

**PHOTOCATALYTIC OXIDATION OF ORGANIC
POLLUTANTS UNDER VISIBLE LIGHT
IRRADIATION: FROM N-DOPED TiO_2
PHOTOCATALYSTS TO THE DESIGN OF A
CONTINUOUS FIXED BED REACTOR**

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LIGHT IRRADIATION: FROM N-DOPED
TiO₂ PHOTOCATALYSTS TO THE DESIGN
OF A CONTINUOUS FIXED BED REACTOR**

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As a consequence of the rapid growth of population in urban areas, water use and reuse has become a major concern, leading to an urgent imperative of developing effective and affordable technologies for the treatment of water and wastewater. Traditional methods for water treatment are usually based on physical and biological processes but, unfortunately, some organic pollutants, classified as bio-recalcitrant, are not biodegradable. In this way heterogeneous photocatalysis may become an effective water treatment technology to remove organic pollutants hardly oxidised by conventional techniques.

Photocatalysis represents one of the main challenges in the field of treatment and decontamination of water and air, because it is able to work at ambient temperature and atmospheric pressure. Heterogeneous photocatalysis is a catalytic process that uses the energy associated to a light source to activate a catalyst with semiconducting properties. The most common used photocatalyst is titanium dioxide (TiO_2), which is able to oxidize a wide range of toxic organic compounds to harmless compounds such as CO_2 and H_2O . However, the following major factors limit both photocatalytic efficiency and activity of TiO_2 :

a) the band gap of anatase TiO_2 is 3.2 eV, i.e. it absorbs light in the UV region, so that only a small portion (5%) of sunlight can be used for a photocatalytic process. This is a great limitation in its use as photocatalyst for the conversion of solar into chemical energy;

b) as in all semiconductors, photogenerated electron-hole couples undergo fast recombination in competition with charge transfer to adsorbed species on the catalyst surface;

c) the use of slurry reactors limits the industrial applications of photocatalysis, since the necessary separation of catalyst powders after liquid phase reactions is troublesome and expensive.

In this context, during this PhD project different routes have been explored to go beyond these limitations:

1. With respect to the use of visible light irradiation, doping with anions belonging to the p-block was investigated in recent years to sensitize TiO_2 towards visible light, either by introducing newly created mid-gap energy states, or by narrowing the band gap itself. However, the role of titania dopants such as N, C, B, S, P, I and F is still not completely understood. The insertion of dopants in the crystalline structure of TiO_2 may induce light absorption in the visible region, but also increases the rate of the undesired recombination of photogenerated charge carriers. This effect becomes relatively lower if the crystallinity of the oxide structure is higher.

Our attention was focused on nitrogen as dopant. N-doped TiO_2 photocatalysts were prepared by sol gel method, via hydrolysis of titanium tetraisopropoxide by aqueous ammonia solution. More in details, the sol- process was carried out at 0°C to limit the evaporation of ammonia due to the exothermic character of the hydrolysis reaction, and then the obtained powders were dried and calcined at 450°C . N/Ti molar ratio and calcination time conditions were optimized. All samples were characterized by BET, UV-vis absorption, Raman spectroscopy, FTIR, SEM-EDAX, TEM and XRD. The effects of the dopant amount on the structural features of the doped materials were systematically investigated in relation to their photocatalytic activity.

The photocatalytic degradation of methylene blue (MB) in aqueous suspension was employed as test reaction. MB is a highly popular test pollutant in semiconductor photocatalysis used in the assessment of such key features as novel photocatalytic materials, photoreactors and light sources.

The best photocatalytic performances in the presence of visible light irradiation have been obtained with a N/Ti molar ratio equal to 18.6 and for a calcination time of 30 minutes.

The photocatalytic behaviour of the optimized N-doped TiO_2 photocatalyst was further explored in other reactions, i.e. the degradation of spyramicin, atrazine, methyl orange and on the inactivation of *E. coli*.

It is also important to evidence that this optimized N- TiO_2 photocatalyst resulted also able to reduce the total chemical oxygen demand (COD) of a highly polluted wastewater such as tannery wastewater.

2. The industrial application of photocatalytic processes is greatly hindered by the insufficient quantum efficiency of the photocatalytic reactions, which results from the relatively high recombination rate of photogenerated electron-hole ($e^- - h^+$) pairs. Therefore, N-doped TiO_2 was coupled with other semiconductors. In particular, ZnS-based phosphors (ZSP) were chosen. The coupling with ZSP not only reduces the charge-carriers recombination rate but also enhances the photons transfer inside the photoreactor, because ZSP emits, under UVA excitation, visible light centred at 440nm, able to photoexcite N-doped titania catalyst.

Also in this case a simple sol-gel method was adopted and the amount of N-doped TiO₂ on the surface of ZSP was optimized. All samples were characterized by BET, UV-vis absorption, Raman spectroscopy, FTIR, SEM-EDAX, TEM and XRD. The effects of coupling (N-doped TiO₂/ZSP) were systematically investigated in relation to their photocatalytic activity. In particular, the photocatalytic activity of N-doped TiO₂/ZSP was firstly evaluated for the removal of MB and of atrazine under UVA light irradiation. Enhanced performance in comparison to either pure N-doped TiO₂ nanoparticles or bare ZSP was obtained. The photocatalyst N-doped TiO₂/ZSP at 30 wt % of N-dopedTiO₂ loading (30N-TiO₂/ZSP) exhibited the highest photocatalytic activity for the removal of MB and atrazine.

A study of the reaction intermediates during the photocatalytic removal of atrazine was also carried out by LC-QTOF and LC/MS/MS analyses. The degradation mainly involved dealkylation reaction and alkyl chain oxidation both in presence of 30N-TiO₂/ZSP and ZSP. It has been found that the presence of N-doped TiO₂ particles dispersed on ZSP surface led to a change of selectivity, lowering the number of intermediates formed during irradiation. It is important to underline that in the presence of ZSP support no dechlorination of aromatic structure occurred, and thus no formation of cyanuric acid was observed. This study clearly demonstrates the importance of using the ZSP as a supporting material for N-doped TiO₂ nanoparticles.

3. The development of an optimized reactor in slurry configuration was then performed. In this case, the experimental results were carried out by using different light sources, such as white LEDs, blue LEDs and UV lamps, with the aim to evaluate the process efficiency at different operating conditions. From the collected experimental data it was developed a simplified mathematical model to correlate the power input of the used light source, and the geometrical properties of the reactor and of the emitting sources spectra with the performances of the photocatalytic reaction. This simplified mathematical model may represent a valuable tool to design and optimize photocatalytic processes for wastewater treatment.

The most limitation of the photocatalytic processes in slurry reactors is the low activity of N-doped TiO₂ in powder form, mainly due to the aggregation phenomena between nanoparticles. Therefore, to understand the effect of aggregation, a dispersing agent was added to the N-doped TiO₂ suspension and the influence of particles aggregate size on the photocatalytic activity was evaluated. The control of the dispersion and aggregation of the nanoparticles resulted crucial to exploit the advantages of the N-doped TiO₂ particles in photocatalytic activity: a lower aggregate size increased the amount of MB adsorbed on the catalyst surface and enhanced the photocatalytic activity. In particular, after 120 minutes of visible light irradiation, MB degradation in the presence of dispersing agent was about 80%, markedly higher than the value (about 50%) reached without the dispersing agent.

Moreover, taking into account the problem related to the scattering and screening of the light by the catalyst and the accessibility of the catalytic surface to photons and reactants, a novel way to achieve high dispersion of the photocatalyst was also investigated. It consists in dispersing it in a light-transparent support, permitting the penetration of the radiation in the inner core of the photocatalyst. , In particular, N-doped TiO₂ was dispersed in transparent syndiotactic polystyrene monolithic aerogel (s-PS) which, due to its high specific surface area, allows a better dispersion of the catalysts, strongly limiting the aggregation phenomena that typically occur when the catalyst is suspended in water solutions. These features increased the photocatalytic activity of the N-doped TiO₂ under visible light irradiation in comparison with the powder sample dispersed in solution.

4. One of the most important drawbacks of photocatalytic process is that photocatalysts are used in slurry reactors. With this type of reactor, photocatalysts must be recovered from the purified water after the treatment, and the cost of this separation stage may even invalidate economically this technique. With the aim to overcome this technical limitation the N-doped TiO₂ photocatalyst was immobilized on glass spheres to design a fixed bed continuous photoreactor. With respect to the methods reported in literature for the immobilization of N-doped TiO₂ (mainly carried out through sputtering technique or chemical vapour deposition), the method developed is a simple sol-gel method that uses ammonia aqueous solution as the only doping source. The effect of sol-gel synthesis temperature on the crystallization and crystallite size of N-doped TiO₂ was investigated; the best temperature for the immobilization through dip-coating process was found at -20°C.

The decolorization of MB and eriochrome black-T (EBT) aqueous solutions was tested in a traditional batch reactor to evaluate the photocatalytic activity of the immobilized photocatalyst. The optimization of N-doped

TiO₂ amount on glass spheres was established. It was found that until to four dip-coating steps, the photocatalytic activity increased. Moreover, the N-doped TiO₂ immobilized on glass spheres (NdTcg) can be easily separated from the reaction mixture, and maintained excellent photocatalytic activity and durability after four cycles. Finally, NdTcg showed a high photocatalytic activity in the decolourization of MB and EBT both under UV and visible light irradiation.

The optimized NdTcg structured catalyst was used to design a continuous fixed bed photoreactor.

The geometric characteristics of the reactor were chosen to maximize the exposition of catalysts to the light source. The fluid dynamic in the packed bed reactor was also deeply studied. In particular, the inlet conditions of liquid phase were experimentally obtained in order to have a uniform distribution of pollutant concentration along the catalytic bed in the absence of reaction. In addition, a CFD model (COMSOL Multiphysics 4.2a) was utilized to determine the shape and the dimension of the transparent support for N-doped TiO₂. A Langmuir–Hinshelwood kinetic model was applied for estimating the kinetic parameters of the catalyst, starting from experimental data collected at different contact times. In order to simplify the model of light distribution inside the reactor, instead of the traditional LVRPA, the Helmholtz equation set with the Dirichlet conditions on the boundary was used. The kinetic expression, together with the spatial photons distribution, was incorporated in the mass balance to achieve the theoretical distribution of the pollutant concentration in the reactor. The developed mathematical model allows determining the best irradiation conditions of the photoreactor to minimize the reactor volume required to achieve the complete removal of organic pollutants from liquid phase.