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Enhanced Performances of a Photocatalytic Reactor for Wastewater Treatment Using Controlled Modulation of LEDs Light

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One of the main limitations related to the industrial utilization of a photocatalytic process is the use of UV lamps that have several disadvantages such as the low quantum efficiency (QE). One of the approaches to increase the QE consists in the use of controlled periodic illumination (CPI). In this regard, Light Emitting Diodes (LEDs) are the best choice as light sources, since they can be electronically controlled by using LED dimming techniques, allowing variable turn-on and turn-off times on a microsecond time-scale.
The aim of this work is to investigate the influence of controlled modulation of LEDs light on the performances of a photocatalytic reactor for wastewater treatment using TiO_2 immobilized on glass spheres (TiO_2/GS).
The experiments were realized with a pyrex cylindrical batch photoreactor irradiated by three power UV-LEDs and placed surrounding the external body of the cylindrical photoreactor.
The system adopted for the controlled modulation of LEDs light is composed by a photovoltaic panel (PV), a dc–dc converter dedicated to the maximum power point tracking of the PV panel and a dc–dc converter dedicated to drive the UV LEDs. A system controller is also included, whose goal is to ensure matching between the maximum available PV power, the LED power and the resulting low-frequency LEDs dimming modulation. The experimental results showed that the use of certain types of duty-cycle dimming modulation waveforms, including periodic and non-periodic waveforms and combinations of them, have been discovered to improve the photo-catalytic reactor performances. In particular, the use of a modulation of LEDs dimming like sinusoidal and pseudo-sinusoidal waveforms is more effective than the fixed dimming. The best results in terms of methylene blue degradation (about 25% in less than 1 h) have been achieved with a pseudo-sinusoidal waveform.

1. Introduction

The main causes of surface and groundwater contamination are industrial effluents, excessive use of pesticides, fertilizers (agrochemicals) and domestic waste landfills. The traditional wastewater treatment is usually based on physical and biological processes. These processes have the limitation to transfer the organic pollutants from one phase to another phase leading to the need of further treatment. Advanced Oxidation Processes (AOPs) may become the most widely used water treatment technologies for organic pollutants (Vaiano et al., 2016) not treatable by conventional techniques (Sacco et al., 2015) due to their high chemical stability and/or low biodegradability (Pera-Titus et al., 2004).
TiO_2 is a well-known effective semiconductor photocatalyst for the purification of water and air due to its high photocatalytic activity, chemical as well as biological stability, relatively low-cost and especially non-toxicity (Lee and Park, 2013). However, photocatalysts are often used in slurry reactors (solid-liquid-gas system) and the treatment of industrial effluent with the TiO_2 based photocatalytic reaction in dispersion medium needs separation of catalyst and the recovery of the ultrafine catalyst from the treated liquid. Moreover the use of photocatalysts in powder form causes damages to the recirculation pumps (expensive). This disadvantage is overcame realizing heterogeneous fixed bed reactors, in which the photocatalyst is supported in granular form

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(Vaiano et al., 2014a) or thin film on transparent support (Vaiano et al., 2015b). However, one of the main limitations related to the industrial utilization of a photocatalytic reactor is the use of UV lamps that have several disadvantages such as low quantum efficiency (QE) (Wang and Ku, 2006). One of the approaches to increase the QE consists in the use of controlled periodic illumination (CPI). In this regard, Light Emitting Diodes (LEDs) are the best choice as light sources, since they can be electronically controlled by using LED dimming techniques, allowing variable turn-on and turn-off times on a microsecond time-scale. LEDs sizes are much smaller that UV lamps, allowing a spatial arrangement that guarantees a highly uniform illumination, with a reduced waste of light energy. Moreover, thanks to their controllable-energy generation, LEDs can realize operating temperatures lower than those of traditional UV lamps, with a consequent reduction of cooling and electrical energy costs (Mottier, 2010). The additional use of a renewable energy source, such as a photovoltaic (PV) panel feeding the LEDs in a light-to-light converter (Femia et al., 2013), and of an electric storage unit to stabilize the renewable energy production (Femia and Zamboni, 2012), opens perspectives of further innovation in LED-lighting applications.
The aim of this work is to investigate the influence of controlled modulation of LEDs light on the performances of a photocatalytic reactor for wastewater treatment using TiO_2 immobilized on glass spheres.

2. Experimental: preparation of photocatalyst and photocatalytic activity tests

2.1 Sol–gel synthesis

The sol-gel synthesis was carried out following the method reported by Vaiano et al. (Vaiano et al., 2015b). In particular Triton X-100 (nonionic surfactant, Sigma–Aldrich) has been used as binder (Vaiano et al., 2015b). Triton X-100 was dissolved in isopropyl alcohol (i-PrOH, 99.8 wt %, Sigma–Aldrich) and the pH of solution was adjusted with sulfuric acid (H_2SO_4, 95-98 wt %, Carlo Erba) until to reach a value of about 3. Then, titanium (IV) isopropoxide (TTIP, 97%, Sigma–Aldrich), used as titania precursor, was added to the mixture. The molar ratio of the ingredients was Triton X-100:i-PrOH:TTIP:sulfuric acid = 1:45:1:1. The obtained solution was stirred for 24 h at room temperature. After this time, the solution was slightly yellow, and appeared homogeneous and stable. The final solution was used for the immobilization of TiO_2 on glass spheres.

2.2 Immobilization of TiO_2 on glass spheres

Pyrex spheres (d_p=5.3 mm, from Microglass Heim) were used as glass substrate for the immobilization of TiO_2, which has been performed through dip-coating technique.
Before dip-coating, the whole surface of glass spheres was rinsed with MilliQ grade water and calcined at 450°C for 30 minutes. TiO_2 coating was realized by immersing the glass spheres in the solution prepared as reported in the section 2.1. The glass spheres were maintained in the solution for 30 minutes and then calcined for 30 minutes at 450°C. The dip-coating and calcination processes were repeated four times (Vaiano et al., 2015b). The final structured catalyst is named TiO_2/GS. The TiO_2 amount coated on glass spheres has been measured using precision balance (Mettler Toledo).

2.3 Photocatalyst characterization

TiO_2/GS catalyst was characterized by several techniques. Specific surface area (BET) was evaluated from dynamic N_2 adsorption measurement at -196°C, performed by a Costech Sorptometer 1040 after pretreatment at 150°C for 30 min in He flow. The Raman spectra were recorded with a Dispersive MicroRaman system (Invia, Renishaw), equipped with 514 nm diode-laser, in the range 100-900 cm^{-1} Raman shift. Total TiO_2 content on glass spheres was determined by X-ray fluorescence spectrometry (XRF) in a thermoFischer ARL QUANT'X EDXRF spectrometer equipped with a rhodium standard tube as the source of radiation and with Si-Li drifted crystal detector.

2.4 Photocatalytic activity tests

Methylene blue (MB) was used as model dye. The experiments were carried out with initial concentration of MB equal to 5 mg L^{-1}, at ambient temperature and pressure.
The experiments were realized with a pyrex cylindrical batch photoreactor (ID = 2.5 cm; height=18 cm) (Vaiano et al., 2014b) equipped with an air distributor device (Q_{air} = 150 cm^3 min^{-1} under standard temperature and pressure conditions) to assure the presence of oxygen in the liquid medium. The amount TiO_2/GS catalyst used during the photocatalytic test was equal to 60 g in a total solution volume of 80 mL.
The continuous mixing of the aqueous sample was realized by external recirculation of the aqueous solution through the use of a peristaltic pump. Thermocouple was inserted inside the reactor to monitor the temperature during irradiation. The photoreactor was irradiated with three power UV LEDs (5 W of nominal maximum power, 700 mA of nominal current and emission spectrum centred at 400 nm). The UV LEDs are placed surrounding the external body of the cylindrical photoreactor. The schematic picture of experimental

set-up is reported in a previous paper (Vaiano et al., 2014b). The system was left in dark until reaching MB adsorption equilibrium, and then photocatalytic reaction was initiated under UV light. Liquid samples were analyzed continuously by spectrophotometric measurement. In particular, a special assembly with a flow quartz cuvette and an external pump for the recirculation of liquid was used, permitting to determine the change of MB measured at λ = 663 nm.
The electronic system adopted for the experimental tests is composed by a PV panel, a dc–dc boost converter dedicated to the maximum power point tracking of the PV panel and a dc–dc buck converter dedicated to drive the LEDs array. A system digital controller is also included, whose goal is to ensure matching between the maximum available PV power, the LED power and the resulting low-frequency LEDs dimming modulation.
The average LEDs current (I_{avg}) depends on the on-state LED current (I_f) and on the dimming duty-cycle d_{dim}, defined as the ratio between the time during which the buck converter is in operation feeding the LEDs array (t_{on}) and the total duration of the dimming period (T_{dim}), according to Eq(1) and Eq(2):

$$I_{avg} = d_{\dim} \cdot I_f \tag{1}$$

$$d_{\dim} = \frac{t_{on}}{T_{\dim}} \tag{2}$$

The average LEDs current was modified according PWM approach, which consists in modulating the duration of current pulses at fixed on-state LED current.
In this work, PWM technique have been investigated and tested. Such modulation approaches have been performed both at fixed (100 %) and at variable dimming duty-cycle. In particular, two kind of variable dimming duty-cycle have been herein considered, based on a sinusoidal and on a pseudosinusoidal modulation of the duty.
In the case of sinusoidal dimming, the duty-cycle is modulated according to Eq(3):

$$d_{\dim}(t) = D_{\min} + \frac{D_{\max} - D_{\min}}{2} \cdot \left[1 + sen(\omega \cdot t)\right] \tag{3}$$

where D_{min} and D_{max} are the minimum and maximum dimming duty-cycle values. In the case of pseudo-sinusoidal dimming, the duty-cycle is modulated according to Eq(4):

$$d_{\dim}(t) = D_{\min} + \frac{D_{\max} - D_{\min}}{2} \cdot \left[1 + sen(\omega(t) \cdot t)\right] \tag{4}$$

where the angular frequency $\omega(t)$ is not a constant value, but varies in a certain range, as shown in Figure 1 (c). The sinusoidal and pseudosinusoidal modulations of the dimming duty cycle used in this work are reported in Figure 1.

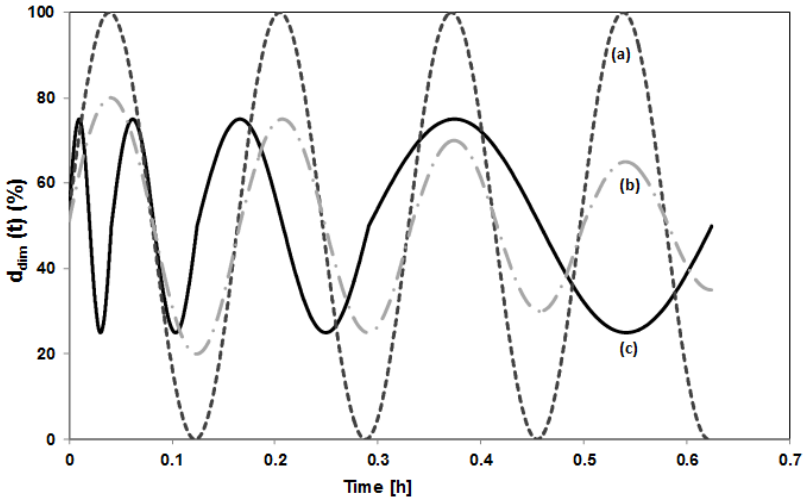

Figure 1: Behaviour of the dimming duty-cycle as a function of run time: (a) sinusoidal modulation with constant amplitude and constant frequency; (b) pseudo-sinusoidal modulation with constant frequency and variable amplitude; (c) pseudo-sinusoidal modulation with constant amplitude and variable frequency.

3. Results and Discussion

3.1 Characterization of TiO_2/GS photocatalyst

Specific surface area (SSA) values for TiO_2/GS and uncoated glass spheres are reported in Table 1. SSA of TiO_2/GS was is 0.96 $m^2 g^{-1}$, while a lower value (0.08 $m^2 g^{-1}$) was found for uncoated glass spheres.
The increase of surface area of TiO_2/GS could be ascribed to the formation of TiO_2 coating on the surface of glass spheres which results in a porous and rough surface, as previously observed for N-doped TiO_2 immobilized on glass spheres (Vaiano et al., 2015a).
The total amount of TiO_2 effectively deposited was determined by XRF (Table 1) and it was equal to 0.6 wt %. The real TiO_2 content well agrees to the TiO_2 content evaluated with the precision balance, indicating a good yield of the dip-coating process under the used preparation conditions.

Table 1: List of the samples and their characteristics

Sample	SSA, $m^2 g^{-1}$	TiO_2 loading wt% (balance)	TiO_2 measured loading wt% (XRF)	TiO_2 crystallite size nm (Raman)
Glass spheres	0.08	-	-	-
TiO_2/GS	0.96	0.6	0.57	6

The Raman spectra of the uncoated glass spheres in comparison with TiO_2/GS structured catalyst is shown in Figure 2. Uncoated glass spheres showed no Raman signals while TiO_2/GS sample displayed bands at 144, 396, 514 637 cm^{-1} and a weak shoulder at 195 cm^{-1} due to the anatase form of TiO_2 (Sannino et al., 2013) meaning that the coating method is able to induce the formation of anatase TiO_2 deposited on the surface of glass spheres. The TiO_2 particle size immobilized on glass spheres has been estimated by Raman spectra following the method finding that the value is about 6 nm, accordingly to previous results (Vaiano et al., 2015b).

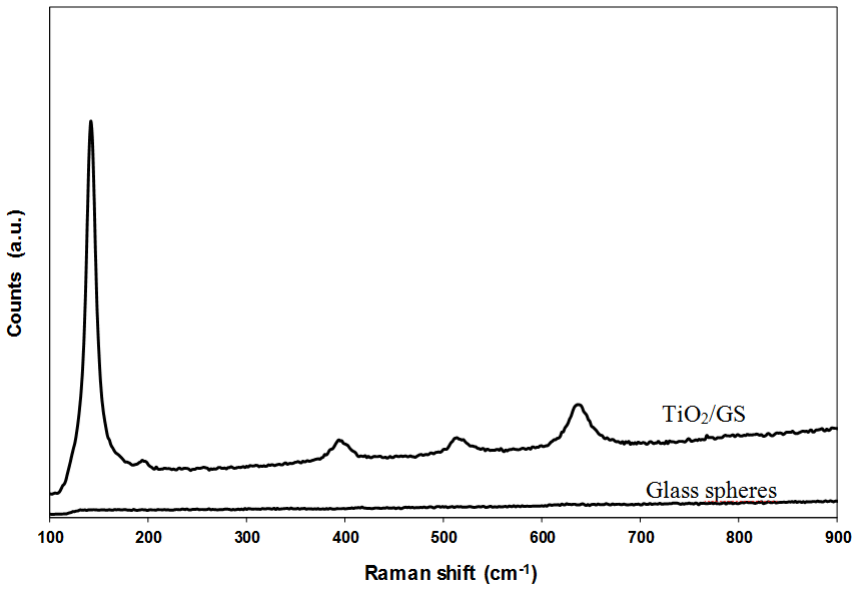

Figure 2: Raman spectra of glass spheres and TiO_2/GS.

3.2 Photocatalytic activity results

Preliminary experiments were carried out in order to verify that MB was degraded by the heterogeneous photocatalytic process. In the absence of TiO_2/GS photocatalyst, no significant decrease in MB concentration was observed during the UV irradiation.
Figure 3 reports the comparison between the photocatalytic activity of TiO_2/GS at fixed (100 %) and at variable LEDs dimming duty-cycle (according to the profiles reported in Figure 1).

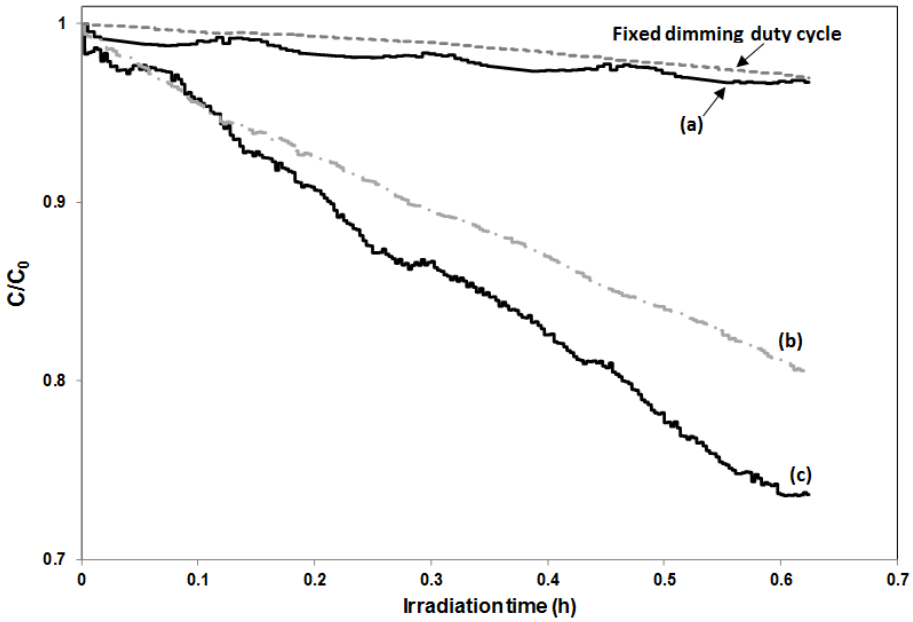

Figure 3: Behaviour of the MB relative concentration as a function of UV irradiation time obtained at fixed dimming duty cycle (100%), with sinusoidal modulation with constant amplitude and constant frequency (a), with pseudo-sinusoidal modulation with constant frequency and variable amplitude (b) and with pseudo-sinusoidal modulation with constant amplitude and variable frequency (c).

The effect of the light intensity modulation on the photocatalytic activity is clearly evident.
The sinusoidal modulation (a) did not promote the photocatalytic performances with respect to the irradiation realized at fixed dimming duty cycle. When the pseudo-sinusoidal modulation changes both in frequency and in amplitude, an increase of photocatalytic activity was achieved. The best results in terms of methylene blue degradation (about 25% in less than 1 h) have been achieved with a pseudo-sinusoidal modulation with constant amplitude and variable frequency (curve c of Figure 3).
Such PWM techniques provide an optimal trade-off between the photocatalytic performances and the energy consumption caused by the lighting system. In fact, variable duty-cycle in PWM dimming techniques may help in improving the effectiveness of the photocatalytic process and the energy efficiency of the lighting system, even if the average LED current (and relevant power consumption) and the resulting light intensity are lower than those ones obtained with fixed duty-cycle based PWM dimming.

4. Conclusions

The influence of controlled modulation of LEDs light on the performances of a photocatalytic reactor for wastewater treatment using TiO_2 immobilized on glass spheres has been studied. The experiments were realized with a pyrex cylindrical batch photoreactor irradiated by three power UV-LEDs and placed surrounding the external body of the cylindrical photoreactor. The system adopted for the controlled modulation of LEDs light is composed by a photovoltaic (PV) panel, a dc–dc converter dedicated to the maximum power point tracking of the PV panel and a dc–dc converter dedicated to drive the UV LEDs.
Photo-catalytic reactor performances has been improved by means of the time domain modulation of the square-wave LEDs light dimming, realized by means of the duty-cycle modulation waveforms.
The use of certain types of duty-cycle dimming modulation waveforms, including periodic and non periodic waveforms and combinations of them, have been discovered to improve the photocatalytic reactor performances. In particular, the duty-cycle has been run-time modulated during the experimental tests allowing to achieve superior photocatalytic performances. In particular, the best results in terms of methylene blue degradation (about 25% in less than 1 h) have been achieved with a sinusoidal modulation with constant amplitude and variable frequency.

References

Femia, N., Fortunato, M. & Vitelli, M. 2013. Light-to-Light: PV-Fed LED Lighting Systems. IEEE Transactions on Power Electronics, 28, 4063-4073.

Femia, N. & Zamboni, W. Photovoltaic-fed LED lighting system with SOC-based dimmable LED load. IECON 2012 - 38th Annual Conference on IEEE Industrial Electronics Society, 25-28 Oct. 2012 2012. 1132-1137.

Lee, S.-Y. & Park, S.-J. 2013. TiO_2 photocatalyst for water treatment applications. Journal of Industrial and Engineering Chemistry, 19, 1761-1769.

Mottier, P. 2010. Frontmatter. LEDs for Lighting Applications. ISTE.

Pera-Titus, M., García-Molina, V., Baños, M. A., Giménez, J. & Esplugas, S. 2004. Degradation of chlorophenols by means of advanced oxidation processes: a general review. Applied Catalysis B: Environmental, 47, 219-256.

Sacco, O., Vaiano, V., Han, C., Sannino, D., Dionysiou, D. D. & Ciambelli, P. 2015. Long afterglow green phosphors functionalized with Fe-N doped TiO_2 for the photocatalytic removal of emerging contaminants. Chemical Engineering Transactions.

Sannino, D., Vaiano, V., Sarno, G. & Ciambelli, P. 2013. Smart tiles for the preservation of indoor air quality. Chemical Engineering Transactions, 32, 355-360.

Vaiano, V., Sacco, O., Pisano, D., Sannino, D. & Ciambelli, P. 2015a. From the design to the development of a continuous fixed bed photoreactor for photocatalytic degradation of organic pollutants in wastewater. Chem. Eng. Sci., 137, 152-160.

Vaiano, V., Sacco, O., Sannino, D. & Ciambelli, P. 2015b. Nanostructured N-doped TiO_2 coated on glass spheres for the photocatalytic removal of organic dyes under UV or visible light irradiation. Applied Catalysis B: Environmental, 170-171, 153-161.

Vaiano, V., Sacco, O., Sannino, D., Ciambelli, P., Longo, S., Venditto, V. & Guerra, G. 2014a. N-doped TiO_2/s-PS aerogels for photocatalytic degradation of organic dyes in wastewater under visible light irradiation. Journal of Chemical Technology and Biotechnology, 89, 1175-1181.

Vaiano, V., Sacco, O., Sannino, D., Stoller, M., Ciambelli, P. & Chianese, A. 2016. Photocatalytic removal of phenol by ferromagnetic N-TiO_2/SiO_2/Fe_3O_4 nanoparticles in presence of visible light irradiation. Chemical Engineering Transactions.

Vaiano, V., Sacco, O., Stoller, M., Chianese, A., Ciambelli, P. & Sannino, D. 2014b. Influence of the photoreactor configuration and of different light sources in the photocatalytic treatment of highly polluted wastewater. Int. J. Chem. React. Eng., 12, 1-13, 13.

Wang, W.-Y. & Ku, Y. 2006. Photocatalytic degradation of Reactive Red 22 in aqueous solution by UV-LED radiation. Water Research, 40, 2249-2258.