



Contents lists available at ScienceDirect

Catalysis Today

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

Removal of the anti-inflammatory drug ibuprofen from water using homogeneous photocatalysis

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ARTICLE INFO

Article history:

Received 31 August 2013
Received in revised form 4 December 2013
Accepted 9 December 2013
Available online xxx

Keywords:

Advanced oxidation process
Photo-Fenton
Ibuprofen
Hydroxyl radicals
TOC removal

ABSTRACT

In this paper the photocatalytic degradation of the 0.2 mM ibuprofen (2-(4-(2-methylpropyl)phenyl)propanoic acid) in aqueous solution (pH 3) has been carried out by the homogeneous photocatalysis (photo-Fenton) process. This method consists of coupling Fenton's reagent and UV-C irradiation in order to catalyse the in situ generation of hydroxyl radicals, a powerful oxidizing agent which leads to degradation of organic pollutants until total mineralization. The effect of H₂O₂ and Fe³⁺ (catalyst) concentration on the TOC removal has been examined and the performances of photo-Fenton process have been also compared with other photochemical processes such as direct photolysis (UV alone) and H₂O₂ photolysis (H₂O₂/UV). The results have shown that the photo-Fenton process appeared more effective than the other systems studied and the TOC removal decreased in the sequence: photo Fenton > H₂O₂/UV > UV alone. The kinetics study showed that the TOC removal follows the second-order kinetics. It was found that the concentrations of H₂O₂ and ferric iron constitute key factors governing the TOC removal and that the optimal concentrations are equal to 10 mM of H₂O₂ and 0.25 mM Fe³⁺. In these conditions, 96% of initial TOC has been removed after 8 h of irradiation time.

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1. Introduction

The widespread use or abuse of pharmaceuticals and personal care products results in increasing quantities of these compounds in the aquatic environment. Concentration levels in the range from ng to μg dm⁻³ have been ubiquitously found in surface waters [1]. While researchers are still improving current knowledge on the possible adverse ecological and human health effect of low concentrated pharmaceuticals, other studies are devoted to develop efficient treatments to achieve the removals of these drugs from waters and wastewaters [2]. It has been demonstrated that physicochemical and biological processes are often inadequate to remove completely pharmaceuticals [3] and thus more effective powerful oxidation methods, such as advanced oxidation processes (AOPs) have to be used for their disposal.

AOP are based on the generation in situ of hydroxyl radicals (•OH) which are able to non-selectively oxidize organic pollutants up to their ultimate oxidation degree, i.e. mineralization, yielding CO₂, water and inorganic ions as final products. Many AOPs have been proposed and efficiently used for the degradation of pharmaceutical pollutants, including Fenton oxidation

[4,5], electrochemical processes [6–11], air wet oxidation [12], ozonation [13,14], photochemical oxidation [15–18] and combination of oxidants (e.g. H₂O₂/O₃; H₂O₂/UV; H₂O₂/O₃/UV, etc.) [14,19,20]. Among them photo-Fenton [21–25] process has been intensively studied and seems to be a promising process for commercial application because of its high efficiency and cost effectiveness compared with other AOPs [26,27]. In solar photo-Fenton (Fe²⁺/H₂O₂/solar radiation), hydroxyl radicals are generated by the well-known Fenton's reactions (Eq. (1)) that is catalysed by photolysis of Fe(OH)²⁺, which is the predominant Fe(III) species at pH 3 (Eq. (2)) providing supplementary •OH:



Recently UVA-photo-Fenton (Fe²⁺/H₂O₂/UVA), also called “photo-Fenton like”, process has shown to be equivalent to the classical solar-photo-Fenton system, and additional amount of •OH are also produced by photolysis of H₂O₂ (Eq. (3)) [27]:



UVC light irradiation (wavelength 280–100 nm) in photo Fenton system has not been widely studied but some promising results have been obtained [28–30]. For example, Evgenidou et al. [31] reported that methyl parathion, an organophosphorus pesticide,

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is slightly mineralized by photo-Fenton with UVA light irradiation (wavelength 400–315 nm), while Diagne et al. [32] demonstrated that the use of UV-C lamp enhances the degradation of methyl parathion.

Ibuprofen (2-(4-(2-methylpropyl)phenyl)propanoic acid) is a nonsteroidal anti-inflammatory drug (NSAID) of the propionic acid and it is one of the most worldwide consumed drugs, and concentration of ibuprofen below $10 \mu\text{g dm}^{-3}$ has been detected in river waters [33–35]. Thus many researches have been performed on the degradation of ibuprofen, including electrochemical oxidation [36–38], ozonation [39,40], UVA irradiation and solar photoelectro-Fenton [41], combination of oxidants $\text{O}_3/\text{H}_2\text{O}_2$ [42], thermal decomposition treatments [43] and also photo Fenton [44]. For example, Zwiener et al. [42] observed that simple ozonation was ineffective to remove ibuprofen (i.e. 12% of degradation efficiency) while the application of AOP $\text{O}_3/\text{H}_2\text{O}_2$ [38] almost quantitatively degraded the drugs (i.e. 99.4%).

We recently reported on the electrochemical abatement of ibuprofen from aqueous solution by anodic oxidation using a Pt or thin-film boron-doped diamond (BDD) anode [37]. The results have shown that ibuprofen has been mineralized in all the conditions tested; however, BDD enables higher removal rates than Pt, because the former produces greater quantity of $\cdot\text{OH}$. The degradation of ibuprofen has also been comparatively studied by electro-Fenton, UVA and solar photoelectro-Fenton by Skuomal et al. [41], and they obtained that the most potent method is solar photoelectro-Fenton. On the other hand, Méndez-Arriaga et al. [44] investigated the degradation of ibuprofen by UVA photo-Fenton using a solar artificial irradiation. After 2 h of irradiation a complete depletion of ibuprofen was observed but TOC removal was only 40% meaning that many refractory by-products are formed.

The degradation of ibuprofen by photo-Fenton under UV-C irradiation has not yet reported, and thus the aim of this work were to study the degradation of a synthetic solution of ibuprofen, taken as model drug, by UV-C photo-Fenton process. The effect of some operating parameters such as iron catalyst and H_2O_2 concentration was explored.

2. Experimental

2.1. Chemicals

Ibuprofen 2-(4-(2-methylpropyl)phenyl)propanoic acid ($\text{C}_{13}\text{H}_{18}\text{O}_2$) was purchased in the reagent purity available from Sigma-Aldrich and was used without further purification. Pentahydrated ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$) used as ferric iron ions (catalyst) source was analytical grade from Fluka. Deionized water used for the preparation of solutions was obtained from a Millipore Milli RO6 system, with resistivity $> 18 \text{ M}\Omega \text{ cm}$. Sulfuric acid used for pH adjustment were supplied by VWR International. H_2O_2 (30%, ACS reagent quality) was supplied by Sigma-Aldrich.

2.2. Photoreactor

Photo-Fenton, water photolysis and H_2O_2 photolysis experiments were carried out at room temperature in batch Pyrex photoreactor of 1.3 L useful volume that is schematized in Fig. 1 and described in more details in a previous publication [32].

The reactor was equipped with a hollow cylindrical quartz tube and a 40 W low-pressure mercury lamp from Heraeus Noblelight GmbH (Germany) emitting at 253.7 nm. The UV-lamp nominal power was 12 W, and the photon flow entering the reactor was $11.2 \times 10^{-6} \text{ Einstein s}^{-1}$. The vessel was covered with aluminium foil. The reaction mixture which set initially to pH 3 was continuously pumped through the photoreactor with a peristaltic

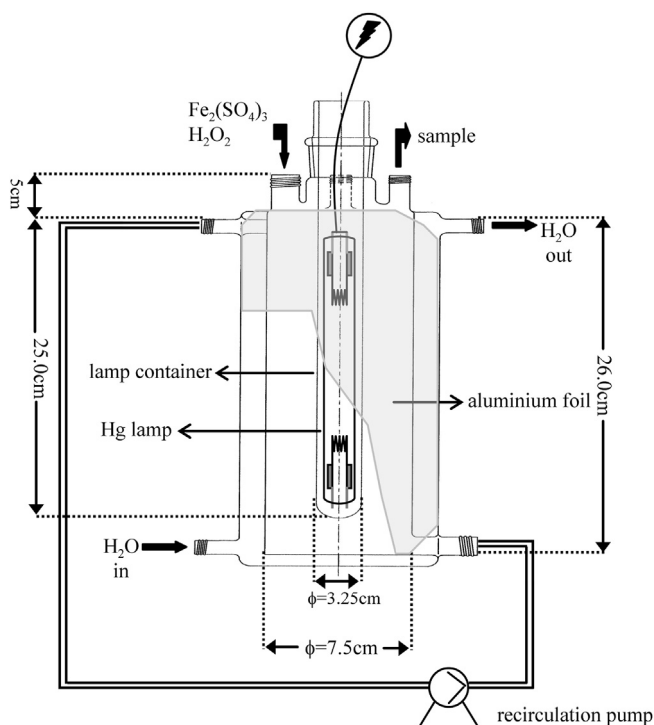


Fig. 1. Schematic representation of the photochemical flow reactor. Reprinted from Diagne et al. [32].

pump (Heidolph, type 523.030) by means of PTFE tubing at a flow rate of 3 L min^{-1} . The cooling water was circulated through a Pyrex jacket surrounding the reactor allowed maintaining the reaction solution at room temperature. Two top orifices in the reactor allowed the introduction of reagents as well as the sampling at selected times. Zero time corresponded to the instant when the lamp was switched on. The value of incident photon flux, $I_0 = 4.14 \times 10^{-7} \text{ Einstein L}^{-1} \text{ s}^{-1}$ was calculated on the basis of the ferrioxalate actinometry measurements [45]. The apparent quantum yield (ϕ_{app}) was determined by chemical actinometry using potassium ferrioxalate system giving the value of $\phi_{\text{app}} = 0.25$. The quantum yield of photochemical reactions mainly depends upon the characteristics of the photo-reactor used. Thus the ϕ_{app} values found for our photoreactor are significantly higher than that of 0.0125 [46] and 0.05 [47].

Aqueous solutions of 0.20 mM (40.25 mg L^{-1}) of ibuprofen were studied with several concentrations of ferric ions and hydrogen peroxide. The solution pH was fixed to 3, since much higher pH values hamper the development of Fenton-based systems due to the $\text{Fe}(\text{OH})_3$ precipitation, which lead to both the decrease of dissolved iron ion [48]. The solution pH was measured with a CyberScan pH 1500 pH-metre from Eutech Instruments.

2.3. Analytical procedures

The degradation of ibuprofen during photochemical AOPs was monitored by following the mineralization kinetics, i.e. its transformation to CO_2 and H_2O , in terms of TOC removal. The mineralization of the Ibuprofen solutions was assessed from the decay of their dissolved organic carbon, which can be considered as the total organic carbon (TOC) when treating highly water soluble organic compounds such as ibuprofen. The TOC values were determined on a Shimadzu VCSH TOC analyser. Samples withdrawn from the treated solution at different electrolysis times were microfiltered onto a hydrophilic membrane (Millex-GV Millipore, pore size

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