Degradation of metronidazole simulated water by nanosecond pulsed DBD plasma

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Abstract. In this work, nanosecond pulsed dielectric barrier discharge (nsp-DBD) plasma was used to degrade metronidazole simulated water under Air gas. The effects of initial concentrations, pulse peak voltages and air flow rates on metronidazole degradation were investigated, respectively. The role of hydroxyl radical in the metronidazole degradation was emphasized. The variations of solution pH value and conductivity during the discharge process were measured. Experimental results show that nsp-DBD plasma can effectively degrade metronidazole simulated water. When the initial concentration was 100 mg/L, the pulse peak voltage was 15 kV, and the air flow rate was 3 L/min, the degradation efficiency and energy yield of metronidazole were 92% and 1.83g/kWh, respectively, after 25 min treatment. The mineralization rate reached 39% after 60 min of treatment. The scavenger experiment proved that the hydroxyl radical was the main active species in metronidazole degradation. The solution pH was significantly reduced, and the conductivity was greatly increased after plasma treatment, which were corresponded to the formation of NO₃⁻, NO₂⁻ and intermediate products in the degradation process.

1. Introduction
Metronidazole (MNZ), a representative nitroimidazole antibiotic, is widely used in the treatment of infectious diseases caused by anaerobes [1]. When untreated metronidazole contaminated water is discharged into the natural environment, it will cause adverse effects on the ecosystem and harm human health. As one of the advanced oxidation technologies, non-thermal plasma technology can effectively degrade various pollutants by applying high-voltage on the electrodes and generating active radicals, hydrogen peroxide, ozone and UV light between the electrodes [2]. Many researchers used plasma technology to effectively degrade many drugs, including antibiotics [3]. But it also exposed some problems such as low degradation efficiency and high energy consumption. In this paper, nanosecond pulse power supply was used as plasma source to drive dielectric barrier discharge, which can greatly improve the degradation efficiency and energy yield. This work provides guidance for the effective and feasible application of low temperature plasma technology in the treatment of antibiotic contaminated wastewater.

2. Materials and Methods

2.1 Experimental materials
Reagent: Metronidazole (purity>99%, Aladin), Isopropanol (AR, Beijing Chemical Plant), Air was produced by air compressor, and the experimental water was all deionized water.
Instruments: Ultraviolet-visible spectrophotometer (UV-2600) was purchased from Shimazu Co., LTD. pH meter (PHS-2F) and conductivity meter (DDSJ-318) was purchased from Shanghai YiDina. TOC analyzer was purchased from TE Instrument Co., LTD. Nanosecond pulse power supply was purchased from Senyuan Science and Technology Co., LTD.

2.2 Experimental device
Figure 1 shows the self-made water treatment system in the laboratory. It consists of quartz tube reactor, power supply, oscilloscope and gas supply system. The inner electrode stainless steel tube is used as high-voltage electrode, the dielectric layer is quartz glass, and the outer electrode is grounded stainless steel net. In the experiment, the simulated metronidazole entered the reactor from the top of the liquid storage tank through peristaltic pump, and formed a liquid film on the internal electrode, which was generated between the uniform plasma internal electrode liquid and quartz tube. During the experiment, samples were taken every 5 minutes for parameter analysis.

Nanosecond pulse power supply parameters: voltage is 0~16 kV, 0~15kHz pulse frequency, pulse width 0.5 s ~ 0.8 s, pulse rise along the 104~112ns, pulse fall along the 465~480ns.

2.3 Determination of metronidazole concentration
Metronidazole solutions with different concentrations were prepared. The characteristic absorption peak of the solution at 318nm was measured by UV-visible spectrophotometer and the standard curve corresponding to absorbance and concentration was drawn. In the experiment, absorbance of different reaction solutions at different times can be measured, and the residual concentration of metronidazole in the solution can be calculated and evaluated by the standard curve.

2.4 Metronidazole removal rate, input power, energy efficiency, dynamic constant calculation method
The degradation efficiency \( D(\%) \), input power \( P(W) \), energy yield \( Y (g/kWh) \) and kinetic constant \( k \) of metronidazole were calculated by equations (1), (2), (3) and (4) respectively:

\[
D = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}
\]

\[
P = f \int_{t_1}^{t_2} U I \, dt \tag{2}
\]

\[
Y = \frac{C_0 \times V \times D}{P \times t} \times 100 \tag{3}
\]

\[
\ln \left( \frac{C_0}{C_t} \right) = kt \tag{4}
\]

Where \( C_0 \) (mg/L) and \( C_t \) (mg/L) were metronidazole concentrations in the water before and after treatment, \( f \) was pulse frequency, \( U (t) \) was instantaneous voltage, \( I (t) \) instantaneous current, \( V \) (L) was the volume of metronidazole solution in the reactor, and \( t \) (h) was the treatment time.

Figure 1. The schematic diagram of experimental setup system
3 Results and Discussion

3.1 Determination of metronidazole concentration

Figure 2(a) shows that UV-visible absorption spectrum of the solution at 200-450nm after plasma treatment for different times. With the extension of treatment time, the characteristic absorption peak intensity of metronidazole at 318nm decreased continuously, indicating that plasma can effectively degrade metronidazole in water. The absorption peak strength around 227nm keeps increasing, which was related to the organic acids, NO3− and H2O2 formed in the solution [4].

Figure 2(b) shows the degradation efficiency of metronidazole at different initial concentrations. It can be seen that the degradation efficiency decreased from 92% to 62% as the initial concentration increased from 100mg/L to 250mg/L. When the initial concentration of metronidazole solution was 100, 150, 200 and 250mg/L, the reaction kinetic constants were 0.088, 0.062, 0.049 and 0.037, respectively. With the increase of initial concentration, the degradation efficiency and reaction kinetic constants was decreased, the reason was that under the fixed avenge power, the concentration of active species remained constant, with the increase of initial concentration of metronidazole, plasma produced by the active species were in short supply, and this will lead to reduce the degradation efficiency and the reaction kinetic constants. In addition, there was also a competitive relationship between intermediate by-products and metronidazole pollutants for the reaction of active oxidizing substances, which reduced the degradation efficiency and reaction kinetic constants.

3.2 Effect of pulse peak voltage

The change of the pulse peak voltage of the power supply was the change of the applied power. Figure 3(a) shows the influence of the peak voltage on the degradation efficiency of metronidazole. When the peak voltage was 15kV (average power 24.2W), 13kV (average power 17.1W) and 11kV (average power 11.1W), the degradation efficiency was 92%, 80% and 65%, respectively. Higher pulse peak voltage, greater E/N, enhanced space charge density, more high-energy electrons, stronger UV light generation, and higher concentration of active substances (such as H2O2, •OH, O3, etc.) lead to increased degradation efficiency of metronidazole [5]. Figure 3(b) shows the variation of energy yield with discharge time at different peak voltages. With the increase of voltage, the energy yield decreased gradually. This can be explained as, on the one hand, with the increase of pulse peak voltage, the energy in the input system increased, and when the metronidazole concentration was constant, the energy utilization efficiency decreased. On the other hand, the increase of voltage will cause more electric energy to be converted into heat energy, resulting in energy loss.
3.3 Effect of air flow rates

Different types of discharge gases used in plasma discharge usually produce different degradation effects [6]. The purpose of this study is aim to practical application of DBD technology. In particular, we are interested in using low-cost air as plasma discharge working gas to study the effects of different air flow rates (0, 0.5, 2.0, 3.0 and 5.0L/min) on metronidazole degradation. As shown in Figure 4, when the treatment time was 25min, the degradation efficiency of metronidazole was 57% when the gas flow rate was 0L/min (without air input). When the air flow rates were 0.5, 2.0 and 3.0L/min, the degradation efficiency was 69%, 86% and 92%, respectively. However, when the air flow rate increased to 5L/min, the degradation efficiency decreased to 81%. The influence of gas flow rates on the active substances in plasma was mainly the residence time of the active species in the reactor, the concentration and the reaction time between them and the organic pollutant molecules. With the increase of air flow rate, the degradation efficiency of metronidazole was improved due to the increase of active species and the increase production of active nitrogen/oxygen particles in the gas phase, which improved the degradation efficiency of metronidazole. When the gas flow rate exceeded a certain value, the degradation efficiency of metronidazole decreased. Because the reactive nitrogen/oxygen particles stay in the discharge area for a short time, reducing the reaction time with organic compounds in water and the amount of reactive nitrogen/oxygen that penetrates into the water phase and reacts with metronidazole molecules.

Table 1 shows the reported degradation results of antibiotics by plasma technology. In order to compare with other technologies, the calculation method of energy yield was unified (Eqn. (3)). It can be seen that compared with other discharge modes, the degradation efficiency and energy yield of nsp-DBD to degrade metronidazole are greatly improved, which proves that nsp-DBD is a promising technology to reduce the energy consumption of plasma water treatment.

Table 1. Comparison with other reported plasma systems for degrading antibiotics in water

| Plasma discharge mode | Compounds     | concentration (mg/L) | volume (L) | Degradation efficiency (%) | Energy yield (mg/kWh) | Ref |
|-----------------------|---------------|----------------------|------------|---------------------------|-----------------------|-----|
| nsp-DBD               | metronidazole | 100                  | 200        | 92                        | 1826                  | -   |
| AC-DBD                | metronidazole | 40                   | 150        | 90                        | 79                    | [7] |
| NFD                   | metronidazole | 40                   | 150        | 88                        | 32.4                  | [8] |

Figure 3. The pulse peak voltage versus the degradation efficiency (a) and energy yield (b) of metronidazole (initial concentration: 100 mg/L; air flow rate: 3 L/min)
3.4 Changes of TOC degraded by metronidazole
The mineralization of organic compounds is also an important index to evaluate its final degradation. In order to determine the effectiveness of metronidazole degradation by nanosecond pulsed DBD plasma, the mineralization rate of metronidazole with time was measured. Figure 5 shows that with the extension of treatment time, the TOC concentration decreased continuously, and at 60min, the concentration drops to 28.85mg/L, and the mineralization rate is 39%. This indicated that the species produced by plasma can effectively oxidize metronidazole and decompose it into inorganic small molecule compounds, and finally part of it degraded into CO2 and H2O.

3.5 Effect of hydroxyl radical scavenger on metronidazole degradation
Plasma technology has been playing an important role in the degradation of high-energy electrons, ozone and active radicals in organic pollutants. In order to determine the degradation of active species in metronidazole by nanosecond pulsed DBD plasma, isopropanol was added to metronidazole solution as hydroxyl radical scavenger [9] to clarify the role of hydroxyl radical.

Figure 6 shows the effect of different doses of hydroxyl radical scavenger on the degradation efficiency of metronidazole. After the addition of 0.5 and 1.0g/L scavenger, the degradation efficiency decreased by 45% and 62% respectively. With the increase of the dose of hydroxyl radical scavenger, the degradation efficiency of metronidazole decreased. With the hydroxyl radical scavenger was added to exceed 1g/L, the degradation efficiency decreases slowly. For example, when 1.5g/L is added, the degradation efficiency decreases 63.8%, which was basically the same as that when 1g/L is added, indicating that the hydroxyl radical had been completely quenched in the system after a certain amount of scavenger was added, and will not play a role in metronidazole degradation. Analysis of hydroxyl radicals in metronidazole degradation contribution rate was about 70%, namely in the nanosecond pulse DBD plasma degradation of metronidazole reaction of hydroxyl radicals may be play a major role, but there were still part of the metronidazole degradation is caused by plasma produced by other active species, such as reactive nitrogen and ozone oxidation material [10].

![Figure 4. Effects of air flow rates on the degradation efficiency of metronidazole (initial concentration: 100 mg/L; pulse peak voltage: 15 kV)](image)

![Figure 5. The variation of metronidazole TOC with the treatment times (initial concentration: 100mg/L; pulse peak voltage: 15 kV; air flow rate: 3 L/min)](image)
4. Conclusion
In this paper, the degradation of metronidazole in water by nanosecond pulsed DBD plasma was experimentally studied. The effects of initial concentration of metronidazole, pulse peak voltage and air flow rate on the degradation effect of metronidazole were mainly investigated. The conclusions were as follows:

1) Initial concentration, pulse peak voltage and air flow rate have an impact on metronidazole degradation. Under the initial concentration of 100 mg/L, peak voltage of 15 kV, and air flow rate of 3 L/min, the degradation efficiency can reach 92% and the energy efficiency can reach 1.83 g/kWh at the treatment time of 25 min. After 60 min of treatment, the mineralization rate reached 39%. Nsp-DBD was proved to be an efficient and energy-saving water treatment technology.

2) The pH and conductivity of the solution decreased significantly after treatment, which proved the generation of reactive nitrogen species and the generation of degradation intermediates.

3) Hydroxyl radical scavenger experiments show that hydroxyl radical was the main active species in the process of metronidazole degradation by nanosecond pulsed DBD plasma.

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