

Study on the Treatment of Veterinary Antibiotic Wastewater by Advanced Oxidation Synergized with Biofilm

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Abstract. The discharge of veterinary antibiotics into natural water bodies can lead to the spread of environmental antibiotic resistance genes, disrupt ecological balance, and pose threats to human health. This study employed advanced oxidation technology synergized with biofilm to conduct in-depth treatment research on production wastewater containing two veterinary antibiotics, Tylosin (TYL) and Tylvalosin (TAT), and investigated the degradation characteristics of TYL and TAT by advanced oxidation technology. The results showed that the degradation efficiency of ozone (O₃) was significantly superior to that of hydrogen peroxide (H₂O₂) and sodium chlorite (NaClO₂). Under acidic conditions (pH=5), the degradation rates of TYL and TAT by O₃ exceeded 92% within 3 minutes. Kinetic analysis confirmed that the oxidative degradation process of TYL and TAT by O₃ followed a pseudo-first-order kinetic model. Based on the characteristics of the actual wastewater from the enterprise, a pilot-scale device integrating "ozone oxidation + biofilm + anaerobic/aerobic + coagulation sedimentation" was constructed. After debugging and biofilm acclimation, a continuous 10-day treatment trial using simulated wastewater demonstrated significant wastewater treatment effectiveness by this system. The degradation rates for TYL and TAT reached 97.1% and 95.8%, respectively; the degradation rates for COD and BOD₅ both exceeded 98%; and the degradation rate for NH₃-N was 88.6%.

Keywords: Biofilm; Tylosin; Tylvalosin; Veterinary Antibiotics

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1 Introduction

Antibiotics are a class of chemicals produced by microbial metabolism that can kill or inhibit bacterial growth [1]. Their main mechanisms of action include inhibiting cell wall synthesis, altering cell membrane permeability, inhibiting nucleic acid and protein synthesis, and disrupting metabolism [2]. Classified by chemical structure, most prescription antibiotics can be categorized into sulfonamides, tetracyclines, fluoroquinolones, macrolides, β -lactams, aminoglycosides, lincosamides, polypeptides, chloramphenicols, etc. [3]. Among them, macrolide antibiotics contain a 12-16 carbon lactone ring and can bind to the 50S subunit of bacterial ribosomal protein, inhibiting bacterial reproduction by suppressing protein synthesis [4].

Tylosin is a 16-membered macrolide antibiotic obtained from the culture broth of *Streptomyces fradiae*[5]. It mainly consists of four active components: Tylosin A, Desmycosin (Tylosin B), Macrocin, and Relomycin, with the A component exhibiting the highest activity in organisms [6]. Tylosin is widely used for treating diseases and promoting growth in poultry. For example, when combined with dietary management, tylosin can effectively control rumen acidosis and liver abscesses. Min et al. [7] conducted a systematic study on tylosin from toxicological and microbiological perspectives, establishing health guidance values and maximum residue limits,

thereby providing a scientific basis for the safe use of tylosin. Tylosin residues can cause damage to the human cochlear nerve and vestibular function, and in severe cases, may lead to serious damage to the kidneys, liver, and hematopoietic system [8]. Tylvalosin, also known as Acetylisovaleryltylosin Tartrate, is a 16-membered ring macrolide antibiotic synthesized through a series of reactions including acetylation, isovalerylation, and alcoholysis using tylosin as the raw material [20]. Due to its immunomodulatory functions, strong antibacterial activity [9], low cost, broad antibacterial spectrum, and high stability, it is commonly used to treat respiratory and intestinal infectious diseases in livestock and poultry [10]. Research indicates that this antibiotic is more effective in certain aspects compared to other antibiotics and is expected to become a best-selling drug in the global veterinary antibiotic market. As it is a new, third-generation, animal-specific broad-spectrum antibiotic, most current studies focus on its production methods, biotransformation, and medicinal effects [11-13], with limited research on removing its pollution.

With the rapid development of the social economy and the improvement of living standards, the demand for livestock and poultry products has gradually increased. The livestock and poultry breeding industry has shifted from individual scattered farming to large-scale intensive farming [14]. This breeding method is more prone to infectious diseases, which spread faster, causing higher economic losses for breeders. Because antibiotics can inhibit bacterial infections and adding small amounts of antibiotics to feed can promote animal growth, they are widely used in animal husbandry and aquaculture [15]. Furthermore, the global demand for veterinary antibiotics is increasing year by year. China is the largest consumer of antibiotics globally, accounting for 45% of total global usage. In 2017, the global consumption of veterinary antimicrobials was 93,309 tons, and it is projected to increase by 11.5% to 104,079 tons by 2030 [16]. Antibiotic production processes generate large amounts of wastewater. If discharged into the environment untreated, antibiotic residues in the wastewater can lead to the proliferation of antibiotic-resistant bacteria, potentially causing water pollution [17] and soil pollution, disrupting the ecological balance [7], and even endangering human health in severe cases. Many countries have set limits on antibiotic residues in water samples. China stipulates that macrolide antibiotics in wastewater must not exceed 850 mg/t [18].

Antibiotic pharmaceutical wastewater primarily originates from multiple stages of the antibiotic production process and is characterized by complex composition, high concentration, and high toxicity [19]. (1) Fermentation wastewater. This wastewater contains large amounts of residual culture medium, fermentation metabolites, and mycelium, with COD concentrations typically ranging from 5000 to 80,000 mg/L, and contains a certain concentration of antibiotic residues. (2) Wastewater containing organic solvents, acids, alkalis, etc. Wastewater from the extraction and refining processes contains organic solvents, acids, alkalis, and other chemicals, as well as incompletely extracted antibiotic products. This wastewater not only has high COD but also contains large amounts of salts and pigments. (3) Cleaning wastewater. Equipment cleaning wastewater contains residual fermentation broth, extraction liquid, and product components. Although the single discharge volume is small, the pollutant concentration is high. (4) Cooling water. The main components include sugars, proteins, fats, and inorganic salts, which are residual nutrients after fermentation. Cooling water often has abundant volume but relatively low pollutant content, and its volume is also affected by seasonal changes. It is worth noting that some enterprises also discharge small amounts of laboratory wastewater, which may contain various experimental reagents and trace highly active substances [31]. The mixture of these different sources of wastewater forms antibiotic pharmaceutical wastewater with bio-inhibitory and refractory characteristics, posing great challenges for subsequent treatment. Residual antibiotics in the wastewater may also induce the production of resistant bacteria in the environment, posing potential threats to the ecological environment and human health. Antibiotic pharmaceutical wastewater has complex composition, high organic concentration, biotoxicity, poor biodegradability, large water quality fluctuations, and limited biological degradability. It features high treatment difficulty, large investment, high operating costs, and difficulty in achieving stable discharge standards. Antibiotic pharmaceutical wastewater is rapidly becoming one of the most serious environmental and public health problems in the world [20].

The core mechanism of AOPs lies in introducing energy (such as light energy, electrical energy, or thermal energy) and/or chemicals (such as O_3 , H_2O_2) into the wastewater, undergoing a series of physical and chemical reactions to generate highly oxidizing free radicals in situ, such as hydroxyl radicals ($\bullet OH$), superoxide radicals ($\bullet O_2^-$), and sulfate radicals ($\bullet SO_4^-$) [21]. These radicals can directly mineralize these refractory organic pollutants into carbon dioxide and water, or oxidize them into low-toxicity or non-toxic small molecular substances [22]. The Fenton

method is widely used due to its mild reaction conditions, simple equipment, and good treatment efficiency. It primarily utilizes the reaction between peroxide (usually H_2O_2) and Fe^{2+} to generate highly active free radicals (usually $\bullet\text{OH}$), leveraging the strong oxidizing power of the radicals to remove pollutants [23]. Researchers have found that the classic Fenton process requires maintaining the system at acidic conditions ($\text{pH}=2\sim 4$) to ensure Fe^{2+} stability. For example, Dehghani et al. [24] found that when $\text{pH}=4.5$ and $\text{H}_2\text{O}_2:\text{Fe}^{2+}=1.5:1$ (mol), the degradation rate of sulfonamide antibiotics could reach 99.99%, and the degradation effect significantly decreased as pH increased. To reduce the limitations of the Fenton method and lower costs, scholars often dope the Fenton system with some metals or metal ions. Commonly used dopants include zero-valent iron. For instance, Conde-Cid [25] found that doping the Fenton system with zero-valent iron nanoparticles could effectively improve antibiotic degradation efficiency, achieving a 95% removal rate for sulfadiazine antibiotic within 5 minutes. Some studies also introduce photoelectric effects to enhance the treatment efficiency of the Fenton method. For example, Zhang [26] used the Fenton method combined with electrocatalysis (electro-Fenton) and the Fenton system introduced with UV (UV-Fenton) to treat antibiotics in aquaculture wastewater. The results showed that the antibiotic removal rate by electro-Fenton reached 95%, and the UV-Fenton method achieved a 90% removal rate, with shorter required reaction times.

Given that the ultimate goal of the research is to apply the treatment process to actual wastewater degradation, it is necessary to conduct in-depth research on integrated treatment processes to maximize treatment benefits. In the biodegradation process, antibiotics are toxic to microorganisms. Advanced oxidation technology is usually used as a pretreatment step to reduce pollutant toxicity and avoid fatal effects on microorganisms in subsequent biological treatment [27]. Furthermore, before advanced oxidation treatment, physical or chemical methods are usually used to remove most insoluble impurities. From the perspective of practicality and effectiveness, combined processes are expected to become the best solution for treating antibiotic-containing wastewater. However, existing combination strategies still have problems such as single technology and high treatment cost. For example, Silva et al. [28] used a biological method - photo/Fenton oxidation - biological method process to treat landfill leachate, with a treatment capacity of $100\text{ m}^3/\text{day}$ and a cost of $6.8\sim 11.3\text{ €/m}^3$. This cost is still higher than practical application requirements. Torres et al. [29] used physical flocculation pretreatment + solar/Fenton oxidation + biological post-treatment process to treat landfill leachate, with a treatment capacity of $40\text{ m}^3/\text{day}$. The biodegradability of the waste liquid after solar/Fenton oxidation exceeded 70%, and biological post-treatment could completely remove pollutants, with a total cost of about 4.3 €/m^3 , of which H_2O_2 consumption cost accounted for 72%.

In view of this, this study proposes using advanced oxidation technology synergized with biofilm as a solution for treating antibiotic pharmaceutical wastewater. By optimizing and controlling operating parameters to improve treatment efficiency, it provides a reference for treating actual antibiotic wastewater and enhances the treatment effect of real antibiotic wastewater. Meanwhile, this solution aims to block the generation and spread of resistance genes, providing a guarantee for environmental ecological protection and human health.

2 Experimental Process

2.1 Investigation of Factors Influencing Antibiotic Degradation by Advanced Oxidation Technology

This study used a quartz ozone tubular generator (dielectric barrier discharge technology) with industrial-grade oxygen (purity $\geq 95\%$) as the gas source to produce ozone. The maximum ozone production of this device was 10 g/h , with an operating power of $70\text{-}80\text{ W}$ (rated voltage 220V). The experimental system was equipped with a fine sand microporous aeration head. At the start of the reaction, the oxygen flow rate was controlled at 1.0 L/min . Before the formal reaction, the aeration head was pre-operated in distilled water for 3 minutes to eliminate systematic errors during the initial equipment startup. To explore the optimal process parameters for the degradation of TYL and TAT by advanced oxidation technology, the experiment used a single-factor variable method. Under the premise of keeping basic parameters such as oxidant dosage and ozone aeration rate (1 L/min) constant, the following key factors were systematically investigated: (1) types of oxidants (O_3 , H_2O_2 , and NaClO_2); (2) solution pH gradient (5, 6, 7, 8, and 9); (3) co-substrate glucose concentration (2000 , 5000 , 8000 mg/L); (4) antibiotic concentration (50 , 100 , 200 , 300 , and 400 mg/L).

2.2 Oxidant Concentration Analysis Method

The residual oxidant concentration in water was tested using the N,N-diethyl-1,4-phenylenediamine (DPD) spectrophotometric method. Specific steps were: DPD indicator preparation: Dissolve 1.0g of N,N-diethyl-1,4-phenylenediamine hydrochloride reagent in 1L of chlorine-free distilled water, add 8mL of dilute sulfuric acid (25%) and 0.2g of Na₂EDTA, and store in a brown stoppered bottle for later use. Phosphate buffer solution preparation: Dissolve 24g of anhydrous Na₂HPO₄, 46g of anhydrous KH₂PO₄, 0.8g of Na₂EDTA, and 0.02g of HgCl₂ in 1L of distilled water, adjust to pH=6.5. Standard curve drawing: Dissolve 0.891g of KMnO₄ in distilled water, and dilute 100 times as the standard working solution. Take 7 identical 10mL brown colorimetric tubes, add 0, 0.1, 0.2, 0.5, 1.0, 2.0, 4.0mL of the standard working solution respectively, then add 0.5mL of phosphate buffer solution and 0.5 mL of DPD indicator sequentially, mix well, and dilute to 10mL with distilled water. Using distilled water as a reference, measure the absorbance of different standard solutions at the maximum absorption wavelength of 515nm using a spectrophotometer, and draw the standard curve. Determination of residual oxidant concentration in water samples: Take 10mL of water sample, add 0.1g of KI, 0.5mL of buffer solution, 0.5mL of DPD indicator, measure the absorbance at 515 nm, read after stabilizing for 2 minutes, and then calculate the oxidant concentration using the standard curve.

2.3 Pilot-scale Equipment Setup

Based on the wastewater quality of the pharmaceutical enterprise, a suitable treatment process system was selected. This experiment designed and built a pilot-scale equipment integrating "ozone oxidation + biofilm + anaerobic/aerobic + coagulation sedimentation", with a designed treatment capacity of 0.5 t/d.

2.3.1 Equalization Tank

The volume of the equalization tank for this project was 310L. The raw water and the secondary biochemical effluent were two independent pipelines (PVC-U pipes), with an inner diameter of 40mm, each equipped with an inflow flow meter to detect the inflow. The two pipelines converged into a main pipe before the equalization tank. A sampling valve was installed on the main pipe to sample the incoming water for analysis of various indicators and monitor the raw water quality. After the converging main pipe, the wastewater pH was adjusted to 5 to improve the subsequent pre-oxidation efficiency. An inlet valve was installed to control the inflow into the tank. The equalization tank was equipped with a mixer to fully mix the wastewater with the secondary biochemical water. The inlet of the equalization tank was equipped with 2 raw water lift pumps and one liquid level gauge.

2.3.2 Pre-oxidation Tank

This study used a high-efficiency ozone system to pre-oxidize the effluent from the equalization tank to improve wastewater biodegradability. The system was equipped with a quartz ozone tubular generator (dielectric barrier discharge technology), using industrial-grade oxygen (purity ≥95%) as the gas source to produce ozone. The maximum ozone production of this device was 10 g/h, with an operating power of 70~80W (rated voltage 220V). The reactor adopted a dual-chamber series design. The front chamber was equipped with a fine sand microporous aeration device (aperture 10~20μm). Under an oxygen flow rate of 1.0L/min, uniform micro-bubbles were generated, and the aeration head was inserted into the bottom of the pre-oxidation tank to achieve mass transfer of ozone from the gas phase to the liquid phase, creating favorable reaction conditions for subsequent biofilm treatment while maximizing ozone utilization efficiency. In the rear chamber, KI was used to absorb the residual oxidant in the wastewater.

2.3.3 Biofilm Tank

Constructed biofilm was added to the biofilm tank to treat the water from the pre-oxidation tank. This tank was designed with dual chambers, ensuring sufficient contact between the biomass and the wastewater, avoiding biofilm clogging issues, and providing a reliable solution for the efficient removal of refractory organic compounds like antibiotics.

2.3.4 Anaerobic Tank

The anaerobic reaction system designed in this study used an innovative stirring device to ensure treatment efficiency. The reactor was configured with a large stirrer, consisting of three sets of blade inclination angle 45° symmetrically distributed at 120 degrees. This prevented sludge sedimentation or scum accumulation during anaerobic treatment, facilitating fuller reaction between the wastewater and anaerobic microorganisms.

2.3.5 Aerobic Tank

The aerobic treatment tank utilized an electromagnetic air pump with an exhaust volume of 88L/min to intermittently aerate air, providing living conditions for aerobic microorganisms. The aeration head was a fine sand microporous aeration device.

2.3.6 Flocculation Sedimentation Tank

In this module, the coagulant was prepared by mixing a 5% polyaluminum chloride (PAC) solution and a 0.3% polyacrylamide (PAM) solution at a volume ratio of 3:1. A pump was used to inject the mixed coagulant into the flocculation sedimentation tank at a flow rate of 60 mL/min. This coagulation sedimentation tank consisted of 3 compartments. The first two compartments were equipped with stirrers to ensure thorough mixing of the coagulant and wastewater, thereby enhancing the coagulation and sedimentation effect. In the last compartment, the fully mixed wastewater underwent sedimentation separation. The supernatant was discharged from the upper outlet, while the sediment flowed into the sand filter tank through the lower outlet for further purification.

2.3.7 Sand Filter Tank

The sand filter tank consisted of a layer of fine sand of appropriate depth, with a layer of gravel or coarse sand laid at the bottom as a support layer to prevent fine sand loss and enhance filtration. Additionally, activated carbon was added to the sand filter tank to further improve the adsorption capacity for organic matter and odors. When water passed through the sand filter tank, particulate matter in the water was intercepted by the fine sand layer, thereby purifying the water quality. To ensure the filtration effect of the sand filter tank, it needed to be cleaned regularly. If long-term lack of cleaning caused severe sand layer clogging and difficult cleaning, the sand filter tank needed to be replaced and reloaded.

3 Results and Discussion

3.1 Investigation of Factors Influencing Antibiotic Degradation by Advanced Oxidation Technology

This study used three oxidants (O_3 , H_2O_2 , and $NaClO_2$) to treat water samples containing TYL and TAT, both at a concentration of 100 mg/L.

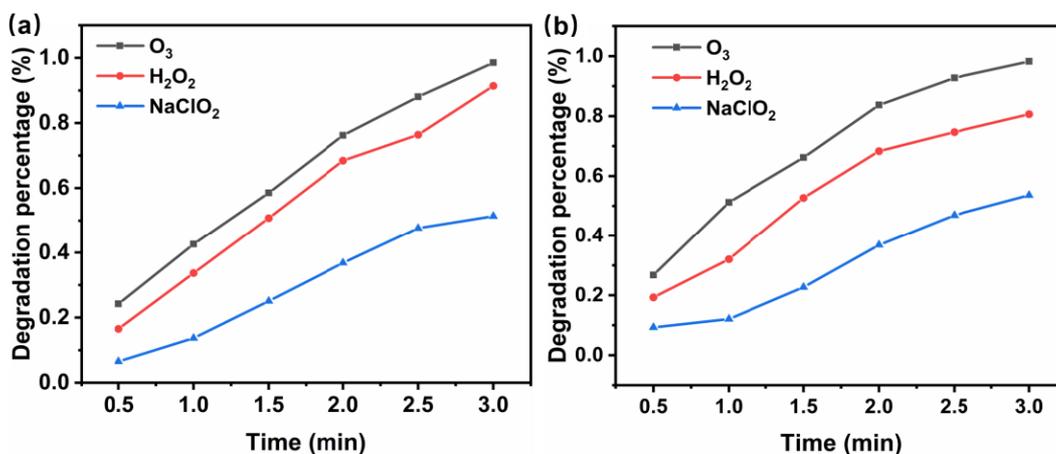


Figure 1 Effect of different oxidants on degradation of TYL (a) and TAT (b).

As shown in Figure 1, under the same reaction conditions, the degradation effects of these three oxidants on the two antibiotics showed significant differences [30]. Among them, O₃ exhibited the highest degradation efficiency, with degradation rates for TYL and TAT both exceeding 98% within 3 minutes. This is the result of the combined action of direct oxidation by ozone molecules and the •OH radicals generated. In comparison, H₂O₂ showed the next best degradation effect on TYL and TAT, with degradation rates of 91.4% and 80.7%, respectively; while NaClO₂ had the lowest degradation efficiency, only 51.4% and 53.6%. This differential performance may be related to the oxidation potentials of the different oxidants and their specific reactions with the molecular structures of the target compounds. In summary, ozone was selected as the primary oxidant for further in-depth treatment of antibiotic pharmaceutical wastewater.

This study investigated the influence of water sample pH on oxidant concentration and its degradation effect during the wastewater treatment process using ozone oxidation technology. As shown in Figure 2, the lower the pH, the higher the oxidant concentration in the water sample. When pH=5, the oxidant concentration reached equilibrium within 7 minutes, at which point the oxidant concentration in the water sample was 4.64 mg/L; under the same experimental conditions, when pH=11, the oxidant concentration in the water sample at equilibrium was only about 1.44 mg/L. This is because pH significantly affects the form of ozone in the water sample. In a high pH environment, ozone can hardly exist stably in the water sample in molecular form [31], hence the effective oxidant concentration decreases. pH not only affects the form of ozone in the water sample and the oxidant concentration but also directly affects its ability to degrade antibiotics. As shown in Figure 2, the lower the pH, the better the antibiotic degradation effect. Under the condition of pH=5, the degradation rates of TYL and TAT in the water sample both exceeded 92.0% within 6 minutes, showing the best degradation efficiency. As the pH increased, the degradation effect of the antibiotics gradually decreased. Therefore, when using ozone oxidation technology to treat TYL and TAT pharmaceutical wastewater, it should be conducted under the condition of pH=5 to improve treatment efficiency.

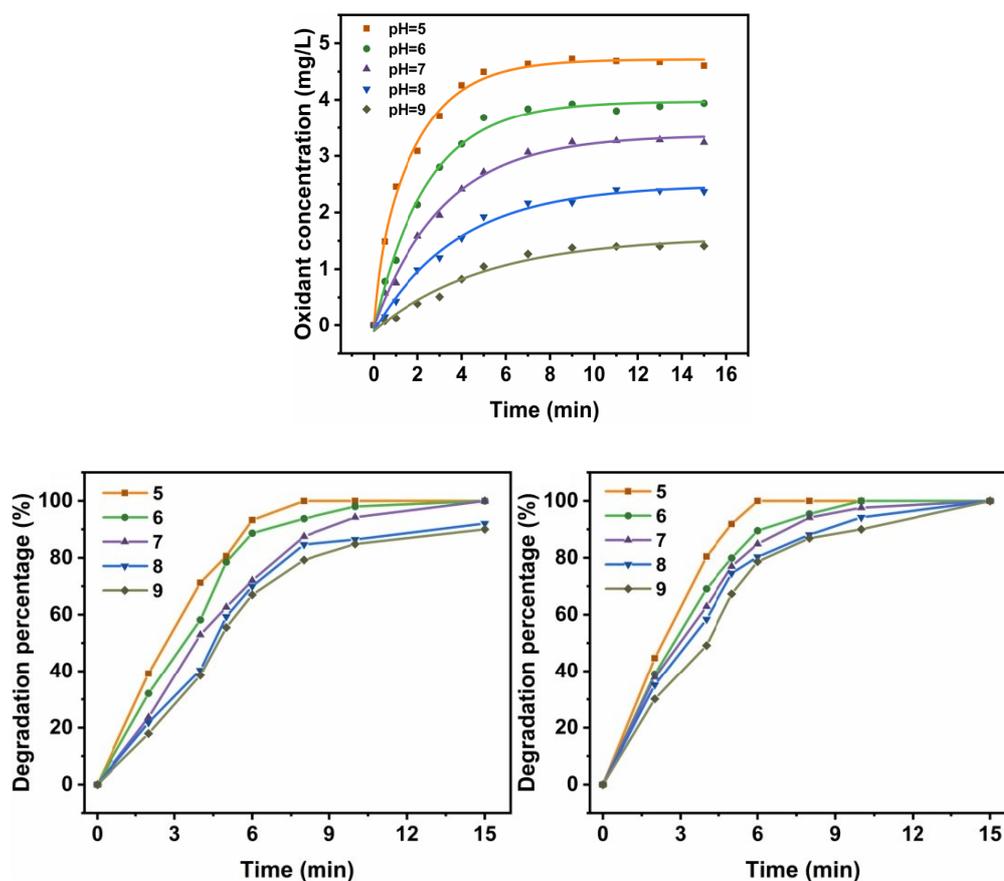


Figure 2 Oxidant concentration in solution at different pH; Effect of pH on advanced oxidative degradation of TYL and TAT

To investigate the effect of COD on the degradation efficiency of antibiotics by ozone, this study first detected the COD values of glucose solutions at different concentrations and performed linear fitting analysis. The results are shown in Figure 2, revealing a significant positive correlation between glucose concentration and COD. This finding provides important basic data for accurately assessing the impact of COD on the degradation efficiency of antibiotics by ozone in subsequent studies. Three water samples with pH=5 and TYL and TAT concentrations of 200 mg/L were prepared, with glucose concentrations of 2000, 5000, and 8000 mg/L added respectively, corresponding to COD values of 1784, 4461, and 7136 mg/L. Ozone oxidation technology was used for treatment to observe the effect of different COD levels on antibiotic degradation efficiency. The experimental results are shown in Figure 2. At a glucose concentration of 2000 mg/L, a high degradation effect was observed, with degradation rates for TYL and TAT reaching 94.3% and 98.0% respectively within 3 minutes; at 5000 mg/L, the degradation effect was slightly lower, at 85% and 95.4% respectively; while at 8000 mg/L, the degradation rates were only 78.1% and 83.9%. This indicates that the lower the COD value in the water sample, the better the degradation effect of ozone on antibiotics. Therefore, in the treatment process of actual antibiotic wastewater, the concentration of organic pollutants in the water body and their potential inhibitory effect on the ozone oxidation process should be fully considered, and the COD concentration should be reduced as much as possible to more effectively utilize this technology to remove TYL and TAT residues from the water.

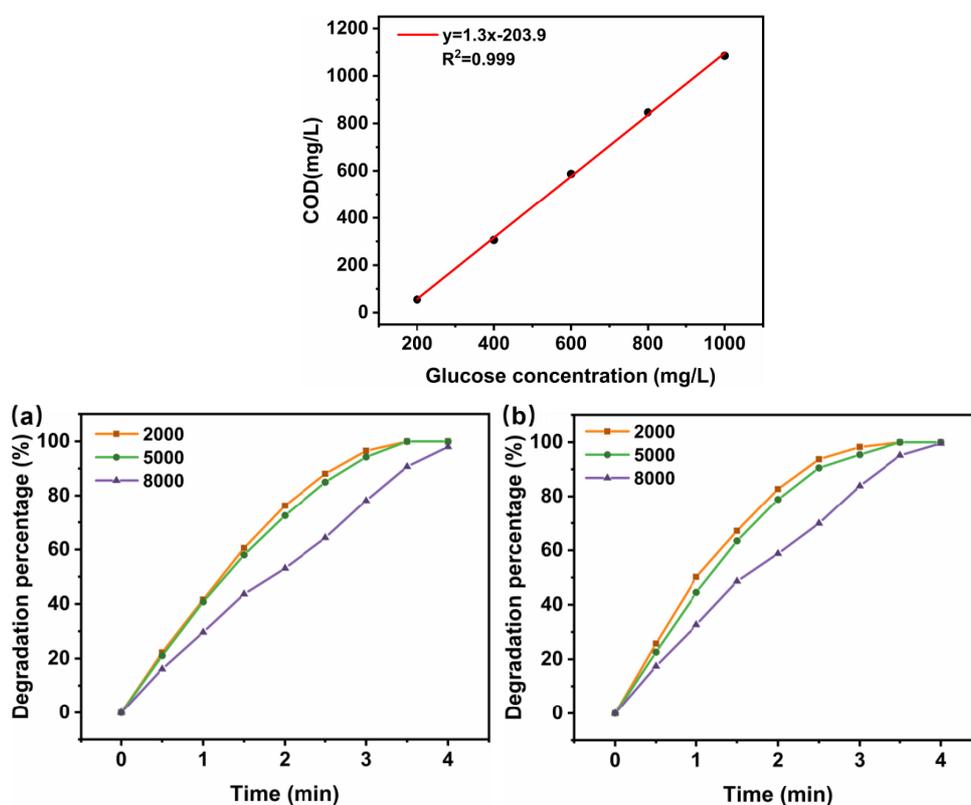


Figure 3 Linear fitting of the relationship between glucose concentration and COD; Effect of glucose concentration on advanced oxidative degradation of TYL (a) and TAT (b).

To investigate the effect of antibiotic concentration on the wastewater treatment efficiency of ozone oxidation technology, this study prepared water samples with TYL and TAT concentrations of 50, 100, 200, 300, and 500 mg/L, respectively, and adjusted them to pH=5. Ozone oxidation technology was used to treat the above water samples to observe the effect of different initial antibiotic concentrations on degradation efficiency. The results are shown in Figure 4. As the initial antibiotic concentration increased, the degradation effect gradually worsened. When the concentrations of TYL and TAT were 50 mg/L, the degradation rates were 97.3% and 94.2%, respectively, showing the best degradation effect. This is because, under conditions where other factors remain constant, simply increasing the antibiotic concentration reduces the mass transfer efficiency of ozone in the water body, leading to a decrease in the degradation rate [32].

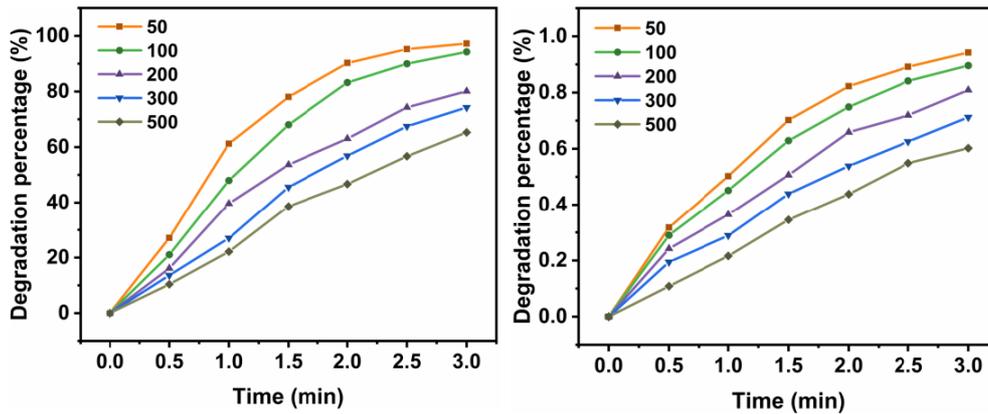


Figure 4 Effect of antibiotic concentration on advanced oxidative degradation of TYL (a) and TAT (b)

3.2 Kinetic Simulation

This study conducted kinetic analysis to deeply explore the degradation patterns of antibiotics at different concentrations (50, 100, 200, 300, and 500 mg/L) during the ozone oxidation treatment process. The results are shown in Figure 5. The degradation process of antibiotics by ozone within 3 minutes conformed to a pseudo-first-order kinetic model, with linear regression coefficients (R^2) all exceeding 0.989. The $t_{1/2}$ increased with the initial concentration. As the initial antibiotic concentration increased, the reaction rate constant gradually decreased, meaning the degradation rate slowed down. This is because when the antibiotic concentration is low, ozone molecules and hydroxyl radicals can react with them rapidly [33], resulting in higher degradation efficiency. However, as the antibiotic concentration increases, the competitive effect between pollutant molecules intensifies, and mass transfer resistance increases, thereby reducing the number of effective collisions per unit time and the reaction rate, leading to a decrease in the degradation rate. Additionally, high antibiotic concentrations may consume more active free radicals, further inhibiting the degradation process.

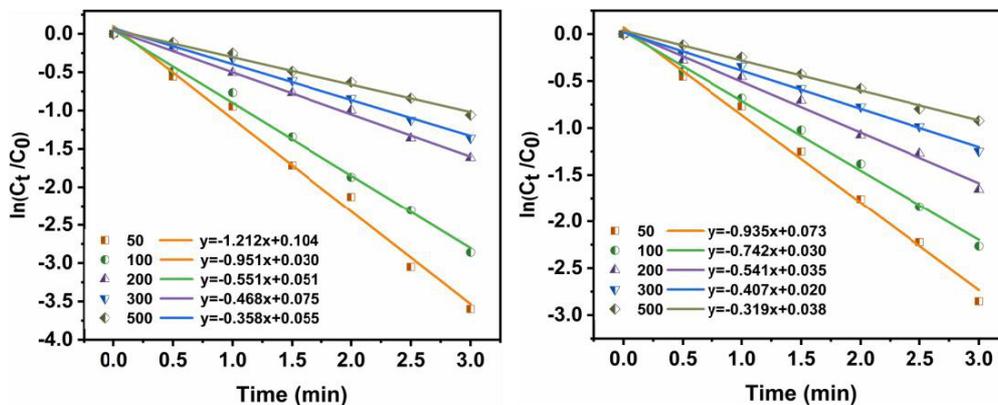


Figure 5 Degradation kinetics model of ozone oxidation technology at different initial concentrations of TYL (a) and TAT (b).

3.3 Pilot-scale Equipment Operation

(1) Pre-operation Preparation

a. Tighten the valves of all drainage pipelines, check for leaks at each interface, and check if the oxygen supply is sufficient.

b. Before the formal operation of the equipment, a 3-day trial operation was conducted. The main purpose of the trial operation was to complete the debugging of the ozone equipment, concentration detection equipment,

and ozone tail gas absorption device, and to ensure the entire treatment system reached a stable operating state.

c. 10 hours before the trial operation, activated sludge acclimated under aerobic conditions was added to the aerobic tank, and continuous aeration was maintained; activated sludge acclimated under anaerobic conditions was added to the anaerobic tank, and sealed aeration was performed.

d. The wastewater pH in the equalization tank was adjusted to around 5 using HCl and NaOH.

e. Coagulant preparation: A 5% polyaluminum chloride (PAC) solution and a 0.3% polyacrylamide (PAM) solution of equal volume were mixed for later use. After equipment startup, the mixed coagulant was pumped into the flocculation sedimentation tank at a flow rate of 5 mL/min.

(2) Operation Process

To verify the feasibility of the designed process system, this experiment used artificially prepared simulated wastewater as the research object and conducted a 10-day operation effect observation and analysis. During the experiment, by adjusting the wastewater flow rate in each tank, the water exchange rate was maintained at about 70%. A complete operation cycle was set at 2 days. The specific hydraulic retention times for each section were: pre-oxidation tank 5h, biofilm tank 8h, anaerobic tank 15h, aerobic tank 12h, flocculation sedimentation tank 5h, and sand filter tank 3h. The operational effects of each section in the reaction system were also compared and analyzed.

(3) Analysis of Operation Effect within 10 Days

During the 10-day operation trial, the concentrations of TYL and TAT in the influent and effluent of the pilot-scale equipment were monitored. The results are shown in Figure 6. The average influent concentrations of TYL and TAT were 54.66 mg/L and 44.55 mg/L, respectively, while the effluent concentrations of TYL and TAT remained stable below 1.56 mg/L and 1.89 mg/L, meeting the discharge standards. This indicates that the process system operated stably. After multiple treatment stages, it effectively degraded the antibiotics in the wastewater. The antibiotic degradation rate in each operation cycle exceeded 95%. This result verifies the high efficiency and reliability of this process system in treating high-concentration veterinary antibiotic wastewater, providing strong technical support for practical applications.

During the 10-day operation trial, the COD and BOD₅ levels in the influent and effluent of the pilot-scale equipment were also monitored. The results are shown in Figure 6. The average influent concentrations of COD and BOD₅ were 2143 mg/L and 841 mg/L, respectively, while the average effluent concentrations of COD and BOD₅ were 35.17 mg/L and 15.66 mg/L, respectively, achieving a degradation rate of 98%. This indicates that the system has good organic pollutant treatment capacity, significantly reducing the content of organic pollutants. Furthermore, the BOD₅/COD ratio at the effluent outlet remained stable within the range of 0.39-0.48, indicating good biodegradability of the treated wastewater.

During the 10-day operation trial, the NH₃-N levels in the influent and effluent of the pilot-scale equipment were also monitored. The results are shown in Figure 6. The average influent NH₃-N concentration was 23.75 mg/L, far exceeding the discharge limit of 5 mg/L for fermentation wastewater, while the average effluent NH₃-N concentration was 2.7 mg/L, stably meeting the discharge standard, with a degradation rate exceeding 85%. This indicates that the process system also demonstrated high treatment efficiency and stability in removing inorganic pollutants like NH₃-N, providing a reliable guarantee for the efficient treatment of veterinary antibiotic pharmaceutical wastewater.

This study systematically analyzed the operational data of each treatment section within one operation cycle (2 days) of the pilot-scale equipment, revealing the degradation patterns of pollutants during operation and the treatment efficiency of the process. The ozone oxidation in the pre-oxidation tank significantly altered the wastewater characteristics: pH decreased from 7.5 to 5.4, color and turbidity were reduced by 54.3% and 20.8% respectively, COD degradation rate reached 35.5%, and biodegradability BOD₅/COD increased from 0.61 to 0.88.

The biological treatment unit (biofilm tank + anaerobic/aerobic) showed specific degradation advantages for the characteristic pollutants TAT and TYL, with degradation contribution rates reaching 72.0% and 74.4%, respectively. The combined anaerobic/aerobic process played a major role in the degradation of COD and BOD₅ in the entire process, with degradation contribution rates of 55.7% and 71.3%, respectively. These data indicate that the biological treatment unit can deeply degrade biodegradable organic matter, exhibiting excellent pollutant degradation capability. In the flocculation sedimentation tank, the effluent water quality achieved a qualitative improvement: the final degradation rates for color and turbidity reached 99.4% and 98.0%, respectively. The concentrations of COD and BOD₅ decreased to 30.5 mg/L and 14.9 mg/L, respectively, fully meeting the GB21904-2008 discharge standard. The combined process showed significant degradation effects on antibiotics, with final degradation rates for TAT and TYL reaching 100% and 99.82%, respectively, and effluent concentrations below the detection limit. Within a complete cycle, each section played a unique and crucial role in treating the antibiotic wastewater, fully demonstrating the effectiveness and efficiency of using advanced oxidation synergized with biofilm for treating veterinary antibiotic pharmaceutical wastewater, providing strong experimental evidence for the feasibility of this process in practical applications.

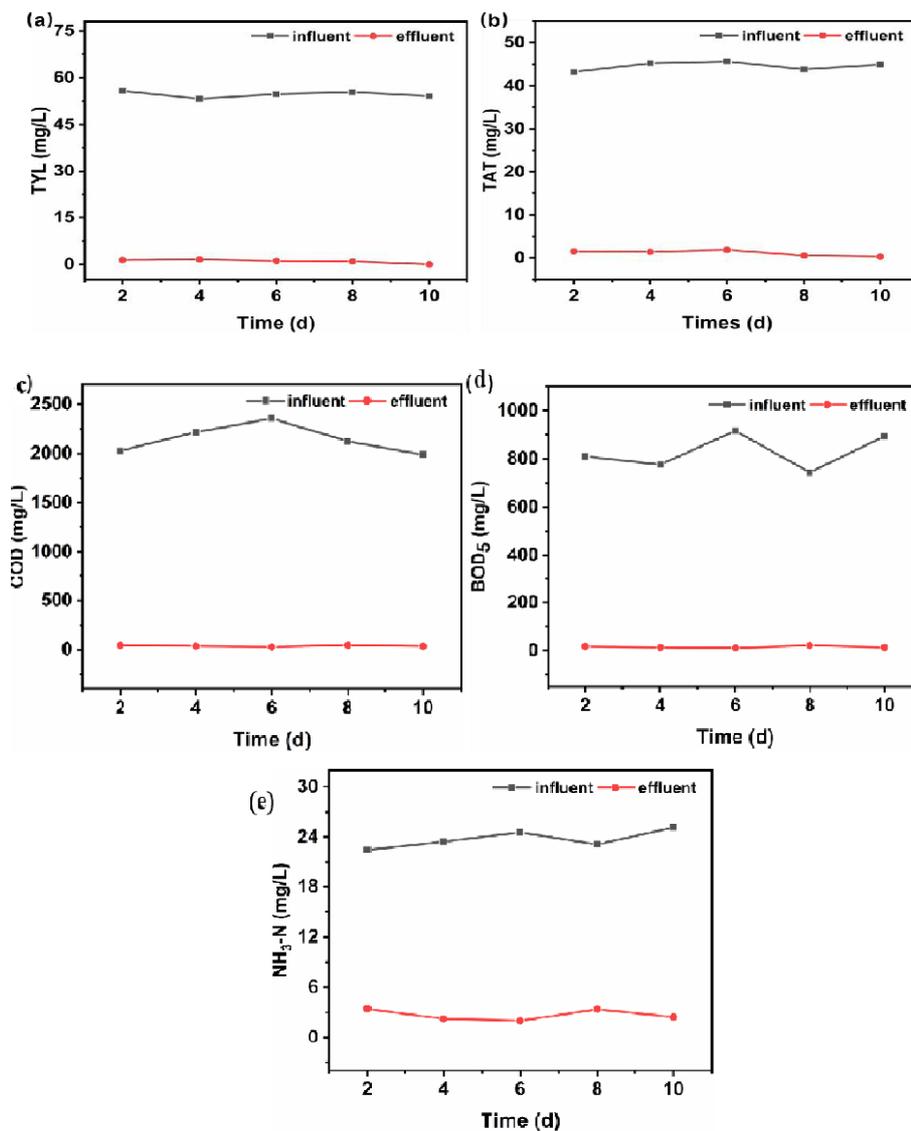


Figure 6 TYL (a) and TAT (b) at influent and effluent within 10 days operation; COD (c) and BOD (d) at influent and effluent within 10 days operation; NH₃-N at influent and effluent within 10 days operation (e)

4 Conclusion

The degradation characteristics of TYL and TAT by advanced oxidation technology were investigated to better utilize the role of the pre-oxidation tank in the subsequent simulated operation of treating antibiotic pharmaceutical wastewater using advanced oxidation technology synergized with biofilm, thereby improving wastewater treatment efficiency. The specific research contents are as follows:

(1) The effects of different water sample pH (5, 6, 7, 8, 9) on the degradation efficiency were compared. When pH=5, the oxidant concentration in the water sample was the highest, and the degradation effect of ozone on TYL and TAT was the best, with degradation rates both exceeding 92.0%. However, as the pH increased, the antibiotic degradation effect gradually decreased. This indicates that the lower the pH, the higher the oxidant concentration in the water sample, and the better the antibiotic degradation effect. The effects of different antibiotic concentrations (50, 100, 200, 300, and 500 mg/L) in the water sample on the degradation efficiency were compared. When the concentrations of TYL and TAT were 50 mg/L, the degradation rates were 97.3% and 94.2%, respectively, showing the best degradation effect. As the antibiotic concentration increased, the degradation effect gradually worsened. Through kinetic analysis, the degradation patterns of antibiotics at different concentrations during the ozone oxidation treatment process were deeply explored. The results showed that the degradation process of antibiotics by ozone within 3 minutes conformed to a pseudo-first-order kinetic model, with linear regression coefficients (R^2) all exceeding 0.989. The $t_{1/2}$ increased with the initial concentration, and the reaction rate constant gradually decreased as the initial antibiotic concentration increased.

(2) Based on the actual wastewater quality of the veterinary antibiotic pharmaceutical enterprise, a pilot-scale equipment integrating "ozone oxidation + biofilm + anaerobic/aerobic + coagulation sedimentation" was designed and constructed, with a treatment capacity of 0.5 t/d. Using a mixed culture of antibiotic-degrading bacteria and activated sludge from the wastewater outlet of the pharmaceutical enterprise as a composite inoculum source, and using ceramic filler as the carrier, a biofilm treatment system was successfully constructed after 7 days of directional acclimation. During the acclimation process, the average influent COD concentration was 822 mg/L. After 4 days of cultivation, the system tended to stabilize, and the effluent COD concentration remained below 600 mg/L. Using simulated wastewater as the treatment object, the pilot-scale equipment was started, and a continuous 10-day operation trial (each 2 days as an operation cycle) was conducted to verify the feasibility of the combined process for treating high-concentration antibiotic wastewater. The results showed that in each operation cycle, the degradation rates of TYL and TAT both exceeded 95%, the degradation rates of COD and BOD_5 reached 98%, and the degradation rate of NH_3-N also exceeded 85%. The effluent quality of this treatment system was stable and fully met the requirements of the GB21903-2008 standard, providing a reliable and efficient technical solution for the treatment of veterinary antibiotic wastewater.

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