



Catalytic ozonation of ibuprofen with ultrasound and Fe-based catalysts



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ABSTRACT

The study is about a novel method of decomposing and mineralizing the emerging contaminant ibuprofen (IBP) by catalytic ozonation using catalysts such as high-frequency ultrasound (US) and soluble/insoluble Fe-bearing species. Preliminary experiments with single processes were run to select the optimum values of IBP concentration, O_3 flow rate and specific US power as $50 \mu\text{M}$, 12 mg min^{-1} , and 0.23 W mL^{-1} , respectively. It was found that the most critical operation parameter was pH, as it controlled the mass transfer and decomposition of O_3 , as well as the diffusion of solutes from the bulk solution to the gas–liquid and solid–liquid interfaces. As such, ozonation and sonication alone were most effective at pH 9.0 and 3.0, respectively owing to the higher rate of $\cdot\text{OH}$ production and gas–liquid interfacial reactions at these conditions. Catalytic ozonation with Fe-bearing species but no ultrasound was most effective at pH 6.5, with a maximum degree of IBP decay in the presence of FeSO_4 . Catalytic ozonation with ultrasound and solid particles was effective at pH 6.5, but maximum degree of oxidation/mineralization was obtained with nanoparticles of zero-valent iron (ZVI) at pH 3.0 (100%, 58%). The synergy of US+ZVI at acidic pH was attributed to: (i) the massive surface areas enriched with extensive reaction and nucleation sites, (ii) the role of reactive Fe (furnishing out from the metal core onto the catalyst surface) and reactive oxygen species as promoters of Fenton-like reactions, and (iii) the contribution of hydrodynamic shear forces to continuous enhancement and cleaning of the catalytic surfaces.

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1. Introduction

Non-steroidal anti-inflammatory drugs (NSAIDs) with more than 70 million global prescriptions annually are a special group of pharmaceuticals that exhibit “persistent toxic waste” character [1,2]. One of the most important members of this group is ibuprofen (IBP), which is readily discharged with urine to sewage treatment facilities with partial degradation resulting in final concentrations of $0.002\text{--}24.6 \mu\text{g L}^{-1}$ in treated sewage effluents [3]. As such, the compound is transferred to natural waters, where it is recognized with biochemical activity and moderate toxicity even at very small concentrations [4–6]. This is why IBP is listed under “emerging contaminants” in the “Water Frame Directive” [7] and must therefore be totally eliminated to prevent its transport into water distribution networks.

Advanced Oxidation Processes (AOPs) have so far emerged as promising solutions to the elimination of refractory micropollutants in water [8,9]. There are several studies in the literature

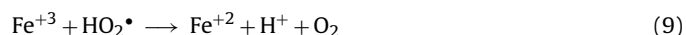
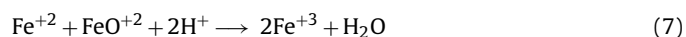
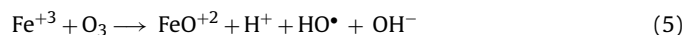
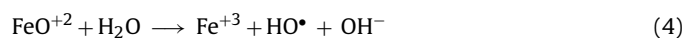
reporting the degradation of IBP by AOPs such as ozonation, photocatalytic oxidation, photo-Fenton, sonocatalysis and sono-photo catalysis [2,4–12]. These studies have revealed that elimination of IBP is generally possible by adjusting the ambient conditions and selecting the right dose of the additives; however mineralization required very long contact times. Some of them have also reported the oxidation byproducts, particularly the formation of mono- and de-hydroxylated derivatives [10,12]. Two of these studies contain comments on the toxicity of the oxidation byproducts and the increase in toxicity with increasing reaction time and ozone flow rates [10,13].

Catalytic ozonation is a modified AOP technology, whereby the rate of ozonation is accelerated by the addition of active metallic catalysts, which also lead to a reduction in the operation cost despite the additional cost of catalyst separation. A similar argument can be found in the literature on the cost efficiency of catalytic ozonation [14]. The process can be operated heterogeneously via complex formation between the organic compound and catalyst; or homogeneously with the decomposition of ozone by active metal species [15]. The governing mechanism of the heterogeneous process is “chemisorption” of ozone, organics or both on the catalyst surface leading to the formation of active oxidizing species and

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redox reactions, the efficiency being dictated by the type and surface properties of the catalyst and the operation pH [15].

Among a wide variety of heterogeneous catalysts to enhance the rate of ozonation of organic compounds, Fe-bearing minerals have been found highly effective [16–19]. A simplified reaction scheme that describes $O_3/Fe(II)/Fe(III)$ heterogeneous system is given in Eqs. (1)–(9) showing the formation of ozonide, superoxide and hydroxyl radicals, all of which were more reactive than ozone with the test contaminants [14,20–22]:



Ultrasonication (US) is also an advanced oxidation technology, whereby very reactive species including the hydroxyl radical are produced by thermal fragmentation of water molecules and organic solutes via the implosive collapse of gaseous cavity bubbles [23]. Recombination of HO^{\bullet} produces H_2O_2 , which in the presence of Fe-like species facilitates Fenton-like reactions. Additionally, ultrasound is recognized with its unique properties for enhancing the mass transfer rates of solutes and improving surface properties of solid particles, thus acting as a ubiquitous catalyst in aqueous reaction systems [24,25]. As such, sonolysis has received considerable attention during the last decade for the complete destruction of color and a large range of recalcitrant compounds, but with insufficient efficiency for carbon mineralization [2,26–33]. This is why recent research with ultrasound has particularly focused on hybrid techniques such as US/O_3 , US/UV , $US/Fenton$ and $US/solids$ with the aim of enhancing the degree of mineralization [34–42]. The O_3/US application has received considerable attention due to the advantages obtained by enhanced rate of ozone mass transfer and the thermal decomposition of the gas inside the collapsing cavity bubbles to generate additional reactive species [27,43].

There are only three studies in the literature related to the catalytic ozonation of IBP, but they all involve heterogeneous catalysis with MnO_2 , Goethite or bio-solids obtained from activated sludge [44–46]. The current study, therefore, has aimed to investigate the effects of some novel catalysts such as ultrasonic irradiation and a variety of homogeneous/heterogeneous Fe-bearing species on ozonation of IBP. The processes were compared at their optimized conditions for their relative efficiencies in accelerating the oxidation and mineralization of IBP during 1-h ozonation.

2. Materials and methods

Ibuprofen was purchased from Sigma with >98% purity and used as received. The chemical structure and some of its environmental properties that are of significance are as given [47,48]:

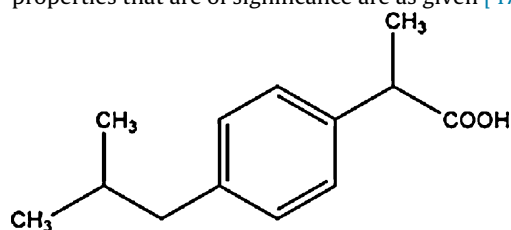


Table 1
The catalysts and their properties.

Catalyst	Type	Label	Relative size range
Fe(OH)O (35%)	Insoluble	Goethite	Micro-(0.08–1.74 μm)
Fe ₂ O ₃ (>99%)	Insoluble	Hematite	Micro-(<5 μm)
Fe ₃ O ₄ (98%)	Insoluble	Magnetite	Nano-(10 nm)
Ni-Fe ₂ O ₄ (98%)	Insoluble	Ni-supp. Ox.	Nano-(<50 nm)
Zero valent iron (I)	Insoluble	ZVI	Micro-(45–150 μm)
Zero valent iron (II)	Insoluble	ZVI-graphite	Nano-(20–100 nm)
FeCl ₃ ·6H ₂ O	Soluble	Chloride	
FeSO ₄ ·7H ₂ O	Soluble	Sulfate	

MW: 206.3 g mol⁻¹; solubility: 21 mg L⁻¹; pKa (20 °C): 3.5–4.9; log Kow: 2.5–4.0.

Fresh test samples of IBP were prepared by dissolving the compound in proper volumes of ultrapure water (Mili-Q) at 45 °C during magnetic stirring. HPLC grade acetonitrile, H₃PO₄, reagent grade NaOH, H₂SO₄, KHP, NaH₂PO₄ were all obtained from Merck, Istanbul. Potassium indigo tri-sulfonate used for analyzing the residual ozone in the samples was obtained from Sigma, Istanbul.

The catalysts, their commercial or given names and particle properties of the solid forms are listed in Table 1. Note that we used two different zero-valent iron species: the first one (ZVI) was purchased from Hepure (USA) in micro-size and the second one (ZVI-graphite) was synthesized in Kanbar Laboratory for Nano-materials at Bar-Ilan University, Israel [49,50]. All the rest were purchased from Sigma–Aldrich, Istanbul.

2.1. Experimental

Preliminary experiments with ozone alone were carried out in 250 mL glass chambers to estimate the ozone mass transfer coefficient at varying pH levels (3.0, 6.5 and 9.0) and ozone flow rates (3, 6 and 12 mg min⁻¹, corresponding to inlet concentrations of 2, 4 and 8 g m⁻³, respectively). Ozone was generated onsite using an Ozonelab-100 Model generator and dry pure oxygen flowing at 1.5 L min⁻¹. Single experiments with solid catalysts alone were carried out at pH 3.0 and 6.5 to assess the degree of IBP adsorption and the extent of solids leaching into the sample solutions, using A Julabo SW22 shaker. The concentration of IBP, the mixing rate and the contact time were 50 μM , 250 rpm and 24 h, respectively. The catalyst dose in each test was adjusted so as to maintain 5 mg L⁻¹ Fe in all samples.

Catalytic experiments with Fe-bearing species were run with 50 μM IBP (10 mg L⁻¹) and 5 mg L⁻¹ Fe-equivalent of each catalyst during a gas flow rate of 12 mg min⁻¹ for 1-h at pH 6.5 unless stated otherwise. The experiments with ultrasound were carried out in a high-frequency plate-type ultrasonic reactor (500 mL) equipped with a 120 W generator (operated at 90% of capacity) and a piezo-electric transducer (22 cm²) emitting 861 kHz (Ultraschall-Meinhardt, Germany). The reactor was operated at a specific power of 0.23 W mL⁻¹ (as determined by calorimetry), cooled by circulating water to maintain constant temperature (20 ± 0.5 °C), and occupied by a sample volume of 250 mL. The flow rate of O₃ into the reactor was 12 mg min⁻¹ throughout the reaction time. A schematic diagram of the experimental system is presented in Fig. 1.

2.2. Analytical

IBP was analyzed by HPLC using a Shimadzu LC-20AT HPLC with a 20A UV-Vis photo diode array detector set at 220 nm, and equipped with Inertsil ODS-3 V (C18) (Hypersil BDS), 250 mm × 4.6 mm, 5 μm particle size column. The mobile phase consisted of 75:25 acetonitrile and 0.1% phosphoric acid flowing at 0.8 mL min⁻¹. Sample injection volume and retention time were 10 μL and 4.7 min, respectively. The aqueous iron concentration

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