Chemical Engineering Science 137 (2015) 152–160

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

From the design to the development of a continuous fixed bed photoreactor for photocatalytic degradation of organic pollutants in wastewater

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HIGHLIGHTS

- Design and development of a continuous flat-plate fixed bed photoreactor.
- Visible light active N-doped TiO_2 photocatalyst supported on glass spheres.
- Fluid dynamic conditions were chosen to have plug flow behavior.
- The photons distribution has been modeled by using the Helmholtz equation.
- The kinetic behavior of the photoreactor was studied by Langmuir–Hinshelwood model.

ARTICLE INFO

Article history:
Received 9 April 2015
Received in revised form
3 June 2015
Accepted 15 June 2015
Available online 24 June 2015

Keywords:
Fixed bed continuous photoreactor
Design and development
Visible light
UV light
Wastewater treatment

ABSTRACT

For industrial applications of photocatalytic processes aimed to the removal of pollutants from wastewater, a good solution for a final scale-up would be the choice of a continuous catalytic fixed bed photoreactor, able to work both with artificial light and with solar light. The optimal design needs a deep study starting from fluid dynamic considerations, together with the evaluation of the light's distribution inside the reactor core. In this work, flat plate geometry was chosen and a structured bed photoreactor for wastewater treatment was designed and implemented starting from an optimized N-doped TiO_2 photocatalyst immobilized on glass spheres. The fluid dynamic study of the structured bed reactor was intensely carried out through a CFD model. Instead of the traditional LVRPA, the Helmholtz equation, set with the Dirichlet conditions on the boundary, was used to model the light distribution inside the photoreactor. Based on the results of the modeling optimization, a laboratory scale photoreactor was developed. In order to obtain kinetic parameters, photocatalytic tests were carried out using a model pollutant. The Langmuir–Hinshelwood kinetic model was applied for estimating the kinetic parameters of the catalyst, starting from experimental data collected at different inlet pollutant concentrations. The kinetic expression together with the photons' spatial distribution was incorporated in the mass balance to achieve the theoretical distribution of the pollutant concentration in the reactor. The model was validated comparing the experimental data obtained at different contact times. The developed mathematical modeling allows to determine the best operating conditions to optimize the irradiation and the reactor volume, being a flexible method for a further scale-up of the photoreactor. The developed flat plate structured bed photoreactor was able to operate in continuous mode.

1. Introduction

During the past 30 years, the advanced oxidation processes (AOPs) have been increased considerably for involving the use of light irradiation and catalysts for treating gaseous streams and wastewater containing refractory and inhibitory organics (Palmisano et al., 2009; Parrino et al., 2014; Sannino et al., 2013a, 2013b, 2013c).

Titanium dioxide (TiO_2) photocatalyst in the anatase form seems to have the most interesting attributes, such as high stability, good performance and low cost (Fujishima and Zhang, 2006; Ruzmanova et al., 2013; Stoller et al., 2011). In this respect, the photodecomposition ability of TiO_2 can be advantageously used to mineralize a wide variety of pollutants present in water (Ahmed et al., 2011; Sacco et al., 2015; Vaiano et al., 2015b).

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http://dx.doi.org/10.1016/j.ces.2015.06.023
0009-2509/

The most useful reactors for the wastewater treatment are heterogeneous phototoreactors, where the photocatalysts can be present in suspended modes (slurry reactor) or immobilized on transparent support (fixed bed reactor). Most of the early photoreactors have employed a TiO_2 suspension because it offers a high surface area for the reactions. The disadvantages of the slurry photocatalysis include (1) difficulty and time consuming process of separation or filtration of the photocatalyst after the photocatalytic process; (2) particle aggregation and agglomeration at high photocatalyst concentration; and (3) difficulty of using the suspended photocatalyst in continuous processes (Sopyan et al., 1996). To overcome these drawbacks, immobilized photocatalysts are usually recommended. Photocatalysts could be immobilized on various supports such as glasses (Neti et al., 2010; Wang et al., 2014), silica (Van Grieken et al., 2002), polymers (Kasanen et al., 2009; Vaiano et al., 2014a), and clays (An et al., 2008).

The efficiency of an immobilized system is less than the slurry photoreactor's one, but the photocatalyst is continuously used for a longer period of time.

In spite of the potential advantages of using photocatalytic reactors, there are still issues to be addressed. One of the main problems in photocatalytic reaction engineering is correspondent to the photoreactor scale-up. Different literature approaches were used for modeling a large scale photoreactor.

The scale-up can be facilitated by the availability of simpler mathematical models that retain the essential elements of rigorous models but are easier to use for scale-up and design purposes (Ghafoori et al., 2014).

One of the most robust methods to design a large-scale photoreactor is to use a precise simple mathematical modeling that involves at least four sub-models that are cross-linked to the material and energy balances. These sub-models are as follows: (1) a radiation emission model (Alfano and Cassano, 2009; Marugán et al., 2009), (2) a radiation absorption–scattering model, (3) a fluid-dynamic model, and (4) a kinetic model.

The design of the photoreactor needs to start from considering the fluid flow across the photocatalytic packed bed. This has to be done to develop a system with no recirculation or dead zones. In order to achieve this design, different solutions could be taken into account, with a final goal of obtaining a plug-flow behavior inside the packed bed.

However, it is necessary to take into account that the performances of a photoreactor strictly depend also on the light sources and the light distribution inside the reactor volume.

Therefore, in order to carry out a practical scaling-up and to optimize a photoreactor, special considerations to the radiant existence must be taken into account. In fact, precise determination of the radiation field is a difficult task. One major problem is the lack of suitable radiation models as well as kinetic models and design procedures (Li Puma and Brucato, 2007; Li Puma and Yue, 2003). Particularly, the behavior of light inside the heterogeneous media and its impact on the pollutant local degradation rate are still not well understood (Minero, 1999).

Regarding photocatalytic reaction engineering, the Local Volumetric Rate of Photon Absorption (LVRPA) is a property of major interest (Li Puma, 2005).

It is important to mention that the LVRPA has been only indirectly estimated solving the radiative transfer equation (RTE) (Alfano et al., 2000; Brandi et al., 2000).

Moreover, the accurate determination of the LVRPA spatial distribution within the photocatalytic reactor is an important factor (Alfano et al., 1994), mainly due to both the inability to render precise kinetic information from averaged photon absorption rates (Brandi et al., 2003) and the strong non-uniformities inherent to light propagation in scattering–absorption media.

Practically, it is possible to measure the light intensity only on certain subsets of physical space (e.g. on some surfaces) surrounding the solid. Therefore, the problem arises how to reconstruct the radiation field from such experimental data (Millar, 1983).

Recently, the light distribution inside the solid media was modeled by the Helmholtz equation with two constant parameters, the scattering coefficient and the absorption coefficient (Mottin et al., 2010). This equation has been studied in various applications including biomedical imaging (Arridge, 1999), impedance imaging (Bryan and Leise, 2010) and wave propagation and scattering (Bryan and Leise, 2010). No paper reports the use of the Helmholtz equation to describe the photons' distribution in the reaction zone.

The aim of the present paper is to show a simple method for the scale-up of a continuous fixed bed photocatalytic reactor for wastewater treatment, through (i) studies of fluid dynamic conditions in order to obtain a plug flow behavior inside the photocatalytic bed (ii) the choice of the geometric characteristics for maximizing the exposition of the catalyst to the light sources (iii) modeling of photons' distribution inside the photoreactor (The Helmholtz equation).

With the designed continuous photocatalytic reactor, the influence of contact time on photocatalytic performances has been analyzed and the evaluation of kinetic parameters has been achieved using the experimental data and results obtained from the light distribution in the reactor. Finally, the developed mathematical model has been used to determine the best irradiation conditions with the aim to minimize the reactor volume.

2. Reactor design

2.1. Synthesis of structured photocatalyst (N-doped TiO_2 on glass spheres)

For the design and the final implementation of the continuous fixed bed photoreactor, firstly the visible light active N-doped TiO_2 photocatalyst was immobilized on pyrex spheres (d_p=4.3 mm, from Microglass Heim) through dip-coating technique (Vaiano et al., 2015a).

Before dip-coating, the whole surface of glass spheres was rinsed with MilliQ grade water and calcined at 450 °C for 30 min. N-doped TiO_2 coating was prepared by immersing the glass spheres support in a solution of Triton X-100 (nonionic surfactant, Sigma-Aldrich) as binder (Rosu et al., 2009). Triton X-100 was dissolved in isopropyl alcohol (i-PrOH, 99.8 wt%, Sigma-Aldrich) and the pH of solution was adjusted with nitric acid (HNO_3, 65 wt %, Carlo Erba) until to reach a value of about 2. Then, titanium (IV) isopropoxide (TTIP, 97%, Sigma-Aldrich), used as titania precursor, was added to the mixture. The synthesis temperature of N-doped TiO_2 on glass spheres was −20 °C.

Once the solution reached the temperature conditions, an ammonia aqueous solution (30 wt%, Sigma-ldrich) was added as nitrogen precursor. The molar ratio N/Ti was equal to 18.6 and corresponds to an optimized catalyst formulation found in a previous work (Sacco et al., 2012). The glass spheres were maintained in the solution for 10 min and then calcined for 30 min at 450 °C. The dip-coating procedure was repeated four times until to reach the amount of N-doped TiO_2, equal to 0.34 wt%, and corresponding to the optimal loading.

2.2. Design of the fixed bed reactor: choice of the photoreactor geometry

The geometry of a photoreactor is strongly related to the source of irradiation, in particular, it has to be designed so as to collect the