

Photocatalytic Removal of Tartrazine Dye from Aqueous Samples on LaFeO₃/ZnO Photocatalysts

Vincenzo Vaiano, Giuseppina Iervolino*, Diana Sannino

Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy
 giervolino@unisa.it

Dyes represent a very important group of water pollutants that appear in the effluents of different industries. These contaminants, by preventing the penetration of light, can have negative effects on the aquatic environment, causing problems to the ecosystem, and possibly being carcinogenic and genotoxic on human health. In particular tartrazine is a commonly not-biodegradable dye used in food industries and it, in high amount, could cause allergic and/or intolerance reactions. In the past decade only few effective photocatalysts for organic dye degradation under visible-light irradiation has been reported. Effective photocatalysts, such as ZnO, however, exhibit photodegradation activity only under ultraviolet irradiation. The coupling of ZnO, having a band gap of 3.2 eV, with low band gap photocatalysts could induce the removal of the dyes under visible light. So, in this work, LaFeO₃, which has a band gap of about 2.1 eV, was supported on ZnO surface. The aim of this work was to evaluate the efficiency of LaFeO₃/ZnO on the degradation of tartrazine under UV but also under visible light. Furthermore it was evaluated the optimal composition in terms of LaFeO₃ amount on ZnO.

1. Introduction

The textile and food industries use organic dyes that represent an important source of environmental contamination. Most of dyes are toxic on aquatic creatures and have carcinogenic effects on humans (Salem et al., 2009). Moreover, these compounds, because of their chemical nature, are considered as persistent in the environment (Oancea and Meltzer, 2013). One of them is tartrazine, which is an azo dye whose presence in foods and drugs has been reported as a possible cause of asthma, urticaria, and angioedema (Modirshahla et al., 2007) and potentially phototoxic (Iervolino et al., 2015). In Malaysia, tartrazine (also known as Yellow Dye No. 5) is widely used in the food industries as coloring agent. Tartrazine, derived from coal tar, has been tested for its toxicity, carcinogenicity, and ability to cause mutations in lab animals. It also has a high solubility in water. Some people are extremely sensitive to tartrazine as it can cause breathing difficulties. Therefore, it is crucial to treat tartrazine present in liquid waste from the food industries with appropriate, affordable technology before being released into the environment.

Food azo dyes are not biodegradable, so conventional biological treatment processes are not efficient for the degradation of these contaminants present in wastewater (Mafra et al., 2013). Therefore, chemical and chemical-physical processes (such as coagulation, flocculation, adsorption, chemical oxidation etc.) are typically applied for azo dyes wastewater treatment. Unfortunately, the most of them are removal processes resulting in the production of sludge that must be properly treated and disposed of. An interesting alternative for the treatment of food azo dyes is represented by the advanced oxidation processes (Vaiano et al., 2015). An experimental approach reported the degradation of the tartrazine through the Photo-Fenton process by using a UV radiation at the wavelength of 254 nm (Iervolino et al., 2015). Photocatalysis is another potential process. In fact, this process, in presence of UV or visible light irradiation, degrades the dyes, giving rise to both discoloration and mineralization. In fact, this process, in presence of UV or visible light irradiation, is able to degrade the dyes, reaching discoloration and mineralization (Vaiano et al., 2016).

When the semiconductor is illuminated, it can generate electron-hole pairs by promoting an electron from the valence band to the conduction band, thus leaving a gap in this band. These holes can absorb H₂O or

hydroxyl groups from the reaction medium and produce highly reactive hydroxyl radical species. Radical hydroxyls are strong oxidizing agents that can degrade organic compounds or their intermediaries to reach final products such as CO₂, H₂O (Rupa et al., 2007).

Most of the literature data on the photocatalytic degradation of tartrazine provide the use of TiO₂ activated by UV light (Rupa et al., 2007). In the photocatalytic process, another very active semiconductor that can be used as a suitable alternative to TiO₂ is ZnO (Pung et al., 2012). However ZnO exhibit photodegradation activity only under ultraviolet irradiation. In order to activate the zinc oxide, having a band gap of 3.2 eV, also under visible light, it may be coupled with lower band gap photocatalysts. This could induce the removal of the dyes under visible light. So, in this work, LaFeO₃, which has a band gap of about 2.1 eV, was supported on ZnO surface. These photocatalysts were prepared using different amount of LaFeO₃ on ZnO. In particular reaction products were monitored by discoloration in liquid phase and total organic carbon (TOC) analysis.

2. Experimental

2.1 Photocatalysts synthesis and characterization

LaFeO₃/ZnO composites were prepared by solution combustion synthesis using citric acid as organic fuel and metal nitrates. Given amounts of Fe(NO₃)₃·9 H₂O, La(NO₃)₃·6 H₂O and citric acid were completely dissolved in 100 ml of distilled water, and the solution was kept stirred continuously at 60 °C. Ammonium hydroxide (Carlo Erba, 37 wt.%) was slowly added to adjust the pH of the solution up to 7.0. Finally, ZnO (Sigma Aldrich) was added to the solution. The solution was dried at 130 °C and then calcined at 300 °C for 3 hours to ignite the solution combustion reaction (Iervolino et al., 2016).

Different wt. % of LaFeO₃ (from 2.5 to 30 wt. %) was deposited on ZnO surface. All the materials were characterized using different techniques. The Raman spectra of the samples were recorded with a Dispersive MicroRaman system (Invia, Renishaw), equipped with 785 nm diode-laser, in the range 100-1000 cm⁻¹ Raman shift. X-ray diffraction patterns were obtained with an X-ray diffractometer (Assing), using Cu-K α radiation. UV-vis reflectance spectra of powder catalysts were recorded by a Perkin Elmer spectrometer Lambda 35 using a RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). All spectra were obtained using an 8° sample positioning holder, giving total reflectance relative to a calibrated standard SRS-010-99 (Labsphere Inc., North Sutton, NH). Equivalent band gap determinations of the photocatalysts were obtained from Kubelka-Munk function $F(R_{\infty})$ by plotting $[F(R_{\infty}) \times hv]^2$ vs. hv (Sannino et al., 2011).

2.2 Photocatalytic tests

Photocatalytic experiments were carried out with a pyrex cylindrical reactor (ID = 2.5 cm) equipped with an air distributor device, irradiated with a strip of UV-LEDs (nominal power: 10 W) emitting in the range 375-385 nm or visible LEDs with the main wavelength emission at 440 nm (nominal power: 10 W). LEDs strip was positioned around and in contact with the external surface of the reactor to make reaction volume uniformly irradiated by the light source. The catalyst dosage was 3 g L⁻¹ in an 80 mL aqueous solution containing 10 mg L⁻¹ of tartrazine. The suspension was left in dark conditions for 2 hours to reach the adsorption-desorption equilibrium of tartrazine on the photocatalyst surface, and then the reaction was started under UV (or visible) light up to 3 hours. The liquid samples were collected at fixed time and analyzed to determine the change of colour of aqueous samples, measured with a Perkin Elmer UV-Vis spectrophotometer at $\lambda_{max} = 426$ nm. TOC of the collected aqueous samples was measured from CO₂ obtained by catalytic combustion at T = 680 °C (Sannino et al., 2013).

3. Results

3.1 Photocatalysts characterization

The list of photocatalysts and their band-gap energy are reported in Table 1.

Table 1: Photocatalysts and their characteristics

Photocatalysts	Nominal LaFeO ₃ content [wt%]	Equivalent band gap energy [eV]
ZnO	0	3.2
LaFeO ₃	100	2.1
2.5LaFeO ₃ /ZnO	2.5	3.1
5LaFeO ₃ /ZnO	5	3.07
15LaFeO ₃ /ZnO	15	2.25
30LaFeO ₃ /ZnO	30	1.94

Figure 1 reports the XRD patterns of the photocatalysts. XRD showed well indexed diffraction peaks for all the samples. In particular, for unsupported LaFeO_3 photocatalyst, the results clearly indicate the formation of orthorhombic perovskite type structure, as reported in literature (Tijare et al., 2012) while for ZnO support, the analysis evidenced that ZnO is in hexagonal phase (wurtzite), as indicated in literature (Sakthivel et al., 2003). No significant impurity phases have been observed in the XRD spectra of the all samples. For all the $\text{LaFeO}_3/\text{ZnO}$ photocatalysts with a perovskite loading lower than 30 wt %, it was possible to observe the characteristic patterns of ZnO but not those ones related to LaFeO_3 . Moreover it was possible to note a reduction of the characteristic peaks of ZnO and in particular the disappearance of the peaks at 66.47° , 72.66° and 77.30° due to the coverage of the ZnO surface by the LaFeO_3 . It was possible to note that a diffraction signal of LaFeO_3 (at about 47°) appears only for the highest loading of LaFeO_3 on the ZnO surface. Raman spectra of photocatalysts, recorded using a 785 nm diode laser, are reported in Figure 2 showing the common peak located at 439 cm^{-1} due to the E_2 (high) vibration characteristic of the wurtzite phase of ZnO. All the other samples showed bands in the range $100 - 1,000\text{ cm}^{-1}$, associated to the LaFeO_3 structure (Phokha et al., 2014). The modes caused by La vibrations are present below 200 cm^{-1} , at 153 and 176 cm^{-1} . The bands in the range $400 - 450\text{ cm}^{-1}$ are due to the oxygen octahedral bending vibrations. It was possible to note that by increasing the amount of LaFeO_3 on ZnO, the signals related to perovskite become more visible. This is consistent with the conclusions of structural analysis obtained from the XRD spectra.

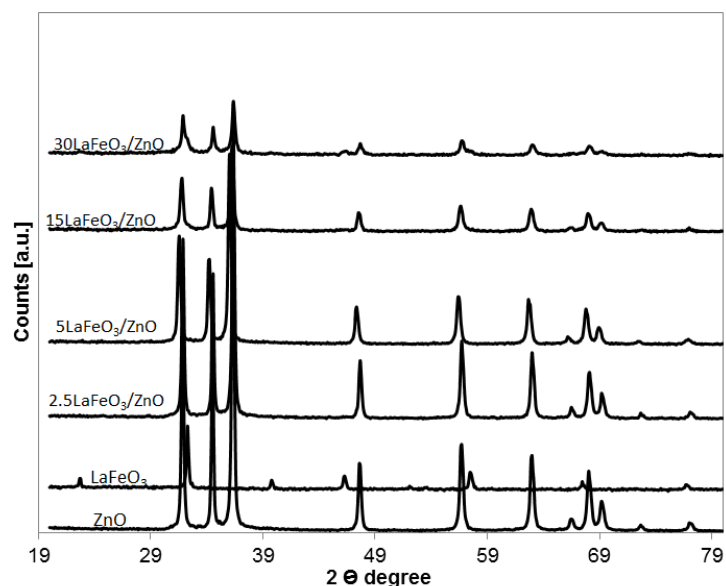


Figure 1: XRD spectra of the photocatalysts

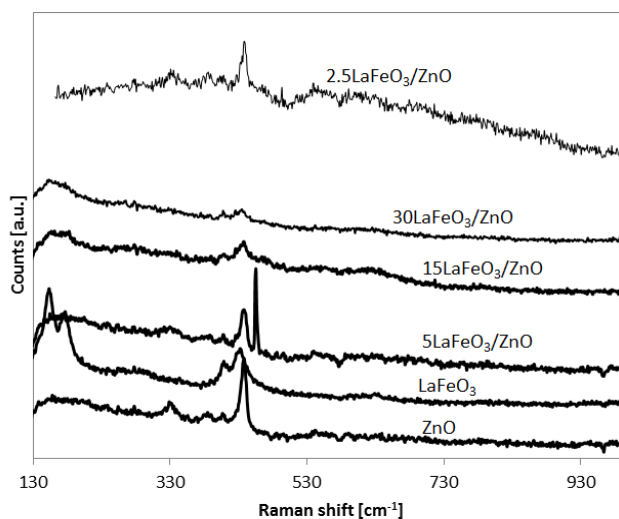


Figure 2: Raman spectra.

The data obtained from UV–Vis reflectance spectra were used for evaluating the band-gap energy of LaFeO₃, ZnO and the other photocatalysts. As shown in Table 1, the coupling of ZnO, having a band gap of 3.2 eV, with different amount of LaFeO₃, influenced significantly the band-gap energy, whose value decreases with the increase of LaFeO₃ dispersed on the ZnO surface. In particular for the photocatalyst prepared with 30% wt of LaFeO₃ on ZnO surface it was possible to observe a decrease of band gap value from 3.2 (for ZnO support) up to 2 eV.

3.2 Photocatalytic activity results

The efficiency of the photocatalysts prepared and characterized was evaluated in the photocatalytic removal of tartrazine. In order to verify that the target dye was converted in a heterogeneous photocatalytic process, blank experiments were performed. In particular, tests carried out in dark conditions did not evidence any oxidation activity. Moreover, additional control tests were carried out in the presence of tartrazine dye and irradiating the photoreactor with UV-LEDs or visible LEDs (photolysis reaction) in the absence of photocatalyst. Also in this case, no degradation of the tartrazine was detected. Figure 4(a) shows the evolution of the discoloration of the tartrazine as a function of run time, obtained over ZnO and LaFeO₃ photocatalysts in comparison with LaFeO₃/ZnO photocatalysts. In dark conditions a decrease of tartrazine concentration was observed during the first 30 min of the test and it was almost unchanged up to 120 min, indicating that the adsorption equilibrium of the dye on catalyst surface was reached. After the dark period, the solution was irradiated with UV light and the reaction started to occur. As it can be observed, an important decrease of the dye concentration was obtained in presence of LaFeO₃/ZnO samples. In particular, the highest discoloration (84 % after 3 h of irradiation) was observed on the photocatalyst 30LaFeO₃/ZnO.

The discoloration of dye does not necessary correspond to the oxidation and mineralization of the molecule. Moreover, it is known that reaction intermediates that can be formed during the oxidation of azo dyes could be more toxic than their parent compounds (Lucas and Peres, 2006). Therefore, it is necessary to understand the mineralization degree of the azo dye tartrazine to evaluate the mineralization level by photocatalytic reaction. In Figure 4(b) it is reported the percentage of discoloration with mineralization after 3 h of UV irradiation. It was observed that the highest mineralization of the dye was achieved on the sample 30LaFeO₃/ZnO. In particular with this photocatalyst, a discoloration and a TOC removal (evaluated starting from the irradiation time) of 84 and 58 % respectively, were obtained after 180 min of UV irradiation. So, in presence of UV light, the photocatalytic performances of the composites were much higher than those obtained with the bulk ZnO (20 and 11 % of discoloration and TOC removal, respectively) or with unsupported LaFeO₃ (46 and 23 % of discoloration and TOC removal, respectively). Coherently, the composites 30LaFeO₃/ZnO exhibited good photoactivity in the visible light driven removal of tartrazine (Figure 5), both in the discoloration (70 %) and in mineralization (45 %). This result is in agreement with the low band gap value evaluated for the composites 30LaFeO₃/ZnO, equal to 1.94 eV.

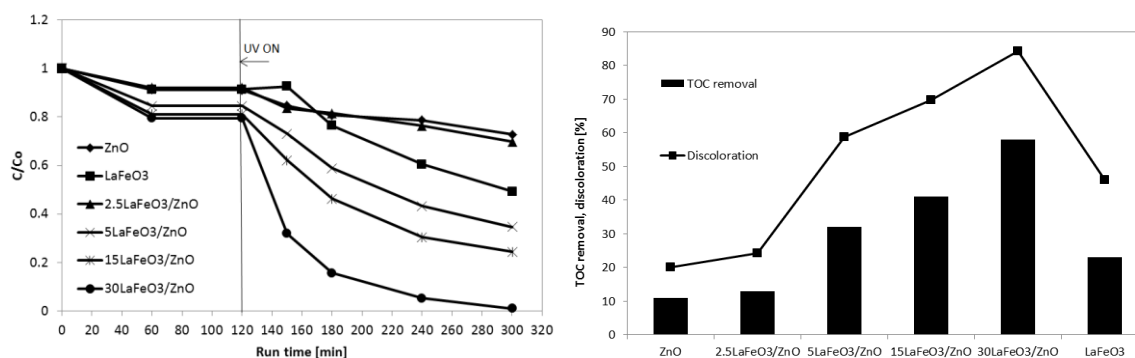


Figure 4: (a) Tartrazine discoloration for the different photocatalysts under UV light; (b) percentage of discoloration and mineralization of the tartrazine after 3 hours of UV irradiation

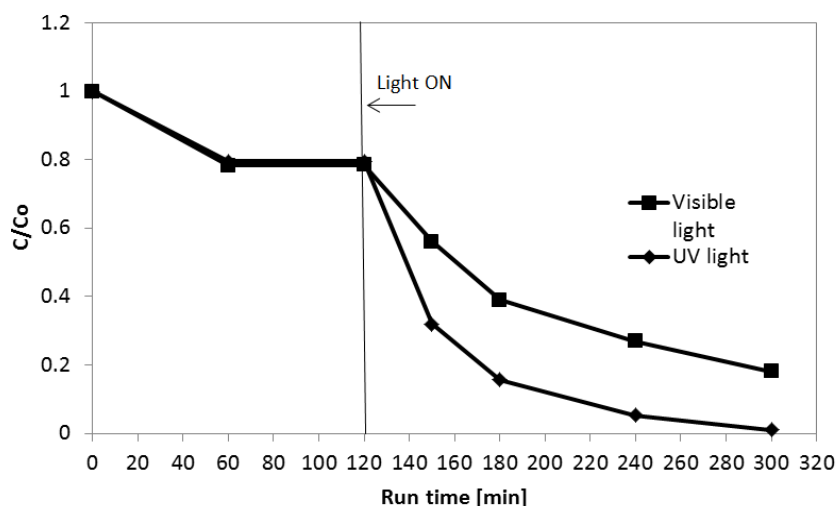


Figure 5: Comparison of the tartrazine discoloration under UV or visible light

4. Conclusions

In this work the photocatalytic removal of the tartrazine dye with LaFeO₃/ZnO photocatalysts has been addressed for the first time. In particular, it was possible to enhance the properties of zinc oxide under visible light through the coupling with LaFeO₃ perovskite. Characterization results evidenced that the deposition of LaFeO₃ on ZnO surface induced a decrease of band gap value from 3.17 eV to 1.94 eV, yielding in visible light active photocatalysts. In presence of UV irradiation, the photocatalytic performances of the composites were much higher than those obtained with the bulk ZnO or LaFeO₃. An optimal composition was found at 30 wt% of LaFeO₃ on ZnO. The composites LaFeO₃/ZnO exhibited good photoactivity in the visible light driven removal of tartrazine, evidencing abilities both in the target dye discoloration and in mineralization. The found performances have been attributed to the band gap decrease with the LaFeO₃ load, which improves the absorption of visible light.

Reference

- Iervolino G., Vaiano V., Sannino D., Rizzo L., Ciambelli P., 2016. Production of hydrogen from glucose by LaFeO₃ based photocatalytic process during water treatment. *International Journal of Hydrogen Energy*, 41, 959-966.
- Iervolino G., Vaiano V., Sannino D., Rizzo L., Sarno G., Ciambelli P., Isupova L.A., 2015. Influence of operating conditions in the photo-fenton removal of tartrazine on structured catalysts. *Chemical Engineering Transactions*, 43, 979-984.
- Lucas M.S., Peres J.A., 2006. Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation. *Dyes Pigm.*, 71, 236-244.
- Mafra M.R., Igarashi-Mafra L., Zuim D.R., Vasquez E.C., Ferreira M.A., 2013. Adsorption of Remazol Brilliant Blue on an orange peel adsorbent. *Braz. J. Chem. Eng.*, 30, 657-665.
- Modirshahla N., Behnajady M.A., Kooshaiian S., 2007. Investigation of the effect of different electrode connections on the removal efficiency of Tartrazine from aqueous solutions by electrocoagulation. *Dyes Pigm.*, 74, 249-257.
- Oancea P., Meltzer V., 2013. Photo-Fenton process for the degradation of Tartrazine (E102) in aqueous medium. *J. Taiwan Inst. Chem. Eng.*, 44, 990-994.
- Phokha S., Pinitsoontorn S., Maensiri S., Rujirawat S., 2014. Structure, optical and magnetic properties of LaFeO₃ nanoparticles prepared by polymerized complex method. *J. Sol-Gel Sci. Technol.*, 71, 333-341.
- Pung S.-Y., Lee W.-P., Aziz A., 2012. Kinetic study of organic dye degradation using ZnO particles with different morphologies as a photocatalyst. *Int. J. Inorg. Chem.*, 608183, 9 pp.
- Rupa A.V., Manikandan D., Divakar D., Revathi S., Preethi M.E.L., Shanthy K., Sivakumar T., 2007. Photocatalytic degradation of tartrazine dye using TiO₂ catalyst: salt effect and kinetic studies. *Indian J. Chem. Technol.*, 14, 71-78.

- Sakthivel S., Neppolian B., Shankar M.V., Arabindoo B., Palanichamy M., Murugesan V., 2003. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO₂. *Sol. Energy Mater. Sol. Cells*, 77, 65-82.
- Salem M.A., Al-Ghonemiy A.F., Zaki A.B., 2009. Photocatalytic degradation of Allura red and Quinoline yellow with Polyaniline/TiO₂ nanocomposite. *Appl. Catal.*, B, 91, 59-66.
- Sannino D., Vaiano V., Ciambelli P., Eloy P., Gaigneaux E.M., 2011. Avoiding the deactivation of sulphated MoO_x/TiO₂ catalysts in the photocatalytic cyclohexane oxidative dehydrogenation by a fluidized bed photoreactor. *Applied Catalysis A: General*, 394, 71-78.
- Sannino D., Vaiano V., Ciambelli P., Isupova L.A., 2013. Mathematical modelling of the heterogeneous photo-Fenton oxidation Of acetic acid on structured catalysts. *Chemical Engineering Journal*, 224, 53-58.
- Tijare S.N., Joshi M.V., Padole P.S., Mangrulkar P.A., Rayalu S.S., Labhsetwar N.K., 2012. Photocatalytic hydrogen generation through water splitting on nano-crystalline LaFeO₃ perovskite. *Int. J. Hydrogen Energy*, 37, 10451-10456.
- Vaiano V., Iervolino G., Sannino D., Murcia J.J., Hidalgo M.C., Ciambelli P., Navío J.A., 2016. Photocatalytic removal of patent blue V dye on Au-TiO₂ and Pt-TiO₂ catalysts. *Applied Catalysis B: Environmental*, 188, 134-146.
- Vaiano V., Iervolino G., Sannino D., Rizzo L., Sarno G., Ciambelli P., Isupova L.A., 2015. Food Azo-Dyes Removal from Water by Heterogeneous Photo-Fenton with LaFeO₃ Supported on Honeycomb Corundum Monoliths. *Journal of Environmental Engineering (United States)*, 141.