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Research on the Degradation of Oxacillin in Water by Strong Ionization Discharge

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Abstract. The degradation of oxacillin in aqueous solution by strong ionization dielectric barrier discharge (DBD) was explored. The effects of input voltage, initial pH, initial concentration of solution and hydroxyl (·OH) inhibitor on the removal efficiency of OXA were investigated. The results showed that the removal efficiency of OXA with initial concentration of 20mg/L reached 91.5% under the optimal treatment conditions of 3.8 kV and 7.3 pH. With the higher voltage and the lower initial concentration, the removal effect was better. The pH of the solution has little effect on the removal efficiency, and the removal effect is the best in neutral aqueous solution. The inhibition effect of TBA was stronger than that of CO32- and HCO3-. Moreover, ·OH was the main active substance in the process of strong ionization discharge, which played a major role in the removal of OXA. In addition, two main by-products were identified, the transformation pathways including hydroxylation (+16 Da), decarboxylation (-44 Da) were observed. This study provided a theoretical basis for the effective removal of antibiotics in water by strong ionization discharge.

Keywords. Dielectric barrier discharge, oxacillin, ozone, strong ionization discharge

1. Introduction

Penicillins is among the most used antibiotic classes in the world, β-lactam oxacillin (OXA) as a typical representative of penicillins for the treatment of aerobic Gram-positive cocci [1]. OXA was often detected in wastewater plants (WWTPs) and natural water bodies, which will cause serious problems of the existence of drug-resistant bacteria and superbacteria in natural aqueous [2]. The main cause of the OXA pollution was due to the traditional process of the existing WWTPs cannot be effectively removed OXA. Therefore, it is necessary to find an effective way to eliminate OXA from aqueous.

In order to remove antibiotics from water, various advanced oxidation processes (AOP) were studied, such as ozonation, Fenton process, photochemical oxidation, photocatalysis [3-5]. These processes aim to generate strong oxygen oxidants, especially hydroxyl radicals (·OH), which can oxidize almost all organic compounds and react non selectively with various types of pollutants. However, the existing AOPs are mostly combined with activated carbon fiber, Fe_3O_4, $MnFe_3O_4$, TiO_2, ZnO, CdS, WO_3 and other catalysts [6-7]. Although the treatment effect is good, there are still has some problems

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such as high treatment cost and difficult catalyst recovery. With the development of plasma technology, especially the maturity of dielectric barrier discharge (DBD) technology, DBD technology has advantages in degradation and removal of antibiotic pollutants [8, 9]. However, the existing DBD technology has a problem of low ·OH production. Therefore, how to produce ·OH with low cost and high yield is the research focus. In this paper, the strong ionization dielectric barrier discharge technology is proposed to treat OXA in aqueous, O_3 concentration and the effects of voltage, pH, initial concentration, ·OH inhibitors on the degradation efficiency are investigated.

2. Material and Methods

2.1. Experimental Materials

β-lactam oxacillin (OXA), phosphoric acid, acetonitrile, methanol, hydrochloric acid, sodium bicarbonate and sodium carbonate were purchased from China Pharmaceutical Co., Ltd. Tertiary butanol alcohol (TBA) was supplied by Aladdin Industrial Corporation Ltd. (China).

2.2. Experimental Apparatus

The experimental system includes DBD system and water treatment circulation system, as shown in figure 1. The strong ionization DBD reactor adopts dielectric barrier plate structure, the discharge electrode is made of sintered silver metal, its outer surface is sprayed with a thin dielectric layer (α-Al_2O_3) composed of dense insulating layer, and the grounding electrode is made of stainless steel shell. The discharge gap is 2.6 mm. The sizes are 16cm×16cm×0.5cm and 16cm×16cm×0.2cm, respectively.

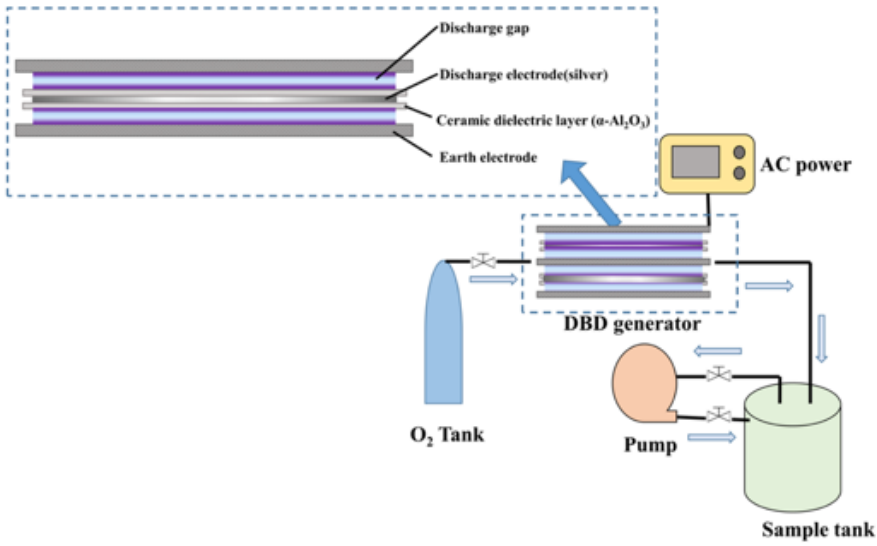

Figure 1. The flow-process diagram of water treatment systems of strong ionization discharge.

The power supply is CTP2000k power supply with discharge frequency of 5-20kHz and discharge voltage of 0-30kV. The electric field strength (E_g) formed between the plates of the generator is as high as 800 Td, the electron density between the plates is $10^{15}/cm^3$, the average electron energy (T_e) is increased to 13 eV, and the energy density of the gap discharge is 2.1 w/cm^2, which is called strong ionization discharge [10]. Under the action of 2 t/h circulating pump, Venturi jet is added in the water circulation system to increase the reaction between active substances and pollutants, which can be recycled and the removal effect is optimized. The degradation experiment of 20 mg/L OXA solution was carried out by strong ionization DBD reaction system. The concentrations of OXA in water samples were detected at 5 min, 10 min, 30 min and 60 min, respectively.

2.3. Analytical Methods

The absorption wavelength of OXA was measured by UV-visible spectrophotometer (UV22450, Shimadzu, Japan). The concentration of OXA was determined by high performance liquid chromatography (HPLC, LC-1260, Agilent, USA) and waters XBridge C18 column at 225 nm. The eluent was composed of phosphate buffer (0.02 mmol/L, pH 5)/acetonitrile/methanol, 64/27/9 (V/V/V), and the flow rate was 0.4 ml/min. High concentration ultraviolet dissolved water ozone analyser (CL-7685, B&C electzanice, Italy) was used to measure the concentrations of O_3 generated during the process. The intermediate byproducts of OXA were measured by high-performance liquid chromatography mass spectrometry (LC/MS/MS) (7890B-5977B, Agilent, USA).

3. Results and Discussion

3.1. Effects of Input Voltage on OXA Degradation

The input voltage *U* affects the production of active particles and the removal efficiency η of pollutants. As shown in figure 2, under *U* of 2.1kV, 3.0kV and 3.8kV, η of OXA increased to 72.0%, 75.4% and 83.6%, respectively, after 30 min strong ionization DBD treatment. With the extension of reaction time, η increased to 82.3%, 87.4% and 91.5% respectively. Similarly, figure 3 showed that the kinetic constant *R* can be enhanced when the increased of *U*. At *U* of 3.8 kV, *R* can reach up to 0.049 min^{-1}. As shown in figure 4, under the same reaction time and different voltage, the amount of O_3 was also different. When *U* reaches 3.8kV, the O_3 concentration reaches 14.3 mg/L. It is worth emphasizing that the concentration of O_3 produced by the strong ionization DBD reactor increased with the increase of *U*. Therefore, increasing *U* can improve η of OXA solution, and the strong ionization DBD under *U* is a feasible way to improve η of antibiotic wastewater.

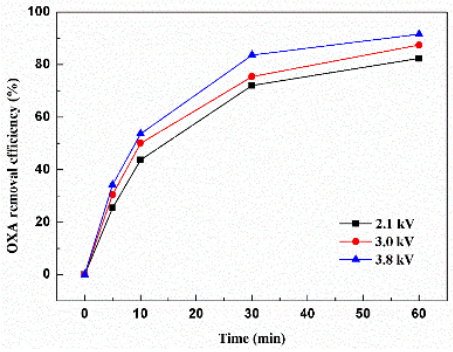

Figure 2. Effect of the input voltage on OXA removal efficiency.

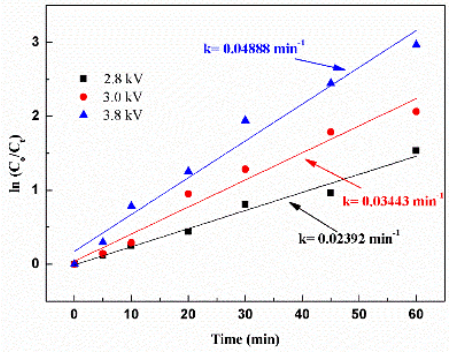

Figure 3. Effect of the input voltage on OXA degradation kinetic constant.

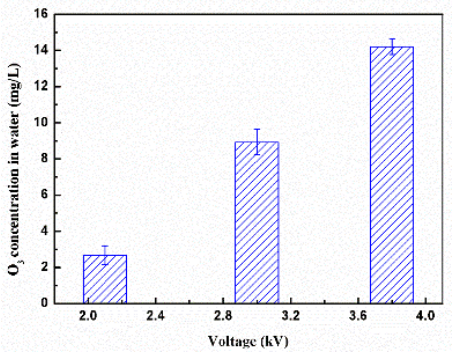

Figure 4. O_3 concentration in water on different voltage.

3.2. Effects of pH on OXA Degradation

The pH value of the solution has an effect on the amounts of active particles and the reaction mechanism between active particles and pollutants. Therefore, it is of great significance to study the degradation of OXA solution by strong ionization discharge at different pH values. As illustrated in figure 5 summarizes the removal efficiency of water samples under different treatment time and pH conditions. Under the same conditions, when the pH values are 3.8, 7.3 and 9.8 respectively, η of OXA after 60 min treatment are 85.3%, 91.5% and 80.5% respectively. Analogously, greater kinetic constant can be obtained at natural pH (7.3), as shown in figure 6, showing that pH value has little effect on η of quinoline. It can be seen that OXA has a better degradation effect under neutral conditions, and η under alkaline conditions is better than that under acidic conditions. This can be explained by the fact that O_3 is more stable but less soluble under acidic conditions [11, 12]. In addition, under alkaline conditions, ·OH can promote the decomposition of O_3, and O_3 can produce more O_2 [13]. Therefore, a large number of active particles can degrade OXA faster. The results show that the strong ionization discharge DBD system is suitable for the removal of pollutants in both acidic and alkaline solutions.

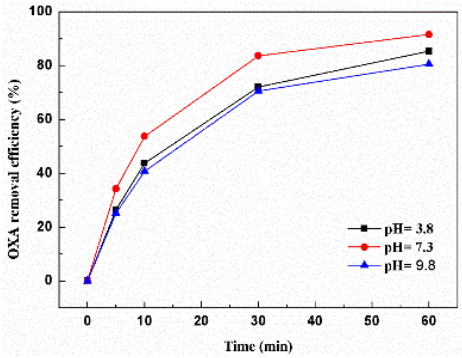

Figure 5. Effect of the pH on OXA removal efficiency.

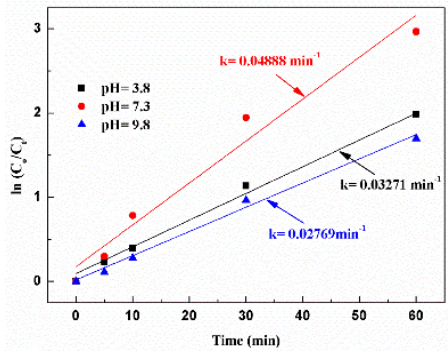

Figure 6. Effect of the pH on OXA degradation kinetic constant.

3.3. Effects of Initial Concentration on OXA Degradation

Under the conditions of *U* 3.8 kV, discharge frequency 20 kHz and pH value 7. 3, the effect of initial concentration on η of OXA was investigated. As shown in figure 7, after 60 min strong ionization discharge treatment, η of OXA decreased with the extension of time, the initial concentration of OXA increased from 5 mg/L to 40 mg/L, η of OXA were 99.0%, 91.5.8% and 78.7%, respectively. Similarly, figure 8 showed that *R* can be decreased when the initial concentration on quinoline were increased, which can reach 0.065 min^{-1}, 0.049 min^{-1} and 0.024 min^{-1}. The higher the initial concentration of the solution, the more active particles are consumed by the strong ionization discharge, η is reduced. It is further confirmed that the high concentration of pollutants in water is greatly affected by the strong ionization discharge.

3.4. Effects of ·OH Inhibitors on OXA Degradation

Based on the theory of dielectric barrier discharge, not only O_3, but also ·OH is one of the representatives of active particles in strong ionization discharge system. However, the effects of different inhibitors on the degradation of OXA by strong ionization discharge need to be investigated. As shown in figure 9, when the concentrations of TBA, CO_3^{2-} and HCO_3^- were 30 mg/L, η of OXA were 46.1%, 70.2% and 54.5% respectively in the 60 min strong ionization discharge oxidation process. *R* decreased from 0.049 min^{-1} to 0.021 min^{-1}, 0.014 min^{-1} and 0.011 min^{-1} in strong ionization discharge DBD system with TBA, CO_3^{2-} and HCO_3^-, respectively (figure 10). η was 91.5% without any inhibitors. The results showed that the addition of inhibitors had obvious inhibition on the degradation of OXA, and TBA had the strongest inhibition effect. These inhibitors (TBA, CO_3^{2-} and HCO_3^-) can inhibit the formation of ·OH. Therefore, ·OH is the main active particles of OXA degradation [12].

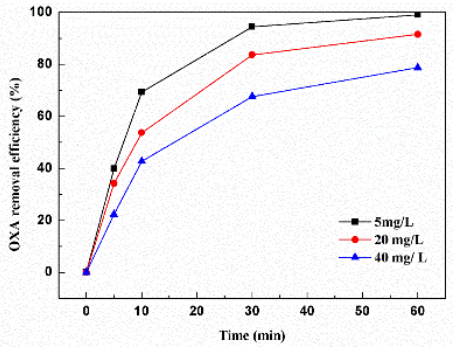

Figure 7. Effect of the initial concentration on OXA removal efficiency.

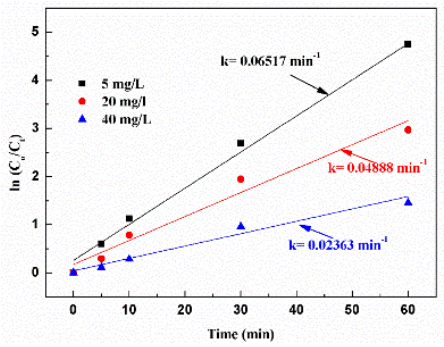

Figure 8. Effect of the initial concentration on OXA degradation kinetic constant.

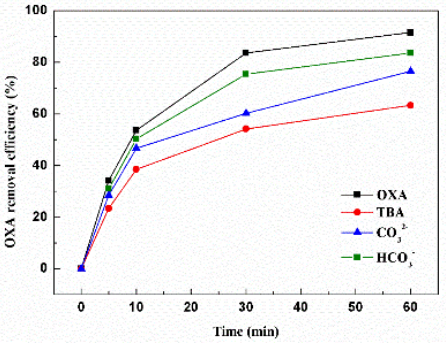

Figure 9. Effect of the ·OH inhibitors on OXA removal efficiency.

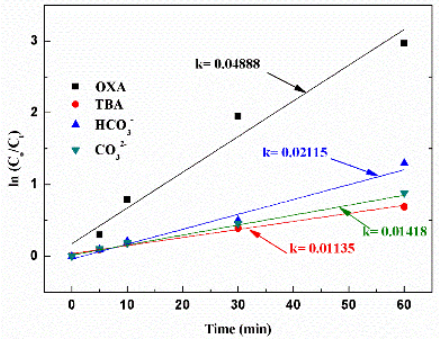

Figure 10. Effect of the ·OH inhibitors on OXA degradation kinetic constant.

3.5. Possible Degradation Mechanism and Pathway of OXA

Based on the LC-MS results the two by-products of OXA (m/z 420, m/z 374) identified and as indicated in figure 11, different transformation pathways were proposed including hydroxylation (+16 Da), decarboxylation (−44 Da). Compound m/z 420 was found in the oxidation process, which could have been generated from the hydrolysis of OXA at the beta-lactam ring. This is a common degradation pathway that has been previously reported for the removal of ß-lactam antibiotics by non-thermal plasma, the photo-Fenton process and the sonochemical treatment [13, 14]. Further reaction of the product m/z 420 with ·OH results in the decarboxylation, which could evolve into m/z 374, might be resulted from the strong electrophilic agent property of ·OH, favoring the decarboxylation process.

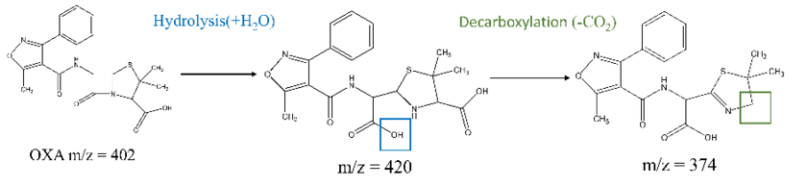

Figure 11. Proposed reaction pathway for the degradation of OXA by a strong ionization discharge.

4. Conclusions

In order to solve the problem of low efficiency and poor treatment ability in traditional treatment methods, a strong ionization DBD reaction system was studied to degrade OXA in water. The effects of different *U*, initial pH value, initial concentration and ·OH inhibitors dosage on η of OXA were investigated. The results showed that η of OTC increased with the increase of *U* and the decrease of initial concentration. At the same time, the addition of TBA, CO_3^{2-} and HCO_3 effectively inhibited the removal of OXA in aqueous solution by inhibiting the existence of hydroxyl groups. It should be noted that pH has little effect on η of ·OH, and the best removal condition is neutral. Under different *U*, with the higher *U*, the more O_3 was produced in the system. In addition, two main by-products (m/z 420 and m/z 374) from OXA of the strong ionization discharge progress were observed.

Acknowledgements

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References

[1] Nomura R, Nakaminami H, Takasao K, Muramatsu S and Noguchi N 2020 A class a β-lactamase produced by borderline oxacillin-resistant staphylococcus aureus hydrolyzes oxacillin *Journal of Global Antimicrobial Resistance* **22**.

[2] Watkinson A J, Murby E J, Kolpin D W and Costanzo S D 2009 The occurrence of antibiotics in an urban watershed: from wastewater to drinking water *Sci. Total Environ* **407** 2711-2723.

[3] Hua Z H, Guo K H, Kong X J, Lin S K, Wu Z H, Wang L P, Huang H and Fang J Y 2019 PPCP degradation and DBP formation in the solar/free chlorine system: Effects of pH and dissolved oxygen *Water Res.* **150** 77-85.

[4] Choi S, Sim W, Jang D, Yoon Y, Ryu J, Oh J, Woo J S, Kim Y M and Lee Y 2020 Antibiotics in coastal aquaculture waters: Occurrence and elimination efficiency in oxidative water treatment processes *Hazard Mater.* **396** 122585.

[5] Watkinson A J, Murby E J and Costanzo S D 2007 Removal of antibiotics in conventional and advanced wastewater treatment: Implications for environmental discharge and wastewater recycling *Water Res.* **41** 4164-4176.

[6] Wang J, Sun Y B, Feng J W, Xin L and Ma J Z 2016 Degradation of triclocarban in water by dielectric barrier discharge plasma combined with TiO_2/activated carbon fibers: Effect of operating parameters and by products identification *Chem. Eng. J.* **300** 36-46.

[7] Uslu M O and Balcioglu I A 2009 Comparison of the ozonation and Fenton process performances for the treatment of antibiotic containing manure *Sci. Total Environ.* **407** 3450-3458.

[8] Yi R J, Guo H, Wang H J, Du D L, Zhang Q and Yi C W 2021 Multiple production of highly active particles for oxytetracycline degradation in a large volume strong ionization dielectric barrier discharge system: Performance and degradation pathways *Sep. Purif. Technol.* **274** 119103.

[9] Yi R J, Yi C W, Du D L, Zhang Q, Yu H J and Yang L 2021 Research on quinoline degradation in drinking water by a large volume strong ionization dielectric barrier discharge reaction system *Plasma Sci. Technol*. **23** (8).

[10] Zhang Y B, Bai M D, Chen C, Meng X Y, Tian Y P, Zhang N H and Yu Z 2013 OH treatment for killing of harmful organisms in ship's ballast water with medium salinity based on strong ionization discharge *Plasma Chem. Plasma Process* **33** 751-763.

[11] Bao Y, Lee W J, Lim T T, Wang R and Hu X 2019 Pore-functionalized ceramic membrane with isotropically impregnated cobalt oxide for sulfamethoxazole degradation and membrane fouling elimination: Synergistic effect between catalytic oxidation and membrane separation *Appl. Catal. B. Environ.* **254** 37-46.
[12] Fu Y Y, Wu G, Geng J J, Li J C, Li S N and Ren H Q 2019 Kinetics and modeling of artificial sweeteners degradation in wastewater by the UV/persulfate process *Water Res.* **150** 12-20.
[13] Lueddeke F, Hess S, Gallert C, Winter J, Guede H and Loeffler H 2015 Removal of total and antibiotic resistant bacteria in advanced wastewater treatment by ozonation in combination with different filtering techniques *Water Res.* **69** 243-251.
[14] Magureanu M, Piroi D and Mandache N B 2011 Degradation of antibiotics in water by non-thermal plasma treatment *Water Research* **45** (11) 3407-3416.