



Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Antipyrine removal by TiO₂ photocatalysis based on spinning disc reactor technologyA.J. Expósito^a, D.A. Patterson^{b, **}, W.S.W. Mansor^b, J.M. Monteagudo^a, E. Emanuelsson^b, I. Sanmartín^a, A. Durán^{a, *}^a Department of Chemical Engineering, Grupo IMAES, Escuela Técnica Superior de Ingenieros Industriales, Instituto de Investigaciones Energéticas y Aplicaciones Industriales (INEL), Universidad de Castilla-La Mancha, Avda. Camilo José Cela 3, 13071, Ciudad Real, Spain^b Bath Process Intensification Laboratory and Centre for Advanced Separations Engineering, Department of Chemical Engineering, University of Bath, BA2 7AY, UK

ARTICLE INFO

Article history:

Received 2 September 2016

Received in revised form

21 October 2016

Accepted 6 November 2016

Available online xxx

Keywords:

AOPs

Emerging contaminant

Neural networks

Pathway

Pharmaceuticals

UV radiation

ABSTRACT

The photo-degradation of the emerging contaminant antipyrine (AP) was studied and optimized in a novel photocatalytic spinning disc reactor (SDR). A heterogeneous process (UV/H₂O₂/TiO₂) was used. TiO₂ was immobilized on the surface of a glass disc using a sol-gel method. A factorial design of experiments followed by a Neural Networks fitting allowed the optimal conditions to be determined for treating 50 mg/L of AP. Under these conditions (pH = 4; [H₂O₂]₀ = 1500 mg/L; disc speed = 500 rpm; flowrate = 25 mL/s), AP was completely degraded in 120 min and regeneration of the disc allowed 10 cycles with no loss in efficiency. The value of the apparent volumetric rate constant was found to be 6.9 · 10⁻⁴ s⁻¹ with no apparent mass transfer limitation.

Based on the main intermediates identified, a mechanism is proposed for antipyrine photo-degradation: Firstly, cleavage of the N–N bond of penta-heterocycle leads to the formation of two aromatic acids and *N*-phenylpropanamide. An attack to the C–N bond in the latter compound produces benzenamine. Finally, the phenyl ring of the aromatic intermediates are opened and molecular organic acids are formed.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Emerging contaminants (EC) have received significant attention in the recent years since they are new chemicals whose effects are unknown on environment and human health (Durán et al., 2013). Therefore, EC are shown as potential pollutants which must be removed. Antipyrine (AP), which is included in this group, is a common analgesic and anti-inflammatory drug used ubiquitously by the pharmaceutical industry. AP is a complex molecule which is not able to be removed by the traditional techniques used in wastewater treatment, hence it can be accumulated in the natural water cycle (Verlicchi et al., 2012). At present, low concentrations of antipyrine have been measured in previous works at up to the µg/L level in municipal sewage effluents, ground water and drinking

water (Cai et al., 2013).

Advanced Oxidation Processes (AOPs) have been shown to be a potential technique that is able to remove refractory molecules. These processes are based on the production of highly reactive radicals Liu et al., 2016). The radicals have a short life, reacting quickly and can mineralize the organic pollutants. One of the most interesting AOPs consists of the use of semiconductors as photocatalysts. The semiconductor TiO₂ has been extensively studied because of its high photo-reactivity, stability to corrosion/dissolution, low price, ready availability and ability to generate electron-hole pairs when illuminated by UV which initiate both radical generation and direct oxidation of organic pollutant species, enabling mineralization to be achieved (Naem and Ouyang, 2013; Domínguez et al., 2015). In addition, it is not toxic, it is biologically and chemically inert and it can be regenerated several times without significant loss of activity. However, comparing TiO₂ results between different scales and configurations is difficult, complicating its applicability (Rao and Chu, 2009; Domínguez et al., 2015). This is in the main due to the almost universal application of

* Corresponding author.

** Corresponding author.

E-mail addresses: antoniojose.exposito@uclm.es (A.J. Expósito), d.patterson@bath.ac.uk (D.A. Patterson), antonio.duran@uclm.es (A. Durán).

TiO₂ as a powder suspension, which when applied in different reactor systems and at different scales produces a difficult to predict change in photo-reactivity due to complex to model effects such as light scattering, shadowing, mass transfer limitations in multiphase flow systems (such as is the norm in gas-liquid-solid or liquid-solid photocatalytic systems). Recovery of the suspended catalyst can also complicate and increase the cost of the overall process, which may be a further barrier to implementation and comparison between different configurations. Consequently, using immobilized/supported TiO₂ is a simple way to overcome most, if not all, of these problems, in particular enabling simpler scale-up since there is no solid phase creating multiphase flow, shadowing and avoiding the need for photocatalyst separation (Boiarkina et al., 2011). Sol-gel coating is an established method for the synthesis of thin and porous layers of TiO₂ and as such is used in this work (Miranda-García et al., 2014).

The use and properties of H₂O₂ as an oxidant is thoroughly known. It can be easily activated by UV light generating hydroxyl radicals. Furthermore, H₂O₂ is cheap, easily stored and it is soluble in water, with negligible mass transfer limitations (Li et al., 2015). There are several studies which have shown the improvement of TiO₂ effectiveness in the presence of H₂O₂ because it can react with TiO₂ giving rise to the formation of Ti-OOH complexes (Li et al., 2001; Domínguez Sánchez et al., 2013). This complex has a coloured surface which enhances the photocatalyst effect (Li et al., 2001).

Despite all of the extensive work on photocatalysis and processes based on TiO₂ they still suffer from particularly show slow kinetics and low mass transfer. It is therefore necessary to find new ways able to improve the efficiency. Intensification processes can reduce costs, increase the intrinsic safety and minimize the environmental impact, as well as enhance the efficiency (Ling et al., 2004). The Spinning Disc Reactor (SDR) is an intensification process based on the creation of a thin film. The reactor consists of a spinning disc, where the feed fluid is fed to the center top surface of the disc. In the photocatalytic SDR, the surface of the disc is coated with the photocatalyst. The feed fluid is spread out over the surface of the disc because of the centrifugal acceleration, generating a thin film of 20–200 µm (Boodhoo and Jachuck, 2000). The thin film improves the mass and heat transfer, especially in solid-liquid systems, and the penetration of UV light to the surface of the disc, which can be an advantage over other types of photoreactor systems when using coloured and/or UV light absorbing solutions, since this facilitates higher light penetration to the photocatalyst per volume of feed on the catalyst, increasing the volumetric efficiency of the reaction. Moreover, shorter retention times are needed since the efficiency is increased. Boiarkina et al. (2011) verified that the effect of the flow and the speed of the disc were important in this kind of reactor because these two parameters have a significant influence on the flow regime and therefore in the mass and heat transfer to and from the photocatalyst surface.

The behavior of the photocatalytic SDR for pollutant removal has been studied for methylene blue (Ling et al., 2004; Boiarkina et al., 2011, 2013) as a common reference pollutant and dehydroabiatic acid (Boiarkina et al., 2013), a pollutant from the paper industry.

Therefore, the aim of this paper is to study the applicability of a TiO₂ photo-degradation process to efficiently degrade a synthetic effluent containing antipyrine in a novel spinning disc reactor (SDR). We are the first to comprehensively map out the effect of the important operating parameters of the photocatalytic spinning disc reactor, by applying statistical experimental design. As this has not been done for SDRs in general, this paper is the first comprehensive assessment of the operating space for this important class of process intensification reactor. To this end, a factorial design of experiments which is a proven technique successfully used in

removal of pollutants with AOPs (Monteagudo et al., 2008b) was used changing four variables. Later, experimental results of antipyrine degradation were fitted with neural networks (NNs) since they have shown to be robust and applicable in almost all situations (Khatae and Kasiri, 2010). In addition, by analysis of reaction products liquid chromatography-mass spectroscopy (LC-MS), this paper proposes a comprehensive photocatalytic degradation pathway for antipyrine.

2. Experimental

2.1. Materials

Antipyrine (99%) was obtained from Acros. 30% hydrogen peroxide (H₂O₂) and methanol (99.8%) were purchased from Fisher Scientific and VWR-Chemical respectively and were used as received. The pH of the solution was adjusted with H₂SO₄ and NaOH.

Acetic acid (99.7%, Sigma Aldrich), acetylacetone (99%, Sigma Aldrich) and isopropanol (99.5%, Sigma Aldrich) were used for sol-gel preparation. Deionized water used for preparing solutions was obtained from a purifying machine (ELGA PURELAB). Glass discs (200 mm in diameter, 3 mm thick) were supplied by Roman Glass (Bath, UK).

2.2. Experimental set-up and procedure

The experimental setup is shown in Fig. 1. The experiments were carried out in recirculating batch mode. For the UV/H₂O₂/TiO₂ process, the solution to be treated (750 mL) is initially kept in a 1 L reservoir under constant magnetic stirring. After pH fitting, the solution is fed with a peristaltic pump (MasterFlex Easy-load II) into a tightly sealed glass flask, which avoided the flow pulsations generated in the pumping process. Then the solution is fed into the spinning disc reactor. Both the reservoir and the flask were covered with aluminum foil in order to avoid the light incidence in case some TiO₂ particles were detached from the disc. The solution is cooled with tap water with a Liebig cooler. The liquid containing AP goes into through the center of the disc where it falls down on the disc spreading out the solution. During this process, the solution is irradiated by a low pressure mercury UV lamp inside a quartz tube (20 W, monochromatic, λ = 254 nm, Steriflow, supplied by Davey Water Products NZ, part nr. GPH369N/S). The lamp is situated at the focus of a parabolic mirror in order to leverage the maximum possible radiation. The liquid is collected by a funnel beneath the disc and is returned to the reservoir by gravity.

The speed and flow were set for every experiment according to the experiment design as explained below. The lamp was switched on and the H₂O₂ was added after 20 min in the dark to allow pollutant adsorption by the TiO₂. Sodium sulfite anhydrous, Na₂SO₃ was used for quenching immediately after sampling. pH was kept constant (±0.1) during the experiments. In exceptional cases, addition of drops of sulfuric acid or sodium hydroxide were needed.

2.3. Analytical methods

The removal of antipyrine was evaluated immediately after sampling using a Gilson 231 XL high performance liquid chromatography (HPLC) system with UV detection under an isocratic mode and an Eclipse XDB-C18 column (5 µm, 4.6 × 250 mm). 60:40 (v/v) methanol/(water with 0.1% acetic acid) mixture at acidic pH was used as the mobile phase (detection wavelength, λ = 252 nm; flow rate of 0.6 mL min⁻¹).

Total organic carbon concentration was determined using a TOC analyzer (Shimadzu TOC-5000A). H₂O₂ concentration was

Download English Version:

<https://daneshyari.com/en/article/5117400>

Download Persian Version:

<https://daneshyari.com/article/5117400>

[Daneshyari.com](https://daneshyari.com)