

# Visible Light-Driven Photocatalytic Performance of ZnO Coupled with Up-Conversion Phosphors for the Removal of Methylene Blue

Olga Sacco, Mariantonietta Matarangolo, Vincenzo Vaiano\*, Diana Sannino

University of Salerno, Department of Industrial Engineering, Via Giovanni Paolo II, 132, 84084 Fisciano (SA)

[vvaiano@unisa.it](mailto:vvaiano@unisa.it)

In this work it was investigated the photocatalytic activity of ZnO coupled with inorganic “up-conversion” phosphors for the treatment of aqueous solutions polluted with methylene blue (MB), in the presence of visible light irradiation. Specifically, the successfully prepared “up-conversion” phosphors nanoparticles emit, when excited with visible light, UV light with main emission at 365 nm. The photocatalytic tests were carried out in a cylindrical pyrex photoreactor equipped with a magnetic stirrer to ensure the continuous mixing of the physical mixtures of “up-conversion” phosphors and commercial ZnO nanoparticles in the solution and irradiated by visible light instead of UV light normally required to excite ZnO. Experimental results were analysed by evaluating the MB decolourization through spectrophotometric method and the total organic carbon (TOC) through high temperature combustion method. In particular, it was found that the photocatalytic performances obtained using ZnO nanoparticles coupled with “up-conversion” phosphors are strongly increased compared to the use of ZnO alone. These results confirmed the enhancement of photocatalytic performances induced by UV photons emitted by “up-conversion” phosphors nanoparticles, able to activate ZnO, demonstrating how their use in photocatalytic systems can be an alternative to the traditional UV lamps, thus preserving human health, environmental and, at the same time, allows to save the energy in process management.

## 1. Introduction

The environment and human health are threatened continuously by a lot of pollutants present in waters discharged by chemical and pharmaceutical industries. Because most of these pollutants are bio-recalcitrant, they are difficult to remove by conventional treatments. Photocatalysis, known as an advanced oxidation process (AOPs), has been proved to be a promising approach for the degradation of organic pollutants (Jiang et al., 2012). In particular, heterogeneous photocatalysis appears a valid alternative because it is suitable for the oxidation of a large range of toxic organic compounds into harmless products such as CO<sub>2</sub> and H<sub>2</sub>O by light irradiation (Janotti and Van de Walle, 2009). Among different semiconductors, ZnO photocatalyst demonstrated high degradation efficiency under UV light irradiation (Lee et al., 2016) but it has limited absorption of radiation in the visible range because of its wide band gap energy that is about 3.3 eV (Vaiano et al., 2018). For this reason, for the use of ZnO in photocatalytic systems irradiated by sunlight, its optical properties should be modified. In order to extend the absorption ability of ZnO to the visible-light region, many strategies, such as dye sensitizing (Georgekutty et al., 2008), heterostructure (Wang et al., 2009) as well as ion doping (Vaiano et al., 2017a; Vaiano et al., 2017b) have been developed.

However, the use of ZnO based photocatalysts still suffers from disadvantages due to the non-uniform photon distribution inside the reactor core that can negatively affect the activity of the photocatalysts. Therefore, since the improving of the photocatalytic activity is correlated to an efficient irradiation of the catalytic surface, the possibility to couple photocatalyst particles with light carriers such as emitting phosphorescent particles (generally known as phosphors) has been successfully verified for organic dyes removal (Vaiano et al., 2017c) and emerging pollutants degradation (Sacco et al., 2015).

Generally, phosphors are materials having optically active centers that can absorb an incident radiation, which is re-emitted at shifted specific wavelengths. When phosphors are present together with a suitable photocatalyst, they can catch the radiation coming from external light sources and emit their specific radiation in the core of photoreactor, transferring additional photons to the photocatalyst in its close proximity, so improving the photons transfer also in the darker zones of a photoreactor (Vaiano et al., 2017c).

A reasonable consequence for the intensification of the photocatalytic process seems to be the use of ZnO coupled with “up-conversion” phosphors, able to convert visible light into UV light.

In order to achieve high efficiency in visible light utilization, formation of composite between the high performance “up-conversion” phosphors and photocatalyst particles should be realized. In this case, visible light is not directly utilized for photocatalysis but it is firstly absorbed by the “up-conversion” phosphors and then the UV light emitted by phosphors themselves is able to activate the photocatalytic reactions. In “up-conversion” and quantum cutting process, critical aspects are the low phonon energy and high chemical stability. Recently, BaGd<sub>2</sub>ZnO<sub>5</sub> doped with Dy<sup>3+</sup> and Yb<sup>3+</sup> has shown “up-conversion” properties, converting visible light into UV light (Yang et al., 2014) and therefore it could be a promising material to be coupled with UV light active ZnO.

In this work, the photocatalytic system consisting of BaGd<sub>2</sub>ZnO<sub>5</sub> based “up-conversion” phosphors (able to emit UV radiation when excited by visible light) and commercial ZnO photocatalyst has been investigated in the degradation of methylene blue (MB) organic dye.

## 2. Experimental

### 2.1 Synthesis of “up-conversion” phosphors

“Up-conversion” phosphors were obtained by the dissolution of several chemicals in distilled water: barium nitrate Ba(NO<sub>3</sub>)<sub>2</sub> (*Honeywell*), gadolinium chloride GdCl<sub>3</sub> (*Sigma-Aldrich*), zinc nitrate Zn(NO<sub>3</sub>)<sub>2</sub> (*Sigma-Aldrich*), praseodymium nitrate PrNO<sub>3</sub> (*Sigma-Aldrich*) and metallic ytterbium Yb. In particular, 0.12 g of metallic ytterbium was first dissolved in 100 ml of distilled water at pH equal to 2 (obtained by HNO<sub>3</sub> addition), the solution was kept under stirring on a heating plate until to get the complete dissolution of metallic ytterbium. Once the single-phase mixture was obtained, the following reagents were sequentially added: Ba(NO<sub>3</sub>)<sub>2</sub> (2.19 g), GdCl<sub>3</sub> (6.24 g), Zn(NO<sub>3</sub>)<sub>2</sub> (1.6 g) and PrNO<sub>3</sub> (0.11 g). Once all the reagents were added in the solution, the obtained sample was dried at 130 °C for about 12 hours and then the obtained gel was calcined at 1000 °C for 10 hours with a heating rate of 10 °C min<sup>-1</sup>.

In order to have the catalytic sample, the obtained “up-conversion” phosphors were physically mixed with commercial ZnO (*Sigma-Aldrich*; BET surface area: 5 m<sup>2</sup> g<sup>-1</sup>; phase composition: wurtzite; crystallite size: 24 nm) by means of the use of an agate mortar.

### 2.2 Photocatalytic tests

The photocatalytic experiments were carried out with a pyrex cylindrical reactor (ID = 2.6 cm, L<sub>TOT</sub> = 41 cm and V<sub>TOT</sub> = 200 mL) equipped with an air distributor device (flow rate of 142 N cm<sup>3</sup> min<sup>-1</sup>). The photoreactor was irradiated by four visible lamps (Philips, nominal power: 8 W each) with an emission in the range 400–650 nm (Figure 1). The lamps surrounded the photoreactor external surface and positioned at an equal distance from it (about 30 mm) in order to irradiate the volume of the solution uniformly.

The photon flux at reactor external surface, obtained using a spectro-radiometer (StellarNet Inc), was about 260 W m<sup>-2</sup>. The pH of the solutions was not modified and it was about 6.5 for all the photocatalytic tests. The physical mixture (0.3 g of commercial ZnO mixed with 0.15 g of “up-conversion” phosphors) was dispersed in 100 mL of aqueous solution containing 10 mg L<sup>-1</sup> of methylene blue (MB) concentration. The suspension was left in dark conditions for 120 min until to reach the complete MB adsorption/desorption equilibrium. Subsequently, the photocatalytic test under visible light was performed up to 180 min. Volumes (3 mL) of solution were taken at regular time intervals and then centrifuged to remove the sample powders. In order to measure the MB dye concentration, UV–vis spectrophotometer (Evolution 201) was used to analyse the MB absorbance at the wavelength of 663 nm while the total organic carbon (TOC) was measured by the high temperature combustion method on a catalyst (Pt-Al<sub>2</sub>O<sub>3</sub>) in a tubular flow microreactor operating at 680 °C, with a stream of hydrocarbon free air to oxidize the organic carbon (Sannino et al., 2013).

## 3. Results

### 3.1 Characterization of the “up-conversion” phosphors

The emission spectra of the synthesized phosphors and visible lamps were measured using a StellarNet spectro-radiometer. The phosphors emission spectrum was obtained evaluating it from a thin layer of material deposited on a transparent glass support.

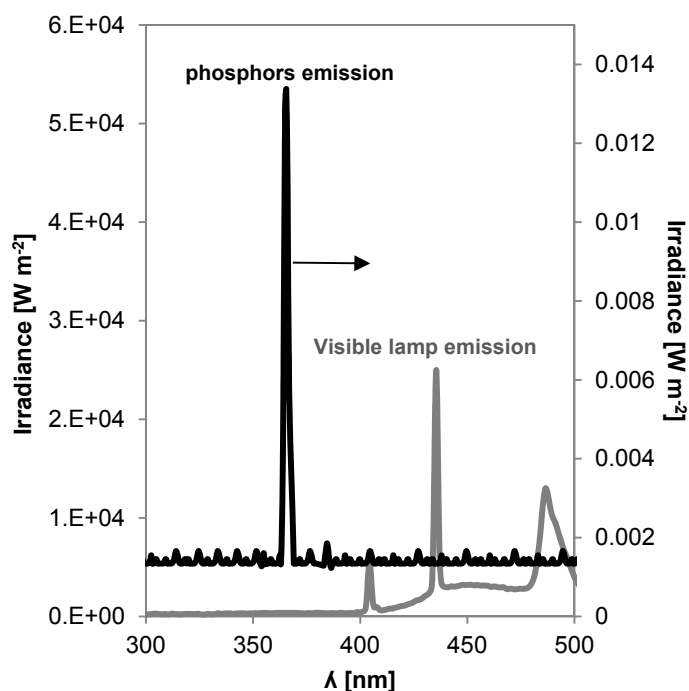


Figure 1: The emission spectra of visible lamps and “up-conversion” phosphors

In this way the phosphors were exposed to the light emitted by the visible lamps (positioned under the glass support) thus obtaining the corresponding emission spectrum from the Figure 1.

The comparison between the emission spectrum of the visible lamps and that one related to the phosphors (Figure 1) shows that the phosphors emission do not overlap with any other peak of the emission bands of the visible lamps. In fact, the main emission peak was found at about 365 nm for “up-conversion” phosphors. This means that phosphors are able to emit in the UV region when they are excited by visible light radiation confirming that the synthesized phosphors have “up-conversion” properties.

### 3.2 Photocatalytic activity results

#### 3.2.1 Influence of “up-conversion” phosphors on photocatalytic activity of commercial ZnO

Figure 2 shows the results in terms of MB discoloration and Total Organic Carbon (TOC) using commercial ZnO and the physical mixture (commercial ZnO+up-conversion phosphors) under visible light. In particular, it is possible to note that no contribution of MB photolysis is present while an important decrease of MB relative concentration was observed using commercial ZnO. Although ZnO is usually active only under UV light, this result can be justified by sensitization phenomena of the photocatalyst surface in the presence of dye molecules such as MB (Rehman et al., 2009). However, compared to the results obtained with only commercial ZnO, the photocatalyst coupled with “up-conversion” phosphors allowed to achieve higher values both in terms of MB discoloration and TOC removal after the same irradiation time. Specifically, the physical mixture was able to reach the almost complete MB discoloration (Figure 2a) and about 90 % of TOC removal (Figure 2b) after 180 min of visible light irradiation. In order to understand the influence of “up-conversion” phosphors presence on photocatalytic activity, the kinetic constant of MB discoloration was evaluated. For this purpose it was considered that the MB discoloration reaction follows the pseudo-first-order kinetic (Salehi et al., 2012). The photodegradation rate ( $r$ ) depends on MB concentration ( $C$ ) in accordance with the following equation Eq(1):

$$r = k \cdot C \quad (1)$$

Where  $C$  is the concentration of MB in  $\text{mg}\cdot\text{L}^{-1}$  and  $k$  is the kinetic constant in  $\text{min}^{-1}$ .

Considering the MB mass balance, reported in Eq(2) and integrating it between initial time ( $t=0$ ) and a generic irradiation time  $t$ , it was obtained the equation Eq(3).

$$\frac{dC}{dt} = -k \cdot C \quad (2)$$

$$-\ln\left(\frac{C}{C_0}\right) = k \cdot t \quad (3)$$

The values of the kinetic constant  $k$  can be calculated by the slope of the straight line obtained by plotting  $-\ln(C/C_0)$  versus irradiation time ( $t$ ) and the obtained results for all the photocatalytic tests previously described are reported in Figure 3. It is evident that the  $k$  value for the system “commercial ZnO+up-conversion phosphors” ( $0.0251 \text{ min}^{-1}$ ) is significantly higher than that obtained for commercial ZnO ( $0.0124 \text{ min}^{-1}$ ). This confirms that the UV radiation emitted by the “up-conversion” phosphors is able to activate the photocatalyst improving its performance in the presence of visible light.

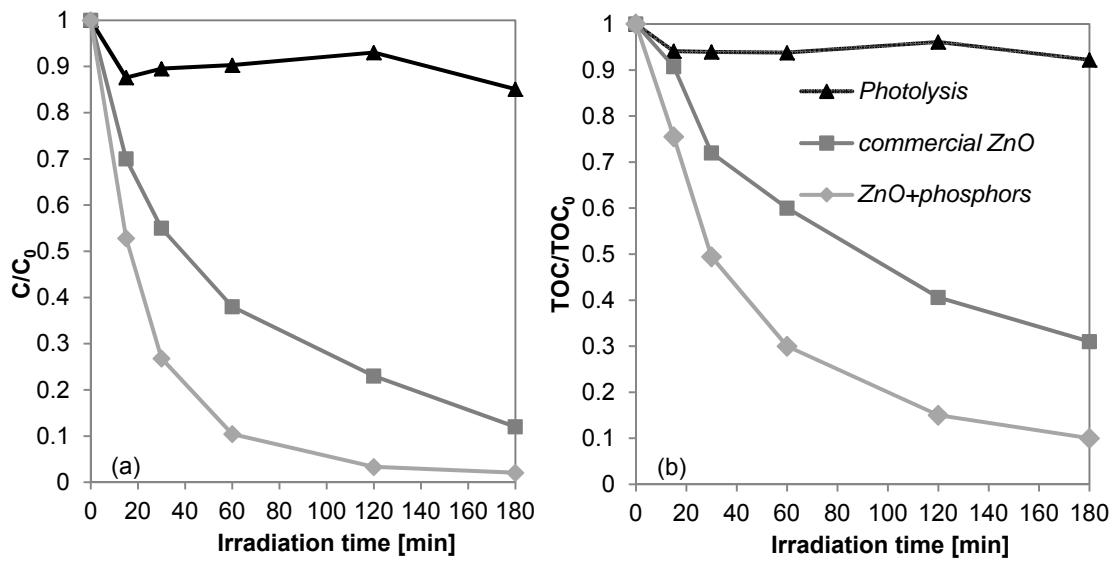


Figure 2: Photocatalytic MB discoloration (a) and Total Organic Carbon (TOC) behaviour (b) under visible light as a function of irradiation time

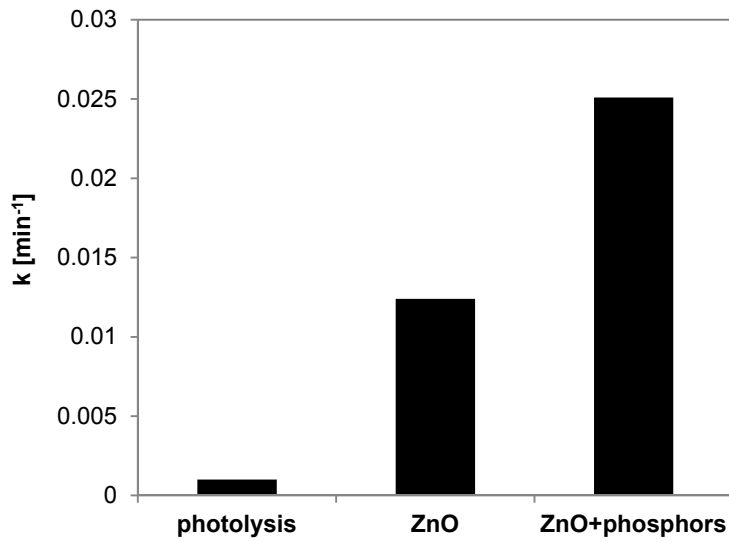


Figure 3: Kinetic constant value for MB degradation

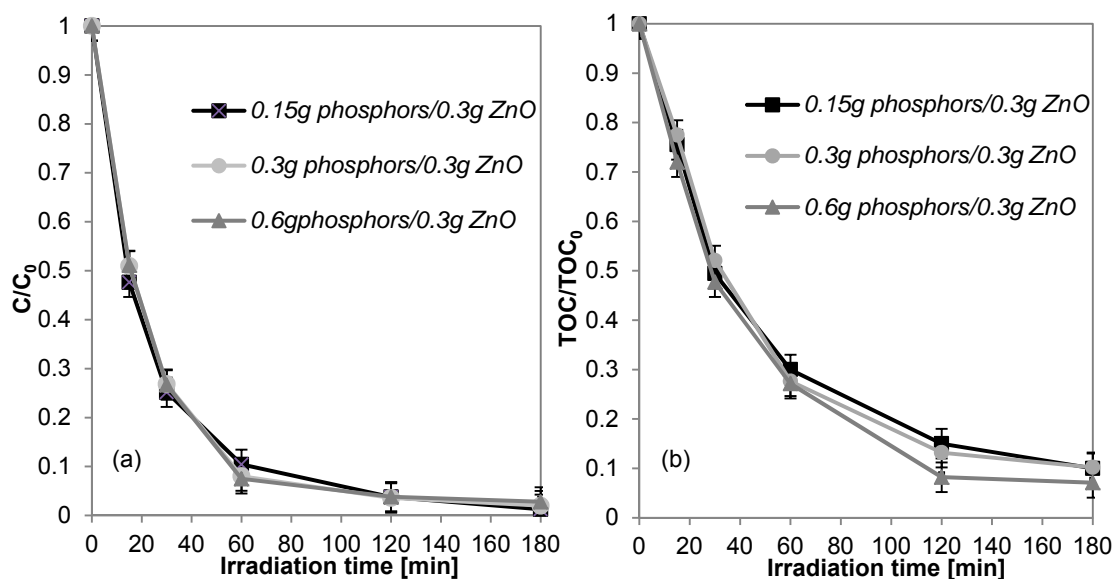


Figure 4: Photocatalytic MB discoloration (a) and TOC behaviour (b) under visible light using 0.3 g of commercial ZnO mixed with different phosphors dosage (in the range 0.15 – 0.6 g).

### 3.2.2 Influence of “up-conversion” phosphors content on ZnO photocatalytic performances

The influence of phosphors dosage was investigated in the range 0.15-0.6 g keeping the amount of commercial ZnO constant and equal to 0.3 g. Figures 4 evidences that the photocatalytic performances was almost the same because both photocatalytic MB discoloration (Figura 3a) and mineralization (Figura 3b) did not change significantly with the increased of phosphors dosage. This result could be explained considering the balance of two effects: i) the increase in the turbidity of the suspension due to the increase of solid content in the solution that induces a decrease of external light penetration (Vaiano et al., 2017c) and ii) the effectiveness of the phosphors that guarantee a good light propagation in the reaction volume, allowing the MB discoloration without changing the kinetic of the process

## 4. Conclusions

The aim of this work was to investigate the photocatalytic activity of ZnO coupled with inorganic “up-conversion” phosphors for the treatment of aqueous solutions polluted with methylene blue (MB) in the presence of visible light irradiation. The synthesized “up-conversion” phosphors are able to emit UV radiation at 365 nm when excited by visible light as confirmed also by characterization results. The photocatalytic treatment of MB aqueous solutions has been studied using the physical mixture between “up-conversion” phosphors and commercial ZnO under visible light irradiation.

The results showed that the presence of “up-conversion” phosphors allows to increase significantly the photocatalytic performances of commercial ZnO reaching the almost complete MB discoloration and a TOC removal of about 90 % after 180 min of visible light irradiation.

The evaluation of apparent kinetic constant ( $k$ ) for the discoloration process evidenced that the  $k$  value for the system “commercial ZnO+phosphors” was equal to  $0.0251 \text{ min}^{-1}$ , two times higher than the value obtained for commercial ZnO ( $0.0124 \text{ min}^{-1}$ ). This confirms that the UV radiation emitted by the “up-conversion” phosphors is able to activate the photocatalyst improving its performance in the presence of visible light.

From the results obtained in this work, it is possible to argue that the “up-conversion” phosphors coupled with a suitable photocatalyst may be an alternative to traditional UV lamps, obtaining both an energy saving and the protection of human and environmental health.

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