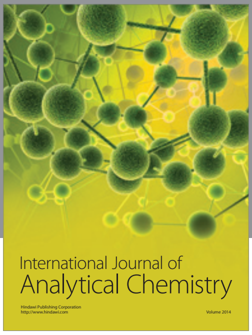
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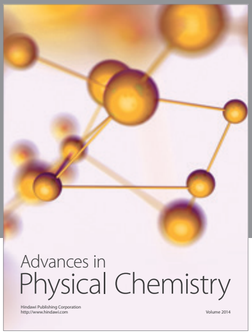
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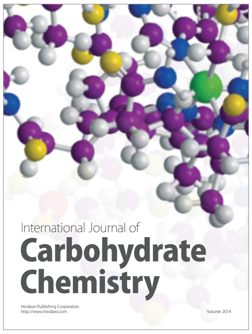
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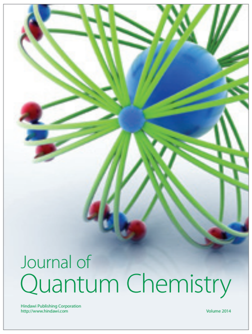
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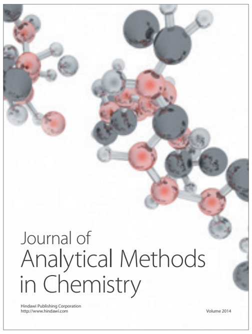
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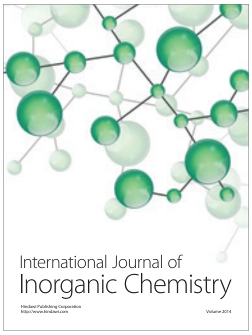
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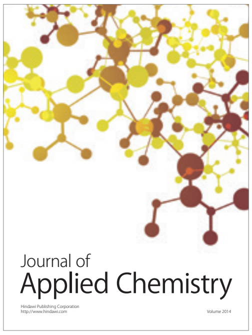
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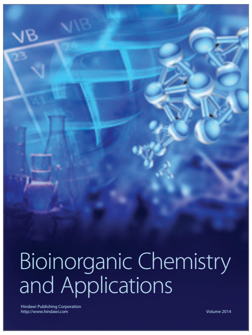
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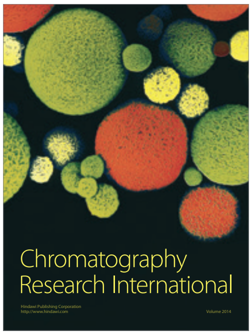
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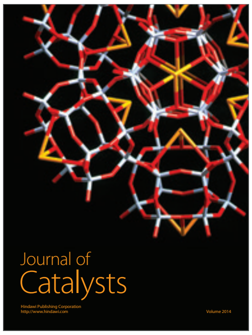
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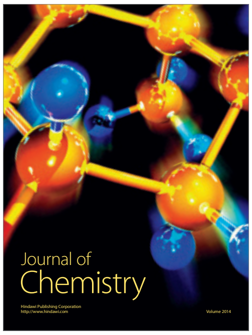
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