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# Dielectric barrier discharge induced the degradation of the emerging contaminant ibuprofen in aqueous solutions

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## ABSTRACT

This study focused on the degradation of the worldwide nonsteroidal anti-inflammatory drug (NSAID) ibuprofen (IBP) by dielectric barrier discharge (DBD). Factors affecting IBP degradation efficiency were examined, such as output power, initial ibuprorfen concentration, solution pH values, and various additives ($H_2O_2$, t-BuOH, humic acid). When IBP concentration of 18 mg/L and the output power of 70 W were chosen, 95.6% of IBP was removed after 5 min treatment. Humic acid and 0.3% $H_2O_2$ additives enhanced the IBP degradation process, while 1% $H_2O_2$ additive restrained the degradation process of IBP. The addition of t-BuOH also hindered the degradation process of IBP. The degradation of IBP was found to be affected by solution pH, with higher degradation efficiency occurring under strong acidic condition than alkaline and neutral conditions. The solution pH values became lower with the increasing of discharge time. High-performance liquid chromatography (HPLC) and electrospray ionization mass spectrometry (ESMS) techniques were employed to identify the IBP derivatives. The mono-hydroxylates of IBP, and the products due to the oxidation of propanoic acid, and isobutyl substituents of IBP were identified.

*Keywords:* Degradation; Ibuprofen; Dielectric barrier discharge

## 1. Introduction

In recent years, the presence of various pharmaceutical pollutants in the environment has received much attention due to the unknown environmental impact and possible damages to the botany [1,2]. These compounds and their metabolites can reach sewage systems, where they are not easily degraded under the typical biological treatments in the municipal wastewater treatment plants (WTPs). The major sources of pharmaceutical pollutants are the continuous disposal of wastewaters released from the pharmaceutical industries and excretory products of medically treated humans and animals [3].

Pollutant found with more than 70 million annual prescriptions in the world was the nonsteroidal anti-inflammatory drug (NSAID), one of the most consumed medications corresponds to the classification. The compound 2-[3-(2-methylpropyl)phenyl]propanoic acid, commercially available as ibuprofen (IBP), is widely used as an NSAID especially prescribed for

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the treatment of fever, migraine, muscle aches, arthritis, and tooth aches [4]. Several kilotons of IBP were produced worldwide each year, part of which was rejected to the effluents, excreted by patients in its original form, or as metabolites from human biodegradation [5]. A lot of research showed the presence of IBP and metabolites, in effluents of WTPs [6,7]. The concentrations of IBP in the environment were reported between 10 ng/L and 169 μg/L [8]. Although the concentration of IBP in natural environment was very low in aquatic systems, but it may present a potential hazard for human, the metabolites are more harmful than the parent organic compounds [9–11].

Recently, dielectric barrier discharge (DBD) has attracted the attention of many researchers for the application of pollutant degradation in aqueous solutions. It is an excellent source for producing ideal energetic electrons with 1–10 eV and high density [12]. In humid air, DBD could produce UV light and many reactive species such as free electrons, negative ions, positive ions, uncharged short-lived radicals, OH, $HO_2^{\cdot}$, $H_2O_2$, and $O_3$ [13,14]. The detailed mechanisms are as follows (Eqs. (1)–(10)). This technology that integrates light, electronic, and chemical oxidation into one process has a collective effect on degrading organic species

$$O_2 \xrightarrow{e^-} O^{\cdot} + O^{\cdot} \tag{1}$$

$$O^{\cdot} + O_2 \longrightarrow O_3 \tag{2}$$

$$O^{\cdot} + H_2O \longrightarrow {}^{\cdot}OH + {}^{\cdot}OH \tag{3}$$

$$O^{-} + H_2O \longrightarrow {}^{\cdot}OH + OH^{-} \tag{4}$$

$$O^{-} + H_2O \longrightarrow HO_2^{\cdot} + OH^{-} \tag{5}$$

$$2H_2O \xrightarrow{e^-} 2H_2O_2 + H_2 \tag{6}$$

$$O_3 + H_2O_2 \longrightarrow {}^{\cdot}OH + O_2 + HO_2^{\cdot} \tag{7}$$

$$O_3 + HO_2^{\cdot} \longrightarrow {}^{\cdot}OH + O_2 + O_2 \tag{8}$$

$$O_3 + H_2O \xrightarrow{hv} H_2O_2 + O_2 \tag{9}$$

$$H_2O_2 \xrightarrow{hv} {}^{\cdot}OH + {}^{\cdot}OH \tag{10}$$

IBP is not easily degraded by typical biological treatments in municipal WTPs. So, many enhanced technologies that can reduce IBP presence in environment have been carried out, such as photodegradation, solar photodegradation methods [15], biological treatments [16,17], and advanced oxidation processes [4,18]. However, the degradation of IBP by DBD has not been fully studied.

Therefore, the purpose of the present work is to investigate the degradation behavior and degradation mechanism of IBP in aqueous solutions by DBD. At the same time, several factors affecting the degradation efficiency of IBP are studied.

## 2. Experimental details

### 2.1. Chemicals and reagents

IBP, $CH_3CN$, $CH_3OOH$, and $CH_3OH$ (High performance liquid chromatography (HPLC) grade) were purchased from Sigma-Aldrich. High-purity humic acid was also obtained from Sigma–Aldrich. $H_2O_2$, HCl, and NaOH (analytical-grade) were obtained from Shanghai Chemicals Factory, China. Ultrapure water was generated with a Milli-Q system (Elix5 + Milli-Q A10).

### 2.1.1. Experimental procedures

*2.1.1.1. Experimental apparatus.* The experimental apparatus was bought from Nanjing Suman Electronics Co., Ltd., PR China and shown in Fig. 1. It consisted of a reaction cell (DBD-50) and a power supplier (CTP-2000 K) that could provide a steady voltage of 100 V. The reaction cell, which was between the high voltage electrode and ground electrode, consisted of two parts. The upper part of the reaction tank was a little bigger than the lower part. The lower part was used to contain the solution, which was 84 mm in inner diameter, 88 mm in outer diameter, and 6 mm in height.

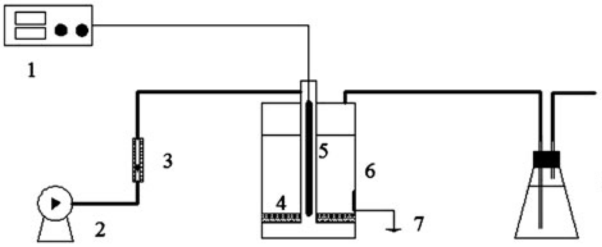


Fig. 1. Scheme of the experimental apparatus (1. plasma power; 2. air pump; 3. flow meter; 4. aeration device; 5. high voltage electrode; 6. discharge reactor; 7. grounding electrode; and 8. tail gas absorber).

The reaction tank was put in the center of the two electrodes. The power was supplied by an AC source, which could be operated at an adjustable amplitude voltage. The intensity of discharge in the reaction tank could be denoted by the input power, which was calculated by the average voltage and current of the AC power. The dielectric barrier was made of quartz.

*2.1.1.2. Sample preparation.* Eighteen milligram per liter IBP solution was prepared in water purified by a Millipore Milli-Q system. It was employed to test the effect of operational parameters on degradation efficiency, and to examine the change of solution pH and TOC after DBD treatment. The different additives ($H_2O_2$, and t-BuOH) were added into IBP aqueous solution to examine their effects on the degradation efficiency of IBP. HCl (0.01 mol/L) and NaOH (0.01 mol/L) were used to examine the effect of pH value on the degradation efficiency of IBP.

*2.1.1.3. Analysis.* The concentration of IBP was analyzed by a HPLC system (Agilent, USA, 1,200 Series) equipped with Hypersil ODS HPLC column (250 × 4.6 mm i.d., 5 m, Agilent, USA), a multiple wavelength UV diode array detector, and an auto sampler controlling under a chemstation data acquisition system. The eluent consisted of 70% acetonitrile and 30% acetic acid (0.25 mol/L), and the flow rate was 1 mL/min. The column temperature was kept at 30˚C and a sample volume of 20 μL was injected from an autosampler. The determination wavelength was set at 254 nm. Five or six point linear standard calibration curves were constructed periodically throughout the analyses period to verify the stability of the system.

The degradation efficiency of IBP was calculated from the following Eq. (11).

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \tag{11}$$

where $\eta$ is the degradation efficiency of IBP (%), $C_t$ is the residual concentration of IBP after discharge treatment (mg/L), and $C_0$ is the initial concentration of IBP before discharge treatment (mg/L).

The identification of IBP and its degradation products was performed by liquid chromatography-mass spectrometer (LC-MS) (ThermoQuestLCQ Duo, USA) with ZORBAX Rx-C18 HPLC column (150 × 2.1 mm i.d., 5 m, Agilent, USA). About 20 μL IBP solutions after DBD treatment were injected automatically into the LC-MS system. The eluent consisted of 30% of 1.0 mmol/L acetic acid in water and 70% acetonitrile. The flow rate was 0.2 mL/min and the other LC conditions were the same as the conditions used in determining IBP concentration. The spray voltage was 3.5 kV and the sheath gas flow rate was 18 arb. The spectra were acquired in the negative ion scan mode, over the $m/z$ range from 50 to 1,000. All the experiments were repeated twice, the experimental error was below 5% and the average data were reported.

Total organic carbon (TOC) was determined by TOC analyzer (Shimadzu, TOC-5000A). The pH value was measured by pH monitor (Shanghai Kangyi Instrument Co. Ltd., China, PHS-2C).

## 3. Results and discussion

### 3.1. The factors affecting degradation of IBP

#### 3.1.1. Effect of output power on IBP degradation process

In this work, the DBD was generated over the treated water. Some vapor was generated in the discharging space as the result of exothermic reaction. Thus, the reactive species mentioned in Eqs. (1)–(10) were formed in the DBD reactor. The reactive species produced in the gas phase would be further carried to the water by the gas agitation caused by the ion wind [19]. When these reactive species reached the liquid film, the aqueous reactive species would also be produced [20]. There these reactive species would be reactive with organic compounds [21].

Fig. 2 describes the change of IBP degradation efficiency by DBD with output power intensity. The result shows that 18 mg/L IBP could be effectively removed from aqueous solutions by DBD. The concentration of IBP decreased with the increasing output power intensity. When 5 min of discharge time was selected, the degradation efficiency of IBP was 95.6%

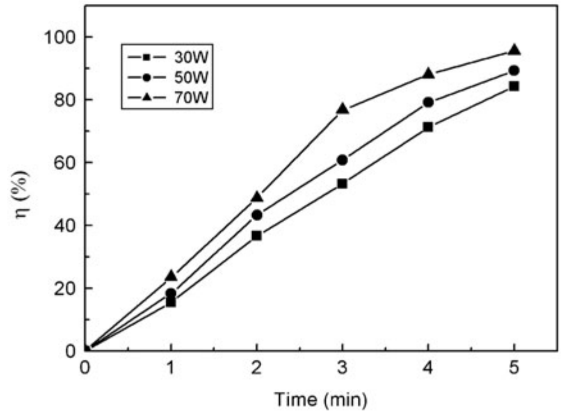


Fig. 2. Change of IBP degradation efficiency with different output power ($C_0 = 18$ mg/L, air flow rate = 0.50 $m^3$/h).

at a 70 W of output power intensity. These results show that DBD could effectively remove IBP in the aqueous solution.

### 3.1.2. Effect of IBP initial concentration on the degradation process

Fig. 3 shows the effect of the initial concentration on IBP degradation by DBD. As shown in Fig. 3, the degradation value decreased with the increasing of the initial concentration at the same discharge time. It was indicated that the initial concentration greatly affected IBP degradation behavior.

In order to compare the reaction rates in the DBD reactor, the experimental data were fitted by the following Equation:

$$\ln\frac{C_0}{C_t} = kt \tag{12}$$

where $C_0$, $C_t$, and $k$ are the initial concentration of IBP before discharge treatment (mg/L), the residual concentration of IBP after discharge treatment (mg/L), and the rate constant ($\text{min}^{-1}$), respectively. When ln $(C_0/C_t)$ was plotted vs. time, a good correlation was obtained for every set of data, which indicated that the degradation of IBP by DBD fitted first-order kinetics. When the initial concentration of IBP was 9 mg/L, the rate constant was 0.4896 $\text{min}^{-1}$. However, when the initial concentrations were 18 and 27 mg/L, the rate constants were 0.3687 and 0.2648 $\text{min}^{-1}$. It shows that rate constants increased with lower initial IBP concentrations.

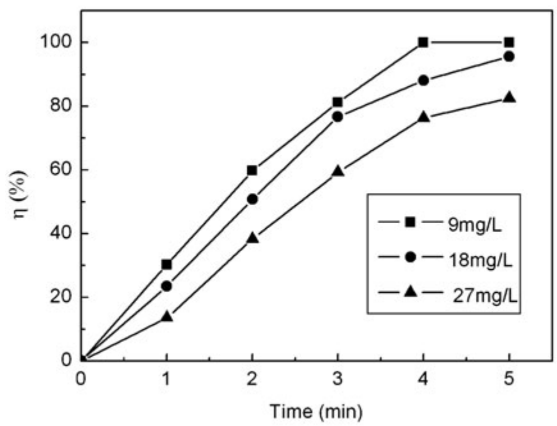


Fig. 3. Effect of the initial concentration on IBP degradation (output power = 70 W, air flow rate = 0.50 $m^3$/h).

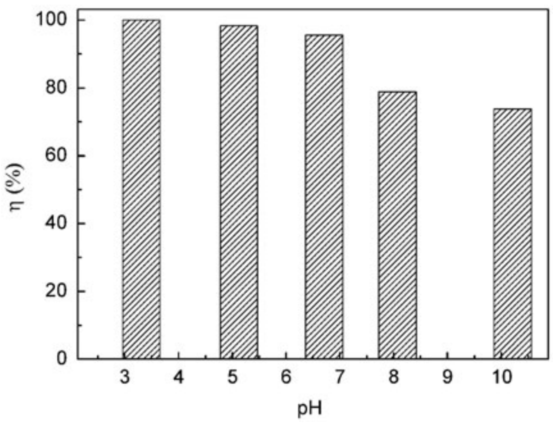


Fig. 4. Effect of the pH value on IBP degradation ($C_0$ = 18 mg/L, output power = 70 W, air flow rate = 0.50 $m^3$/h, discharge time = 5 min).

### 3.1.3. Effect of pH values on IBP degradation process

The effects of solution pH values on IBP degradation process are shown in Fig. 4. The results obtained indicate that pH value was significantly affected by the IBP degradation. The degradation efficiency of IBP was higher under acidic conditions than in alkaline conditions. For example, the degradation efficiency of IBP reached 100% after 5 min of discharge time at pH value of 3.31, whereas the degradation efficiency was only 73.8% at pH value of 10.0. It is well known that the major active species, which are useful for the degradation of organic pollutants in aqueous solutions by pulsed discharge, are $^{\cdot}OH$, $O_3$ and $H_2O_2$ [20,21]. Under acidic conditions, more $^{\cdot}OH$ radicals were produced and $H_2O_2$ decomposition was inhibited [21–23], thus the degradation efficiency of IBP increased. While in alkaline media, $HO_2^{\cdot}$ ion would be decomposed by the discharge, which scavenged $^{\cdot}OH$, thus the degradation efficiency of IBP decreased [24].

### 3.1.4. Effect of $H_2O_2$ additive on IBP degradation process

It is well known that $H_2O_2$ is $^{\cdot}OH$ radical promoter, it could accelerate the degradation of pollutions in aqueous solutions. In order to test the effect of $H_2O_2$ on IBP degradation by DBD, $H_2O_2$ were added at different concentrations of 0.3 and 1.0%. The results obtained are shown in Fig. 5. It was indicated that the degradation value in the presence or absence of $H_2O_2$ was improved with the increasing of discharge time and $H_2O_2$ enhanced IBP degradation process at the concentration of 0.3%, however, hindered the degradation at 1.0%. This result indicated that IBP degradation by DBD could be enhanced when $H_2O_2$

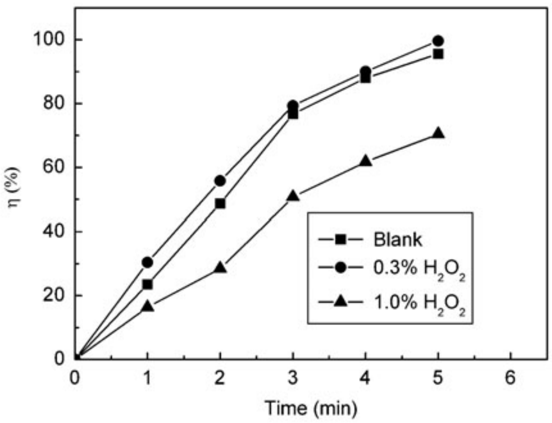


Fig. 5. Effect of $H_2O_2$ on IBP degradation ($C_0 = 18\,mg/L$, output power = 70 W, air flow rate = 0.50 $m^3/h$).

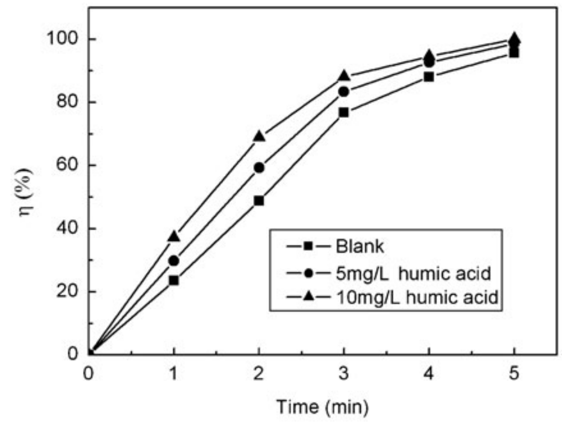


Fig. 7. Effect of humic acid on IBP degradation ($C_0 = 18\,mg/L$, output power = 70 W, air flow rate = 0.50 $m^3/h$).

was added at the appropriate concentration. It might be the reason that when $H_2O_2$ was added at the concentration of 0.3%, $^{\cdot}OH$ was formed by the decomposition of $H_2O_2$ (Eq. (10)) and then $^{\cdot}OH$ concentration increased, so the IBP degradation process enhanced. However, when $H_2O_2$ was added at 1.0%, the hydroxyl radicals generated hydroperoxyl radicals ($HO_2^{\cdot}$) in the presence of a local excess of $H_2O_2$ and then $^{\cdot}OH$ concentration decreased [25,26].

### 3.1.5. Effect of the presence of t-BuOH on IBP degradation

Results obtained when the t-BuOH was added are shown in Fig. 6. In the presence or absence of t-BuOH additive, IBP degradation efficiency increased with the increasing of discharge time. While the degradation efficiency of IBP in the presence of t-BuOH was much lower than in the absence of t-BuOH with the same discharge time. The effect of t-BuOH is due to a well-known fact that it reacts more rapidly than IBP with $^{\cdot}OH$ and $e_{aq}^-$ in aqueous solutions [27]. These reactions will reduce the yield of $^{\cdot}OH$ and $e_{aq}^-$, resulting in the decrease of IBP degradation efficiency.

### 3.1.6. Effect of humic acid additive on IBP degradation

Results obtained when humic acid was added are shown in Fig. 7. In the presence or absence of humic acid additives, the degradation efficiency of IBP increased with the increasing of discharge time. The degradation efficiency increased with the increasing concentrations of humic acid. The reason was that humic acid could absorb light and generate excited triplet states ($^3HA^*$) and various reactive oxygen species, including hydroxyl radicals ($^{\cdot}OH$), singlet oxygen ($^1O_2$), and hydrogen peroxide ($H_2O_2$) [28], so the radical concentrations for reaction with IBP increased.

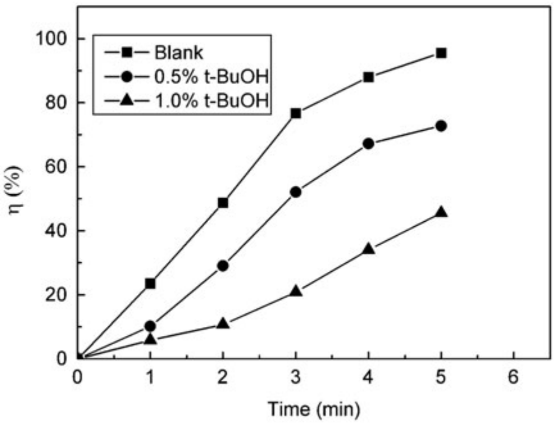


Fig. 6. Effect of t-BuOH on IBP degradation ($C_0 = 18\,mg/L$, output power = 70 W, air flow rate = 0.50 $m^3/h$).

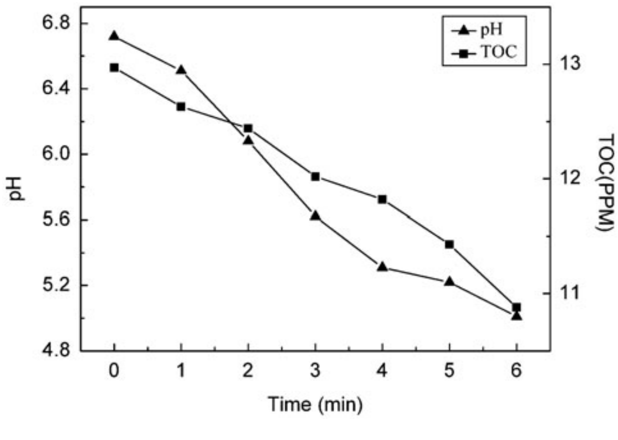
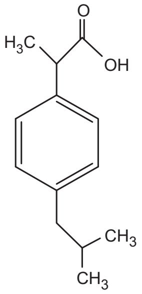
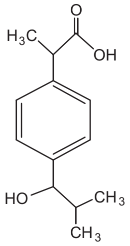
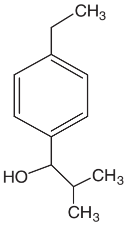
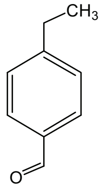
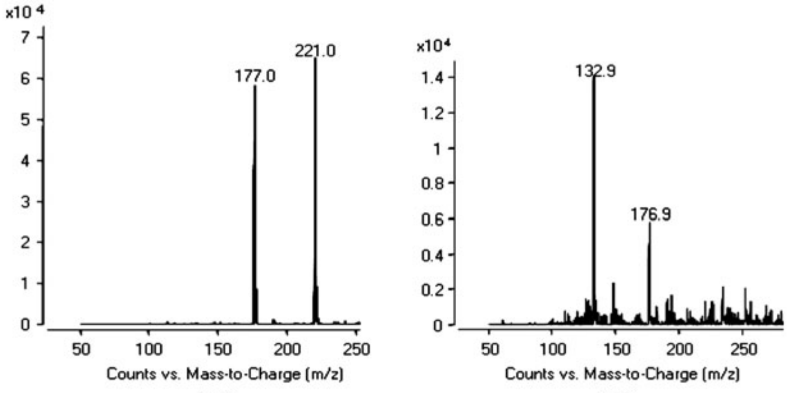


Fig. 8. pH and TOC values variation of IBP solution.

Table 1
Degradation products observed for IBP during DBD treatment.

| | | | |
|---|---|---|---|
|  |  |  |  |
| Ibuprofen | I | II | III |
| $m/z$ 205 | $m/z$ 221 | $m/z$ 176 | $m/z$ 133 |



(a) (b)

Fig. 9. The mass spectra of IBP byproducts.

### *3.2. Variations of solution pH and TOC*

The effect of DBD on solution pH value is shown in Fig. 8. The solution pH value decreased with the increasing of discharge time, pH values decreased from 6.72 to 5.01 at the discharge time of 1 and 5 min. The decrease of pH values was possibly due to a large amount of $H_3O^+$ produced during degradation process. Fig. 8 also describes the TOC values change of IBP aqueous solutions. The solution TOC values decreased with the increasing of discharge time, which indicated that DBD could lead to both degradation and partial mineralization of IBP in aqueous solutions. But the mineralization efficiency was not high with 5 min dischare time.

### *3.3. The by-products of IBP*

In order to identify the reactive by-products of IBP degradation, samples collected at different absorbed dose were analyzed by means of HPLC-electrospray ionization mass spectrometry (ESMS). The results indicated that DBD could induce the degradation of IBP. The by-products were shown in Table 1. It was observed that an attack of hydroxyl radicals on both the propanoic acid and isobutyl substituents of the IBP structure results in the formation of products such as 2-[4-(1-hydroxyisobutyl)phenyl]propionic acid (I), 1-ethyl-4-(1-Hydroxy)iso-Butylbenzene (II), and 4-ethylbenzaldehyde (III). In Fig. 9(a), the peaks that appear at $m/z$ 221 show the formation of monohydroxylated products of IBP, such as products (I). Fig. 9(a) also shows the peaks of $m/z$ 176, it indicates the formation of product (II). The peak of $m/z$ 133 appears in Fig. 9(b), it shows the formation of product (III).

## 4. Conclusions

DBD could effectively degrade IBP in aqueous solutions. The degradation efficiency was 95.6% when the output power was 70 W and 5 min was selected as the discharge time. The degradation reaction of IBP followed first-order-like kinetics.

The pH value affected the IBP degradation process. The degradation yield was higher under acidic conditions than in alkaline media. IBP degradation efficiency decreased with the increase of initial concentration. $H_2O_2$ as the additive enhanced the degradation process at the concentration of 0.3%, however, hindered the degradation at 1.0%. Humic acid additives enhanced the degradation of IBP. But, t-BuOH additives inhibited IBP degradation. The pH values and TOC of IBP solution decreased with the increasing of discharge time. IBP by DBD treatment leads to the formation of its mono-hydroxylated intermediates, and the products due to the oxidation of propanoic acid and isobutyl substituents of the IBP were also identified.

## Acknowledgment

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