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Degradation of pharmaceutical contaminant ibuprofen in aqueous solution by cylindrical wetted-wall corona discharge

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HIGHLIGHTS

- Non-thermal plasma technology was firstly applied to treat ibuprofen wastewater.
- Reaction order and kinetics of ibuprofen degradation are investigated.
- The byproducts are evaluated and possible pathway of IBP degradation is proposed.

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ABSTRACT

Non-thermal plasma in cylindrical wetted-wall reactor was used to evaluate the degradation feasibility of non-steroidal anti-inflammatory drug ibuprofen (IBP) in aqueous solution and the corresponding kinetics were investigated. The influences of initial concentration and pulse repetition rate were studied. After 80 min plasma treatment, 91.7% removal of IBP was achieved and the degradation yield was 6.9 g/kW h for the initial concentration of 60 mg/l. The decomposition of IBP was in accordance with the first order reaction and the rate constant was $30.3 \times 10^{-3}\ min^{-1}$. Degradation byproducts during plasma treatment were obtained by HPLC–MS and the possible degradation pathway was proposed. The total organic carbon (TOC) in the residual solution remained high although IBP was almost completely degraded. However, the high biodegradable index (BOD_5/COD) indicated that it can be further degraded by the biological treatment.

1. Introduction

The release of the pharmaceutical drugs in water has received the increasing attention due to their wide usage and adverse effects on the botany and fauna [1]. Non-steroidal anti-inflammatory drugs (NSAIDs), one of the analgesic drugs, are the most consumed medications all over the world [2]. The wastewater with NSAIDs is derived from its production, unused medicine disposal and human and animal medical care [3]. In particular, the 2-[3-2(methylpropyl)phenyl] propanoic acid, known as ibuprofen (IBP), is regarded as one of the most used NSAIDs. In some countries, such as Finland, Spain and Sweden, IBP is the most popular drug for pain relief [4]. The production per year exceeds 15,000 tons in the world which is around one-third of the use of aspirin [5]. IBP is a persistent pollutant because it cannot be completely eliminated during wastewater treatment which usually inhibited biological degradation. Thus, it is an emerging issue to remove IBP effectively from wastewaters before discharging them.

Various advanced oxidation processes (AOPs) which are based on the generation of the hydroxyl radicals have been studied for water or wastewater treatment in recent years. The hydroxyl radical is the second strongest oxidizing species known after fluorine, and it can be able to non-selectively react with the organic pollutants. For the removal of IBP in water, advanced oxidation processes, such as photo-Fenton [6–8], photoelectron-Fenton [9], photolysis [10,11], TiO_2 photocatalysis [12,13], heated persulfate catalysis [14], ozonation [15,16] and sonochemistry [17] have been investigated. Though the AOPs mentioned above may be effective in the degradation of IBP, they require high energy consumptions and need subsequent separation of the catalysts. To solve these problems, the feasibility of non-thermal plasma is to be investigated.

Non-thermal plasma (NTP) generated by high voltage electrical discharge has also been an alternative approach for water

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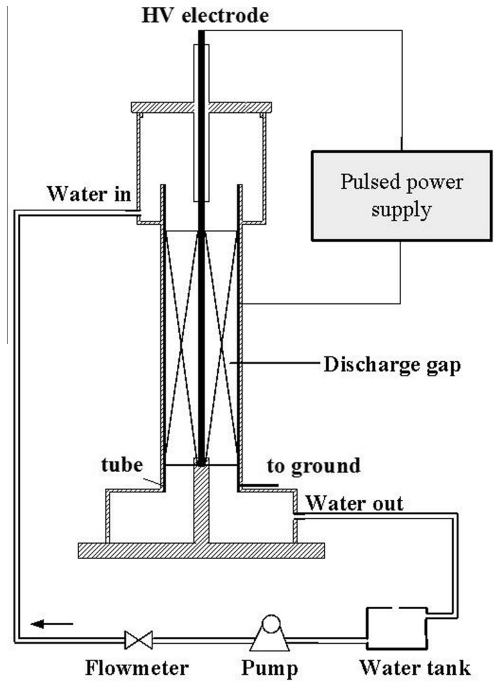

Fig. 1. Experimental set-up.

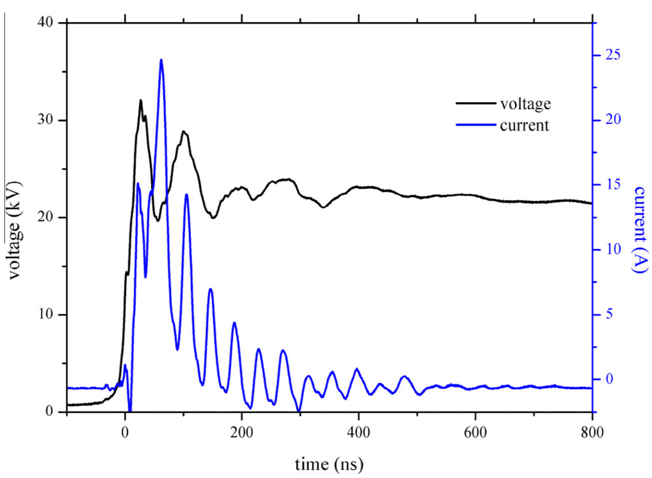

Fig. 2. Typical waveforms of the discharge voltage and current.

treatment [18–26]. NTP can be achieved by electrohydraulic discharge, water surface discharge and hybrid gas–liquid discharge with various discharge reactors, leading to different discharge types, such as corona discharge, dielectric barrier discharge, gliding arc discharge and contact glow discharge. Comparing to most of the other AOPs, NTP does not need additional catalysts to generate hydroxyl radicals. Much more reactive chemical species other than hydroxyl radical can be produced, such as hydrogen peroxide, hydroperoxyl and ozone. Zimmerman et al. devoted to the investigation of the ozone formation reaction in a microchannel plasma reactor [27,28]. Furthermore, shock waves and UV light formed by discharge also can be favorable during water treatment [29].

To the best of our knowledge, degradation of IBP by plasma has not been reported yet. Herein, the cylindrical wetted-wall reactor was used to generate non-thermal plasma in the present study, and the objective was to examine the potential effectiveness of NTP for the decomposition of IBP as well as to evaluate the biodegradability of the identified byproducts after the treatment.

2. Materials and methods

2.1. Chemicals and reagents

IBP (Energy-Chemical, >99% purity) solutions were prepared in a phosphate buffer (pH = 7.4). HPLC grade methanol, acetonitrile and acetic acid (Tedia Company, Inc., USA) were used to prepare the HPLC mobile phase. All solutions were prepared using Milli-Q water (Millipore Synergy 185, >18 MΩ cm).

2.2. Plasma experimental set-up

The plasma reactor, a cylindrical wetted-wall discharge system was described in our previous work [30]. The HV electrode was made of stainless steel with an inner radius of 1.5 mm. The ground electrode was made of graphite with a length of 25 cm and an inner radius of 2.5 cm, as shown in Fig. 1. The reagent (500 ml) was circulated (64 L/h) in this system with the water tank fixed at the temperature of 25 °C.

Initial IBP aqueous solution was pumped from the feeding tank and was fed to the overflow tank. A uniform falling film could be formed in the inner surface of the reactor. The effluent left the water out port and flowed back to the feeding tank. The flow rate of the solution was controlled by a flowmeter. The temperature of the effluent was maintained at 25 °C by a thermostatic water bath.

The high voltage pulses were generated by charging a capacitor of 0.9 nF, which was then discharged with a rotating spark-gap

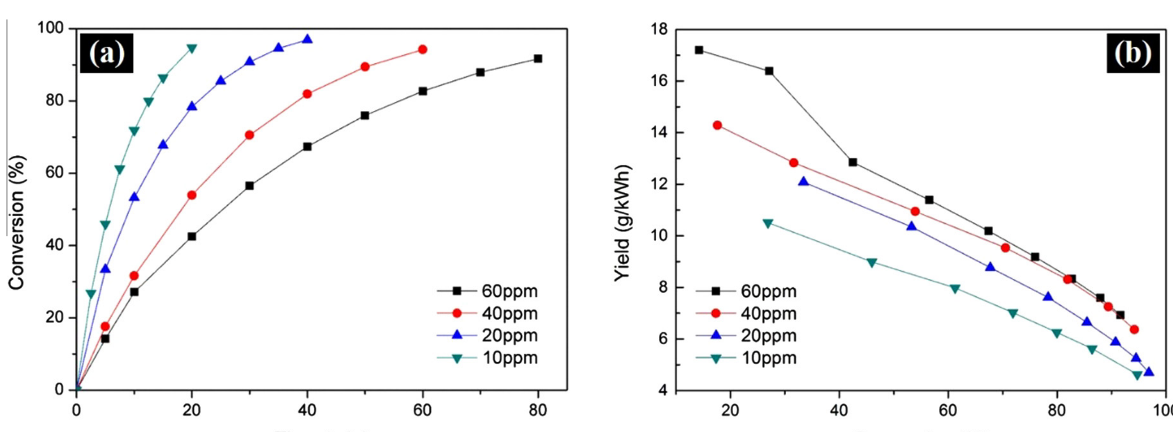

Fig. 3. (a) Ibuprofen conversion as a function of treatment time; (b) ibuprofen degradation yield as a function of conversion for initial concentrations of 10, 20, 40 and 60 mg/l. (T = 25 °C, Q = 64 L/h, V_p = 32 kV, f = 100 Hz).