

# Photocatalysis in Darkness: Optimization of Sol-Gel Synthesis of NP-TiO<sub>2</sub> Supported on a Persistent Luminescence Material and its Application for the Removal of Ofloxacin from Water

Alberti S<sup>1\*</sup>, Locardi F<sup>1</sup>, Sturini M<sup>3</sup>, Speltini A<sup>3</sup>, Maraschi F<sup>3</sup>, Costa GA<sup>1,2</sup>, Ferretti M<sup>1,2</sup> and Caratto V<sup>1</sup>

<sup>1</sup>Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy

<sup>2</sup>SPIN-CNR, Genoa, Italy

<sup>3</sup>Department of Chemistry, University of Pavia, Pavia, Italy

## Abstract

In the present work, a new photocatalyst based on a new persistent luminescence phosphor, PeLM, and NPs-TiO<sub>2</sub> was synthesized and the synthesis was optimized using a chemometric approach. A solid-state synthesis was used to obtain the persistent luminescence material while a sol-gel synthesis was used to obtain anatase NPs-TiO<sub>2</sub>. Each sample was then characterized by means of XRD, SEM and BET analysis, while the photocatalytic activity was evaluated testing the percent degradation of a methylene blue aqueous solution. Two different kinds of experiments were performed on the optimized sample, using a continuous irradiation or halving it with darkness cycles. It's been demonstrated that the PeLM acts as an internal source for TiO<sub>2</sub>, providing the excitation required for the photocatalysis and so allowing to continue photon absorption even in darkness conditions. The two materials were coupled by means of a solid-state synthesis, varying the ratio between the reagents (1, 6), the heating temperature (350, 550°C) and time (1, 6 hours) through a chemometric approach, in order to find the optimized values. Validating the model led to the conclusion that the parameters affecting the synthesis have no significant interactions among them. The obtained results demonstrated the real applicability of this coupled system in the removal of Ofloxacin from water solution as probe of emerging organic pollutants.

**Keywords:** Photocatalysis; Sol-gel synthesis; Persistent luminescence; Titanium dioxide; Fluoroquinolone; Methylene blue

## Introduction

Emerging pollutants, such as drugs [1,2], are becoming a serious threat to the aquatic environment as they result to be resistant to aerobic degradation and hydrolysis, and because the current water treatment processes are unable to provide quantitative abatements [3] and, often, are energy and capital intensive [4]. Special concern is involved by the widespread of pharmaceutically active compounds, as indeed antibiotics are, due to stimulation of bacterial resistance [2]. Among these, Fluoroquinolone (FQs) antibiotics were detected in different environmental waters and wastewater effluents at concentrations from nanograms to micrograms per liter [5,6]. Together with their photoproducts FQs residues were proved to possess residual antimicrobial activity and to exert biotoxic effect [7,8]. In the recent years, the development of VIS-light activated photocatalysts based on earth abundant materials is growing in importance [9,10], since many aromatic refractory compounds have proven to be mineralized totally to CO<sub>2</sub>, H<sub>2</sub>O and small molecules, in the presence of either natural and artificial radiation [11-13]. Heterogeneous photocatalysis can be applied to several research areas, especially for environmental applications; among these, water remediation [14] and wastewater decolorization are important fields the scientific research is focusing on. TiO<sub>2</sub> in nanometric size is one of the most preferable material [15], due to its strong oxidizing ability, excellent chemical stability, long durability, non-toxicity, water insolubility, super hydrophilicity, low cost and high surface to volume ratio [1,4,12,16-18]. An important feature of TiO<sub>2</sub> photocatalysis is the sorption affinity of the catalyst for the pollutant(s) considering that the degradation process is strongly favoured if the target species is adsorbed on the TiO<sub>2</sub> surface. Therefore, it is clear the need for nanoparticle materials, optionally supported on materials with high surface area and high adsorption capacity, such as silica, zeolite, activated carbon or clay [1,4,9,12,17-21]. Thus, solar powered TiO<sub>2</sub> photocatalysis results to be an energy neutral

technique for water purification and pollution control. However, TiO<sub>2</sub> is limited as a sunlight-driven photocatalyst, due to its large band gap (ca. 3.2 eV), which requires for photo-activation a wavelength of energy equal to or greater than the band gap [22]. This means that a UV light source is mandatory (UV represents only 5-8% of the solar spectrum) [17,23,24]. There are two possible ways to overcome this limitation: using a dopant capable to promote a bathochromic shift of TiO<sub>2</sub> absorption towards visible light [11,25], such as N and Fe-doping [23,26-28]; using a supporting material for TiO<sub>2</sub> capable to emit a proper radiation in order to activate internally the photocatalyst [29]. It was documented as the support of photocatalyst onto a persistent luminescence materials (PeLMs) increased the general efficiency [30] and allowed the photocatalytic process to occur even in the darkness [18]. In fact, the PeLM is able to be charged with either natural or artificial radiation [31-33] and, glowing in darkness, provide the necessary photons to the catalyst. The coupled system has potential application in the removal of organic pollutants in conditions in which the single photocatalyst possesses low or no efficiency, such as in low-transparent and turbid wastewater both under natural and artificial radiation [34,35]. Moreover, the capability to work also in darkness is significant in the reduction of electric energy consumption.

**\*Corresponding author:** Stefano Alberti, Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy, Tel: 390103538737; E-mail: [Stefano.alberti@edu.unige.it](mailto:Stefano.alberti@edu.unige.it)

**Received:** February 15, 2018; **Accepted:** February 21, 2018; **Published:** February 26, 2018

**Citation:** Alberti S, Locardi F, Sturini M, Speltini A, Maraschi F, et al. (2018) Photocatalysis in Darkness: Optimization of Sol-Gel Synthesis of NP-TiO<sub>2</sub> Supported on a Persistent Luminescence Material and its Application for the Removal of Ofloxacin from Water. J Nanomed Nanotechnol 9: 501. doi: 10.4172/2157-7439.1000501

**Copyright:** © 2018 Alberti S, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Here we report the synthesis of TiO<sub>2</sub> nanoparticles, prepared via a sol-gel synthesis, supported on (3ZnO:Ga<sub>2</sub>O<sub>3</sub>:2GeO<sub>2</sub>):Cr<sup>3+</sup> PeLM by solid state reaction, optimized with respect to our previous work [18] by a chemometric approach. The catalyst, characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and surface area measurement (by BET), was then tested. In particular, its performance was studied for the photocatalytic abatement of methylene blue (MB) from aqueous solution – representative of organic dyes [36] under simulated solar light. Then the optimized photocatalyst was employed for the removal of Ofloxacin antimicrobial from tap water under natural sunlight.

## Materials and Methods

### Synthesis

The TiO<sub>2</sub> samples supported on (3ZnO:Ga<sub>2</sub>O<sub>3</sub>:2GeO<sub>2</sub>):Cr<sup>3+</sup>, the persistent luminescent material, was prepared using a solid-state reaction. The zinc gallogermanate Cr<sup>3+</sup> doped was prepared using as precursor, ZnO (Alfa Aesar, 99.99%), Ga<sub>2</sub>O<sub>3</sub> (Alfa Aesar, 99.999%), GeO<sub>2</sub> (Alfa Aesar, 99.98%), Cr<sub>2</sub>O<sub>3</sub> (Alfa Aesar, 99.97%), which were mixed together using an agate mortar and then treated in oven at a temperature of 900°C for 2 h and then at 1100°C for 2 h. Between the two heat treatments, the samples were re-grinded and re-homogenized. The titanium dioxide was prepared using a sol-gel route. 12 mL of 2-propanol, 6 ml of titanium isopropoxide and 30 ml of water were mixed together with magnetic stirring for 4 hours. The gel so formed was then treated in oven at 105°C for 12 hours; the xerogel was grinded and homogenized in an agate mortar. These two reagents were placed in an aqueous solution and left under magnetic stirring for 30 min and eventually put in oven for the heating treatment, on the basis of the experimental design (as described in paragraph 2.5).

### Physical-chemical characterization

The optimized sample was characterized by XRD, SEM and BET. Phase identification was performed by XRD analysis using a Philips PW1830 diffractometer (Bragg-Brentano geometry; Cu K $\alpha$ ; Ni filtered; range 20-80 2 $\theta$ ; step 0.025 2 $\theta$ ; sampling time 10 s). SEM images were collected using a Tescan Vega 3 XMV microscope on powders coated with gold in low vacuum. Brunauer-Emmett-Teller (BET) analysis was carried out using an ASAP 2010 physisorption analyzer (Micromeritics Instrument Corp). Before the measurement the sample was pre-treated at 200°C in vacuum.

### Photocatalytic activity

First, the photocatalytic activity was investigated by testing the percent degradation of 25 mL 0.01 g/L MB solution in presence of 0.0125 g catalyst, as seen in our previous work [18]. MB was quantified using a Perkin Elmer UV-Vis spectrophotometer LAMBDA 35 (664 nm). The catalyst was added to the MB solution and, before irradiation, the suspension was equilibrated in the dark under magnetic stirring for 20 minutes. Then, two different tests were performed. In the first set of experiments, the sample was irradiated continuously with simulated solar light (300W Ultra-Vitalux lamp, Osram) for 50 minutes; in the second one, the sample was irradiated for 10 minutes alternately to 10 minutes of darkness for a total time of 50 min (total irradiation time: 30 min).

Later the catalyst was tested under natural solar light (462 W m<sup>-2</sup> VIS, 28 W m<sup>-2</sup> UV, Pavia, 45°11' N, 9°09' E, May 2016) for the degradation of OFL (> 99%, Sigma-Aldrich, Milan, Italy). Tap water solutions (100 mL 20 mg L<sup>-1</sup> OFL, 0.050 g catalyst) were equilibrated for

20 minutes (dark stirring) and then submitted to alternate irradiation/darkness cycles (10 +10 min each). OFL was quantified by HPLC-UV, by using a Shimadzu (Milan, Italy) LC-20AT solvent delivery module equipped with a DGU-20A3 degasser and interfaced with a SPD-20A UV detector. The analysis wavelength selected was 275 nm. 20  $\mu$ L of each sample was injected into a 250  $\times$  4.6 mm, 5  $\mu$ m Analytical Ascentis C18 (Supelco) coupled with a similar guard-column. The mobile phase was 25 mM H<sub>3</sub>PO<sub>4</sub>-acetonitrile (85:15), flow rate 1 mL min<sup>-1</sup>.

All the photocatalytic tests were carried out in triplicate.

### Luminescence analysis

The luminescence analysis on (3ZnO:Ga<sub>2</sub>O<sub>3</sub>:2GeO<sub>2</sub>):Cr<sup>3+</sup> are reported in our previous work [18]. The photos were collected by means of a Fujifilm – FinepixS1 camera set with ISO equal to 12800 and acquisition time of 8 seconds. Samples were charged under simulated solar light (300 W Ultra-Vitalux lamp, Osram) for 5 minutes.

### Multivariate experimental design

In order to find out the most convenient experimental conditions to prepare a catalyst with the highest photocatalytic activity, a chemometric approach was chosen to evaluate the significance of the variables involved in the preparation procedure. A multivariate experimental 2<sup>3</sup> factorial design was carried out considering the variables ratio between TiO<sub>2</sub> and the luminescent support (x1), temperature (x2), and heating time (x3). As reported in Table 1, the experimental domain comprised of different levels of TiO<sub>2</sub>/PeLM ratio (1 and 6), temperature (350 and 550°C) and heating time (1 and 6 h). TiO<sub>2</sub>/(3ZnO:Ga<sub>2</sub>O<sub>3</sub>:2GeO<sub>2</sub>):Cr<sup>3+</sup> ratio equal to 1:1 was the minimum ratio for the complete coverage of the PeLM support, while the temperature interval was chosen considering that, at least, a treatment at 350°C for 1 h was necessary to guarantee the formation of a crystalline phase. Temperature higher than 550°C were not explored to avoid phase transformation from anatase to rutile; no significant differences in the XRD diffractograms of samples prepared at 350°C and 550°C were detected.

Each sample was synthesized in triplicate and then tested for the photodegradation of MB aqueous solutions, under simulated solar light.

## Results and Discussion

### Chemometric optimization of the synthesis

The photocatalytic activity results, obtained from the factorial design experiments, are expressed as MB percent degradation (Table 2).

Figure 1 shows the plot of the coefficients of the model elaborated on the basis of the responses (MB degradation yields, %) reported in Table 2.

The responses were modelled according to the equation:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 \quad (1)$$

and the estimated coefficients of the model are reported in Table 3.

Variable	Level codes	
	+1	-1
TiO <sub>2</sub> /(3ZnO:Ga <sub>2</sub> O <sub>3</sub> :2GeO <sub>2</sub> ):Cr <sup>3+</sup> ratio <sup>a</sup>	6	1
Temperature (°C)	550	350
Time (h)	6	1
<sup>a</sup> Amount of PeLM 0.5 g.		

**Table 1:** Variables experimental domain for the 2<sup>3</sup> factorial design. All the samples were synthesized in triplicate.

Sample	TiO <sub>2</sub> /(3ZnO:Ga <sub>2</sub> O <sub>3</sub> :2GeO <sub>2</sub> ):Cr <sup>3+</sup> ratio <sup>a</sup>	Temperature (°C)	Time (h)	Mean Percent Degradation <sup>b</sup> (SD) (n=3)
1	1	550	1	89(2)
2	1	350	1	87(1)
3	1	350	6	89(6)
4	1	550	6	90(4)
5	6	350	1	91(1)
6	6	350	6	93(2)
7	6	550	6	89(7)
8	6	550	1	92(3)

<sup>a</sup>amount of PeLM 0.5 g.  
<sup>b</sup>irradiation time 50 min.

Table 2: MB percent degradation obtained at different experimental conditions.

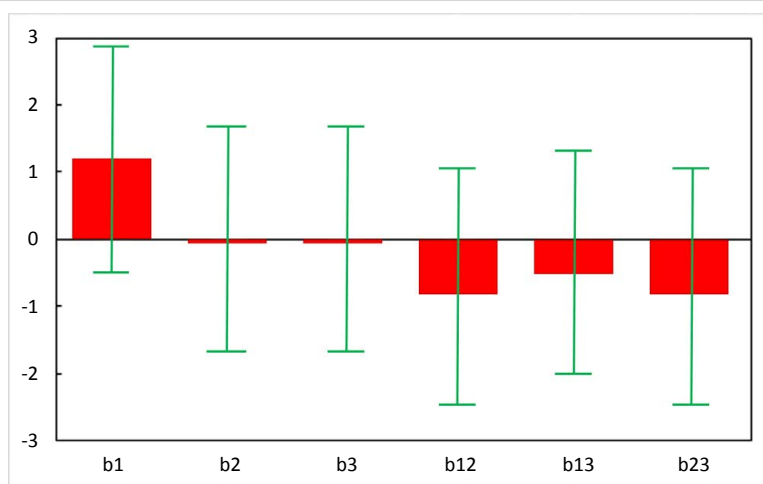


Figure 1: Plot of the coefficients of the model showing the significance of the variables considered in the chemometric study. Error bars indicate the confidence intervals at  $p=0.05$ .

	Coefficient	Standard deviation
$b_0$	89.9	0.8
$b_1$	1.2	0.8
$b_2$	0	0.8
$b_3$	0	0.8
$b_{12}$	-0.7	0.8
$b_{13}$	-0.4	0.8
$b_{23}$	-0.7	0.8

Table 3: Estimated coefficients of regression model for dependent variables.

The significance of each coefficient was evaluated according to usual convention: \* $p<0.05$ , \*\* $p<0.01$  and \*\*\* $p<0.0001$ . As shown in Figure 1, the variables and the interactions between the variables were not significant. This suggests that the synthesis can be conveniently carried out at the low values of the variables reported in the experimental domain (Table 1).

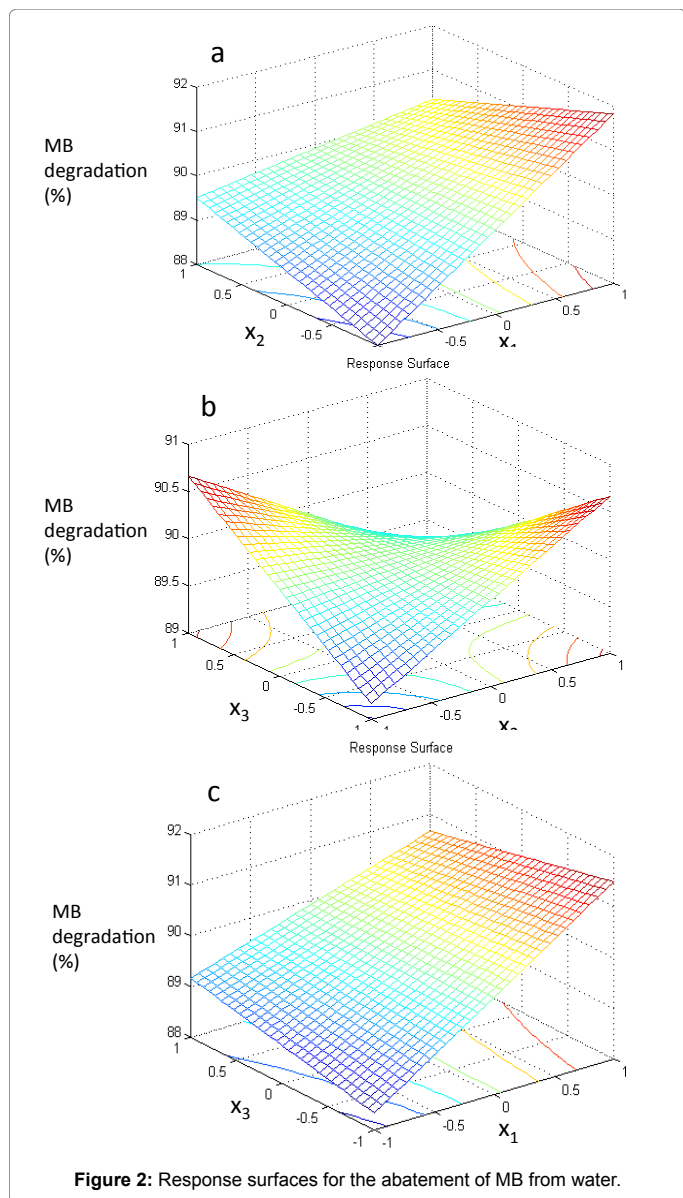
Indeed, even working at the high value of  $x_1$  variable, the photocatalytic efficiency was slightly improved as can be observed from the MB percent degradation reported in Figure 2. The model was validated on a test point ( $x_1=1$ ;  $x_2=0$ ;  $x_3=0$ ) chosen within the experimental domain. The experimentally obtained result, expressed as MB percent degradation ( $90 \pm 6$   $p=0.05$ ,  $n=3$ ) was not significantly different from that predicted according to eqn. (1).

The optimized catalyst, provides the highest value of MB percent degradation (87(1)%), after 50 minutes of continuous irradiation (Figure 3). Moreover, performing the experiment using just half of irradiation time (irradiation/darkness) the same performance was

gained. Compared with our previous results, in which the percent degradation of MB solution reached the value of 79% with continuous irradiation and 70% with alternate irradiation/darkness, respectively, after 50 minutes, we observed a yield increase of about 10% under continuous irradiation and 17% with alternate irradiation/darkness. Therefore, it is possible to state that the synthesis performed under the optimized conditions positively influenced the photocatalytic behaviour of the material. The stability of the catalyst was measured carrying out three experiments in sequence. The results, respectively 87(1)%, 84(1)%, 88(5)% for the first, second and third test, suggested a good durability of the material.

Basing on the excellent results obtained on 0.01 g/L MB solution, the photocatalytic efficiency of the catalyst was tested doubling the concentration of MB, under both continuous and alternate irradiation obtaining 80(1)% and 62(2)% respectively.

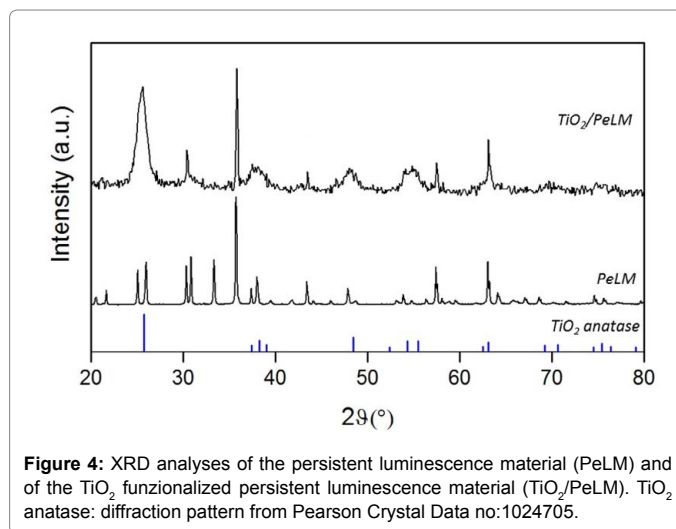
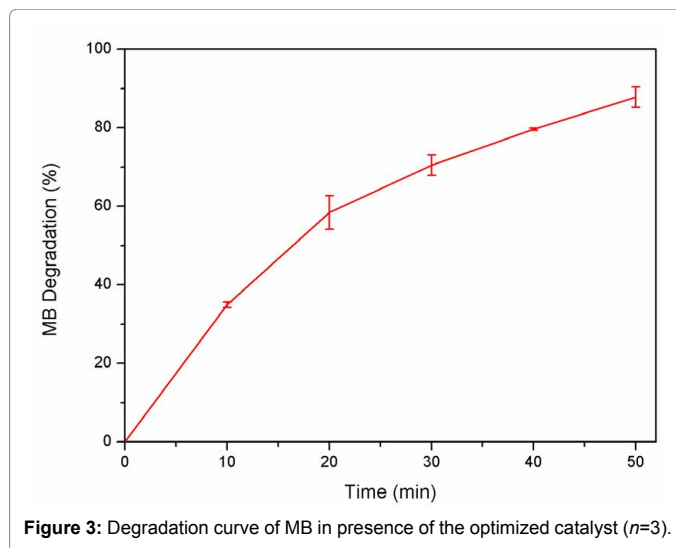
With continuous irradiation, the percent of degradation was actually comparable to the values obtained on 0.01 g/L MB solution (Table 2), with a loss in the percent degradation of just 10%, considering that the amount of catalyst is the same as in previous experiment. Moreover, the percent degradation is similar in both the experiments but the dye/catalyst ratio here employed is twice compared with the previous. The loss in the percent degradation resulted to be about 18% in the alternate irradiation/darkness test. This result can be attributed to the higher absorbance of 0.02 g/L MB solution, which did not allow a full charge of the photoluminescent material during 10 minutes of irradiation. Moreover, at the highest MB concentration all the active sites were reasonably saturated, with a consequent loss in efficiency.



### Physical-chemical characterization

In Figure 4, the XRD analysis on the optimized sample (TiO<sub>2</sub>/PeLM) is reported together with the experimental pattern of the persistent luminescence material (PeLM) and the reference pattern of TiO<sub>2</sub> anatase. The optimized sample presents both the characteristic peaks of anatase and PeLM, according to our previous work [18]. Indeed, the signals of PeLM are lower compared with the non-functionalized material, due to the effect of the crystalline TiO<sub>2</sub> on the surface that smooths the intensity.

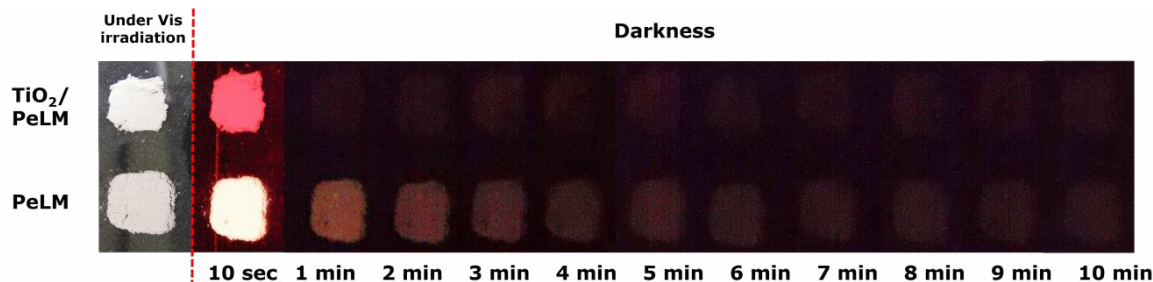
The emission of PeLM is formed by a broad peak centered at ~350 nm and a narrower signal at ~700 nm; hence, the overall emission resulted “white” [18]. Figure 5 reports the behavior of the persistent luminescence both for PeLM and TiO<sub>2</sub>/PeLM. The latter possessed a lower intensity probably induced by the titanium dioxide onto the surface. Indeed, it demonstrates that the coverage occurred. The persistent luminescence was visible up to 10 min, even if instrumentally can be measured still after 30 min [18]. Consequently, it is reasonable



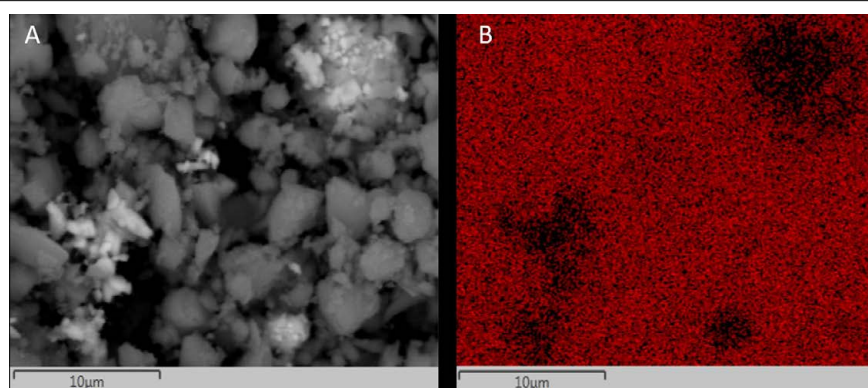
that during this time, the TiO<sub>2</sub> is able to exploit the photons provided by PeLM, allowing the photocatalytic process to occur.

Results from SEM-EDS investigation are reported in Figure 6. The morphology of the final products results inhomogeneous, presenting micrometric particles dispersed in sizes. The TiO<sub>2</sub> coating is not visible even if, through the elementary mapping of Ti through EDS analysis, the distribution onto the PeLM surface results well evident (Figure 6B. Red area indicate titanium signal). The brightest areas in Figure 6A are related to a lack of Ti signal in Figure 6B, indicating a lower amount of TiO<sub>2</sub> in those spots.

According to BET analysis, the surface area of the optimized sample (TiO<sub>2</sub>/PeLM) resulted to be  $62.49 \pm 0.01$  m<sup>2</sup>/g. Comparing with our previous results [18], which showed a surface area of  $4.49 \pm 0.01$  m<sup>2</sup>/g for the PeLM itself, it is well evident that the optimized synthesis allowed to obtain a catalyst with a surface area much closer to that of un-supported TiO<sub>2</sub> ( $88.64 \pm 0.01$  m<sup>2</sup>/g). The material provides a better photocatalytic performance due to the presence of the persistent luminescence material and, at the same time, retains a consistent surface area, which is absolutely important in a phenomenon which takes place at the catalyst interface.



**Figure 5:** Behaviour of the emission intensity, in darkness, of the persistent luminescence material (PeLM) and of the TiO<sub>2</sub> functionalized persistent luminescence material (TiO<sub>2</sub>/PeLM).



**Figure 6:** A: Back scattered image of the optimized sample. B: EDS mapping of Ti referred to image 4A. Red spots indicate titanium signal.

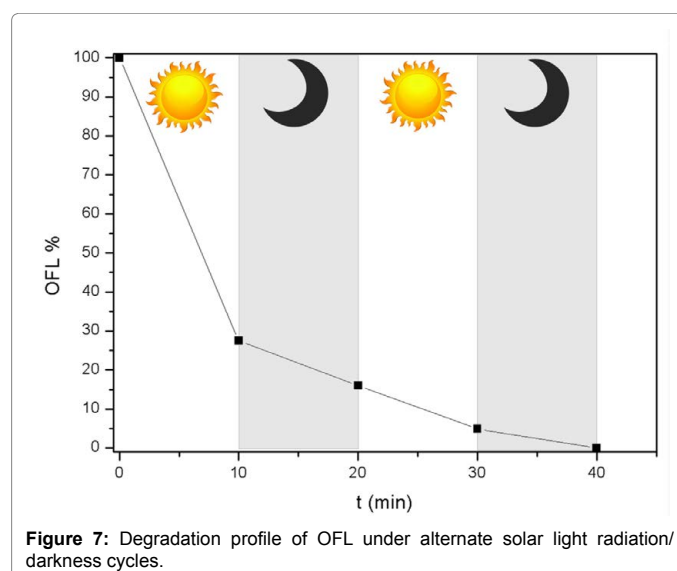
## Ofloxacin test

The optimal catalyst was then tested for the degradation of OFL in aqueous solution (tap water), directly under natural sunlight. This FQ was selected due to its wide presence in environmental matrices [6], and also because it is characterized by a slower photolytic decay in water matrices compared with other related drugs [37]. Before irradiation, spiked samples (20 mg/L OFL, 0.5 g/L catalyst) were stirred in the dark for 20 minutes to achieve sorption equilibrium. Under these conditions, a significant percentage of OFL was adsorbed onto the catalyst, namely 26%. Then the suspension was submitted to alternate irradiation/darkness cycles (10 minutes each).

The degradation profile (Figure 7). The antibiotic was quantitatively degraded (95%) in just 30 min (20 min of irradiation + 10 min of darkness), compared with 110 min required for direct photolysis under natural sunlight and continuous irradiation.

## Conclusions

A new photocatalyst based on TiO<sub>2</sub> nanoparticles supported on the persistent luminescence material (3ZnO:Ga<sub>2</sub>O<sub>3</sub>:2GeO<sub>2</sub>):Cr<sup>3+</sup> was synthesized and optimized by a chemometric approach. The activity of the new catalytic system was tested for the abatement of methylene blue (MB) aqueous solution, and also for removal of Ofloxacin antibiotic. The optimized catalyst reached the highest value of percent degradation (87(1)%) with the most convenient synthesis conditions after 50 minutes of continuous irradiation, while a comparable performance was gained by just half irradiation time, i.e. alternating irradiation/darkness cycles. High degradation of Ofloxacin (>95%) was achieved by 30 minutes of total irradiation, alternating irradiation and darkness cycles, 10 minutes each. These results demonstrated the real



**Figure 7:** Degradation profile of OFL under alternate solar light radiation/darkness cycles.

applicability of coupled system photocatalyst/persistent luminescence material in the removal of organic pollutants from water solution. The capability of the persistent luminescence material to store and release the light allowed the photocatalyst to work also in absence of external irradiation; consequently it could be employed in aqueous cloudy suspension, as indeed wastewaters are.

## Acknowledgement

The Authors are grateful to Professor Raffaella Biesuz for her precious support for chemometric analysis.

## References

- Chen Y, Wang K, Liping L (2004) Photodegradation of dye pollutants on silica gel supported TiO<sub>2</sub> particles under visible light irradiation. *J Photochem Photobiol A: Chem* 163: 281-287.
- Ferro G, Guarino F, Castiglione S, Rizzo L (2016) Antibiotic resistance spread potential in urban wastewater effluents disinfected by UV/H<sub>2</sub>O<sub>2</sub> process. *Sci Total Environ* 560-561: 29-35.
- Sharma VK, Johnson N, Cizmas L, McDonald TJ, Kim H (2016) A review of the influence of treatment strategies on antibiotic resistant bacteria and antibiotic resistance genes. *Chemosphere* 150: 702-714.
- Djellabi R, Ghorab MF, Cerrato G, Morandi S, Gatto S, et al. (2014) Photoactive TiO<sub>2</sub>-montmorillonite composite for degradation of organic dyes in water. *J Photochem Photobiol A: Chem* 295: 57-63.
- Speltini A, Sturini M, Maraschi F, Profumo A (2010) Fluoroquinolone antibiotics in environmental waters: Sample preparation and determination. *Sep Sci* 33: 1115-1131.
- Van Doorslaer X, Dewulf J, Van Langenhove H, Demeestere K (2014) Fluoroquinolone antibiotics: an emerging class of environmental micropollutants. *Sci Total Environ* 500-501: 250-269.
- Sturini M, Speltini A, Maraschi F, Pretali L, Profumo A, et al. (2012) Photodegradation of fluoroquinolones in surface water and antimicrobial activity of the photoproducts. *Water Res* 46-17: 5575-5582.
- Sturini M, Speltini A, Maraschi F, Pretali L, Ferri EN, et al. (2015) Sunlight-induced degradation of fluoroquinolones in wastewater effluent: Photoproducts identification and toxicity. *Chemosphere* 134: 313-318.
- Najafabadi AT, Taghipour F (2012) Cobalt precursor role in the photocatalytic activity of the zeolite-supported TiO<sub>2</sub>-based photocatalysts under visible light: a promising tool toward zeolite-based core-shell photocatalysis. *J Photochem Photobiol A: Chem* 248: 1-7.
- He Y, Sutton NB, Rijnaarts HHM, Langenhoff AAM (2016) Degradation of pharmaceuticals in wastewater using immobilized TiO<sub>2</sub> photocatalysis under simulated solar irradiation. *Appl Catal B - Environ* 181: 132-141.
- Graf C, Ohsen-Wiedmann R, Kreisel G (2007) Preparation and characterization of doped metal-supported TiO<sub>2</sub>-layers. *J Photochem Photobiol A: Chem* 188: 226-234.
- Bel Hadjitaief H, Ben Zina M, Galvez ME, Da Costa P (2016) Photocatalytic degradation of methyl green dye in aqueous solution over natural clay-supported ZnO-TiO<sub>2</sub> catalysts. *J Photochem Photobiol A: Chem* 315: 25-33.
- Speltini A, Sturini M, Maraschi F, Dondi D, Fisogni G, et al. (2015) Evaluation of UV-A and solar light photocatalytic hydrogen gas evolution from olive mill. *Int J Hydrogen Energy* 40: 4303-4310.
- Sturini M, Speltini A, Maraschi F, Profumo A, Pretali L, et al. (2012) Photolytic and Photocatalytic degradation of fluoroquinolones in untreated river water under natural sunlight. *Appl Catal B Environ* 119-120: 32-39.
- Pelaez M, Nolan NT, Pillai SC, Seery MK, Falaras P, et al. (2012) A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl Catal B Environ* 125: 331-349.
- Le Cunff J, Tomašić V, Wittine O (2015) Photocatalytic degradation of the herbicide terbuthylazine: preparation, characterization and photoactivity of the immobilized thin layer of TiO<sub>2</sub>/chitosan. *J Photochem Photobiol A: Chem* 309: 22-29.
- Lin L, Wang H, Luo H, Xu P (2015) Enhanced photocatalysis using side-glowing optical fibers coated with Fe-doped TiO<sub>2</sub> nanocomposite thin films. *J Photochem Photobiol A: Chem* 307-308: 88-98.
- Locardi F, Sanguineti E, Fasoli M, Martini M, Costa GA, et al. (2016) Photocatalytic activity of TiO<sub>2</sub> nanopowders supported on a new persistent luminescence phosphor. *Catal Comm* 74: 24-27.
- Maraschi F, Sturini M, Speltini A, Pretali L, Profumo A, et al. (2014) TiO<sub>2</sub>-modified zeolites for fluoroquinolones removal from wastewater and reuse after solar light regeneration. *J Environ Chem Eng* 2: 2170-2176.
- Maraschi F, Rivagli E, Sturini M, Speltini A, Profumo A, et al. (2015) Solid-phase extraction of vanadium (V) from tea infusions and wines on immobilized nanometer titanium dioxide followed by ICP-OES analysis. *Arab J Chem*.
- Shan AY, Ghazi TIM, Rashid SA (2010) Immobilization of titanium dioxide onto supporting materials in heterogeneous photocatalysis: A review. *Appl Catal A Gen* 389: 1-8.
- Kapilashrami M, Zhang Y, Liu YS, Hagfeldt A, Guo J (2014) Probing the optical property and electronic structure of TiO<sub>2</sub> nanomaterials for renewable energy applications. *Chem Rev* 114: 9662-9707.
- Caratto V, Setti L, Campodonico S, Carnasciali MM, Botter R, et al. (2012) Synthesis and characterization of nitrogen-doped TiO<sub>2</sub> nanoparticles prepared by sol-gel method. *J Sol-Gel Sci Technol* 63: 16-22.
- Schneider J, Matsuoka M, Takeuchi M, Zhang J, Horiuchi Y, et al. (2014) Understanding TiO<sub>2</sub> photocatalysis: mechanisms and materials. *Chem Rev* 114: 9919-9986.
- Zaleska A (2008) Doped-TiO<sub>2</sub>: a review. *Recent Pat Eng* 2: 157-164.
- Macwan DP, Dave PN, Chaturvedi S (2011) A review on nano-TiO<sub>2</sub> sol-gel type syntheses and its applications. *J Mater Sci* 46: 3669-3686.
- Caratto V, Locardi F, Alberti S, Villa S, Sanguineti E, et al. (2016) Different sol-gel preparations of iron-doped TiO<sub>2</sub> nanoparticles: characterization, photocatalytic activity and cytotoxicity. *J Sol-Gel Sci Technol* 80: 152-159.
- Villa S, Caratto V, Locardi F, Alberti S, Sturini M, et al. (2016) Enhancement of TiO<sub>2</sub> NPs activity by Fe<sub>3</sub>O<sub>4</sub> nano-seeds for removal of organic pollutants in water. *Materials* 9: 771.
- Wang J, Li R, Zhang Z, Sun W, Xu R, et al. (2008) Efficient photocatalytic degradation of organic dyes over titanium dioxide coating on immobilized luminescence agent under visible and sunlight irradiation. *Appl Catal A Gen* 334: 227-233.
- Zhang J, Pan F, Hao W, Ge Q, Wang T (2004) Light-storing photocatalyst. *Appl Phys Lett* 85: 5778-5780.
- Pan Z, Lu YY, Liu F (2012) Sunlight-activated long-persistent luminescence in the near-infrared from Cr<sup>3+</sup>-doped zinc gallogermanates. *Nat Mater* 11: 58-63.
- Li Y, Gecevicius M, Qui J (2016) Long persistent phosphors-from fundamentals to applications. *Chem Soc Rev* 45: 2090-2136.
- Caratto V, Locardi F, Costa GA, Masini R, Fasoli M, et al. (2014) NIR persistent luminescence of lanthanide ion-doped rare earth oxycarbonates: the effect of dopants. *ACS Appl Mater Interfaces* 6: 17346-17351.
- Feng PF, Wei YD, Wang YN, Zhang JC, Li HH, et al. (2016) Long persistent phosphor CdSiO<sub>3</sub>:Gd<sup>3+</sup>, Bi<sup>3+</sup> and potential photocatalytic application of CdSiO<sub>3</sub>:Gd<sup>3+</sup>, Bi<sup>3+</sup>@TiO<sub>2</sub> in dark. *J Am Ceram Soc* 99: 2368-2375.
- Garcia CR, Diaz-Torres LA, Salas P, Guzman M, Angeles-Chavez C (2015) Photoluminescent and photocatalytic properties of bismuth doped strontium aluminates blended with titanium dioxide. *Mat Sci Semicon Proc* 37: 105-111.
- Mills A, Hill C, Robertson PKJ (2012) Overview of the current ISO tests for photocatalytic materials. *J Photochem Photobiol A: Chem* 237: 7-23.
- Sunderland J, Tobin CM, White LO, Mac Gowan AP, Hedges AJ (1999) Antimicrobial activity of fluoroquinolone photodegradation products determined by parallel-line bioassay and high performance liquid chromatography. *Drugs* 47: 271-272.