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Research paper

Wavelength dependence of the efficiency of photocatalytic processes for water treatment

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ABSTRACT

The main objective of this work is to present a novel approach to evaluate quantitatively the action spectra and energy efficiency for chemical oxidation and bacterial inactivation of photocatalytic processes using monochromatic LED sources. Two different catalysts with different absorption spectra (TiO_2 and iron citrate complex) were used. In all cases, it was confirmed a direct relationship between the absorption spectrum of the catalyst and the spectral dependence of the photonic efficiency. The best alternative for TiO_2 processes in terms of energy consumption when using artificial lighting is the use of 365 nm. In contrast, for iron complexes it seems more economically feasible the use of longer wavelengths close to the visible range, because the lower absorption of the complex is counterbalanced by the higher energy efficiency of the LED devices. This can be obviously extrapolated to the use of sunlight, where the use of iron-based photocatalytic processes can harvest a higher fraction of the available light. Predictions of the process efficiency under solar irradiation based on the action spectra determined with LED at laboratory scale have been successfully validated by experimental data. The methodology proposed in this work could be easily extrapolated to other wavelength ranges required by novel catalysts or efficient short wavelength monochromatic LED sources available in the future.

1. Introduction

TiO_2 has been widely used as photocatalyst due to its low cost and non-toxicity [1,2]. However one of the main drawbacks of TiO_2 photocatalysis is its relatively high band gap energy (above 3.0 eV for rutile and 3.2 eV for anatase) which requires wavelength below 400 nm, in the UV-A range [3]. Although the effectiveness of the use of sunlight as radiation source for the removal of pollutants has been extensively proved [4,5], since the solar spectrum reaching the Earth's surface contains only 5–7% in the UV region, solar photocatalysis with TiO_2 is limited to areas of the planet with very long periods of sun exposure and high radiation levels. Some authors have pointed out the possibility of doping TiO_2 with other compounds to expand their absorption spectrum [6]. Although its effectiveness in the visible range has been demonstrated [7–9], the synthesis of this type of catalysts would considerably increase the complexity and the costs of the process.

Another possibility for photocatalytic processes is the use of artificial light. The use of this type of illumination has been widely studied; however, it has not been implanted at industrial level because it is strongly limited by the energy consumption. In recent years, the development of LED technology has opened the possibility of implementing the process at industrial level due to the large energy savings compared to traditional lighting systems [10–14].

Additionally, the development of LED technology has derived in the availability of monochromatic light sources with different wavelengths [10]. The possibility of using wavelengths closer to the visible range has the advantage of showing significantly higher energy efficiency [15]. Therefore, the possibility of using catalysts active in the UV-A/Vis range such iron-based complexes in photo-Fenton processes is interesting not only from the possible use of solar light but also for the improvement in the energy efficiency of LED driven processes. However the photo-Fenton processes have the drawback of working at low pH levels in order to avoid the catalyst precipitation which limits its applications, especially for disinfection purposes [16–18]. An interesting alternative to consider is the use of iron–based complexes that do not precipitate at neutral pH such as the iron citrate complex (Fe-citrate). The effectiveness of Fe-citrate has recently been successfully tested for the treatment of both synthetic [19,20] and real water [16,21].

This work reports a novel approach for the quantitative evaluation of the action spectra and energy efficiency of TiO_2 and iron-based photocatalytic processes based on the use of monochromatic LED sources. Comparable LED based systems providing maximum emission

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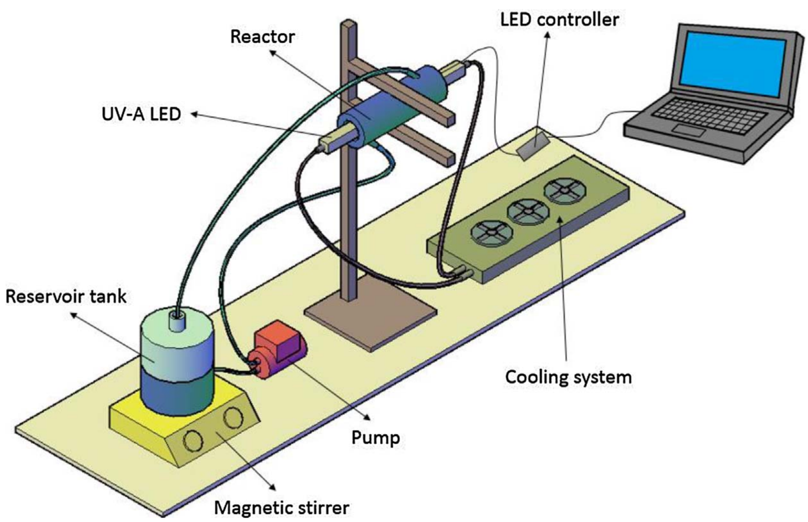

Fig. 1. Schematic representation of the experimental setup.

peaks at different wavelengths were used to determine the action spectra. Taking into account that several authors have pointed out the existence of certain differences between the photocatalytic oxidation of organics and the inactivation of microorganisms [22,23] two different model reactions were selected in order to evaluate the efficiency of each system. The photocatalytic oxidation of methanol to formaldehyde was used as model chemical reaction, whereas *E. coli* was selected as model pathogenic microorganism for disinfection applications. Finally, based on the action spectra, prediction of the process efficiency under solar light irradiation were carried out, being successfully validated by experimental data.

2. Material and methods

2.1. Experimental setup

An annular photoreactor 15 cm length, 3 cm internal diameter and 5 cm external diameter (Fig. 1) was used to get the experimental data to calculate the photonic efficiency data. The reactor was operated in a closed recirculating circuit driven by a centrifugal pump with a reservoir tank, being the total working volume of 1 L. As illumination sources, six different 8-UV-A LED based systems providing maximum emission peaks centered at different wavelengths (Fig. 2) were placed in the axis of the annular photoreactor. The LED-based systems were continuously refrigerated using a liquid cooling system (Koolance EX2-755) and the irradiation power was controlled through the electrical current intensity using the software Eldoled LED driver configuration Toolbox. Potassium ferrioxalate actinometry experiments were carried out in each case in order to calculate the total irradiation power as described elsewhere [24].

2.2. Experimental procedure

Chemical oxidation experiments were carried out using methanol (Sigma-Aldrich, LC–MS) as model of chemical pollutant. The initial concentration was fixed at 100 mM and all solutions were prepared in deionized water. Methanol oxidation was followed through the colorimetric determination of the formaldehyde produced throughout the reaction [25,26], quantitative oxidation product when methanol is in excess [27,28].

As model of microorganism, *Escherichia coli* K12 strains (CECT 4624, corresponding to ATCC 23631, where CECT stands for “Colección Española de Cultivos Tipo”) were used. Fresh liquid cultures were prepared by inoculation in a Luria-Bertani (LB) nutrient medium (Miller’s LB Broth, Scharlab) and incubation at 37 °C for 24 h under constant stirring on a rotary shaker. In all the experiments, the bacterial suspensions (NaCl 0.9%) were prepared with an initial concentration of 10^6 CFU/mL.

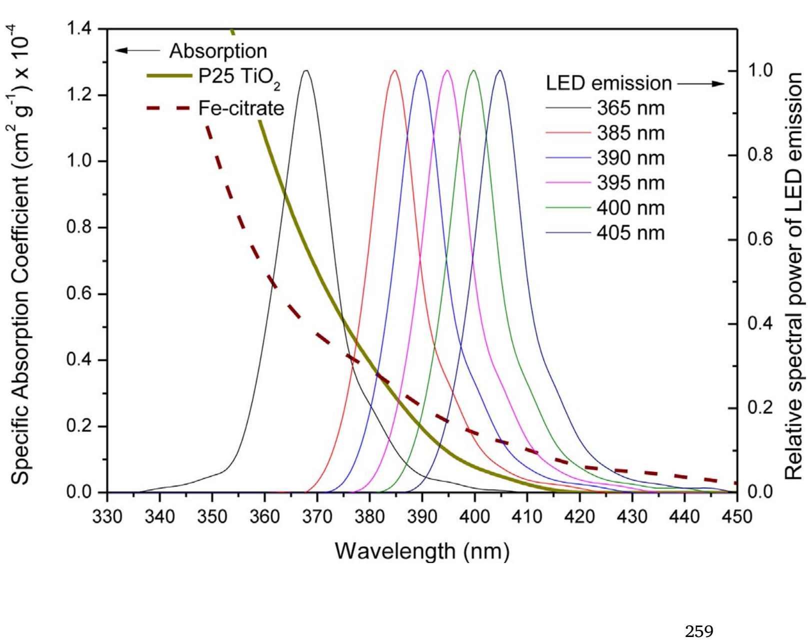

Fig. 2. Spectral emission of the light sources and specific absorption coefficients for TiO_2 and Fe-citrate complex.