

Degradation of the Emerging Contaminant Naproxen in Aqueous Solutions by Dielectric Barrier Discharge

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This study focused on the degradation of naproxen by dielectric barrier discharge. The effects of various parameters such as output power, naproxen initial concentration, solution pH, presence of additives on the degradation of naproxen were investigated. The degradation value was 93.2 % when output power was 60 W and 6 min was selected as the discharge time. The degradation efficiency was higher under acidic conditions than in alkaline media and the degradation efficiency decreased with the increasing of initial concentration at the same discharge time. 0.25 % H₂O₂ additive enhanced the degradation process, however, 1.0 and 1.5 % H₂O₂ additive hindered the degradation. The presence of Fe²⁺ could enhance the degradation of naproxen, however, the increment in degradation efficiency might be suppressed to some extent at a high concentration level. Identification of byproducts has shown that demethylation and decarboxylation are the principal initial processes in the degradation of naproxen under the conditions of this experiment.

Key Words: Degradation, Naproxen, Dielectric barrier discharge.

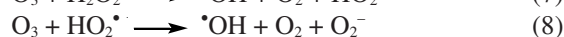
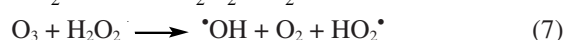
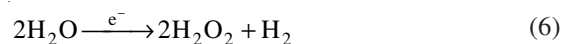
INTRODUCTION

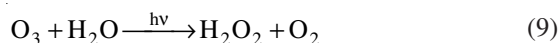
In recent years, the pharmaceutical pollutants in the environment have received much attention due to their unknown environmental impacts and their possible damage to botany^{1,2}. These compounds and their metabolites can reach sewage systems, where they are not easily degraded under the typical biological treatments in the municipal wastewater treatment plants³⁻⁶. Naproxen and naproxen-based products are pharmaceutical pollutants and have been detected in surface water, groundwater, wastewater and even in drinking water in the range from ng L⁻¹ to several µg L⁻¹⁷⁻¹⁰. Their presence has been observed due to their adverse effects on biota such as reducing the lipid peroxidation system of bivalves¹¹, so it is becoming a serious problem.

A lot of research has been carried out to remove naproxen with ozonation, free chlorine, phototransformation and H₂O₂/UV. These treatments usually achieve high removal efficiencies of naproxen, but the mineralization efficiencies of naproxen are not high¹²⁻¹⁵. The degradation of naproxen in biological ways has also been tested, the research results show that the white-rot fungus *Trametes vesicolor* can degrade naproxen in liquid medium and sewage sludge^{3,8,16}. When naproxen initial concentration is 55 µg L⁻¹ in liquid medium, which is the typical level in the environment, the degradation efficiency is 95 %

after 5 h by white-rot fungus *Trametes vesicolor*⁸. In five different wastewater treatment systems, including constructed wetland system, sand filter system and activated sludge system, the enantioselective degradation of naproxen is feasible under aerobic and anaerobic conditions.

Nowadays, dielectric barrier discharge (DBD) is widely used in environmental protection field. It is an excellent source for producing ideal energetic electrons with 1-10 eV and high density¹⁷. In humid air dielectric barrier discharge could produce UV light and many reactive species such as free electrons, negative ions, positive ions, uncharged short-lived radicals, H₂O₂ and O₃. The detailed mechanisms are as follows (eqns. 1-10)¹⁸⁻²¹. This technology that integrates light, electronic and chemical oxidation into one process has a collective effect on degrading organic species.





The degradation behaviour of naproxen by dielectric barrier discharge has not yet been studied. The purpose of this study was to investigate the possibility of naproxen degradation in aqueous solutions by dielectric barrier discharge and propose the possible degradation mechanism. Factors that might affect the degradation efficiency of naproxen were examined.

EXPERIMENTAL

Naproxen was purchased from Sigma-Aldrich and its chemical structure is represented in Fig. 1. CH_3CN , CH_3COOH and CH_3OH were obtained from Sigma-Aldrich and HPLC grade. Humic acid was high purity products from Sigma-Aldrich. The other chemicals were of reagent grade with purity higher than 99%. The ultrapure water was obtained from milli-Q system (Elix5+milliQ A10, USA).

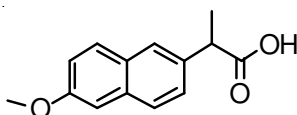


Fig. 1. Chemical structure of naproxen

The experimental apparatus was bought from Nanjing Suman Electronics Co. Ltd., PR China (Fig. 2). It consisted of a reaction cell (DBD-50) and a power supplier (CTP-2000K) 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. 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.

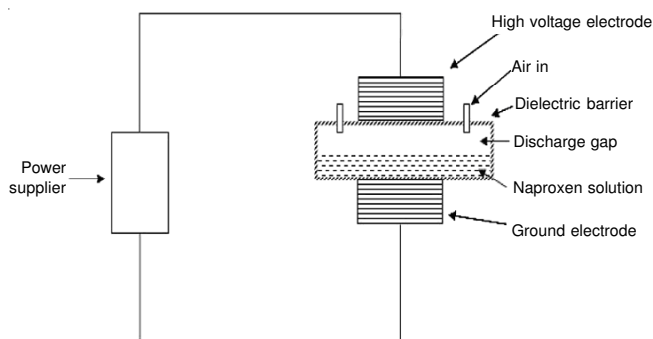


Fig. 2. Scheme of the experimental apparatus

Sample preparation: Naproxen solution at initial concentration of 20 mg L^{-1} was prepared by solid naproxen with ultrapure water. It was employed to be used to test the effect of output power, H_2O_2 , Fe^{2+} , NO_3^- , humic acid and initial pH

value on the degradation and to examine the change of pH value and total organic carbon by DBD. The output power of 60W was employed to investigate the effect of naproxen initial concentration, H_2O_2 , Fe^{2+} , NO_3^- , humic acid and initial pH value on the degradation and to determine the change of pH value and TOC by DBD. The pH value of the solution was adjusted using HCl dilute solution or NaOH dilute solution. All the samples were treated at the voltage of 100 V.

Analysis: The concentration of naproxen was determined by using a HPLC system (Agilent, USA, 1200 series high-performance liquid chromatography) equipped with Hypersil ODS HPLC column ($250 \text{ mm} \times 4.6 \text{ mm i.d.}$, $5 \mu\text{m}$, Agilent, USA), a multiple wavelength UV diode array detector and an auto sampler controlling under a chemstation data acquisition system. The mobile phase consisted of 25% phosphate (0.01 mol L^{-1} potassium dihydrogen phosphate, adjusted with phosphoric acid to pH 3) and 75% methanol and the flow rate was 1 mL min^{-1} . The determination wavelength was set at 230 nm and the column temperature was kept at $30 \text{ }^\circ\text{C}$.

The degradation efficiency (η) of each sample was calculated from the following eqn. 11.

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 \% \quad (11)$$

η : The degradation efficiency of naproxen (%); C_t : The residual concentration of naproxen (mg L^{-1}); C_0 : The initial concentration of naproxen (mg L^{-1}).

The identification of naproxen and its degradation products resulted from the radiolytic degradation were performed by LC-MS (ThermoQuestLCQ Duo, USA) equipped with Beta Basic- C_{18} HPLC column ($150 \text{ mm} \times 2.1 \text{ mm i.d.}$, $5 \mu\text{m}$, Finnigan, Thermo, USA). $20 \mu\text{L}$ naproxen solutions treated by DBD were injected automatically into the LC-MS system. The eluent consisted of 65% of 1.0 mM acetic acid in water and 35% of acetonitrile. The flow rate was 0.2 mL min^{-1} , the other LC conditions were the same as the conditions used in determining naproxen concentration. MS conditions were as follows: the electrospray ionization interface was selected. The capillary temperature was set to $275 \text{ }^\circ\text{C}$ with a voltage of 19.00 V. The spray voltage was 5000 V 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 50-600. 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).

RESULTS AND DISCUSSION

Effect of output power on naproxen 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 eqns. 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 wind²². When these reactive species reached the liquid film,

the aqueous reactive species would also be produced¹⁸. There these reactive species would be reactive with organic compounds²³.

Fig. 3 showed the change of naproxen degradation values with different output powers using DBD. It was indicated that naproxen could be effectively removed from aqueous solutions by DBD. The concentration of naproxen in aqueous solutions decreased with the increasing of output power. When the discharge time was 6 min, 72.8, 93.2 and 96.7 % of naproxen was removed when the output powers were 40, 60 and 80 W, respectively. This results show that DBD is an effective method to remove naproxen in aqueous solutions.

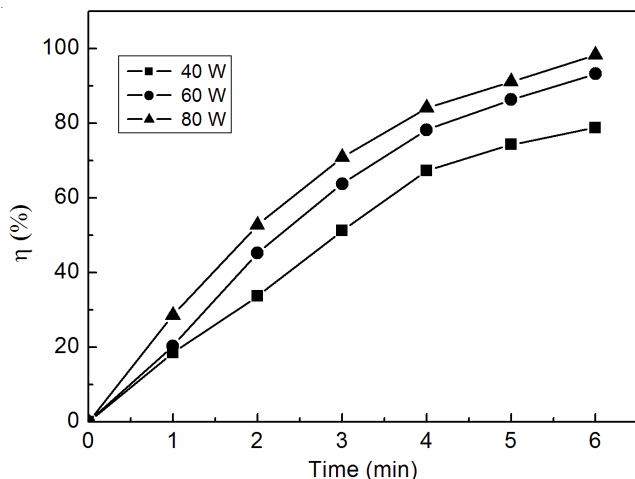


Fig. 3. Change of naproxen degradation values with different output powers ($C_0 = 20 \text{ mg L}^{-1}$, initial pH value = 6.62, air flow rate = $0.50 \text{ m}^3 \text{ h}^{-1}$)

Effect of naproxen initial concentration on the degradation process: Fig. 4(a) showed the effect of the initial concentration on naproxen degradation by DBD. As shown in Fig. 4(a), the degradation value decreased with the increasing of initial concentration at the same discharge time. It was indicated that the initial concentration greatly affected naproxen degradation behaviour.

The degradation kinetics of naproxen followed first order kinetics. The change in $\ln(C_0/C_t)$ as the discharge time were described in Fig. 4(b). Fig. 4(b) shows a trend and the slope of this plot yielded the first order rate constants. When the initial concentration of naproxen was 10 mg L^{-1} , the rate constant was 0.5552 min^{-1} . However, when the initial concentrations were 20 and 30 mg L^{-1} , the rate constants were 0.4026 and 0.2828 min^{-1} . It showed that rate constants increased with lower initial naproxen concentrations. These experimental results are similar to published findings for the degradation of diuron by dielectric barrier discharge²³.

Effect of solution pH on naproxen degradation process: Fig. 5 shows the effect of solution pH on naproxen degradation efficiency. The results indicated that pH value is an important factor that affected the naproxen degradation efficiency. The degradation efficiency of naproxen was higher under acidic conditions than in alkaline media. For example, the degradation efficiency of naproxen reached 95.5 % after 4 min of discharge time at pH value of 3, whereas the degradation efficiency was only 58.7 % at pH value of 10. It is well-known that the major active species, which are useful for the degradation of organic

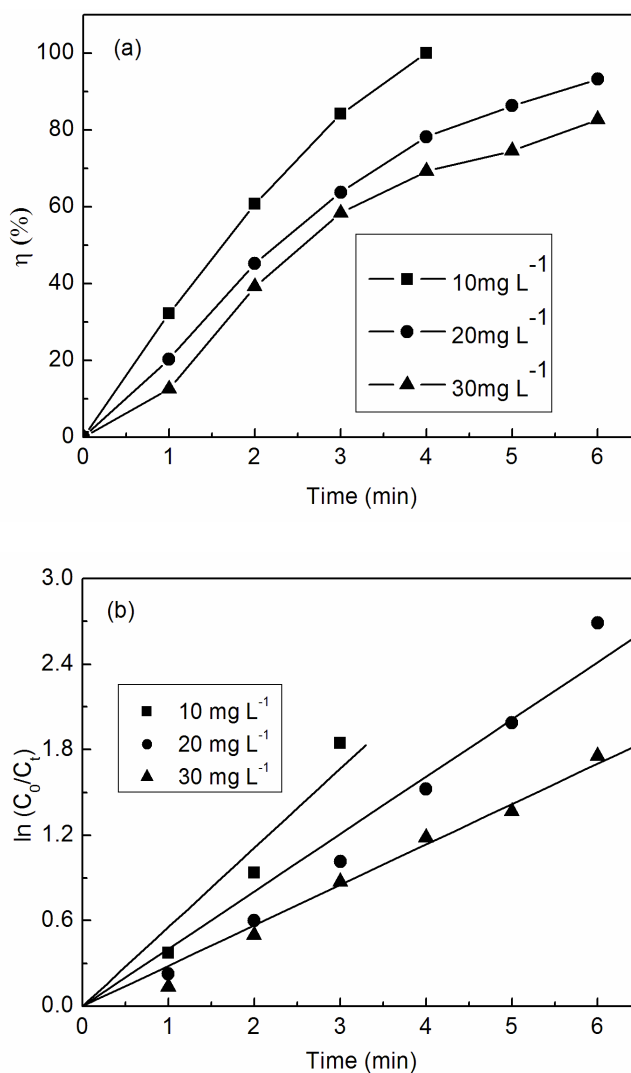


Fig. 4. Effect of the initial concentration on naproxen degradation process (output power = 60 W, initial pH value = 6.62, air flow rate = $0.50 \text{ m}^3 \text{ h}^{-1}$)

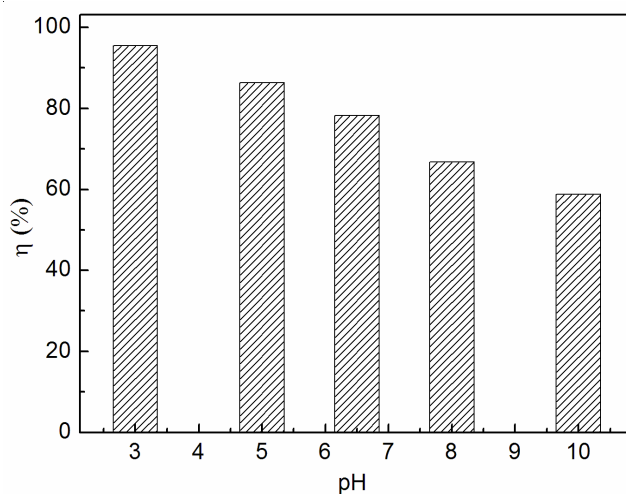


Fig. 5. Effect of the pH value on naproxen degradation ($C_0 = 20 \text{ mg L}^{-1}$, output power = 60 W, air flow rate = $0.50 \text{ m}^3 \text{ h}^{-1}$, discharge time = 4 min)

pollutants in aqueous solution by pulsed discharge, are $\cdot\text{OH}$, O_3 and H_2O_2 ^{18,24,25}. Under acidic conditions, more $\cdot\text{OH}$ radicals

were produced and H_2O_2 decomposition was inhibited²³⁻²⁵, thus the degradation efficiency of naproxen increased. While in alkaline media, HO_2^\bullet ion would be decomposed by the discharge, which scavenged $^\bullet\text{OH}$, thus the degradation efficiency of naproxen decreased²⁶.

Effect of H_2O_2 additive on naproxen degradation

process: It is well-known that H_2O_2 is $^\bullet\text{OH}$ radical promoter, it could accelerate the degradation of pollutions in aqueous solutions. In order to test the effect of H_2O_2 on naproxen degradation by DBD, H_2O_2 was added at different concentrations of 0.25, 1.0 and 1.5 %. The results obtained are shown in Fig. 6. 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 naproxen degradation at the concentration of 0.25 %, however, hindered the degradation at 1.0 and 1.5 %. When the discharge time was 6 min and the concentration of H_2O_2 were 0, 0.25, 1.0 and 2.0 %, the degradation values were 93.2, 94.3, 43.3 and 29.4 %, respectively. This result indicated that naproxen degradation by DBD could be enhanced when H_2O_2 was added at the appropriate concentration. It might be the reason that when H_2O_2 was added at the concentration of 0.25 %, $^\bullet\text{OH}$ was formed by the decomposition of H_2O_2 (eqn. 10)²⁷ and then $^\bullet\text{OH}$ concentration increased, so the degradation process enhanced. However, when H_2O_2 was added at 1.0 and 1.5 %, the hydroxyl radicals generated produced hydroperoxyl radicals (HO_2^\bullet) in the presence of a local excess of H_2O_2 and then $^\bullet\text{OH}$ concentration decreased^{28,29}.

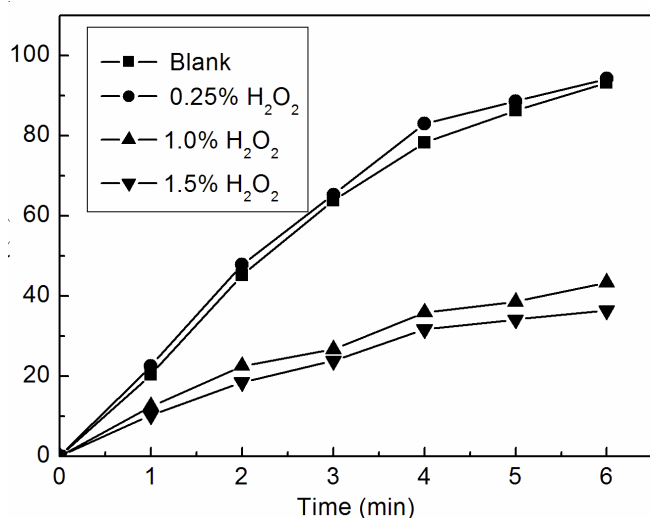


Fig. 6. Effect of H_2O_2 additive on naproxen degradation ($C_0 = 20 \text{ mg L}^{-1}$, output power = 60 W, air flow rate = $0.50 \text{ m}^3 \text{ h}^{-1}$)

Effect of Fe^{2+} additive on degradation of naproxen:

Fe^{2+} has an evidently catalytic effect and the effect is more remarkable when the concentration of Fe^{2+} is higher³⁰. The effect of Fe^{2+} as the additive on naproxen degradation by DBD was tested (Fig. 7). The results showed that the degradation efficiency of naproxen increased dramatically with the presence of Fe^{2+} . When the concentration of Fe^{2+} was 40 mg L^{-1} , the total disappearance of naproxen was achieved at 2 min, however only 70.8 % of naproxen disappeared when Fe^{2+} was added at 120 mg L^{-1} . These results indicated that an appropriate amount of Fe^{2+} could largely enhance the degradation of

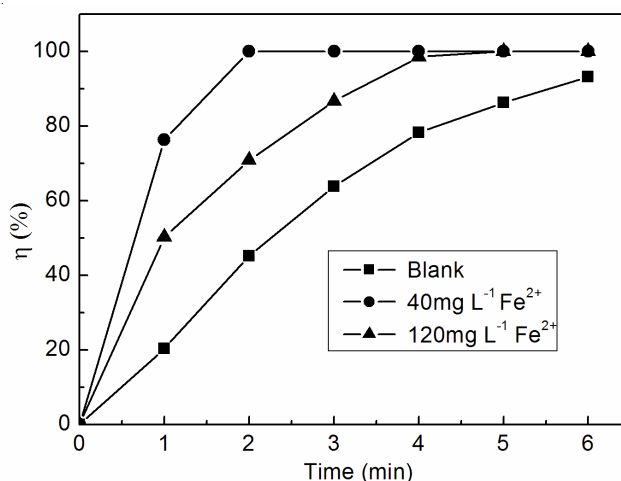
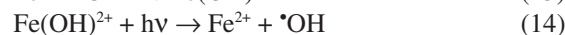
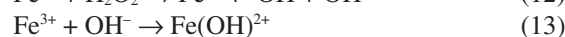


Fig. 7. Effect of Fe^{2+} additive on naproxen degradation ($C_0 = 20 \text{ mg L}^{-1}$, output power = 60 W, air flow rate = $0.50 \text{ m}^3 \text{ h}^{-1}$)

naproxen by DBD. The reason was that the appropriate amount of Fe^{2+} additive enhanced the oxidizing power of H_2O_2 because of the production of $^\bullet\text{OH}$ in the solution (eqn. 12). Furthermore, the regeneration of Fe^{2+} from additional reduction of $\text{Fe}(\text{OH})^{2+}$ benefited the production of $^\bullet\text{OH}$ (eqns. 13 and 14), hence, naproxen degradation process was enhanced. When the concentration of Fe^{2+} was high, it could compete with naproxen for $^\bullet\text{OH}$ (eqn. 15) and therefore the enhancement effect was accordingly weakened^{31,32}.



Effect of NO_3^- additive on degradation of naproxen:

Fig. 8 shows the effect of NO_3^- additive on the degradation of naproxen. The result showed that NO_3^- could enhance the degradation of naproxen, the degradation efficiency increased with the increasing concentration of NO_3^- . When the concentrations of NO_3^- were 2 and 5 mg L^{-1} , the degradation efficiency of naproxen were 92.8 and 100 % at the discharge time of 5 min, but only 86.3 %, in the absence of NO_3^- . The reason was that more $^\bullet\text{OH}$ were produced in the presence of NO_3^- (eqns. 16-18)³³.

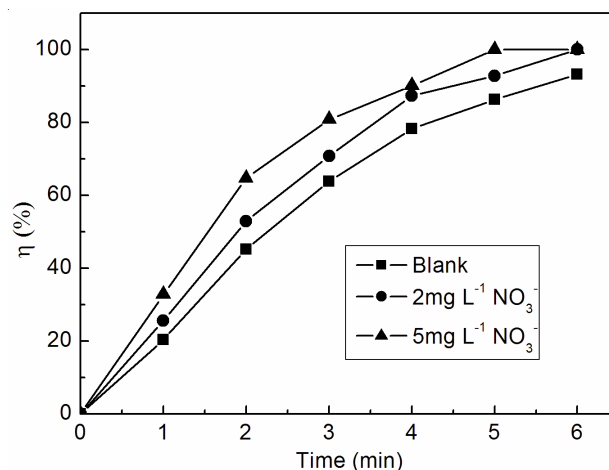
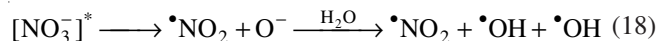
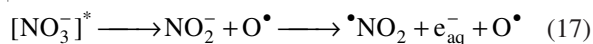
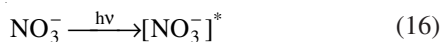


Fig. 8. Effect of NO_3^- additive on naproxen degradation ($C_0 = 20 \text{ mg L}^{-1}$, output power = 60 W, air flow rate = $0.50 \text{ m}^3 \text{ h}^{-1}$)



Effect of humic acid additive on degradation of naproxen:

Results obtained when humic acid was added are shown in Fig. 9. In the presence or absence of humic acid additive, naproxen degradation efficiency increased with the increasing of discharge time. The degradation efficiency increased with the increasing concentrations of humic acid. When the concentrations of humic acid were 2 and 4 mg L⁻¹, the degradation efficiency of naproxen were 90.5 and 97.4 % at the discharge time of 5 min, but only 86.3 % in the absence 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 ([•]OH), singlet oxygen (¹O₂) and hydrogen peroxide (H₂O₂)³⁴, so the radical concentrations for reaction with naproxen increased.

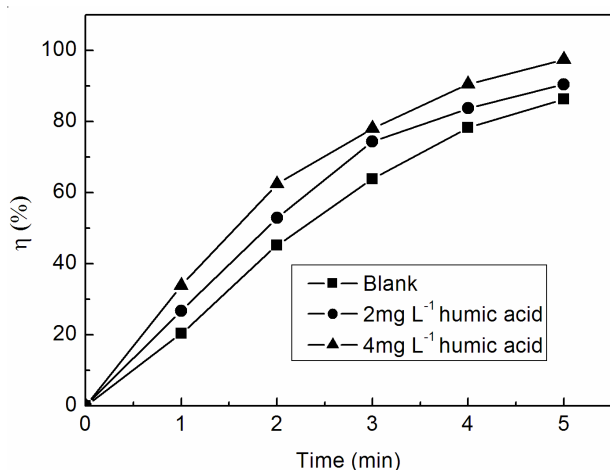


Fig. 9. Effect of humic acid additive on naproxen degradation ($C_0 = 20 \text{ mg L}^{-1}$, output power = 60 W, air flow rate = 0.50 m³ h⁻¹)

Variation of solution pH value: The effect of DBD on pH value is shown in Fig. 10. It was noteworthy that the pH value decreased with the increasing of discharge time, pH values decreased from 6.62 to 5.12, 6.41, 6.18, 5.78, 5.53 and 5.34 at the discharge time of 1, 2, 3, 4 and 5 min. The decrease of pH values was possibly due to a large amount of H₃O⁺ produced during degradation process.

Variation of solution TOC: Fig. 11 shows the change of TOC value of naproxen aqueous solutions. The solution TOC value decreased with the increasing of discharge time, which indicated that DBD could lead to both degradation and partial mineralization of naproxen in aqueous solutions.

Identification of degradation products: In order to optimize the instrumental parameters, a full-scan ESI mass spectrum of naproxen (negative ions) is reported in Fig. 12. The [M]⁻ (m/z 228.8) ion was clearly observed in the spectrum, along with the corresponding isotope peak. Fragmentation of deprotonated naproxen in the ion source leads to the formation of two main product ions, arising from the loss of CO₂ (m/z 184.9) and the consecutive losses of CO₂ and CH₃ (m/z 169.9).

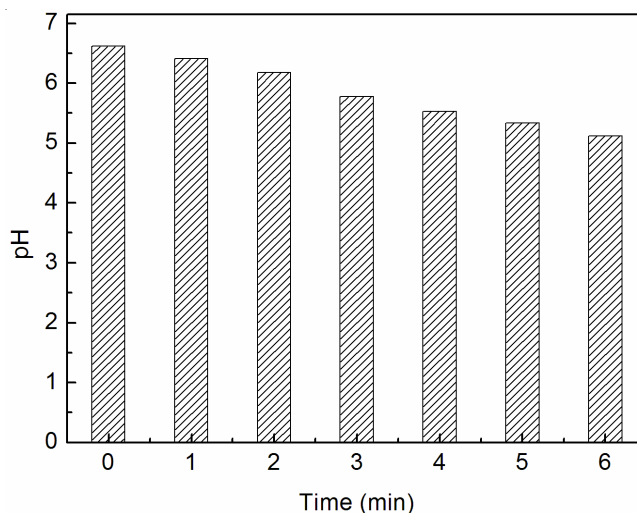


Fig. 10. Change of pH value of naproxen solution ($C_0 = 20 \text{ mg L}^{-1}$, output power = 60 W, air flow rate = 0.50 m³ h⁻¹)

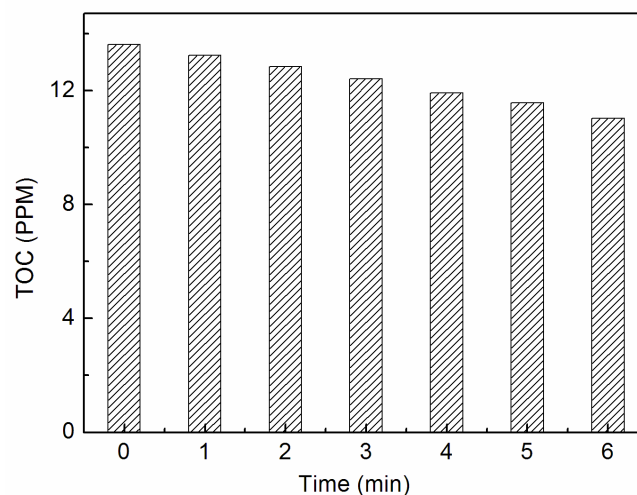


Fig. 11. TOC value variations of naproxen solution ($C_0 = 20 \text{ mg L}^{-1}$, output power = 60 W, air flow rate = 0.50 m³ h⁻¹)

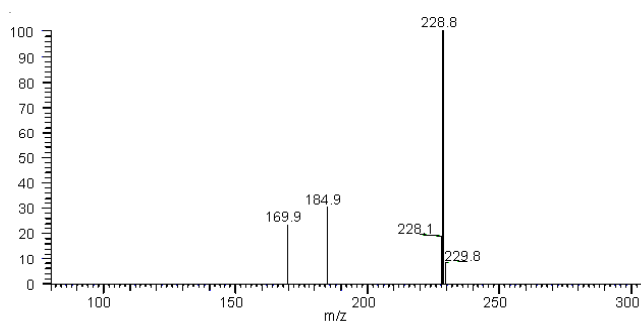


Fig. 12. Full-scan ESI mass spectrum of naproxen (negative ions)

According to Figs. 13 and 14, the major molecular ion ([M]⁻) correlated with the degradation of naproxen by DBD was m/z ions 213.9 and 184.9, 15 and 44 μ lower than the naproxen ion, indicated that the demethylation and decarboxylation reaction generated by DBD. The possible degradation pathway of naproxen by DBD is shown in Fig. 15.

Conclusion

DBD could effectively degrade naproxen in aqueous solutions. The degradation efficiency was 93.2 % when the output

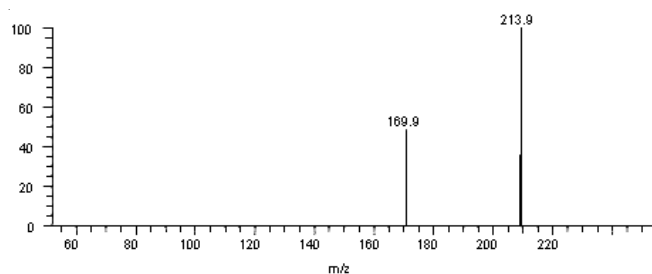


Fig. 13. Full-scan ESI mass spectrum of the m/z ion 213.9

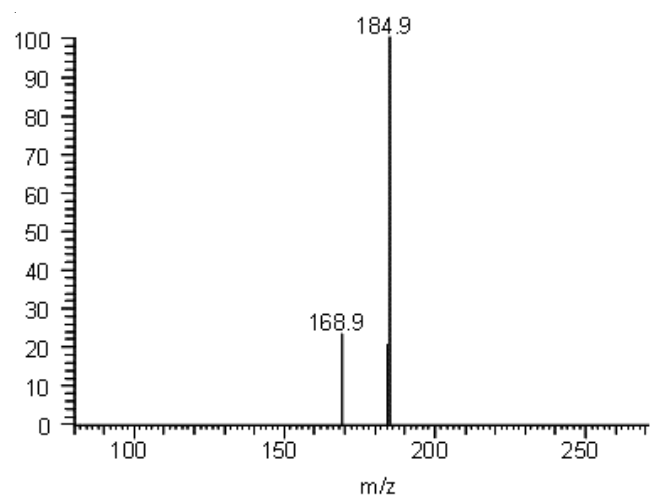


Fig. 14. Full-scan ESI mass spectrum of the m/z ion 184.9

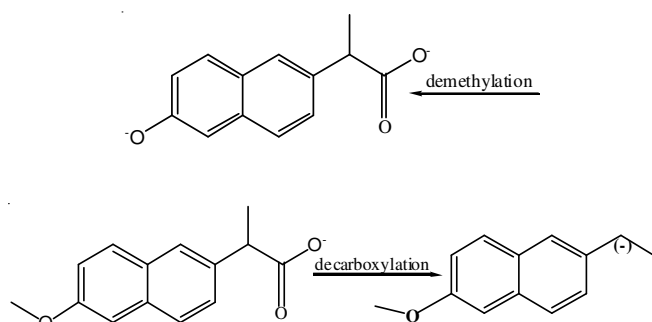


Fig. 15. Possible degradation pathway of naproxen by DBD

power was 60 W and 6 min was selected as the discharge time. The degradation reaction of naproxen followed first-order like kinetics.

The pH value affected the naproxen degradation process. The degradation yield was higher under acidic conditions than in alkaline media. Naproxen degradation efficiency decreased with the increase of initial concentration. H_2O_2 as the additive enhanced the degradation process at the concentration of 0.25 %, however, hindered the degradation at 1.0 and 1.5 %. Fe^{2+} benefited the degradation at 40 mg L^{-1} , however, the enhancement effect was weakened when Fe^{2+} was added at 120 mg L^{-1} . NO_3^- and humic acid additives also enhanced the degradation of naproxen. The pH value and TOC of naproxen solution decreased with the increasing of discharge time. The possible degradation pathway of naproxen was demethylation and decarboxylation reaction.

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