Research progress on antibiotic removal process in wastewater for aquatic environment protection

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Abstract: The serious issue of antibiotic contamination has become a pressing concern. Antibiotic-contaminated wastewater that is not effectively treated can have detrimental effects on both aquatic environments and human health. Therefore, it is imperative to intensify research efforts towards developing efficient and effective processes for removing antibiotics from aquatic environments. This paper provides a comprehensive review of common antibiotic removal processes used in sewage treatment plants, including physical adsorption and membrane filtration. It also examines various chemical treatments such as ozone oxidation, hydrolysis, photolysis, Fenton oxidation, persulfate oxidation, and electrochemical oxidation. In addition, the paper discusses biological treatments including anaerobic biological treatment, aerobic biological treatment, and constructed wetland treatment, as well as the combination of related processes. Through this review of the relevant literature, it is evident that advanced oxidation technology demonstrates superior performance in single removal processes for antibiotics. Furthermore, the combination of different removal processes yields even more effective antibiotic removal outcomes, indicating great potential for future development. Finally, this paper highlights the importance of future research in antibiotic removal to further advance the field and promote the growth of antibiotic removal technology.

Key Words: Antibiotics; Aquatic environment; Combined technology; Sewage; Removal effect

1. Introduction

Antibiotics can affect the structure and function of bacterial cells, change the metabolic state of bacteria, thus inhibiting bacterial growth, reducing reproductive ability and even causing bacterial death [1]. Therefore, antibiotics are essential for the treatment of humans and animals, and are now widely used in various countries. The consumption of antibiotics is also expected to continue to increase in the coming years due to the need to improve health standards in low - and middle-income countries and to treat aging populations in high-income countries [2].Typically, ingested antibiotics have water solubility that is not easily absorbed by the intestine, so 30-90% of antibiotics are usually excreted in the form of feces or urine and form antibiotic wastewater [3].However, a large amount of antibiotics wastewater is directly or indirectly discharged into the river due to the lack of effective removal methods, which causes serious pollution to the environment. As a result, antibiotics are found in almost all kinds of aquatic environments (aquaculture water bodies, rivers, lakes, groundwater, drinking water, etc.), and have a high content. The spread of antibiotic resistance genes (ARGs) caused by the extensive use of antibiotics will cause higher harm than the antibiotic drugs themselves. These ARGs enter the aquatic organisms and harm the human body through the food chain, increasing the human body's resistance to antibiotics and threatening human health

Wastewater treatment plants play a vital role in decreasing the risks posed by the release of pollutants in the receiving environment. Usually, urban sewage treatment plants are the last barrier before antibiotics enter the natural water environment, and they are also the main source of antibiotic contaminants entering the environment. Antibiotics can enter sewage treatment plants for treatment through human waste, livestock manure, and direct medical and industrial wastewater. However, it is considered that the elimination of antibiotics in traditional sewage treatment plants is not enough. The current mainstream urban sewage treatment processes are hydrolysis, photolysis, sludge adsorption, biodegradation, advanced oxidation and other methods to degrade antibiotics [4]. But the overall removal effect is not so good. As a result, only a small amount of antibiotics can be removed during sewage treatment, while more antibiotics remain in the water. In addition, there are other environmental pollutants in sewage, such as metal ions and hard-to-degrade organic pollutants, which may promote the spread of ARGs. Eventually, these antibiotics and resistance genes are released into the natural aquatic environment, causing a series of related environmental problems. There are many new studies showing that the combination of related treatment methods shows better removal results [5]. In summary, the full study of antibiotics in sewage treatment technology will have important practical significance for seeking and improving more effective methods of antibiotic removal in the future.

2. Research status of antibiotic removal technology

2.1 Physical treatments

2.1.1 Adsorption

Adsorption method is the most common physical method. It has been widely used in wastewater treatment because of its fast, efficient, economic, recyclability and other advantage [6]. Physical adsorption is a technique for the removal of antibiotics by fixing them on the surface or inside a porous material with a highly developed pore structure and a large specific surface area. At present, carbon materials and sludge are mainly used as adsorbents to remove antibiotics from water. Liu et al.[7] used activated sludge to treat a solution containing three antibiotics and found significant reductions in the concentrations of all three. Chandrasekaran et al.[8] used acid activated carbon formed from acid-activated wood to carry out adsorption experiments on solutions containing ciprofloxacin (CIP) and amoxicillin (AMX), and found that its maximum adsorption capacity for CIP was 250 mg/g and that for AMX 714.29 mg/g, proving that acid activated carbon can effectively eliminate emerging pollutants such as antibiotics. Kim et al.[9] studied the removal effect of adding biochar to activated sludge on CIP, and found that the removal rate of CIP was significantly increased (up to 94%) under steady state addition, and the removal rate was positively correlated with the volume ratio of biochar.

2.1.2 Membrane filtration

Membrane filtration technology is an effective method to separate water and target pollutants through the interception of surface membrane pores, so it can remove small molecules and low concentration of antibiotics, and has the advantages of high effluent quality, sustainable treatment performance, good separation selectivity, etc., which has attracted much attention in water and wastewater treatment [10].Zhan et al.[11] studied the removal of three antibiotics by polyamide nanofiltration membranes, and found that nanofiltration membrane had good removal effect on three different antibiotics in short-term filtration experiment. Among them, the retention rate of trimethoprim was 82.2%, the retention rate of ciprofloxacin was 93.0%, and the retention rate of ofloxacin was 90.7%. Gaálovád et al.[12] studied modified single-walled carbon nanotube membranes for the elimination of antibiotics in water and found that 3.118 s in the thinnest membrane (2μm) was sufficient to filter 98.8% of SM, 95.5% of TMP, and 87.0% of TET, and the thicker film showed higher adsorption capacity.

2.2 Chemical treatment

2.2.1 Hydrolysis

Hydrolysis plays an important role in the abiotic transformation of antibiotics. Under normal circumstances, antibiotic wastewater is hydrolyzed to varying degrees in the natural water environment. The degree of hydrolysis of antibiotics is influenced by several factors, including pH, temperature, and hydrolyzation-sensitive functional groups in the antibiotic molecular structure, and base-catalyzed hydrolysis is faster than acid-catalyzed and neutral pH hydrolysis [13].Song et al.[14] He hydrolyzed spectinomycin in pure water system and alkaline wate, and found that the hydrolysis rate increased with the increase of temperature in the same environment, and the concentration of hydroxide ion in aqueous solution was conducive to improving the hydrolysis efficiency of spectinomycin. The effects of sulfamic acid, heteropolyacid, sulfonated biochar and TiO2/SO4 on the hydrolysis of spiramycin (SPM) have been studied [15][16].It was found that at 35 ℃, 0.3 g/L sulfamic acid, 1.0 g/L heteropoly acid and 20 mg/L SPM solution could be effectively hydrolyzed within 40 min, and the removal rate of antibacterial titer could reach 100%. When using microwave intensification with microwave power of 200 W, adding 1.0 g/L silicotungstic acid, SPM solution with concentration of 100 mg/L can be effectively removed within 8 min. Selecting the carbon-based solid acid from different sulfonated biochar and using the microwave in combination with the carbon-based solid acid, when the microwave power was 200 W and the dosage was 1.0 g/L, the SPM solution of 40 mg/L could be completely removed in 10 minutes.

2.2.2 Photolysis

Photocatalysis technology uses the energy of sunlight without additional energy and can degrade pollutants at room temperature, so it has become an ideal antibiotic treatment technology. Ultraviolet radiation (UV) is commonly used as a disinfectant in water treatment plants. Ding et al.[17] conducted experiments on ultraviolet photolysis antibiotics and found that a variety of antibiotics were effectively decomposed after 1h ultraviolet irradiation. Keene et al.[18] used low pressure mercury vapor and medium pressure mercury vapor ultraviolet source to carry out photolysis experiments on the solution containing antibiotics, and found that doxycycline, penicillin-G and ciprofloxacin showed degradation through direct photolysis. In the effluent, all compounds showed polychromatic UV degradation. Sudha et al.[19] studied the photolysis of seven sulfonamides in different substrates and found that under ultraviolet (254 nm) irradiation, the sulfonamides with five substituents degraded faster than the six substituents, and the latter had the highest ratio in saltwater, followed by reverse osmosis deionized water and fresh water.

However, compared to all other tested light sources, the removal rates of most sulfonamides are higher in natural water than in reverse osmosis deionized water.

2.2.3 Advanced oxidation

Advanced oxidation processes （AOPs） refer that reactive oxygen species such as hydroxyl radical (•OH) and sulfate radical (SO4•-) produced under high temperature and high pressure, electricity, sound, light irradiation, catalyst and other reaction conditions react with the target pollutants, such as adcombination, substitution, electron transfer or bond breaking, so that the macromolecular pollutants that are difficult to biodegrade in sewage decompose into non-toxic or less toxic small molecular substances technology [20]. Common advanced oxidation technologies include ozone oxidation, Fenton oxidation, persulfate oxidation, electrochemical oxidation and so on.

2.2.3.1 Ozonation

Many studies have confirmed that ozone can be used effectively to oxidize antibiotics. In most cases, this involves changes in one or more reactive functional groups in their molecular structure, such as amine nitrogen, sulfur, carbon-carbon double bonds, and activated aromatic rings. Lie et al.[21] performed ozone-based catalytic processes using ozone /PMS and ozone /PS and found that the only ozone process removed 8.10% of sulfadiazine in 23 minutes. When ozone was involved in the reaction of PS or PMS, the degradation efficiency of sulfadiazine was significantly improved, reaching 6.73% and 7.10%, respectively, within 64 min. Fares et al.[22] investigated the use of ozone as a pre-treatment process for water-containing drugs and conducted experiments on synthetic wastewater, surface water, and effluent from wastewater treatment plants. It was found that in the ozone reaction for 50 s, the concentration of most antibiotics was reduced by 15%. And the percentage of antibiotics removed in the sewage of urban sewage treatment plants is greater than or equal to 98.5%.Omar et al.[23] studied the removal of amoxicillin, doxycycline, ciprofloxacin, and sulfamediazine by ozonation in aqueous solutions and milk samples, and found that the removal rate reached 75%–100% at ozone doses as low as 95 mg/L. The removal efficiency of antibiotics in milk samples was higher and the rate constant was faster.

2.2.3.2 Fenton oxidatio

Fenton reaction refers to the rapid oxidation of organic substances into inorganic substances in a solution containing iron ions and H. Fenton reagent is a strong oxidizing agent based on the oxidation of ferrous ions, hydrogen peroxide and hydroxyl radicals produced by the catalytic decomposition of hydrogen peroxide in acidic solution [24].Somayyeh et al.[25] studied the degradation of sulfonamides antibiotics in aquatic environment by Fenton oxidation process, and found that under the best conditions, Fenton reaction can effectively degrade sulfonamides antibiotics (99.99%).Francesco et al.[26] used the Fenton process based on zero-valent iron（ZVI-Fenton）to explore its degradation of specialty antibiotics in hospital wastewater, and found that CFZ, IMI, and VNM were completely or almost completely degraded with zero-valent iron + H at pH 1-5 within 7 hours. Qian et al.[27] conducted comparative experiments of Fenton-like oxidation and Fenton-like oxidation. Using 0.5 mM iron 2+ and 1.5mM citric acid to pre-mix antibiotics in a Fenton-like reactor （[CA]：[Fe2+] = 3：1） for Fenton-like oxidation experiments, they found that the removal efficiency of antibiotics was significantly improved by about 65%, and the removal efficiency of non-biodegradable TMP reached 80%.

2.2.3.3 Persulfate oxidation

Persulfates (PS) are mainly peroxomonosulfates (PMS) and perdisulfates (PDS), which are commonly used as oxidants in SR-AOP, while often activated by heat, ultraviolet, alkali, carbonous materials and metal based catalysts to produce SO4- with a greater REDOX potential [28].Tang et al.[29] used thermal activated persulfate oxidation to treat antibiotics in wastewater sludge and found that TAP oxidation had obvious antibiotic degradation efficiency, among which the degradation efficiency of macrolides and tetracycline antibiotics was the best (>80%).Ji et al.[30] studied the degradation of tetracycline antibiotics (TTC) by thermally-activated PS oxidation and found that at pH 7.0, about 20% of TTC was destroyed at ambient temperature (20±1°C), and about 40% of TTC was degraded after 240min at 70°C. At 30°C, TTC is completely eliminated within 70 minutes. Zhang et al.[31] studied the degradation of tetracycline (TC) in mariculture wastewater by ultraviolet activated PS, and found that in UV/PS system, UV light and PS showed a greater synergistic effect, significantly improving the TC removal rate. When PS concentration is 95 mg/L and UV irradiation time is 73 min, the TC removal efficiency of mariculture wastewater can reach 30.30%.

2.2.3.4 Electrochemical oxidation

Electrochemical oxidation is a method commonly used in the treatment of organic wastewater. It has many advantages, such as easy control of reaction conditions, simple operation of the equipment, and no additional oxidant required. Therefore, this method has been widely used in the field of organic wastewater treatment. Wang et al.[32] used electrolytic oxidation technology to conduct experimental research on water samples containing common antibiotics oxytetracycline (OTC), tetracycline (TC) and chloromycin (CTC) in aquaculture wastewater, and found that electrolytic oxidation technology can effectively remove antibiotics in aquaculture wastewater. When the electrolytic time is 2 min, the initial pH value is 9, aeration time was 3 h, the removal rates of quinoline, oxytetracycline and aureomycin were the best, reaching 99.1%,90.8%,97.7% and 90.7%, respectively. Xu et al.[33] studied the BDD electrode pulsed electrochemical oxidation degradation of levofloxacin in antibiotic wastewater, and the research results showed that the COD removal efficiency could reach 94.4% under the best conditions. Ganesan et al.[34]

carried out experiments under the conditions of constant current density of 5 mA/cm2, electrolyte concentration of 0.1M Na2SO4 and pH 5.4, and found that under 180 min EO process, the removal rate of CIP, TOC and COD can reach the highest of 99.9%, 46.6% and 60.3% respectively.

2.3 Biological treatment

2.3.1 Anaerobic biological treatment

Anaerobic organisms are a group of organisms that must grow and reproduce in the absence of oxygen. Nowadays, as the standard of wastewater treatment is getting higher and higher, the corresponding cost is also increasing accordingly, therefore, vigorously develop renewable energy and promote the utilization of waste resources, can reduce economic demand. Under anaerobic conditions, organic matter is decomposed into methane and carbon dioxide, which not only completes the degradation of substances but also generates part of the energy. At present, anaerobic digesters have been widely used to treat wastewater from livestock farms. Han et al.35] used anaerobic organisms to treat veterinary antibiotics in pig wastewater with anaerobic digestion (AD). The results showed that after AD treatment, the COD removal efficiency was 81%, and the total amount of antibiotics was reduced to 3.90μg/L. After naturally degrading 73d in the tank, 14% of the total antibiotics were further removed. Zero-valent iron (ZVI) has an enhanced effect on anaerobic digestion，Pan et al.[36] studied at different tetracycline concentrations（1mg/L、10mg/L、30mg/L、50mg/L 、 80mg/L 、 100mg/L 、 150mg/L), the enhancing effect of ZVI on anaerobic digestion. When the concentration of tetracycline was 1mg/L, the removal rate of tetracycline increased from 68% to 76.7%.Zhou et al.[37] studied the effect of ZVI enhanced anaerobic digestion on the removal of different antibiotics. When the SRT was 20 days, the removal rate of sulfamethazine was increased from 18.6% to 74.53%, and the removal rate of sulfamethazole was increased from 76.6% to 97.39%. The Kd value of roxithromycin was 236.02L/kg, and its biodegradability was poor. Roxithromycin was almost not removed when ZVI was not added. When 1g/L ZVI is added, the removal rate can reach 86%.

2.3.2 Aerobic biological treatment

The decomposition of aerobic organisms can also be used to effectively remove antibiotics. Yang et al.[38] studied the degradation of tetracycline in pig wastewater by aerobic organisms and found that the removal rates of COD and tetracycline antibiotics were 91% and 76%, respectively. Aerobic composting is the use of aerobic microorganisms in the appropriate conditions (temperature, humidity, oxygen, C/N(mass ratio), pH, etc.), the organic matter in the compost material decomposition, and ultimately the formation of CO2, NH3, H2O and other small molecular substances and polymer humus. Because of its advantages of low cost and high degradation efficiency, it is now a widely used biodegradation method. Shi et al.[39] conducted aerobic composting experiments of human feces at constant medium temperature (35℃), constant high temperature (55℃) and without temperature control, and analyzed the effect of composting temperature on the degradation of four typical antibiotics. The results showed that the removal efficiency of 4 antibiotics in high temperature compost was the best and the removal rate was above 90% in 20 days of different temperature compost treatment. Liu et al.[40] studied the degradation of tetracycline antibiotics during cattle manure composting and also found that the residual rate of tetracycline gradually decreased as the temperature increased, and the degradation was fastest between 5 and 14 days.

2.3.3 Constructed wetlands

Constructed wetland (CW) is an emerging method of ecological wastewater treatment, which has the advantages of low investment and operating costs, and is well suited for implementation in rural areas of China. CW can remove pollutants through the action of the microorganisms present in it, as well as the action of sunlight, plants and wind. Many studies have also shown that the treatment of antibiotics by microorganisms and plants in constructed wetlands is also effective [41].Yue et al.[42] constructed three kinds of vertical subsurface flow constructed wetland systems under different conditions to explore their removal of aquaculture tail water, and the results showed that the three kinds of vertical subsurface flow constructed wetland systems under different conditions showed good removal effects on ofloxacin and oxytetracycline in spring and summer, with removal rates above 85%. Compared with ofloxacin and oxytetracycin, the removal efficiency of sulfamethoxazole and flufenicol was relatively low. In spring, the removal efficiency of flufenicol and sulfamethoxazole were 17.23%-67.50% and 8.37%-67.87%, respectively. In summer, the removal rates of flufenicol and sulfamethoxazole were 12.01%-41.29% and 19.28%-67.04%, respectively.

2.4 Combined process

The combined process of antibiotic removal usually has a more effective removal effect. It mainly includes the following steps: First, through physical methods such as filtration, precipitation and so on to remove the solid particles in the wastewater; Then, chemical methods such as oxidation, reduction and neutralization are used to convert organic and inorganic substances in wastewater into small molecular compounds that are easy to remove. Finally, microorganisms and other biodegrades the wastewater into harmless substances such as water and carbon dioxide through biological methods such as aerobic and anaerobic treatment. At present, the common combined process is mainly based on the coupling of advanced oxidation method with other processes.

2.4.1 Advanced oxidation coupling process

2.4.1.1 Membrane filtration combined with advanced oxidation
Li et al.[43]developed an electroactive ultrafiltration membrane using electrochemistry and membrane filtration technology, and used it to conduct experiments on water samples containing sulfamethoxazole (SMX). The results showed that the electroactive C/PVDF membrane was effective for SMX removal, and the SMX removal efficiency in the anode filtration process was 95.5% (+2 V). The SMX removal efficiency of the cathode filtration process (−78 V) is 0.2%.Karaolia et al.[44] studied the degradation of sulfamethoxazole, erythromycin and clarithromycin by chlorinated polyethylene (CPE) plate microfiltration membrane and solar Fenton oxidation coupling process. The results showed that the concentrations of sulfamethoxazole and erythromycin were lower than the detection limit, and the removal rate of clarithromycin was as high as 84%.

2.4.1.2 Fenton combined with activated sludge
Elmoll et al.[45] studied the combined photoFenton-SBR treatment of antibiotic wastewater containing amoxicillin and cloxacillin, and found 发现 Antibiotics were completely degraded within 1 min, and under the conditions of molar ratio of H2O2 to COD of 2, molar ratio of H2O2 to Fe2+ of 150, irradiation time of 90 min and HRT of 12 h, the combined treatment effect of photoFenton-SBR was the best, and the comprehensive process efficiency of completely nitrating sCOD removal was 89%.Guo et al.[46] studied the degradation of antibiotic amoxicillin in Fenton activated sludge combined system and found that Fenton activated sludge combined system was completely effective in the degradation of amoxicillin. Under the best conditions, amoxicillin less than 500 mg/L can be completely degraded, and the degradation capacity is limited with the increase of concentration, and 85.13% of amoxicillin can be degraded even if the concentration is increased to 1000 mg/L.

2.4.1.3 Electrochemical oxidation coupling process
The electrochemical oxidation process also has synergistic effect with other oxidation processes. Liu et al. [47] studied the degradation of tetracycline hydrochloride (TCH) by electrochemical (EC) process combined with persulfate (PS) addition. It was found that the PS process alone showed limited TCH removal oxidation (only 19.8%). When electrolysis (EC) was applied alone, 43.8% of TCH was removed while the electrolysis coupled with persulfate oxidation process found that 81.1% of 50 mg/L TCH was removed within 240 min under optimal conditions.

2.4.1.4 Combination of photocatalysis and biodegradation
Tightly coupled photocatalysis and biodegradation are also promising technologies for treating antibiotic wastewater (ICPB). Wang et al.[48] studied the removal of AMO by ICPB and found that at room temperature (about 20°C), the removal rate of AMO by photocatalysis alone was about 40%, the removal rate of biodegradation alone was about 20%, and the removal rate of ICPB reached 55% after the removal of 35% adsorption. Liu et al.[49] studied the degradation effectiveness of sulfamethoxazole in wastewater in a tightly coupled photocatalytic and biofilm system and found that the removal rate of DOC in the ICPB system was significantly higher than that of the photocatalytic system alone and the biofilm system, indicating that the mineralization degree of small SMX in the system was enhanced. Li et al.[50] studied the sequential combination of photocatalysis and microalgae technology on the degradation and detoxification of typical antibiotics. First, norfloxacin (NOR) was treated with photocatalysis, and microalgae were used to further treat the residual NOR and its degradation products after photocatalysis, and it was found that NOR was further degraded and the toxicity of NOR reaction solution was reduced after microalgae treatment.

3. Conclusion

In this paper, the common antibiotic removal processes in wastewater treatment plants are reviewed. In the single antibiotic removal process, advanced oxidation method is always considered to be a method with high removal efficiency, low cost and simple steps, and its removal rate of most antibiotics can reach more than 80%. At the same time, this paper also summarizes the current common combined removal process. Among them, the advanced oxidation method shows the potential of coupling with other methods, and the coupling process also shows better removal efficiency, and the relevant antibiotics can reach more than 95% under the combined process treatment. The contamination of antibiotics in the future is likely to become more and more serious, so new and more effective removal methods are explored based on the current process of removing antibiotics. This study shows that the combined process has greater potential for antibiotic removal research in the future.

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