



## Degradation of ibuprofen by hydrodynamic cavitation: Reaction pathways and effect of operational parameters



Dino Musmarra<sup>a</sup>, Marina Prisciandaro<sup>b,\*</sup>, Mauro Capocelli<sup>c</sup>, Despina Karatza<sup>a</sup>, Pasquale Iovino<sup>d</sup>, Silvana Canzano<sup>d</sup>, Amedeo Lancia<sup>e</sup>

<sup>a</sup> Dipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, Seconda Università degli Studi di Napoli, Real Casa dell'Annunziata, Via Roma 29, 81031 Aversa (CE), Italy

<sup>b</sup> Dipartimento di Ingegneria Industriale e dell'Informazione e di Economia, Università dell'Aquila, viale Giovanni Gronchi 18, 67100 L'Aquila, Italy

<sup>c</sup> Facoltà di Ingegneria, Università Campus Bio-Medico, Via Alvaro del Portillo, 21, 00128 Roma, Italy

<sup>d</sup> Dipartimento di Scienze e Tecnologie Ambientali, Biologiche e Farmaceutiche, Seconda Università degli Studi di Napoli, Via Vivaldi, 43, 81100 Caserta, Italy

<sup>e</sup> Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università "Federico II" di Napoli, Piazzale V. Tecchio, 80, 80125 Napoli, Italy

### ARTICLE INFO

#### Article history:

Received 2 May 2015

Received in revised form 8 August 2015

Accepted 3 September 2015

Available online 5 September 2015

#### Keywords:

Emerging contaminants

Ibuprofen

Reaction mechanism

Venturi reactor

Modeling

Intermediates

### ABSTRACT

Ibuprofen (IBP) is an anti-inflammatory drug whose residues can be found worldwide in natural water bodies resulting in harmful effects to aquatic species even at low concentrations. This paper deals with the degradation of IBP in water by hydrodynamic cavitation in a convergent–divergent nozzle. Over 60% of ibuprofen was degraded in 60 min with an electrical energy per order ( $E_{EO}$ ) of  $10.77 \text{ kWh m}^{-3}$  at an initial concentration of  $200 \mu\text{g L}^{-1}$  and a relative inlet pressure  $p_{in} = 0.35 \text{ MPa}$ . Five intermediates generated from different hydroxylation reactions were identified; the potential mechanisms of degradation were sketched and discussed. The reaction pathways recognized are in line with the relevant literature, both experimental and theoretical. By varying the pressure upstream the constriction, different degradation rates were observed. This effect was discussed according to a numerical simulation of the hydroxyl radical production identifying a clear correspondence between the maximum kinetic constant  $k_{OH}$  and the maximum calculated  $\cdot\text{OH}$  production. Furthermore, in the investigated experimental conditions, the pH parameter was found not to affect the extent of degradation; this peculiar feature agrees with a recently published kinetic insight and has been explained in the light of the intermediates of the different reaction pathways.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The pollution of the aquatic environment has received increasing attention over the last decades because of the presence of emerging compounds (EC), only recently quantified thanks to the development of new analytical techniques [1,2]. These compounds are xenobiotic and bioactive chemicals such as surfactants, pharmaceuticals, endocrine disruptors and illegal drugs that, even at small concentrations, can affect water quality and are potentially harmful for the ecosystem and human health [2]. They reach the environment via the discharge of personal hygiene products, industrial (mainly pharmaceutical) and hospital wastes and medications. Currently, it is estimated that more than 3000 different pharmaceutical compounds are used in the European Union and many of them are susceptible to reach the water cycle [3]. Despite the unpredictable negative impact of these compounds on the

environment and human health, at present there is no regulation limiting their concentrations in water streams. Based on the precaution principle, every four years the Environmental European Agency updates the list of priority substances where pharmaceuticals are included as potential pollutants. The EU Water Framework Directive EEA 2013 [4] recognizes pharmaceuticals as a potential risk for the aquatic environment in Europe and states that the Commission shall develop a strategic approach to monitor and regulate this kind of pollution as far as possible.

The compound 2-[3-(2-methylpropyl)phenyl] propanoic acid, marketed as ibuprofen (IBP, CAS number: 79261-49-7), is a Non-Steroidal Anti-Inflammatory Drug (NSAID) (available for over-the-counter sale) used in the treatment of rheumatic disorders, fever, migraine, muscle aches, arthritis and tooth aches. The main sources of environmental IBP contamination include industrial discharges, excretory products of medically treated humans and animals and the improper disposal of unused medications via the toilet [5]. As many other contaminants, its fate in the aquatic environment depends on biodegradability and physicochemical

\* Corresponding author.

E-mail address: [marina.prisciandaro@univaq.it](mailto:marina.prisciandaro@univaq.it) (M. Prisciandaro).

properties such as solubility in water, octanol–water and organic carbon–water partitioning coefficient [6]: natural attenuation phenomena mainly include sorption on soils or sediments, sunlight photolysis, and other abiotic transformations (i.e. hydrolysis) [7].

The conventional wastewater treatment plants (WWTP) do not seem to effectively remove the IBP from effluents. Some recent studies demonstrate that the conventional treatments, mainly based on the use of microorganisms, are inadequate to effectively destroy these organic compounds with a complex molecular structure and low concentrations [1]. For this reason, IBP can be found in sewage influents, effluent samples and, consequently, in several surface waters located downstream municipal WWTPs [8–12]. IBP, as other micropollutants, can be removed by membrane filtration or adsorption onto activated carbon; however, these two methods can be inhibited by the natural organic matter present in water, that also affects the fouling potential of the membranes or competes for adsorption. Although there have been numerous studies on the adsorption of aromatic compounds in aqueous solutions, the governing mechanisms must still be established to enhance the effectiveness of the process that still suffers from desorption- and regeneration-related issues [13–15]. IBP is also very resistant towards ozonation techniques [16]. For these reasons, new effective EC degradation techniques, known as Advanced Oxidation Processes (AOPs), are currently being studied. They are based on the generation of the hydroxyl radicals. OH-radicals are very reactive and non-selective species, able to react very rapidly with almost every organic substance. The AOPs include, among others, Fenton-like processes, direct ultraviolet photolysis, cavitation, photocatalysis, ozone-based hybrid processes, electro-oxidation and cavitation processes [17].

Cavitation is the formation, growth and subsequent collapse of microbubbles in a solvent with the consequent release of large magnitudes of energy per unit volume over an extremely short interval of time ( $10^{-3}$  ms), resulting in local high pressures (10–500 MPa) and temperatures (1000–10,000 K). The collapses also result in the formation of highly reactive free radicals, the continuous surface and interface cleaning as well as the enhancement of mass transfer rates due to generated turbulence [18]. The phenomenon takes place because of a pressure variation due to the presence of a constriction, designed ad hoc, or to ultrasound waves and is nowadays considered an innovative means to enhance different chemical processes [19]. In the field of pharmaceutical wastewater treatment, the application of ultrasounds was the first to be studied and is widely described in literature [6,20–23]. It shows promising results (also for IBP degradation) particularly if combined with other AOPs: sonophotocatalytic degradation in the presence of homogeneous ( $\text{Fe}^{3+}$ ) and heterogeneous photocatalysts ( $\text{TiO}_2$ ) [10,24].

Hydrodynamic cavitation (HC) has been recently considered as an interesting opportunity to rule out the issue of the high-energy consumption of ultrasounds. Moreover, HC can be considered a sustainable, reliable and easy-to-handle technique. Several papers prove the applicability of HC in degrading emerging organic pollutants [25,26]. Its combination with a chemical AOP seems to have major synergistic effects also in the treatment of pharmaceutical micropollutants, besides the excellent results in terms of power consumption and cost-effective system up-scaling. The most recent research works aim at extending degradation by introducing additional oxidants. Particularly in the case of non-VOC and hydrophilic substances, it is common opinion that, in industrial WWT, the cavitation has to be coupled in hybrid AOP solutions (e.g. with  $\text{H}_2\text{O}_2$ , UV, Fenton). Bagal and Gogate [27] studied the degradation of diclofenac by optimizing a HC hybrid technique (95% degradation using UV/ $\text{TiO}_2$ / $\text{H}_2\text{O}_2$  and hydrodynamic cavitation in a Venturi nozzle at 3 bar and pH 4). It is also worth

mentioning the work carried out by researchers from the University of Ljubljana who investigated the use of shear-induced cavitation for hybrid HC/AOP [28,29]. They obtained promising results in degrading four different pharmaceuticals in a roto-cavitating apparatus with the addition of  $\text{H}_2\text{O}_2$ . They also achieved very high efficiency with the combination of biological treatment, UV and HC/ $\text{H}_2\text{O}_2$  for similar pharmaceutical effluents [30] demonstrating how it is possible to transpose research findings into a directly employable large-scale wastewater treatment and encouraging the research in this field.

The patented Dynajet apparatus is the only example of industrial application of stand-alone HC that is effective in the degradation of a mixture of pharmaceuticals and personal care products; it has also shown that the overall degradation extent for different compounds increases linearly with the logKow while the pressure has a non-linear effect on the kinetics [31]. As long as cavitation alone is not ready to solve the issue of EC degradation, in our opinion it is important to keep performing stand-alone and cavitation experiments and to investigate its phenomenology by coupling the experiments with numerical simulations and by analyzing the degradation mechanisms. To this purpose, our paper is part of a wider study carried out by our research group focused on the experimental and theoretical insight of HC as an advanced oxidation process [25,32]. Hereby we present the experimental results on the degradation of IBP through hydrodynamic cavitation in a convergent–divergent nozzle reactor. The effects of inlet pressure and pH are addressed and discussed by referring to a consolidated mathematical model [32] as well as other relevant literature. The identification of different reaction intermediates in this work, allowed the investigation of the reaction kinetics and the identification of a possible mechanism of degradation that, in the light of a thermodynamic insight and other experimental evidences, might explain the peculiar the pH effect observed.

## 2. Experimental

### 2.1. Apparatus

Fig. 1 depicts the experimental setup. It consists of a closed-loop reactor comprising a holding tank of 1.5 L volume with a cooling system and two pipelines: the main line consists in the reactor provided with two pressure gauges measuring the inlet pressure ( $p_1$ ) and the fully recovered downstream pressure ( $p_2$ ); the second one is used to recirculate the solution bypassing the reactor. The dimensions of the nozzle are shown in Fig. 2. Two control valves regulate the gauge pressure and the flow rate ( $p_1 = 0.20$ – $0.65$  MPa;  $Q = 0.2$ – $0.4$   $\text{m}^3 \text{h}^{-1}$ ) in the main line; the inside diameter of both the main and the by-pass lines is 12 mm while the constriction diameter is 2 mm. Further details can be found in Capocelli et al. [24]. The IBP initial concentration was 200  $\mu\text{g/L}$ , the initial pH was varied in the range 2–9; the temperature was kept during the experiments below the limit of  $T_w = 25$  °C. During testing, 1 ml samples were drawn from the test reservoir and analyzed as described in the next section.

### 2.2. Materials and methods

An ibuprofen sodium salt of analytical grade with purity higher than 98% purchased from Sigma–Aldrich (UK) was used for the experimental activities. The analytical measurement of the total IBP in solution was performed by Gas-Chromatography coupled with Mass Spectrometry (GC/MS) after a solid phase extraction (SPE) step. The SPE step consists in the isolation of the pharmaceuticals from the water samples through a

Download English Version:

<https://daneshyari.com/en/article/1265855>

Download Persian Version:

<https://daneshyari.com/article/1265855>

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