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o-Nitrobenzaldehyde actinometry in the presence of suspended TiO_2 for photocatalytic reactors

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ABSTRACT

In this study the o-nitrobenzaldehyde (o-NB) actinometry is used to measure the photon flow entering a photocatalytic reactor. Two different proposed methods in bibliography are adapted and compared: by following pH or o-NB concentration. In addition, it was studied the influence of suspended TiO_2 particles, inside the photoreactor, on the o-NB actinometry. Particularly, the appearance of photocatalytic products was followed during actinometries with suspended TiO_2. It seems that these photocatalytic products do not come from the o-NB photocatalysis, but from the photocatalytic reaction of its photo-product (o-nitrosobenzoic acid), catalyzed by TiO_2. Therefore, this actinometry, following the o-NB concentration, can be used in the presence of suspended TiO_2 to determine the apparent photon flow entering a photoreactor or apply it to suitable models.

1. Introduction

Water pollution has received an increasing attention worldwide, because water is essential for the economic development of societies, human health and survival. Thus, wastewater treatments are an effective strategy for water conservation.

A large part of wastewater can be effectively treated by traditional methods such as biological processes or adsorption with activated carbon. Nevertheless, there are cases where these kinds of treatments are not enough to reach certain law requirements, or where persistent, toxic and/or non biodegradable organic pollutants appear in effluents from wastewater treatment plants. Therefore, complementary processes such as Advanced Oxidation Processes (AOPs) may be required.

Among AOPs, heterogeneous photocatalysis represents a promising technique for water treatment. Its efficiency has been proved in degrading a wide range of different refractory organics into readily biodegradable compounds, and mineralizing them to innocuous carbon dioxide and water [1–6]. This process is based on the presence of a semiconductor, which absorbs photonic energy higher than or equal to its bandgap energy, generating e^-/h^+ pairs. These pairs induce a series of reductive and oxidative reactions on the semiconductor's surface, which can lead to the degradation of different pollutants. Among semiconductors, titanium dioxide has received high interest since it is active, resistant, safe and cheap. Furthermore, this semiconductor has special interest, since it can use natural (solar) UV of wavelength in the range of 300–390 nm [7].

The strict modeling of photocatalytic reactors is a highly complex assignment, due to the requirement of the analysis of the radiation field. In this process, the radiation can control the kinetic mechanism of contaminants degradation, which is based on the quantity of absorbed photons. Therefore, the interaction assessment between light and TiO_2 particles becomes necessary to understand the overall photochemical mechanism. In this sense, some researches have developed different photocatalytic degradation kinetics including mathematical models of the radiation inside the photoreactor. These models can provide information for both scaling-up and design of commercial photoreactors [8–11].

Thus, to study the kinetic mechanism of a photocatalytic process, radiation should be quantified. Chemical actinometries are often used to calculate the light entering into the system. Actinometries are well known processes based on the reaction of a determined compound, as a result of a photon absorption in a specified wavelengths range. The actinometric reaction rate is related to photons absorption. In the case of AOPs activated by light, actinometries are commonly applied under exactly the same experimental conditions and device, to estimate the irradiance intensity to which the solution is exposed.

Many actinometries have been developed [12]. They are based on diverse chemicals and procedures which lead to the measure of photon absorptions over different and specified wavelength ranges. In this study, o-nitrobenzaldehyde (o-NB) actinometry has been selected, primarily because of its accordance to the TiO_2 absorption

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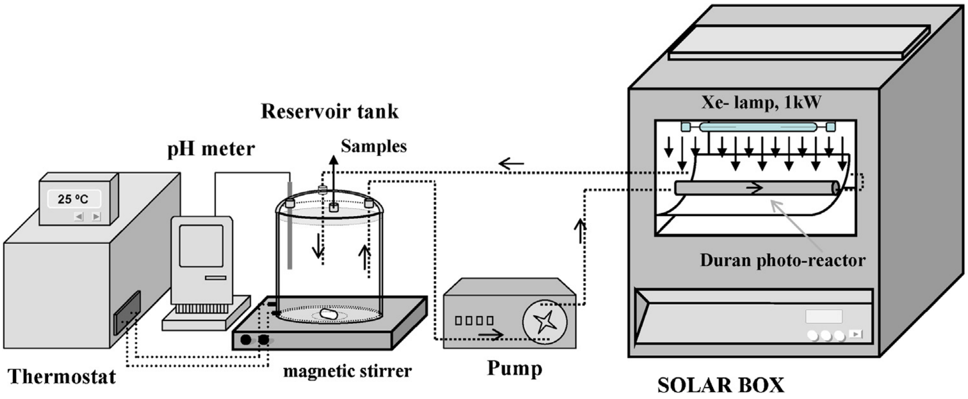

Fig. 1. Experimental device.

wavelength range, giving photon absorption data in the range from 290 to 400 nm. It also entails a safe experimental procedure and easy to perform. Another advantage is that the o-NB actinometry may be used with common UV lamps and also in solar photoreactors. This is an actinometry which has been not deep studied yet. Others, more commonly used and studied, were not selected for different reasons. For instance, the uranyl oxalate actinometry was rejected because of environmental and toxic matters. The potassium ferrioxalate actinometry, which must be developed under dark red light, was not useful in this case.

To characterize the radiation in a TiO_2/UV system, it becomes important to compute the photonic flow reaching the solution inside a photoreactor. Different light phenomena would take place in this system, such as transmission, reflection, refraction or absorption. An option to reach this purpose could be to quantify the light absorbed by an actinometric solution inside the photoreactor, when the heterogeneous catalyst is added [13]. However, when o-NB actinometry is used, it could be possible that photocatalytic reactions would take place, as the o-NB is an organic compound.

Thus, the goal of this study was to contribute to estimate the light entering into a photocatalytic heterogeneous system by using the o-NB actinometry. In order to have an actinometric system which could be used to calculate the radiation absorbed by TiO_2, the influence of adding TiO_2 to the o-NB actinometry has been approached. HPLC chromatograms were considered to detect the appearance of photocatalytic reactions during actinometric measurements. Diverse photocatalytic scavengers have also been used with the objective of deducting possible reacting pathways in these conditions. Furthermore, two different ways of developing the o-NB actinometry have been carried out and compared.

2. Materials and methods

2.1. Chemicals

Solutions of o-NB were prepared in 50% ethanol per 50% Milli Q water and stored in the dark. o-Nitrobenzaldehyde (98%) and ethanol (96%, v/v) were from Panreac Química (Spain), formic acid (85%) and tert-butyl alcohol were from Probus S.A. (Spain), ρ-benzoquinone (for synthesis) from Merck (Germany) and sodium hydroxide (98%) from Panreac (Spain). Synthetic amorphous titanium dioxide (Degussa P-25, Spain) was used as catalyst.

2.2. Analytical procedures

The o-NB concentration was monitored by using a high-performance liquid chromatograph (HPLC) from Waters with a *SEA18* 5 μm 15 × 0.46 Teknokroma column, and a Waters 996 photodiode array detector using the Empower Pro software 2002 Water Co. The mobile phase was composed by water and acetonitrile (40:60), injected with a flow-rate of 0.6 mL min^{-1} and detected at maximum UV absorbance set at wavelength of 258 nm. In order to remove the catalyst, before the HPLC analysis, samples were filtered with a polyethersulfone membrane filter of 0.45 μm. The measurement of pH was carried out by a Crison GLP 22 instrument with pH electrode from VWR international (662-1759).

2.3. Photoreactor

A magnetically stirred reservoir tank (1.0 L) was filled with o-NB solutions (Fig. 1). Reagents as formic acid, tert-butanol, benzoquinone or suspended TiO_2 were added when needed.

Solution was continuously pumped (peristaltic pump Ecoline VC-280 II, Ismatec) into a solar simulator (Solarbox Co.fo.me.gra, 220 V, 50 Hz), and recirculated back to the reservoir tank with a flow of 0.65 L min^{-1}. Inside the Solarbox, a duran tubular photoreactor (0.078 L) was irradiated by a Xe-lamp of 1 kW (Phillips XOP 15-OF 1CT). Reactor was located at the bottom of solarbox in the axis of a parabolic mirror. The solution was maintained at constant temperature of 25 °C; the jacket temperature of the stirred tank was controlled with an ultra-thermostat bath (Haake K10).

Before irradiation started, a 5 mL sample was collected from the reservoir tank representing time zero. After turning on the lamp, samples were collected every 5 min during a total period of 45 min. pH was also monitored.

All connections and pipes employed were made of Teflon and/or glass material to avoid losses by adsorption.

3. Results and discussion

3.1. o-NB actinometry

Experiments were carried out to quantify the irradiance intensity of a Xe-lamp light and to compare two different ways of performing the o-NB actinometry.

The photo-degradation of o-NB has been reported by different authors [14–16] and it is generally accepted that the phototransformation of o-NB leads to o-nitrosobenzoic acid (o-HNB). This reaction involves an intramolecular rearrangement where the first step is a hydrogen migration from the aldehyde moiety to the nitro group, leading to the formation of the nitronic acid which rapidly deprotonates to give the nitronate anion (Fig. 2).

3.1.1. o-NB actinometry based on pH

o-NB actinometry was carried out by adapting the method described by Allen et al. [17]. The procedure used in our work