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# Er-YAG/Er-YAP/$TiO_2$ Composite As A Novel Photocatalyst Using Solar Lights For Treating Aqueous Dye Solutions

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## ABSTRACT

*A new photocatalyst for the treatment of aqueous dye solutions under visible and solar lights was designed and prepared. It is based on* $TiO_2$ *coating a combination of both upconversion luminescence agents:* $Er:Y_3Al_5O_{12}$ *(Er-YAG) and* $Er:YAlO_3$ *(Er-YAP), well known by their ability to transform visible light into UV light.* $TiO_2$ *and Er-YAG/Er-YAP/*$TiO_2$ *composites were characterized by X-ray diffraction (XRD) and Transmission electron microscopy (TEM). The degradation reaction of methylene blue (MB) aqueous solution was used to measure the photocatalytic activity of the prepared photocatalysts. The obtained results showed that (1.5 %* $Er_{0.01}$*-YAG + 0.5 %* $Er_{0.01}$*–YAP)/*$TiO_2$ *composite is strongly more photoactive than pure* $TiO_2$ *and was able to degrade 98 % of MB solution in one hour under sunlight irradiation at pH = 6.5. This efficiency was supported by TOC measurements and was proven to depend on the ionic nature of the dye and the pH of the solution. Consequently, it is a promising photocatalyst for treating aqueous dye solutions by sunlight.*

**Keywords:** Composite materials, Oxides, Upconversion, Photocatalysis, Wastewater.

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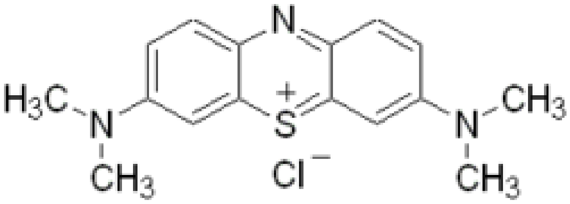
## INTRODUCTION

The removal of dyes and other commercial stains from the industrial wastewaters is a much concern topic of the environmental safety. During last years, Advanced Oxidation Processes (AOPs) such as UV/$H_2O_2$, ozonation, (photo) Fenton, sonolysis, electrochemical oxidation, and photocatalysis have been widely and extensively explored to mitigate a great variety of pollutants present in various environmental media. AOPs have been considered as alternatives to conventional water treatment technologies. Among many AOPs, photocatalysis has received huge attention as one of the most viable environmental cleanup technologies [1, 2]. Among a great number of photocatalysts, titanium dioxide ($TiO_2$) has been used extensively [3, 4]. Its use as photocatalyst is due to some properties such as versatility, physical and chemical stability, abundance, non-toxic as well as a relative low price. However, it is generally accepted that $TiO_2$ is a poor absorber of photons in the visible spectrum and, as a result, its use as an effective photocatalyst demand a UV light source. From a practical point of view, photocatalysts need to have higher activities to be economically competitive as a cleanup technology. One of the most viable and practical approaches in developing better photocatalysts is to modify $TiO_2$ (e.g., impurity doping, sensitization, surface modification/complexation, integration with other nanostructured materials, etc.).For a long time, an immense effort has been provided to extend the absorption wavelength region of $TiO_2$, i.e., making it absorbing the visible lights significantly. Thus, a lot of solutions have been adopted, such as the doping of transition metal ions or/and the non metals and the combination of semiconductors of narrow band gaps [5-8]. These methods allow extending the absorption range of $TiO_2$ appreciably, but they often endure a thermal instability and an increase of recombination centers [9]. Some researchers [10] found out that $TiO_2$ doped with nitrogen (N) absorbs efficiently the visible light without a high increase in its photocatalytic activity. The main reason is that the N-$TiO_2$ photocatalyst undergoes again a raise of the electron-hole recombination.Besides, the visible light is not so energetic, compared to UV light, to activate the particles of $TiO_2$ and degrade many organic pollutants efficiently. Therefore, it could be very useful to think about a method of transformation of visible light into UV light that would be more efficient in the activation of $TiO_2$ particles. Thus, it would be very important to find materials that could transform the visible lights into UV lights to satisfy the real need of the $TiO_2$ photocatalyst.

Fortunately, the materials of the "upconversion" containing rare earth (RE) metals [11] are just what we want to insert into powders of $TiO_2$. Most of research studying the upconversion of light has been achieved by physicists looking for materials that produce Laser of short lengths of the wave. The most studied crystals were $LiYF_4$, $KYF_4$, $Y_3Al_5O_{12}$ (YAG) and $YAlO_3$ (YAP) doped with $Er^{3+}$ ion [12, 13]. Among all the trivalent RE ions, $Er^{3+}$ ion has the richest spectra in the IR-UV range that makes it more adequate for upconversion studies, especially when it is organized in the crystalline matrices of oxides or fluorides [14-17]. The upconversion process depends on the excitation energy, the concentration of doping and the properties of the host crystal.

Lately, these materials have found some interest in photocatalysis, because they may be used to exploit efficiently the inexhaustible solar light in the photodegradation of organic pollutants. Indeed, few studies have especially concerned with upconversion luminescence agents of Er-YAG and Er-YAP type introduced into powders of $TiO_2$ or ZnO [18, 19]. Photoluminescence measurements have shown that Er-YAG and Er-YAP give out UV lights under excitation in the visible wavelength range [20-22]. Emission spectra are discontinuous and contain distinct peaks for the two types of upconversion agents. Therefore, these spectra do not totally cover the UV domain. As a result, the intensity of UV lights emitted from each upconversion luminescence agent is lower than that of the UV halogen lamp. But if we think to add the emission spectrum of both Er-YAG and Er-YAP, the resultant spectrum of the upconversion process should contain many more peaks, leading to an intensification of UV lights exciting the $TiO_2$ semi-conductor. Hence, the idea of this study is to exploit simultaneously the most of the upconversion emission spectrum of both Er-YAG and Er-YAP. The procedure consists in coating them together by the $TiO_2$ powders. This system could improve the kinetics and the yield of the organic pollutants photodegradation. In addition, this system is environmentally feasible since it is based on non-toxic sol-gel synthesized components. Moreover, this system is mainly based on relatively low cost $TiO_2$ powders, and the expensive upconversion oxides are incorporated only in weak proportions (less than 2 %). This system could also be economically reasonable with regards to the improvement that would be realized in the efficiency of the wastewater remediation processes. In this study, methylene blue (MB: methyl thioninium chloride) was chosen as a probe compound and pollutant for the photocatalytic tests. It is a heterocyclic aromatic compound of positive charge and is usually used as representative for dyes commonly discharged in wastewater.

The photocatalytic activity of prepared $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ composite was studied under visible and solar light irradiation. The molecular structure of MB dye is given in scheme 1.



**Scheme 1**: Molecular structure of methylene blue dye.

## MATERIALS AND METHODS

**Synthesis of $Er_{0.01}Y_{2.99}Al_5O_{12}$**: The nanocrystalline Er-YAG was prepared by a salt based sol-gel process [23]. All chemicals were reactive grade and supplied by Aldrich Inc. Yttrium chloride ($YCl_3.6H_2O$) was dissolved in 100 ml of distilled water, previously mixed with 2 ml of acetic acid ($CH_3CO_2H$), and the mixture was stirred for 2 h at 50 °C. In a second beaker, proper amounts of aluminum chloride ($AlCl_3.6H_2O$) and erbium nitrate (Er $(NO_3)_3.5H_2O$) were dissolved in 50 ml of distilled water under stirring for 1 h at room temperature. Then both solutions were mixed and complexed with 2 ml of ethylene glycol and stirred again. The resulting solution was stirred at 80 °C for 24 h to evaporate slowly all the solvents until a pale yellow, viscous gel was formed. The gel was dried at 120 °C for 24 h and then ground in an agate mortar to get a fine powder. This powder was annealed at 900 °C for 2 h (ramp 10 $°C.min^{-1}$). After cooling in air atmosphere, the nanocrystalline $Er_{0.01}Y_{2.99}Al_5O_{12}$ ($Er_{0.01}$-YAG) was obtained.

**Synthesis of $Er_{0.01}Y_{0.99}AlO_3$**: The nanocrystalline Er-YAP was prepared by the modified nitrate-citric acid method described elsewhere [24]. Briefly, proper amounts of yttrium chloride ($YCl_3.6H_2O$) and erbium nitrate (Er $(NO_3)_3.5H_2O$) were dissolved in 100 ml of distilled water. In a separate flask, aluminum chloride ($AlCl_3.6H_2O$) was dissolved in 50 ml of distilled water and stirred for 1 h at room temperature. Both solutions were mixed and solid citric acid was added (mol. ratio of citric acid: metal ion = 3:1). The final solution was further evaporated at 85 °C until a viscous gel was obtained. The obtained gel was dried at 130 °C for 24 h and ground to get a powder. A heat-treatment of 1200 °C for 2 h (ramp 10 $°C.min^{-1}$) was applied to the sample. After cooling in air atmosphere, the nanocrystalline $Er_{0.01}Y_{0.99}AlO_3$ ($Er_{0.01}$-YAP) was obtained.

**Preparation of $TiO_2$ photocatalyst coating upconversion luminescence agents:** The $TiO_2$ photocatalyst coating $Er_{0.01}$-YAG and/or $Er_{0.01}$-YAP upconversion luminescence agents was prepared through the soil-gel process described elsewhere [18]. The two precursor solutions, here denoted precursor A and B, were prepared as follows. Precursor A: Titanium (IV) isopropoxide (40 ml), ethanol (50 ml) and acetic acid (3.0 ml) were mixed and stirred for 10 min at room temperature. Precursor B: distilled water (7.0 ml) and ethanol (50 ml) were mixed and the crystallized powders of $Er_{0.01}$-YAG and/or $Er_{0.01}$-YAP (0.5 g) were added under vigorous stirring to make them dispersed adequately in the solution. Afterwards, the precursor B was added to the precursor A drop wise with vigorous stirring. The resultant mixture was further stirred for 20 min. The sol solution was placed in a culture dish for a day to finish the sol-gel transition and filtered. Filter residue was rinsed with water repeatedly, and then dried at 100 °C for 24 h to get a dried gel. The dried gel was ground and a light-yellow powder was obtained. The powder was then heat treated at 400 °C and 700 °C for 2.0 h (ramp 10 $°C.min^{-1}$) to get a stable $TiO_2$ photocatalyst coating crystallized $Er_{0.01}$-YAG and/or $Er_{0.01}$-YAP. The ratio of ($Er_{0.01}$-YAG + $Er_{0.01}$-YAP) to $TiO_2$ in the photocatalyst is about 2.0 %. The pure $TiO_2$ powder was also prepared using the same procedure without the addition of the upconversion luminescence agents during sol-gel process. The surface areas were determined as 68 and 59 $m^2.g^{-1}$, respectively, for pure $TiO_2$ and $TiO_2$ coating crystallized upconversion luminescence agents annealed at 700°C according to BET method.

**Catalyst characterization:** The X-ray diffraction (XRD) patterns obtained on a D5000X-ray diffractometer (German Bruker) using Cu Kα radiation at a scan rate of 0.02° $s^{-1}$ were used to decide the crystallite size and identity. The average crystallite size was determined according to the Scherrer equation. The transmission electron micrographs (TEM) were recorded with a JEM-3010 (JEOL Company, Japan) electron microscope and were used for observing the shape of prepared particles and estimating the particle size.

**Photoreactor system and experimental procedures:** A Pyrex cylindrical photoreactor was used in the experiments, where a 250 W halogen lamp with emission between 400-800 nm and main emission peak at 650 nm was positioned at the center of the cylindrical vessel and surrounded by a circulating water jacket. The UV emission of the lamp is filtered to approximate to sunlight. The intensity of the emitted light of the lamp was obtained by using radiometric calibration standard (Ocean Optics) and is about 140 $W.m^{-2}$. The reactor, which was wrapped with aluminum foil to prevent the loss of light was immersed into a water bath for maintaining a reaction temperature at 25 °C. A magnetic stirrer was used to induce continuous mixing of the reaction solution throughout the experimental period. The photocatalytic degradation of methylene blue (MB) was employed to investigate the photodegradation effect of the $TiO_2$ catalyst doped with upconversion luminescence agents. The experiments of the photocatalytic degradation of MB in aqueous solution were carried out under the conditions such as 30 $mg.l^{-1}$ MB concentration, 1.0 $g.l^{-1}$ prepared photocatalyst and 125 ml total volume. All photocatalytic experiments were carried out at natural solution pH equal to 6.5. Absorbance measurements were recorded using a UV-Vis spectrophotometer (PerkinElmer Lambda 25 UV-Vis). The wavelength of 665 nm, the maximum absorption wavelength registered experimentally, was used for evaluation of the MB photodegradation. The photocatalytic degradation rate (DR) was calculated by the following formula:

$$DR\ (\%) = (1 - C_t / C_0) \times 100 \qquad (1)$$

Where $C_0$ is the initial concentration and $C_t$ is the concentration of the MB dye solution at the irradiation time (t).

Total organic carbon (TOC) was determined by using a TOC-Ve Analyzer (Shimadzu) to follow the mineralization of MB.

Outdoor Photocatalytic tests were also carried out under solar light irradiation using the same conditions as under lamp excitation, such as V = 125 ml, 1 $g.l^{-1}$ photocatalyst, 30 $mg.l^{-1}$ MB concentration. The cylindrical photoreactor was directly exposed to sunlight.

Blank tests are performed under the following conditions: (a) MB solution + irradiation, (b) MB solution + photocatalyst (pure $TiO_2$ or Er-YAG/Er-YAP/$TiO_2$) in the dark. The results show that the efficiency of the degradation based on the self-photosensitized process is very lower than that using photocatalysis with $TiO_2$ coating crystallized upconversion luminescence agents. Moreover, it reveals that prepared photocatalysts all behave a little adsorption to MB molecules in aqueous solution.

## RESULTS AND DISCUSSION

### XRD of $Er_{0.01}$-YAG and $Er_{0.01}$-YAP

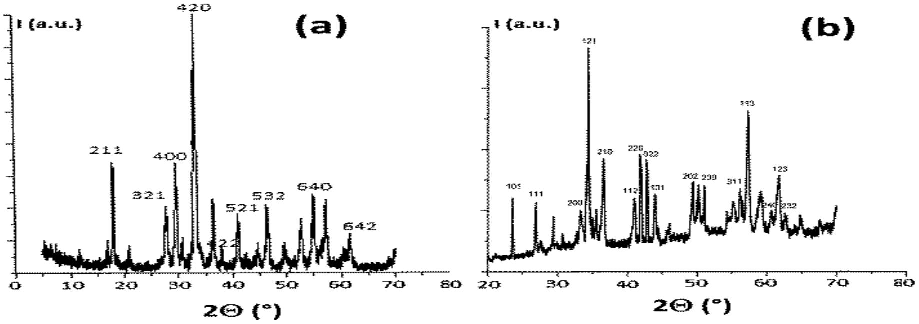


**Fig.1.** XRD of (a) $Er_{0.01}Y_{2.99}Al_5O_{12}$ and (b) $Er_{0.01}Y_{0.99}AlO_3$ powders.

Fig. 1 shows the XRD patterns of $Er_{0.01}$-YAG (a) and $Er_{0.01}$-YAP (b) powders. It shows that the $Er_{0.01}$-YAG powder heat-treated at 900 °C and the $Er_{0.01}$-YAP powder heated at 1200 °C present crystallized forms. The obtained diffraction peaks of $Er_{0.01}$-YAG are in good agreement with the reference data of $Y_3Al_5O_{12}$ (JCPDS file card 33–40) and the XRD pattern of $Er_{0.01}$-YAP exhibit dominant diffraction peaks due to the orthorhombic phase of $YAlO_3$ (JCPDS File no. 70-1677). The main peaks of both structures are centered at $2\theta = 33.5°$ for $Er_{0.01}$-YAG and $2\theta = 34.5°$ for $Er_{0.01}$-YAP. Both patterns present a well-defined one fold crystal structure and no secondary impurity phase such as $Y_4Al_{12}O_9$ is observed. These findings are similar to those obtained by other researchers [25-26].

**XRD and TEM of prepared $TiO_2$ photocatalyst coating upconversion luminescence agents:**Fig. 2 (a, b) shows the XRD patterns of the prepared powders. It can be seen that for pure $TiO_2$ powder annealed at 400 °C (a), the XRD pattern reveals only anatase phase which is characterized by the main peaks observed at 2θ = 25, 38, 48, 54, 56, 62.5 and 68°. The pure anatase phase is still stable even at 700 °C when $TiO_2$ powder is coating (1.5 % $Er_{0.01}$-YAG + 0.5 %$Er_{0.01}$-YAP) (b) which shows that the upconversion luminescence agents have to increase the thermal stability of this phase (XRD of pure $TiO_2$ heated at 700 °C, not shown here, reveals both anatase and rutile phases). Moreover, the XRD pattern of $TiO_2$ coating both $Er_{0.01}$-YAG and $Er_{0.01}$-YAP shows new lines that have been assigned respectively to upconversion luminescence agents YAG and YAP. These lines imply that the particles of upconversion agents and those of $TiO_2$ have integrated indeed.

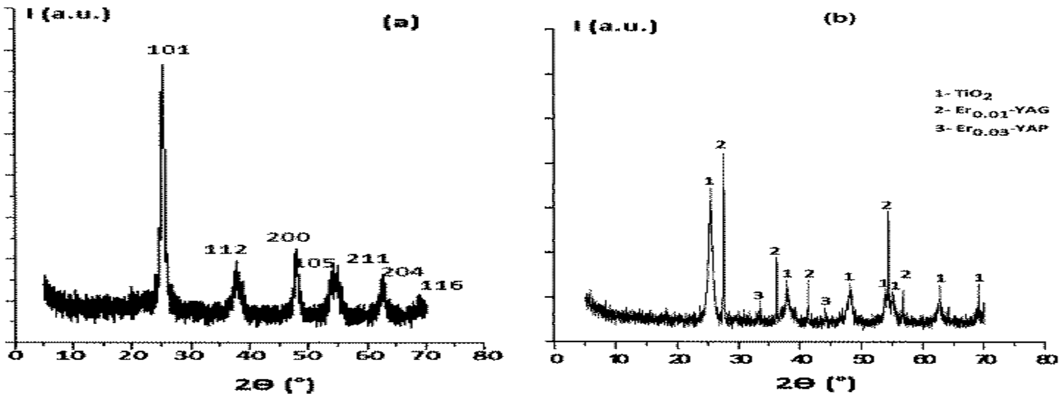


**Fig.2.** XRD of (a) pure $TiO_2$ under 400 °C heat-treatment and
(b) (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$-YAP)/$TiO_2$ composite under 700 °C heat-treatment.

$$\text{The Scherrer equation: } d = \frac{K\lambda}{\beta\cos\theta} \qquad (2)$$

Was used to calculate the average size of crystallites in each sample, where k = 0.89 is the shape factor of particles, β is the peak width at half maximum (radians).

The sizes of crystallized $Er_{0.01}$-YAG and $Er_{0.01}$-YAP powders are about 20-30 nm. The average size of the prepared $TiO_2$ is about 50-60 nm when is coating $Er_{0.01}$-YAG or/and $Er_{0.01}$-YAP. Thus, taking into account these sizes, we consider that the layer of $TiO_2$ particles coating the upconversion agents is suitable for penetrating the visible light and exciting the inner particles of $Er_{0.01}$-YAG and $Er_{0.01}$-YAP, which would result the emission of UV lights.

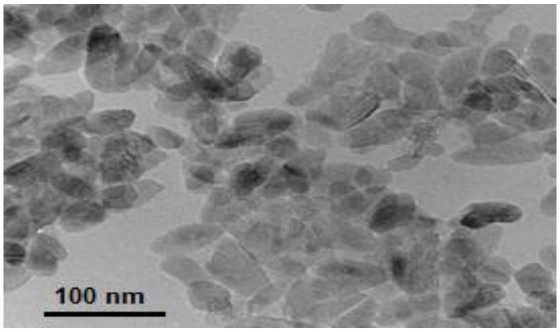


**Fig.3.** TEM of prepared $TiO_2$ particles coating $Er_{0.01}$-YAG and $Er_{0.01}$-YAP after 700 °C heat treatment.

Fig.3 shows the TEM image of the prepared $TiO_2$ powder coating $Er_{0.01}$-YAG and $Er_{0.01}$-YAP. It is found that the prepared $TiO_2$ powder is composed of grayer particles with approximately uniform size and shape. The average size of these particles estimated from the TEM image is about 50-70 nm. The black parts in central regions of many grayer particles can be found clearly, which can be confirmed as the crystallized upconversion luminescence agents particles covered with $TiO_2$ folium.

## Photocatalytic activity

**$Er_{0.01}$-YAG/$TiO_2$ and $Er_{0.01}$-YAP/$TiO_2$ photocatalysts :** In this part, we show the degradation efficiency of the MB solution (of 30 $mg.l^{-1}$ initial concentration) under the visible light irradiation in the presence of $TiO_2$ coating one upconversion luminescence agent ($Er_{0.01}$-YAG or $Er_{0.01}$-YAP) in comparison with the prepared pure $TiO_2$. It can be seen in Fig.4 that the photocatalytic activity of the doped $TiO_2$ is better than that of the undoped one. The degradation ratio in the presence of $TiO_2$ powder doped with $Er_{0.01}$-YAG or $Er_{0.01}$-YAP increases with the irradiation time and attains about 96-98% after 5 h, while the degradation ratio in the presence of undoped $TiO_2$ powder is only 80 % over the same time. These results prove that $Er_{0.01}$–YAG and $Er_{0.01}$-YAP upconversion luminescence agents have improved the photocatalytic activity of $TiO_2$ photocatalyst.

Since blank tests have shown the weak contribution of self - photosensitized and photolysis processes in the degradation reaction of a MB solution under visible light irradiation, thus, it can be deduced that UV lights resulted from the upconversion process are the major responsible for the improvement of the degradation ratio. These deductions accord well with those found in similar studies of photocatalytic activity via the upconversion luminescence process [18, 27]. However, we think that this improvement could be better if we combine the effect of both upconversion agents $Er_{0.01}$-YAG and $Er_{0.01}$-YAP in coating them together with $TiO_2$ powders.

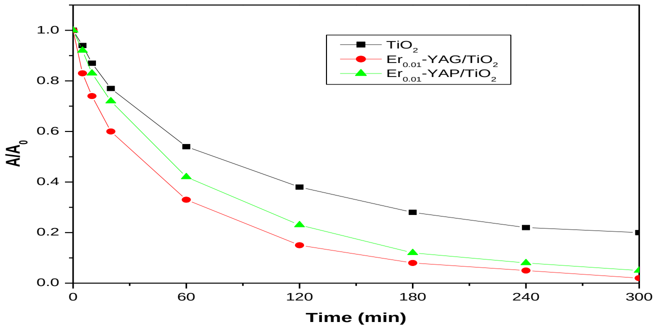


**Fig.4.** Effect of irradiation time on the photocatalytic degradation of MB solution in the presence of pure $TiO_2$, $Er_{0.01}$-YAG/$TiO_2$ and $Er_{0.01}$-YAP/$TiO_2$ respectively. ($C_0$ = 30 $mg.l^{-1}$, $m_{cat}$ = 1.0 $g.l^{-1}$, pH = 6.5).

**The $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ photocatalyst:** The effects of both upconversion luminescence agents $Er_{0.01}$-YAG and $Er_{0.01}$-YAP are combined to get the highest photocatalytic activity of the $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/ $TiO_2$ composite. The total mass ratio of both agents in the composite is kept equal to 2 %. The following combinations are performed:

(1% $Er_{0.01}$-YAG + 1%$Er_{0.01}$-YAP)/$TiO_2$.
(1.5% $Er_{0.01}$-YAG + 0.5 %$Er_{0.01}$-YAP)/$TiO_2$.
(0.5 % $Er_{0.01}$-YAG + 1.5 % $Er_{0.01}$-YAP)/$TiO_2$.

The photocatalytic tests focus on the degradation of BM solutions under the same conditions as before: [BM] = 30 mg.$l^{-1}$, V = 0.125 l, m (catalyst) = 0.125 g, pH = 6.5 (natural). The photocatalysts are annealed at 700 °C for 2 h.

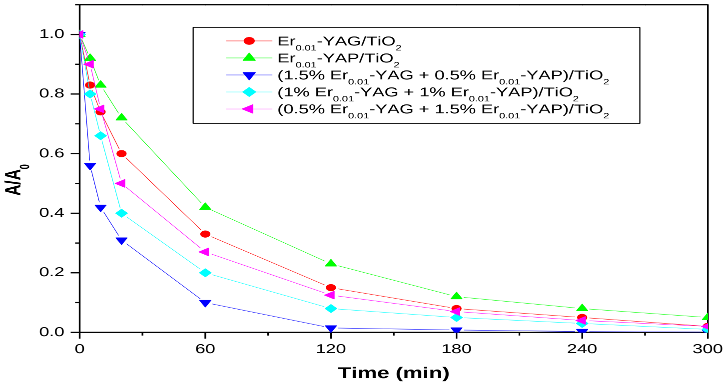


**Fig.5.** Effect of the combination formula between $Er_{0.01}$-YAG and $Er_{0.01}$-YAP on the photocatalytic activity of $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ composite for the degradation of MB solution. ($C_0$ = 30 mg.$l^{-1}$, $m_{cat}$ = 1.0 g.$l^{-1}$, pH = 6.5).

The obtained results are depicted in Fig. 5. In all cases, the degradation ratio of the MB solution in the presence of $TiO_2$ coating a combination of $Er_{0.01}$-YAG and $Er_{0.01}$-YAP is much more than that obtained in the presence of $TiO_2$ powder coating only one upconversion luminescence agent. Moreover, the best combination of the upconversion luminescence agents corresponds to 1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$-YAP. The photocatalyst containing 1.5% $Er_{0.01}$-YAG and 0.5% $Er_{0.01}$-YAP has achieved the highest degradation ratio in the short time of irradiation. Indeed, with this composite, almost complete photodegradation of MB solution has been performed after two hours of visible irradiation. This was firstly supported by the deletion of the absorption spectra of MB solution in the UV-Vis range (Fig. 6).

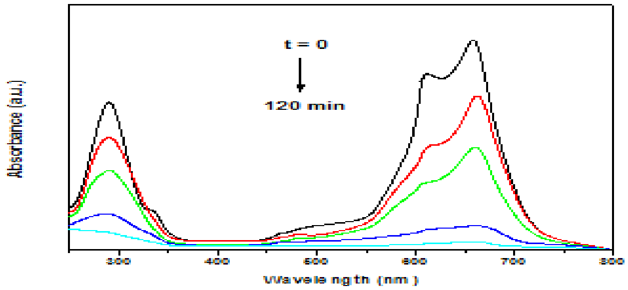


**Fig.6.** Spectra change that occurs during the degradation of MB aqueous solution irradiated by visible light in the presence of (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$-YAP)/$TiO_2$ composite ($C_0$ = 30 mg.$l^{-1}$, $m_{cat}$ = 1.0 g.$l^{-1}$, pH = 6.5).

The blue color of MB solution was almost totally deleted after two hours of irradiation. It may mean that the concentration of MB in solution decreased and it was not only solution decolorization but also photodegradation. The total mineralization of methylene blue using (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$-YAP)/$TiO_2$ composite was also proved by measuring the initial TOC before irradiation (15.60 ppm) and after two hours of visible irradiation and it was found to be equal to 2.1 ppm. This performance has not been achieved by any of the photocatalysts tested throughout this study such as pure $TiO_2$, $Er_{0.01}$-YAG/$TiO_2$ and $Er_{0.01}$-YAP/$TiO_2$. Indeed, the degradation ratio of MB solution after two hours of visible irradiation is only 62, 77 and 85 % in the presence of pure $TiO_2$, $Er_{0.01}$-YAP/$TiO_2$ and $Er_{0.01}$-YAG/$TiO_2$ respectively. In addition, the modeling of the obtained results by the equation:

$$\mathrm{Ln}\,(C_0/C) = \mathrm{Ln}\,(A_0/A) = k.t \qquad (3)$$

shows that the reaction of photocatalytic degradation of MB in the presence of both doped and undoped $TiO_2$ powders accord with the first order kinetics. The related rate constants (table 1) show that the (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$-YAP)/$TiO_2$ composite increases the kinetic reaction more than three times compared to $Er_{0.01}$-YAP/$TiO_2$ or $Er_{0.01}$-YAG/$TiO_2$ and more than seven times compared to the prepared pure $TiO_2$. All these findings allow considering that the combination of both $Er_{0.01}$-YAG and $Er_{0.01}$-YAP leads to an intensification of UV lights from the upconversion process compared to those obtained when only one upconversion luminescence agent is used. The photodegradation efficiency is, therefore, highly improved.

**Table 1:** Rate constants of the degradation reaction of the MB solution in the presence of various photocatalysts under visible irradiation ($C_0$ = 30 mg.$l^{-1}$, $m_{cat}$ = 1.0 g.$l^{-1}$, pH = 6.5).

| Photocatalyst | k $10^3$ ($min^{-1}$) | $R^2$ |
|---|---|---|
| $TiO_2$ | 3 | 0.96 |
| $Er_{0.01}$-YAP/$TiO_2$ | 5 | 0.99 |
| $Er_{0.01}$-YAG/$TiO_2$ | 7 | 0.97 |
| (0.5% $Er_{0.01}$-YAG +1.5% $Er_{0.01}$-YAP)/$TiO_2$ | 8 | 0.95 |
| (1% $Er_{0.01}$-YAG + 1% $Er_{0.01}$-YAP)/$TiO_2$ | 9 | 0.93 |
| (1.5%$Er_{0.01}$-YAG + 0.5% $Er_{0.01}$-YAP)/$TiO_2$ | 21 | 0.99 |

In order to more investigate the kinetics of the photocatalytic degradation of MB in the presence of (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$-YAP)/$TiO_2$ composite irradiated by visible light, the rate constant (k) of the degradation reaction has been studied in relation to the initial concentration of MB solution ($C_0$). Table 2 reports the values of k resulting from the plot of Ln ($C_0$/C) versus time for the photocatalytic degradation of MB, which decreases as the initial reactant concentration increases. This can be ascribed to the decrease in the number of active sites on the catalyst surface due to the covering of the surface with MB molecules, which is directly proportional to the initial concentration of MB.

**Table 2**: kinetic rate constant of photocatalytic degradation of MB in the presence of (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$–YAP)/$TiO_2$ composite under visible light with different initial concentration (pH = 6.5).

| $C_0 = [MB]_0$ (mg.$l^{-1}$) | k ($min^{-1}$) |
|---|---|
| 5 | 0.037 |
| 10 | 0.030 |
| 20 | 0.026 |
| 30 | 0.021 |

The experimental data has been rationalized in terms of the modified form of Langmuir-Hinshelwood (L-H) kinetic model to describe the solid-liquid reaction successfully. The effect of the initial concentration of MB on the initial degradation rate (r) is given by the following equations:

$$r = K_{MB}\,.k_c\,[C].\,(1 + K_{MB}.\,[C_0])^{-1} = k\,[C] \qquad (4)$$

$$1/k = 1/K_{MB}.k_c + [C_0]/k_c \qquad (5)$$

Where, $K_{MB}$ and $k_c$ are the L-H adsorption equilibrium constant and the rate constant of surface reaction, respectively. At concentrations up to 30 mg.l$^{-1}$, the applicability of the L-H equation for the photocatalytic degradation of MB has been confirmed by the linear plot obtained by plotting the reciprocal of the rate constant (1/k) against the initial concentration ($[C]_0$) (not shown here). The values of $K_{MB}$ and $k_c$ are found to be 0.336 (mg$^{-1}$.l) and 0.149 mg.l$^{-1}$.min$^{-1}$, respectively.

**Determination of the Quantum Yield:** The quantum yield (Φ) is a useful parameter in indicating the efficiency of a photodegradation reaction, and is defined as the number of molecules being decomposed per photon absorbed. It can be calculated from the observed first-order degradation rate constant as follows: $\Phi = k / 2.303\,\varepsilon_\lambda\, I_{0,\lambda}\, l$ (6)

Where k (s$^{-1}$) is the pseudo-first-order rate constant, $I_{0,\lambda}$ (Einstein l$^{-1}$s$^{-1}$) is the incident light intensity at wavelength λ which has been calculated on the bases of the ferrioxalate actinometry measurements, $\varepsilon_\lambda$ (cm$^{-1}$M$^{-1}$) is the molar absorptivity at wavelength λ, and l is the cell path length (cm).

The quantum yield values for the photodegradation of MB by direct photolysis and in the presence of (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$-YAP)/$TiO_2$ composite irradiated by a visible lamp at $\lambda_{max}$ = 650 nm are 0.007 and 0.11, respectively. These results indicate that the photocatalysis quantum yield in the presence of (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$-YAP)/$TiO_2$ is higher than that of the direct photolysis, suggesting that the photodecay of MB is dominated by the photocatalysis.

It has to be mentioned that, since r = f (C) follows a Langmuir-Hinshelwood mechanism, with a linear increase of r at low concentrations, this catalytic quantum yield could be consequently higher for higher concentrations. It is high enough to ensure a reasonable degradation rate for diluted colored water solutions.

**Photocatalytic activity of $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ under sunlight:** After being selected as the most effective photocatalyst resulting from the combination of both $Er_{0.01}$-YAG and $Er_{0.01}$-YAP, the (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$-YAP)/$TiO_2$ composite is evaluated under sunlight excitation in comparison with visible light excitation from the halogen lamp. The outdoor experiments (Gabes city, Tunisia) are carried out from a.m. 09:00 to p.m. 14:00 of 10-15 June 2012, where the corresponding temperature varied from 30 to 35 °C, respectively. The obtained results (Fig.7) show that the (1.5% $Er_{0.01}$-YAG + 0.5% $Er_{0.01}$-YAP)/$TiO_2$ composite is very active under sunlight. Indeed, the irradiation time needed to attain a degradation ratio of about 100 % is reduced to half (60 min) compared to that shown with visible irradiation from the 250 W halogen lamp (120 min) in the presence of the same photocatalyst. Furthermore, the rate constant (0.071 min$^{-1}$) is more than three times higher than that found if visible irradiation is used (0.021 min$^{-1}$). Considering the treatment cycle cost, shortening time for the MB treatment is a necessary goal that is achieved with the use of solar light in the presence of the (1.5% $Er_{0.01}$-YAG + 0.5% $Er_{0.01}$-YAP)/$TiO_2$ composite. This performance, which is comparable to those reached when using UV lights directly from the artificial lamp for treating dyes by $TiO_2$ photocatalyst [26], may be explained by the contribution of about 4-5% of sun lights which are in the form of UV radiations, more energetic than visible lights for the excitation of electrons from the valence to the conduction band of $TiO_2$. Besides, the solar lights contain continuous pump wavelengths that make the upconversion process take place more easily in $Er_{0.01}$-YAG and $Er_{0.01}$ –YAP crystals compared to the visible lights from the 250 W power lamp. It is also worthy to notice the improvement of the degradation ratio in the presence of pure $TiO_2$ under sunlight containing UV radiations, but this improvement is still lower than that attained with the new $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ photocatalyst.

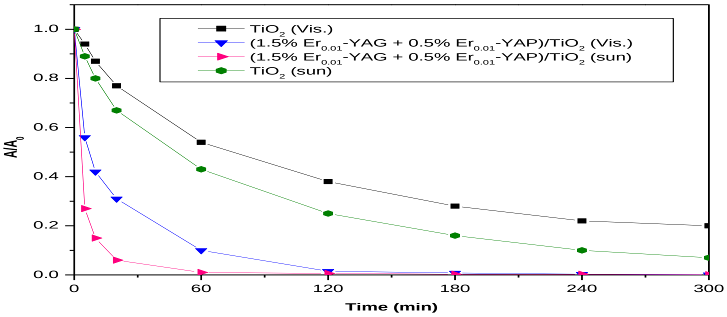


**Fig.7.** Comparison of the photocatalytic activity of (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$–YAP)/$TiO_2$ composite and pure $TiO_2$ under solar and visible light irradiation for the degradation of MB solution. ($C_0$ = 30 mg.l$^{-1}$, $m_{cat}$ = 1.0 g.l$^{-1}$, pH = 6.5).

**Photocatalytic activity of $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ for the degradation of some other dyes under sunlight :** The photocatalytic activity of (1.5% $Er_{0.01}$-YAG +0.5% $Er_{0.01}$-YAP)/$TiO_2$ composite under solar light irradiation is also evaluated with other organic dyes having different molecular structures and chemical compositions such as methyl violet (MV), Congo red (CR) and methyl orange (MO). The manipulative experiments are performed in the same conditions as before (with MB) such as 1 g.l$^{-1}$ photocatalyst, 30 mg.l$^{-1}$ dye concentration and natural pH value. The degradation ratio of each dye is measured after 60 min of solar light irradiation using UV-vis spectroscopy at maximum absorption (MV: 590 nm; CR: 541 nm; MO: 465 nm). Fig.8 shows a high degradation ratio for cationic dyes (MB and MV) and lower ratios for anionic ones (CR and MO). This is obviously explained by the electrostatic attraction or repulsion that has occurred between different organic molecules (cationic or anionic) and $TiO_2$ surface negatively charged at the natural pH value (pH = 6.5). Thus, the degradation ratio of anionic dyes should be higher in the more acidic medium. This was highly supported by experimental results obtained when varying pH conditions in the photocatalytic tests (Table 3). The pH effect can be explained by the zero point of charge of $TiO_2$ surface, usually around 6. The surface of the photocatalyst is positively charged in acidic solutions and negatively charged in neutral and alkaline solutions. As a result, it is not surprising to observe an increase in the adsorption of cationic dye molecules on the surface of photocatalyst in alkaline solutions, leading to an increase in the degradation efficiency of dye. But at low pH, the adsorption of cationic dyes on the positively charged surface of the photocatalyst decreases due to repulsive forces, leading to a decrease in the degradation efficiency. For the anionic dyes, they behave reversely with pH.

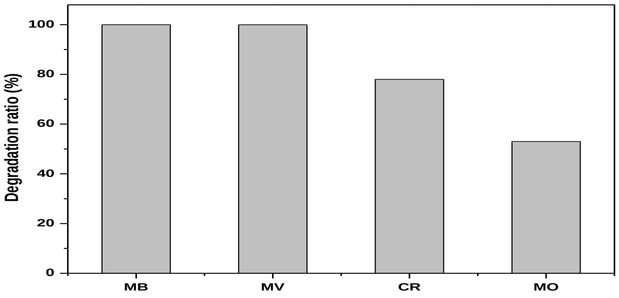


**Fig.8.** Degradation ratios of various organic dyes in the presence of (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$–YAP)/$TiO_2$ composite under solar light irradiation ($C_0$ = 30 mg.l$^{-1}$, $m_{cat}$ = 1.0 g.l$^{-1}$, pH = 6.5).

With reference to experimental results, the (1.5% $Er_{0.01}$-YAG + 0.5% $Er_{0.01}$-YAP)/$TiO_2$ composite shows promise in solar energy applications when the pH conditions are optimized.

**Table 3:** Degradation ratios (DR) of MB (cationic) and MO (anionic) dyes in the presence of (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$–YAP)/$TiO_2$ composite under solar light irradiation at three different pH solutions.

| pH | DR (%) of MB | DR (%) of MO |
|---|---|---|
| 3.5 | 58 | 92 |
| 6.5 | 98 | 53 |
| 9 | 96 | 51 |

**Mechanism discussion:** $Er^{3+}$: YAG and $Er^{3+}$: YAP are known as efficient upconversion agents that enable the visible light to transform into the UV light. For the $Er^{3+}$: YAP, the emission bands around 318.7 and 320.1 nm were observed under the pumping of 486.5 and 542.4 (or 548.8) nm visible light [24, 27], respectively. In addition, the 326-312 nm and 354-359 nm upconversion luminescence by 652.2 (or 657.8) nm pumping was also detected [28]. Many other emission bands of wavelengths inferior to that of excitation source are also observed [21]. When $Er^{3+}$:YAG as the upconversion luminescence agent is pumped by a 488 nm $Ar^+$ laser, the upconversion signals at 271, 317 and 381 nm are observed. Otherwise, the upconversion signal at 320 nm is also found by a 647 nm laser excitation [19, 20]. The solar light (and its visible section) which contains continuous pump wavelengths was used as an excitation source, thus the upconversion process may easily take place in $Er^{3+}$: YAG and $Er^{3+}$: YAP crystals. If both $Er^{3+}$:YAG and $Er^{3+}$:YAP are excited at the same time with continuous visible light, the upconversion signal should contain all their emission bands leading to an intensification of the emitted light from the upconversion process. According to the energy level data given in references [16, 21, 22], the upconversion process can be achieved through the chains of ground state absorption (GSA) and excited state absorption (ESA). As illustrated in fig. 9, the crystallized $Er^{3+}$:YAG and $Er^{3+}$:YAP as upconversion luminescence agents coated by the $TiO_2$ folium, under continuous excitation of visible light, can emit the UV light, which can effectively be absorbed by $TiO_2$ parts to generate the electron-hole pairs. The holes not only directly decompose the MB adsorbed on the surface of $TiO_2$ particles, but also oxidize water molecules to form $^{\cdot}OH$ radicals with high activity and indirectly degrade the MB in the aqueous solution.

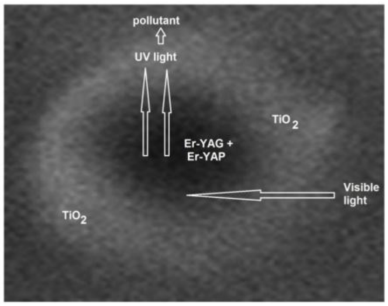


**Fig.9.** Degradation processes of organic dyes catalyzed by $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ composite under solar light irradiation.

## APPLICATION

The Er-YAG/Er-YAP/$TiO_2$ composite shows high efficiency as a photocatalyst for the degradation reaction of some dye aqueous solutions under visible and solar lights. It is able to convert visible lights into more energetic UV lights. Thus, using the upconversion mechanism, the $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ could be used as an efficient photocatalyst for treating dyes aqueous solutions under sunlight irradiation.

## CONCLUSION

A new photocatalyst with high catalytic activity under visible and solar irradiation is prepared. It is based on $TiO_2$ coating a combination of two upconversion luminescence agents: $Er_{0.01}$-YAG and $Er_{0.01}$-YAP. The $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ composite is prepared by the sol - gel method. This composite is found to be more photoactive than pure $TiO_2$ and both $Er_{0.01}$-YAG/$TiO_2$ and $Er_{0.01}$-YAP/$TiO_2$. The (1.5 % $Er_{0.01}$-YAG + 0.5 % $Er_{0.01}$–YAP)/$TiO_2$ combination is found to have the highest photocatalytic activity for the degradation of MB in aqueous solution under visible and solar light irradiation. Shortening time for the MB treatment is a necessary goal that is achieved with the use of solar light in the presence of the (1.5% $Er_{0.01}$-YAG + 0.5% $Er_{0.01}$-YAP)/$TiO_2$ composite. The irradiation time needed to achieve a degradation ratio of about 100 % is reduced to half compared to that shown with visible irradiation from the 250 W halogen lamp. Some other dyes exhibit high degradation ratios in the presence of this composite. Therefore, the $Er_{0.01}$-YAG/$Er_{0.01}$-YAP/$TiO_2$ composite combining the effect of two upconversion luminescence agents may be envisaged as a novel photocatalyst for treating aqueous dye solutions using solar energy.

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