Visible light driven mineralization of spiramycin over photostructured N-doped TiO₂ on up conversion phosphors

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ABSTRACT

A novel visible light-active photocatalyst formulation (NdT/OP) was obtained by supporting N-doped TiO₂ (NdT) particles on up-conversion luminescent organic phosphors (OP). The photocatalytic activity of such catalysts was evaluated for the mineralization process of spiramycin in aqueous solution. The effect of NdT loading in the range 15–60 wt.% on bulk and surface characteristics of NdT/OP catalysts was investigated by several chemico-physical characterization techniques. The photocatalytic performance of NdT/OP catalysts in the removal of spiramycin from aqueous solution was assessed through photocatalytic tests under visible light irradiation. Total organic carbon (TOC) of aqueous solution, and CO and CO₂ gas concentrations evolved during the photodegradation were analyzed. A dramatic enhancement of photocatalytic activity of the photostructured visible active NdT/OP catalysts, compared to NdT catalyst, was observed. Only CO₂ was detected in gas-phase during visible light irradiation, proving that the photocatalytic process is effective in the mineralization of spiramycin, reaching very high values of TOC removal. The photocatalyst NdT/OP at 30 wt.% of NdT loading showed the highest photocatalytic activity (58% of TOC removed after 180 min irradiation against only 31% removal after 300 min of irradiation of NdT). We attribute this enhanced activity to the high effectiveness in the utilization of visible light through improved light harvesting and exploiting. OP particles act as “photoactive support”, able to be excited by the external visible light irradiation, and reissue luminescence of wavelength suitable to promote NdT photomineralization activity. © 2016 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

In recent years, there has been an increasing concern about the penetration of pharmaceutical active compounds (PACs) into the environment and related risks. Among the various PACs present in the environment, special emphasis has to be given to antibiotics, because of their potential role in the development of antibiotic resistant bacteria (Rizzo et al., 2014).

The great concern is that waters contaminated with residual antibiotics can reach waters used for human consumption or municipal water treatment facilities (Ericson et al., 2002). In fact, due to their antibacterial activity, waters containing antibiotics commonly used for animal and human health (antibiotics included) are refractory to natural biological degradation or conventional wastewater treatments (Palominos et al., 2008).

As a consequence, when these effluents are released from the treatment plants into an aquatic body, drug-tainted waters are introduced directly into the aquatic habitat, thus PACs are progressively accumulated into the environment.
For the removal of these compounds from wastewater several alternatives to conventional treatments, including reverse osmosis, adsorption, or advanced oxidation processes (AOPs), such as ozonation, Fenton, photo-Fenton oxidation, and heterogeneous photocatalysis (Reyes et al., 2006), mainly ultraviolet (UV) light-promoted, have been studied. With reference to AOPs, TiO₂ photocatalysis is under developing as an affordable, effective, environmentally friendly and sustainable technology for various chemical transformations. Indeed, amoxicillin (Dimitrakopoulou et al., 2012), nitroimidazoles (Prados-Joya et al., 2011), oxycetracycline (Zhao et al., 2013), and sulfamethoxazole (Xekoukoultakis et al., 2011) are degraded by UV or visible light treatments.

Spiramycin (SP) is a typical antibiotic currently detected in groundwater sources and drinking water supplies. SP can be removed from water by a UV driven photocatalytic process involving TiO₂ (Chekir et al., 2014), however, titania has a very low efficiency when used in a photocatalytic process using the emission spectrum of solar light. Novel photocatalysts, with a photo-response within the visible light (43%) of the electromagnetic radiation reaching the planet’s surface (Ozaki et al., 2007; Di Valentin and Pacchioni, 2013) should be developed.

In particular, intensive efforts have been directed to improve the photocatalytic behavior of TiO₂ under visible light, using non-metal (C, N, F and S) (Vaiano et al., 2015a; Han et al., 2011) dopants. Among all, N-doped TiO₂ photocatalyst (NdT), able to work in the visible-light region (420 nm < λ < 800 nm) with a band gap of 2.5 eV (Sacco et al., 2012), seems to be a promising candidate for the development of a more efficient photocatalytic process under solar irradiation. It has shown that visible light can selectively promote the electrons from the N 2p states to the conduction band (Ozaki et al., 2007; Di Valentin and Pacchioni, 2013; Livraghi et al., 2006).

Really, even if NdT can work with visible light, its use in a photoreaction system suffers of the disadvantage due to the no-uniform photon distribution inside the reactor core. In this respect, an approach based on (i) enhancing the irradiation of the overall catalytic surface through the decrease of the optical path of irradiation towards the photocatalyst, and (ii) harvesting the residual irradiation to be released in close proximity of the photocatalytic surface could be a solution. A reasonable consequence of such an approach for the intensification of the photocatalytic process seems to be the use of photocatalyst components able to convert low-energy photons into high-energy ones. Very recently, we have demonstrated the effectiveness of such an approach by coupling N-doped TiO₂ with organic up-conversion phosphors (Vaiano et al., 2015b). The advantages of organic up-conversion phosphors are a higher absorption coefficient of sensitizer and higher quantum yield with respect to the inorganic ones (Singh-Rachford and Castellano, 2010). We tested this innovative photocatalyst in the decolorization process of several dyes (Vaiano et al., 2015b), but never in the removal of emerging contaminants, such as antibiotics.

In this work, N-doped TiO₂ photocatalyst was supported on organic up-conversion phosphors and studied for the removal of spiramycin in the presence of visible light irradiation emitted by white light emitting diodes (LEDs). At the best of our knowledge, it is the first paper reporting the use of organic up-conversion phosphors as support for N-doped TiO₂ photocatalyst in the photocatalytic mineralization of spiramycin under visible light.

Intentionally, the aim of the work was to investigate the antibiotic mineralization rather than the substrate decomposition, since the rational micropollution abatement in aqueous matrices should involve its complete elimination rather than its transformation to other species.

1. Materials and methods

1.1. Synthesis of N-doped TiO₂ photocatalyst

The N-doped TiO₂ (NdT) photocatalyst was prepared by hydrolysis and condensation reactions between a TiO₂ precursor (titanium tetrathopropoxide, >97 wt.%, Sigma Aldrich) and ammonia aqueous solution (30 wt.%, Carlo Erba) (Sacco et al., 2012). The molar ratio N/Ti is 18.6, the same as in the optimized catalyst formulation found in our previous work (Sacco et al., 2012). To limit the effect of the hydrolysis reaction exothermicity, the synthesis temperature was 0°C and the system has been maintained at this temperature until the formation of a gel. The obtained gel was then centrifuged and washed with distilled water for removing the ammonia excess and the alcohols produced during the hydrolysis reaction. Finally, the sample was calcined at 450°C for 30 min. The characterization of NdT catalyst, yellow in color, by different analytical techniques has been reported in our previous papers (Rizzo et al., 2014; Sacco et al., 2012). The NdT photocatalyst has a band-gap energy of 2.5 eV and for this reason it is very effective in the removing of different organic pollutants under visible light irradiation (Sacco et al., 2015; Vaiano et al., 2015c, 2015d; Vaiano et al., 2014a).

1.2. Preparation of NdT supported on up-conversion phosphors

Blue-emissive up-conversion organic nanoparticles (OP) (with a size ranging between 10 and 22 nm (Liu et al., 2012)) were prepared following the method reported in (Liu et al., 2012). When excited by green light in the range 520–560 nm, the OP particles present a wide emission band between 400 and 500 nm, with a blue peak centered at about 434 nm and two blunter peaks located at 418 and 450 nm (Vaiano et al., 2015b). The blue light emitted by OP is able to activate the NdT photocatalyst, being the latter a semiconductor with band-gap energy of 2.5 eV.

The OP nanoparticles were used as support for NdT catalyst: 0.4 g of OP was dispersed in 25 mL of HCl (0.85 mol/L) aqueous solution and maintained under magnetic stirring for several minutes until to obtain a uniform dispersion. Then, 2 mL of tetraethyl orthosilicate (TEOS) and different amounts of NdT (0.06–0.24 g) were added to the OP aqueous suspension. The mixture was kept under stirring for 48 hr at 25°C and then centrifuged to recover the final NdT/OP solid phase.

The nominal loading of NdT on the OP support was varied in the range 15–60 wt.%.

1.3. Samples characterization

The samples were characterized with several techniques. Specific surface area of catalysts was obtained by N₂
adsorption measurement at ~196°C with a Costech Sorptometer 1040 after pretreatment at 60°C for 120 min in He flow (99.999%). The TiO₂ content of the NdT/OP samples was determined by X-ray fluorescence spectrometry (XRF) in a ThermoFischer ARL QUANT’X EDXRF spectrometer equipped with a rhodium standard tube as source of radiation and with Si-Li drifted crystal detector. X-ray diffraction (XRD) spectra were obtained with an X-ray micro diffractometer Rigaku D-max-RAPID (Cu-Kα radiation). Raman spectra were obtained at room temperature with a Dispersive Micro-Raman spectrophotometer (Invia, Renishaw), equipped with a 514 nm diode-laser, in the range 100–2500 cm⁻¹. Ultraviolet-Visible reflectance spectra (UV–Vis DRS) of catalysts were recorded by a Perkin-Elmer spectrophotometer Lambda 35 using a RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). All spectra were obtained using an 8° sample positioning holder, giving total reflectance relative to a calibrated standard SRS-010-99 (Labsphere Inc., North Sutton, NH).

1.4. Photocatalytic activity tests

The aqueous solutions containing spiramycin were prepared dissolving weighted fractions of pills in bidistilled water, to get a more realistic drug-tainted wastewater. The dissolved amount of spiramycin in bidistilled water corresponded to a total organic carbon (TOC) of 170 mg/L.

Photocatalytic tests were carried out in a pyrex tubular photoreactor (ID = 2.5 cm) equipped with an air distributor device (Qair = 150 mL/min), and a magnetic stirrer to maintain the photocatalyst suspended in the aqueous solution (natural pH = 6). The reaction temperature was controlled being in the range 20–30°C (Vaiano et al., 2015c). The photoreactor was irradiated by a strip composed by 30 white light LEDs (light intensity: 32 mW/cm²) with wavelength emission in the range 400–800 nm. The LEDs strip was positioned around the external surface of the reactor to assure uniform illumination of the reaction volume.

The tests were carried out using 3 g/L of photocatalyst and 100 mL of solution. The system was kept in dark condition for 2 hr to reach the adsorption equilibrium on the catalyst surface, and then the photocatalytic reaction was initiated by lighting on the LEDs. Liquid samples were taken at regular time intervals during the test and centrifuged for 20 min at 4000 rpm for separating the photocatalyst particles. The continuous analysis of gas phase (CO, CO₂) coming from the photoreactor was performed by specific on-line analyzers (ABB Advance Optima).

The photocatalytic activity was measured as TOC removal, a parameter able to quantify the SP mineralization. TOC of solution was calculated from CO₂ obtained by catalytic combustion at T = 680°C. CO₂ produced in gas-phase was monitored by continuous analyzers, measuring CO, CO₂ (Uras 14, ABB) and O₂ (Magnos 106, ABB) gaseous concentrations (Vaiano et al., 2015c).

2. Results and discussion

2.1. Characterization of NdT/OP catalysts

Table 1 reports a list of prepared catalysts together with the nominal and measured NdT loading, specific surface area (SSA), and NdT average crystallite size. The total amount of titania, determined by XRF, well agrees with the nominal TiO₂ amount, indicating that the preparation method is a suitable way to couple NdT with OP phosphors.

The crystal phases of NdT/OP catalysts were determined by XRD analysis (Fig. 1). From the analysis of XRD spectra of NdT/OP compared with those of bare OP and unsupported NdT powder (Fig. 1), the presence of the anatase-TiO₂ peak at about 25.5° in all NdT/OP catalysts was found. With the increase of NdT loading from 15 to 60 wt.%., the intensity of the diffraction peak corresponding to anatase phase also increased. This result suggests that the preparation method did not induce any change in the NdT crystalline structure, as also evidenced by the values of crystallite size, calculated by Scherrer equation at diffraction plane (101) (Table 1). In all NdT/OP samples, the broad band with low intensity centered at 2θ = 23° appears, attributed to silica coming from the hydrolysis of TEOS (Vaiano et al., 2015b). Moreover, the disappearing of the main diffraction signals of OP is found in NdT/OP spectra indicates that the OP surface is covered by silica and NdT.

Raman spectra of NdT, OP and NdT/OP catalysts are shown in Fig. 2. In the range 100–1000/cm NdT showed bands at 144, 396, 514, 637/cm and a weak shoulder at 195/cm, due to the

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NdT nominal loading (wt.%)</th>
<th>NdT measured loading (XRF) (wt.%)</th>
<th>TiO₂ average crystallite size (1 0 1) (nm)</th>
<th>SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdT</td>
<td>–</td>
<td>–</td>
<td>17</td>
<td>30</td>
</tr>
<tr>
<td>OP</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1</td>
</tr>
<tr>
<td>15NdT/OP</td>
<td>15</td>
<td>16</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td>30NdT/OP</td>
<td>30</td>
<td>28</td>
<td>17</td>
<td>8</td>
</tr>
<tr>
<td>15NdT/OP</td>
<td>60</td>
<td>59</td>
<td>17</td>
<td>10</td>
</tr>
</tbody>
</table>

SSA: specific surface area; NdT: N-doped TiO₂; OP: organic phosphors; XRF: X-ray fluorescence spectrometry.

Fig. 1 – XRD patterns of NdT, OP and NdT/OP samples. XRD: X-ray diffraction; NdT: N-doped TiO₂; OP: organic phosphors.
Raman-active fundamental modes of anatase (Rizzo et al., 2014). The NdT/OP catalysts also show the presence of some bands of NdT without any shift in their positions. This indicates that the dispersion of NdT on the OP surface did not cause modification in the crystalline structure of NdT catalyst, as shown by XRD analysis.

The spectrum of OP displayed signals at 281, 366, 536, 582, 847 and 926/cm. These signals disappeared when NdT was supported on the surface of OP.

The data obtained from UV–Vis reflectance spectra of the samples are reported in Fig. 3. As shown in Fig. 3a, the increase of NdT loading on OP surface leads to spectra similar to those of NdT. The increased amount of NdT leads to the decrease of intensity of the absorption bands typical of OP (in the range 520–560 nm), as it is seen in Fig. 3b. More in details, the sample 15NdT/OP shows two defined absorption bands at about 560 nm and 520 nm, while in 30NdT/OP the 520 nm contribution disappeared and only the absorption band centered at 560 nm is detected, indicating that a partial covering of the OP surface is occurring by increasing the NdT content. Finally, with a further increase of the NdT content (60NdT/OP sample), the OP absorption band at 560 nm disappeared completely, so suggesting that a nearly complete coverage of OP surface by NdT particles was achieved.

The strong influence of NdT amount on the final NdT/OP characteristics was also observed with respect to their morphology. Fig. 4 shows a low-magnification scanning electron microscopy (SEM) image of microsized particles of OP and nano/microsized particles of NdT/OP. The morphology of OP (Fig. 4a) was approximately uniform (a smooth exposed surface of OP is observed in the image). All NdT/OP samples show a similar morphology, but with an increased roughness on the surface, due to the deposition of the NdT particles on the OP surface. For 15NdT/OP (Fig. 4b) and 30NdT/OP (Fig. 4c), NdT appears uniformly dispersed on the OP surface, with an aggregate size very similar and lower than 2 μm. The situation is different for 60NdT/OP catalyst (Fig. 4d), where large isles of NdT particle aggregates (larger than 6 μm) are visible in some zones of the OP surface, while in other zones, the OP surface does not present so large aggregates. Therefore, at high NdT load, its surface distribution is not uniform, and the inhomogeneity of the surface increases with the quantity of supported photocatalyst.

The SSA values of NdT and OP are very different, being 30 and 1 m²/g, respectively. It is worthwhile that SSA of NdT/OP catalysts increased by increasing the NdT loading on the surface of OP (Fig. 5). However, from 30 to 60 wt.% NdT nominal loading, the increase of SSA is not linear with the NdT amount, as happens from 15 to 30 wt.% NdT content. This behavior is due to the strong aggregation between NdT particles on OP surface of 60NdT/OP (Fig. 6b), as observed in SEM images (Fig. 6).

2.2. Photocatalytic activity of NdT/OP

Fig. 7 shows the amount of spiramycin adsorbed in dark conditions in terms of TOC reduction at the spontaneous pH of the solution (pH = 6) and photocatalyst dosage of 3 g/L. Moreover, the TOC reduction increased linearly with the increase of NdT loading. It is important to underline that in
the absence of irradiation, the TOC reduction is only due to the adsorption of spiramycin on the catalyst surface, since no formation of CO\(_2\) was detected in the gas phase.

After the dark period, the suspension was irradiated with visible light emitted by white LEDs and the reaction started to occur. Preliminary experiments were carried out in order to verify that spiramycin was removed by the heterogeneous photocatalytic process. We found that in the absence of photocatalyst, no significant decrease in TOC was observed (less than 10%) during 7 hr of illumination (Vaiano et al., 2015c). Therefore, photolysis phenomena occur but at a limited extent. The TOC profiles as function of irradiation time in the presence of photocatalyst are reported in Fig. 8. All catalyst samples effectively removed spiramycin. The TOC removal was 34%, 58% and 24% for 15NdT/OP, 30NdT/OP and 60NdT/OP, respectively, after 180 min. For all the photocatalysts, the analysis of photoreactor outlet gases showed the presence of only CO\(_2\) during the irradiation time, confirming the occurrence of spiramycin mineralization into CO\(_2\) and water. From Fig. 8a a dramatic increase of TOC removal with 15NdT/OP and 30NdT/OP with respect to NdT catalyst is evident.

This dramatic enhancement of photocatalytic activity is related to the specific formulation of the NdT/OP photocatalyst. For 15NdT/OP and 30NdT/OP samples, we suggest that NdT supported on the OP surface is excited both by the blue component of the emission spectrum of the white LEDs, and by the blue emission of the phosphors (OP), excited in turn by the green component emitted by the white LEDs (Fig. 9), as previously observed in the discoloration process of several organic dyes (Vaiano et al., 2015b). This phenomenon contributes to strongly enhance the photoactivity of 15NdT/OP and 30NdT/OP when they are irradiated with white LEDs. On the other hand, similar activity has been observed for NdT and 60NdT/OP catalysts.

These experimental results can be better understood by comparing the apparent kinetic constant of mineralization process.

The apparent kinetic constant was evaluated assuming that in the batch reactor under visible light irradiation, the mineralization of spiramycin follows a pseudo-first order kinetics (Chekir et al., 2014).

Spiramycin mass balance (expressed as TOC) can be written as:

\[
\frac{d\text{TOC}(t)}{dt} = -k \cdot \text{TOC} \cdot a
\]

where, TOC\((t)\) (mg/L) is TOC of solution at any given time \(t\), \(k \ (L/(g\text{NdT} \cdot \text{min}))\) is apparent kinetic constant, \(a \ (g/L)\) is NdT effective dosage (considering the NdT content in NdT/OP catalysts).

The values of \(a\) have been calculated as follows:

\[
a = \frac{W_{\text{NdT}}}{100} \cdot d
\]
where, $W_{\text{NdT}}$ is the NdT content in NdT/OP (wt%) and $d$ is the NdT/OP dosage of 3 g/L.

The initial condition for Eq. (1) is $t = 0$ and $\text{TOC}_0 = 170$ mg/L.

Eq. (1), together with the initial condition, was solved by the Euler iterative method, allowing to identify the apparent kinetic constants $k$ by fitting experimental data reported in Fig. 8 as a function of irradiation time. The fitting procedure was realized by using the least squares approach, obtaining the following value of $k$ of NdT = 0.04 L/(g$_{\text{NdT}}$·min); 15NdT/OP = 0.5 L/(g$_{\text{NdT}}$·min); 30NdT/OP = 0.55 L/(g$_{\text{NdT}}$·min); 60NdT/OP = 0.018 L/(g$_{\text{NdT}}$·min).

The pseudo-first order kinetic constant is the best parameter to compare the results of photocatalytic activity, being independent from the amount of catalyst (Sacco et al., 2015), and only correlated to the NdT active phase loaded on the OP surface. It is important to note that, starting from the values obtained for NdT, the kinetics constant for 15NdT/OP and 30NdT/OP increased of one order of magnitude or more.

The results are summarized in Fig. 10. The value of $k$ is almost the same for 15NdT/OP and 30NdT/OP, meaning that the overall amount of NdT present on OP surface is totally irradiated. On the other hand, when NdT loading is higher than 30 wt.%, the photocatalytic activity decreased. In fact, the catalyst 60NdT/OP showed an apparent kinetic constant of spiramycin mineralization equal to 0.018 L/(g$_{\text{NdT}}$·min), lower than that obtained for 30 N-TiO$_2$/ZSP, equal to 0.55 L/(g$_{\text{NdT}}$·min). In this case, the decrease of reaction rate could be related to the increase of NdT agglomerate size observed by increasing NdT amount from 30 to 60 wt.%. A similar effect was previously observed in the E. coli inactivation (Rizzo et al., 2013) and in the photocatalytic removal of atrazine (Sacco et al., 2015).

The most relevant result is the exceptional promoted photocactivity shown by the NdT/OP photocatalysts up to 30 wt.% of NdT load with respect to the pure NdT powder. It must be remembering that when NdT is dispersed into aqueous solution (pH = 6), it forms aggregates of about 367 nm (Sacco et al., 2012). Taking into account this result, the higher photocactivity (up to 30 wt.% NdT content) could be assigned to the formation of NdT aggregates lower in size with respect to the suspended particles because of the acid conditions used during the immobilization of NdT on OP surface. The decrease of NdT aggregate size should lead to the formation of structured photocatalyst that better exposes the visible active photocatalyst for both mass and light transfer (Safaei-Naeini et al., 2012). Another reason of the peculiar photoactivity of 30NdT/OP could be the action of the photoactive support (OP) that increases the irradiation of the supported NdT nanoparticles in the visible range, giving a higher number of photons useful to activate NdT.

Fig. 6 – SEM images of (a) 30NdT/OP and (b) 60NdT/OP samples. NdT: N-doped TiO$_2$; OP: organic phosphors.

Fig. 7 – TOC reduction in dark condition as a function of NdT nominal loading. TOC: total organic carbon; NdT: N-doped TiO$_2$.

Fig. 8 – TOC profile as function of irradiation time for NdT and NdT/OP photocatalysts.
To better understand this phenomenon, additional photocatalytic tests were carried out by changing the amount of pure NdT in the photoreactor. In particular, an amount of NdT equal to 0.045, 0.09 and 0.18 g (corresponding to the NdT content in 0.3 g of NdT/OP photocatalysts) were used. The obtained data have been used to evaluate the quantum yield ($\phi_0$) of the photoreaction, evaluated according to the following equation (Eq. (3)):

$$\phi_0 = \frac{(\text{TOC}_0 - \text{TOC}_t) \cdot V \cdot N_A}{N_{\text{Photons}} \cdot t}$$

where, TOC$_0$ (mg/L) is initial TOC of spiramycin solution, TOC$_t$ (mg/L) is TOC of spiramycin solution after 180 min of irradiation, V (L) is solution volume, $N_A$ is Avogadro number, $N_{\text{Photons}}$ is number of photons emitted by LEDs useful to activate the NdT photocatalyst, t (min) is irradiation time.

The number of photons emitted by LEDs that have the energy able to photoactivate the NdT photocatalyst can be estimated through the following equation (Eq. (4) in Vaiano et al., 2014b):

$$N_{\text{Photons}} = \sum Y_i \cdot \frac{I_0}{h \cdot c} \cdot S$$

where, $I_0$ (W/cm$^2$) is the overall light intensity emitted by LEDs, $Y_i$ relative emission intensity at $\lambda_i$, $\lambda_i$ (m): wavelength; $S$ (cm$^2$): irradiated surface; $h$ (J s): Planck constant = 6.62 $\times$ 10$^{-34}$, $c$ (m/sec): lux velocity 3·10$^8$.

To assess the $N_{\text{Photons}}$, it has been considered the LEDs emission spectrum and relative emission intensity ($Y_i$) Table 2.

Considering that the wavelength useful for activating NdT is lower than 434 nm, only the relative intensity lower than this value was used for calculating the quantum yield (Fig. 11). The values of $\phi_0$ for pure NdT increased almost linearly by increasing the amount of NdT in the photoreactor, meaning that the overall amount of NdT particles are totally irradiated by the exciting light. This indicates a true heterogeneous catalytic regime without photons transfer limitation phenomena. A dramatic enhancement of $\phi_0$ was achieved for 15NdT/OP and 30NdT/OP if compared to the values obtained for pure NdT with an amount of 0.045 and 0.09 g, corresponding to the NdT content of 15NdT/OP and 30NdT/OP samples. The ratio between the values of $\phi_0$ for 0.045 and 0.09 g of pure NdT, and

### Table 2 - Spectral emission of white light emitting diodes (LEDs) as a function of wavelength ($\lambda$).

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$Y$ (−)</th>
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<tr>
<td>365</td>
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</tr>
<tr>
<td>425</td>
<td>0.05</td>
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<tr>
<td>434</td>
<td>0.095</td>
</tr>
<tr>
<td>475</td>
<td>1</td>
</tr>
<tr>
<td>525</td>
<td>0.3</td>
</tr>
<tr>
<td>575</td>
<td>0.4</td>
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<tr>
<td>625</td>
<td>0.22</td>
</tr>
<tr>
<td>675</td>
<td>0.08</td>
</tr>
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</table>

Fig. 9 – Schematic illustration of the mechanism of photocatalysis of the NdT supported on OP up-conversion phosphors.

Fig. 10 – Apparent kinetic constant of spiramycin mineralization as a function of NdT nominal loading.

Fig. 11 – Quantum yield after 180 min of irradiation for different amount of pure NdT and for NdT/OP photocatalysts.
for 15NdT/OP and 30NdT/OP, is almost equal to 2. Thus, as the NdT aggregate size for 15NdT/OP and 30NdT/OP is similar, (see SEM pictures), the increase of photocatalytic performances with respect to pure NdT, should be mainly attributed to the presence of the OP support able to increase the number of photons useful to excite NdT nanoparticles dispersed on the OP surface.

Moreover, the decrease of photocatalytic activity observed for 60NdT/OP could be explained considering that the OP surface is almost totally masked by NdT particles (as evidenced by characterization results), making ineffective the phosphors excitation by the green component of white LEDs. As a consequence, OP particles, if highly covered by NdT, cannot harvest the exciting radiation and no additional emission of the blue light at 434 nm, able to photoexcite the NdT catalyst, can occur.

In conclusion, we propose that the activity of the most active catalyst, 30NdT/OP, resulting in the highest mineralization rate of spiramycin, is related to a right balance between the absorption of light from both NdT and phosphors and the ability to realize a close re-emission of OP to the NdT particles present on NdT/OP photostructured photocatalyst.

3. Conclusions

The photocatalytic mineralization of spiramycin under visible light irradiation was investigated for the first time with catalysts (NdT/OP) based on N-doped TiO2 (NdT) supported on the surface of organic up-conversion phosphors (OP).

Anatase NdT nanoparticles, deposited on OP, form aggregated particles (size from lower than 2 μm up to NdT amount of 30 wt.% to higher than 6 μm when NdT loading is increased up to 60 wt.%), progressively covering the OP surface with increasing the NdT amount. We have found that the preparation method did not induce modifications of the crystalline structure and light absorption properties of NdT.

Photocatalytic results showed that NdT/OP photocatalysts dramatically increased the removal efficiency of spiramycin under visible light irradiation. The mineralization was confirmed by the analysis of the gas phase coming from the photoreactor: the only product detected was CO2.

The photocatalyst NdT/OP with NdT loading equal to 30 wt.% was the most active. In particular, 58% of TOC was removed after 180 min of visible light irradiation compared to pure NdT, which after 300 min of irradiation showed a TOC removal of only about 31%.

We propose that the NdT particles supported on the OP surface are excited both by the blue component of the emission spectrum of the white LEDs, and by the blue emission of OP excited by the green component emitted by white LEDs. This phenomenon leads to the enhancement of the photocatalytic activity.

For comparing the results as function of the effective NdT amount, the apparent kinetic constant was estimated using a pseudo-first-order kinetic model. Its value was almost the same up to 30 wt.% NdT content, indicating that the overall amount of active phase is well irradiated. Beyond the optimal loading of NdT (30 wt.%), the photocatalytic activity decreased because of the increase in NdT agglomerate size resulting in the masking of the OP surface.

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