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Degradation of pharmaceutical diclofenac and ibuprofen in aqueous solution, a direct comparison of ozonation, photocatalysis, and non-thermal plasma

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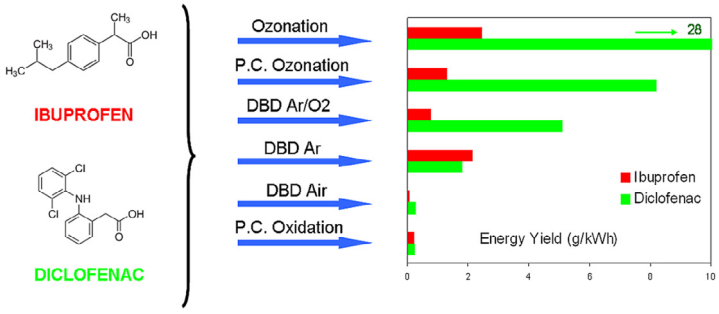
HIGHLIGHTS

- Comparable planar falling film reactors used to compare efficiency of various AOPs.
- Ozonation provides high energetic yield but low mineralization.
- Photocatalytic ozonation results in high energetic yield and high mineralization.
- DBD plasma in argon is effective and the addition of O_2 provides good mineralization.
- Each contaminating compound requires comparative studies of AOPs before realization.

GRAPHICAL ABSTRACT



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ABSTRACT

Ozonation and different advanced oxidation processes (AOPs) such as photocatalytic ozonation, photocatalytic oxidation and non-thermal dielectric barrier discharge (DBD) have been examined for the degradation of the non-steroidal anti-inflammatory drugs (NSAIDs) diclofenac (DCF) and ibuprofen (IBP) in aqueous solution. To enable a direct comparison of the efficiencies of the mentioned methods, a planar falling film reactor with common design has been used.

The results show that the degradation of both pharmaceuticals by photocatalytic oxidation is only moderate. Direct ozonation in darkness, however, is very effective for the degradation of DCF and possesses the highest energy yield of 28 g/kW h. Degradation of IBP by ozonation is slower than that of DCF and the estimated energy yield is 2.5 g/kW h. Ozonation results, however, in poor mineralization even after 90 min treatment. Combination of ozonation with photocatalysis, causes a synergetic effect for the degradation of IBP and the mineralization rate is enhanced for both pharmaceuticals. The degradation by DBD plasma depends on the gas atmosphere and the input energy. The effect of various gas atmospheres and input energies on the generation of hydrogen peroxide as well as on the degradation of DCF and IBP was investigated. The addition of Fe^{2+} to the solution improves the degradation efficiency of DBD in an argon atmosphere due to the Fenton reaction.

The mineralization efficiency of each oxidation methods was followed by the total organic carbon (TOC) removal. The highest TOC removal was obtained by photocatalytic ozonation and by DBD plasma in an Ar/O_2 atmosphere.

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1. Introduction

Among the large number of various organic pollutants that may enter into the water resources, pharmaceutical residues in surface and ground waters have been a major environmental concern [1–3]. Since the use of these pharmaceutical products cannot be controlled or eliminated, due to the population growth, their release into the environment has to be optimized and limited, as it may cause risks to human health, climate and aquatic environments. Many pharmaceutical residues are non-biodegradable and resistant against conventional wastewater treatments [1–3]. Diclofenac and ibuprofen are typical representatives of analgesic non-steroidal anti-inflammatory pharmaceutical compounds (NSAIDs) that have been recently detected in the aquatic environment at trace concentrations (ng to μg/L) [4,5]. This is one of the reason that diclofenac (including 17-beta-estradiol (E2), 17-alpha-ethinylestradiol (EE2), Estrone (E1) and three macrolide antibiotics) was now included in EU First Watch List for emerging water pollutants [6]. The ecotoxicity of NSAIDs such as DCF alone is relatively low, but prolonged exposure to environmentally relevant concentrations or to combinations of various NSAIDs present in water, increases the toxicity considerably and has a negative effect on aquatic life [6,7].

Various advanced oxidation processes (AOPs) have been reported in the literature for the degradation and removal of residual pharmaceuticals from aqueous solution. These methods involve the generation of active, unstable and non-selective oxidizing species like hydroxyl radicals that may oxidize most of the organic pollutants present in water. They are successful and promising methods for the removal of pharmaceutical pollutants found in water bodies [8,9].

Degradation of DCF was investigated in several reports using sonolysis [10,11], ozonation [13,14], and their combined application [14,15]. Removal of DCF was also reported by electron beam technology [16], UV/H_2O_2 [17], Fenton and photo-Fenton oxidation [18–20], photolysis and photocatalytic degradation [21–26], photocatalytic ozonation [27], pulsed corona [28] and dielectric barrier discharge [29].

IBP has already been treated by several oxidation processes including photolysis [30], ozonation [31], electron beam irradiation [32], sonolysis and sonocatalytic degradation [33,34], Fenton and photo-Fenton oxidation [35,36], and non-thermal plasma [37–40].

Most studies on degradation and removal of pharmaceutical pollutants reported in the literature has been focused on the application of only one AOP method using a specific experimental setup, thus a comparative observation of the results is doubtful. Therefore, the main objective of the present work is the direct comparison of degradation efficiencies and energy yields for the decomposition of DCF and IBP in aqueous solution obtained by different methods, including ozonation, photocatalysis and non-thermal DBD-plasma using a planar falling film reactor with a common design. Besides the removal of DCF and IBP, special attention was paid to the degree of mineralization and the formation of byproducts. In fact, this is generally an important aspect because some of the by-products might be more toxic and carcinogenic than the initial pollutant [33,41]. Hence, a maximum mineralization of the pollutants is necessary before releasing them into the ecosystem.

2. Materials and methods

2.1. Materials

All chemicals used in this work were of analytical grade. Diclofenac and ibuprofen sodium salts were obtained from Alfa Aesar (purity > 98.5% Germany) and Fluka (>98% GC) respectively. Oxalic acid (99.5% Merck), sodium chloride (>99.5% Merck), sodium thiosulfate (>99% Fluka), potassium nitrate (99% Merck), potassium titanium oxide oxalate (⩾90% Sigma-Aldrich), maleic acid (>99% Merck), manolic acid (99% abcr), succinic acid (>99% Fluka), liquid hydrogen peroxide (30% GR Merck), sodium carbonate and bicarbonate for ion chromatography (0.1 M Fluka), acetonitrile for HPLC (⩾99.9% Chemsolute), glacial acetic acid (amresco), and H_2SO_4 (95–97% Merck) were used.

2.2. Reactors and equipments

The planar falling film reactor used in the present work is shown in Fig. 1. The design of the reactor is based on our previous

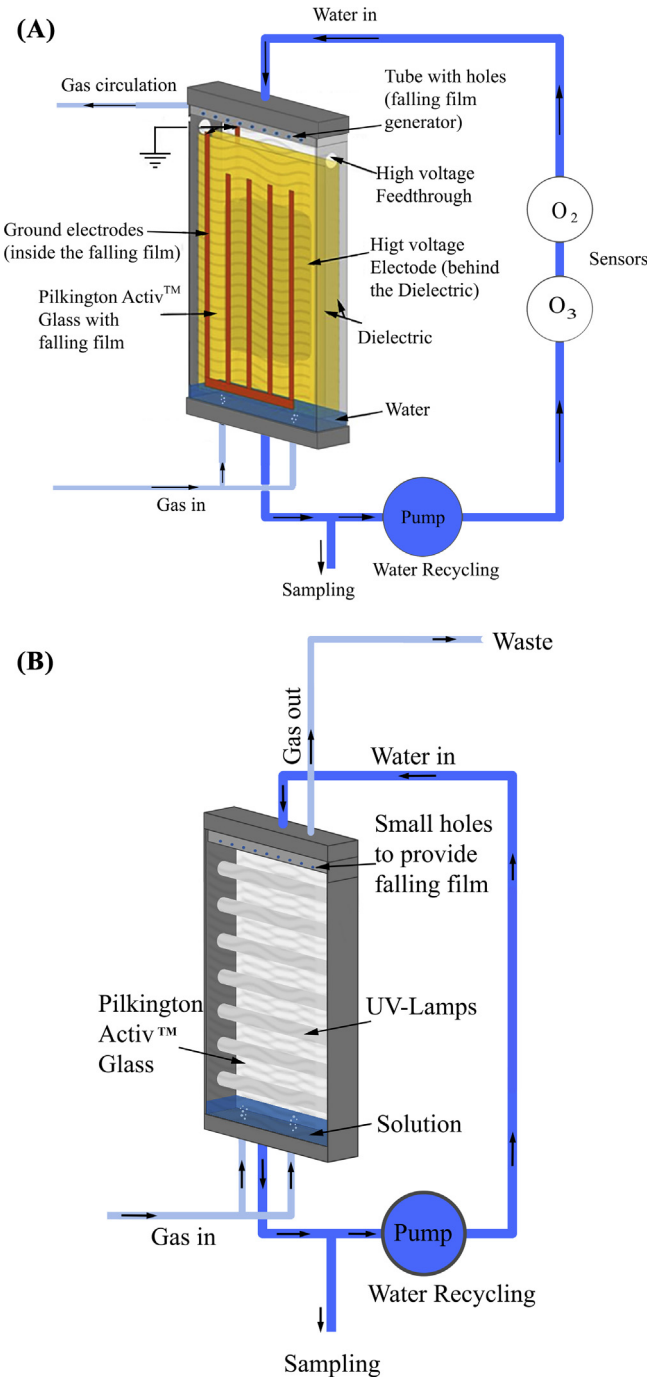

Fig. 1. (A) DBD reactor (top) and (B) photocatalytic reactor (bottom).