ЕСТЕСТВЕННЫЕ НАУКИ

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REMOVAL OF TYPICAL ANTIBIOTICS PRESENT IN HOSPITAL WASTEWATERS: A CRITICAL REVIEW OF CONVENTIONAL TREATMENT TECHNIQUES

This review provides insight into the fate and removal of antibiotics in hospital wastewater, and demonstrates the occurrence and risk of antibiotics in hospital wastewater by different treatment processes and materials. The properties of typical antibiotics such as sulfonamides, tetracyclines and quinones in hospital wastewater were comprehensively understood. Based on the typical antibiotic treatment technology and water treatment materials, the advantages and disadvantages of physical, chemical and biological methods in water treatment are compared and analyzed, so as to guide the design and improvement of relevant water treatment technology.

Keywords: antibiotic removal; hospital wastewater; typical treatment technology; physical method; chemical method; biological method.

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УДАЛЕНИЕ ТИПИЧНЫХ АНТИБИОТИКОВ, ПРИСУТСТВУЮЩИХ В СТОЧНЫХ ВОДАХ В БОЛЬНИЦЕ: КРИТИЧЕСКИЙ ОБЗОР КОНВЕНЦИОНАЛЬНЫХ МЕТОДОВ ОЧИСТКИ

В статье представлен анализ удаления антибиотиков из сточных вод в больнице, демонстрируется риск их попадания при различных процессах очистки. Были изучены свойства таких антибиотиков, как сульфаниламиды, тетрациклины и хиноны, в больничных сточных водах. На основе типичной технологии обработки проводится сравнение преимуществ и недостатков физических, химических и биологических методов для очистки воды.

Ключевые слова: удаление антибиотиков; сточная вода в больнице; типичные технологии обработки; физический метод; химический метод; биологический метод.

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1. Introduction

Hospital activities play a significant role in keeping the society healthier. Although during these activities many unwanted by-products are produced and are not dealt with. As a result, environmental scientists are now paying more attention to wastewater from healthcare facilities, community health centers and hospitals [1]. Hospital effluent is a major source of pharmaceuticals entering aquatic organisms, soil cultures, and wastewater treatment plants Hospital sewage, especially infectious disease hospital sewage, is a special sewage with high risk source and high biological pollution, which can easily cause water pollution [2]. Therefore, it must be disinfected before discharge, and China's Integrated Wastewater Discharge Standard (GB8978-1996) also makes strict regulations on the discharge of hospital sewage. (Santos et al. 2013) For many years, there are some problems in hospital sewage treatment in China, such as incomplete hospital sewage treatment facilities, small scale, low technical level, a large number of halides produced by the use of disinfectants, hospital sewage treatment standards. Therefore, design specifications need to be revised and improved, and these problems that we are facing need to be solved urgently. If not handled properly, it will not only pollute the water environment, but also threaten human health. Moreover, the treatment of hospital sewage in China is far less than that of industrial sewage. Therefore, we should attach great importance to the thorny problem of improper treatment of hospital sewage.

Hospital sewage discharge has been highly valued by the people, and the emission standards is a key parameter. Various emission standards and related regulations have also been promulgated and implemented [3]. And many hospitals have also established their own sewage treatment station, through the sewage sampling, filter tank filtration, sedimentation tank sedimentation, membrane purification and chlorine dioxide disinfection treatment, etc [4]. The common treatment methods of hospital sewage include physical method, chemical method and biological method. The physical method mainly removes the floating matter and suspended matter in the sewage. The chemical method mainly removes the specific ions in the sewage, adjusts the pH value of the sewage, and disinfects the sewage. The biological treatment method refers to the use of microorganisms to reduce carbon and nitrogen [5] as well as organic pollutants such as phosphorus, phenol, cyanide, and LAS pollute hospital sewage. At present, domestic hospitals basically use chlorine disinfection method to disinfect sewage, but the conventional chlorine disinfection method has some shortcomings. For example, the combination of microorganisms and suspended solids in the effluent will weaken the disinfection effect and reduce the disinfection effect, and the large amount of disinfectant input will produce disinfection by-products and pollute the environment. Therefore, the key to hospital sewage treatment is to effectively remove a large amount of suspended solids and organic matter in sewage before disinfection, thus to obtain good disinfection effect.

The purpose of this review several conventional and advanced treatment technology and materials with respect to antibiotics removal are also examined.

2. Conventional treatment techniques

It was essential to economically and efficiently remove residual antibiotics in water. In general, treatment methods of antibiotics in water can be divided into physical method, chemical method and biological method. Physical method mainly adopts adsorption, ion exchange, membrane separation technology, etc. Chemical method is a chemical reaction that degrades large molecules in antibiotics into small molecules or other inorganic substances. It mainly includes chlorination and advanced oxidation (AOPs). Thereinto, AOPs includes Fenton oxidation, photocatalytic oxidation, ozonation, electrochemical oxidation, etc. According to the specific properties of antibiotic wastewater, corresponding treatment methods should be adopted. Biological method is the use of microbial metabolism mechanism, so that antibiotics are degraded naturally. Biological methods can be divided into aerobic biological treatment, anaerobic biological treatment, anaerobic-aerobic biological group method (Figure 1).

2.1. Physical method

2.1.1. Adsorption

Adsorption occurs by the help of intermolecular force between adsorbate and adsorbent. Over the past few decades, efforts have been made to investigate the feasibility of various adsorption materials, including activated carbon, carbon nanotubes, clay minerals, ion-exchange resins, and biochar. The performance of adsorbents is usually evaluated by equilibrium or maximum adsorption capacity. Experimental conditions such as the initial concentration of the adsorbent, the amount of the adsorbent, and the contact time between the adsorbent and the adsorbent vary widely among published studies, it is technically preferred to compare the

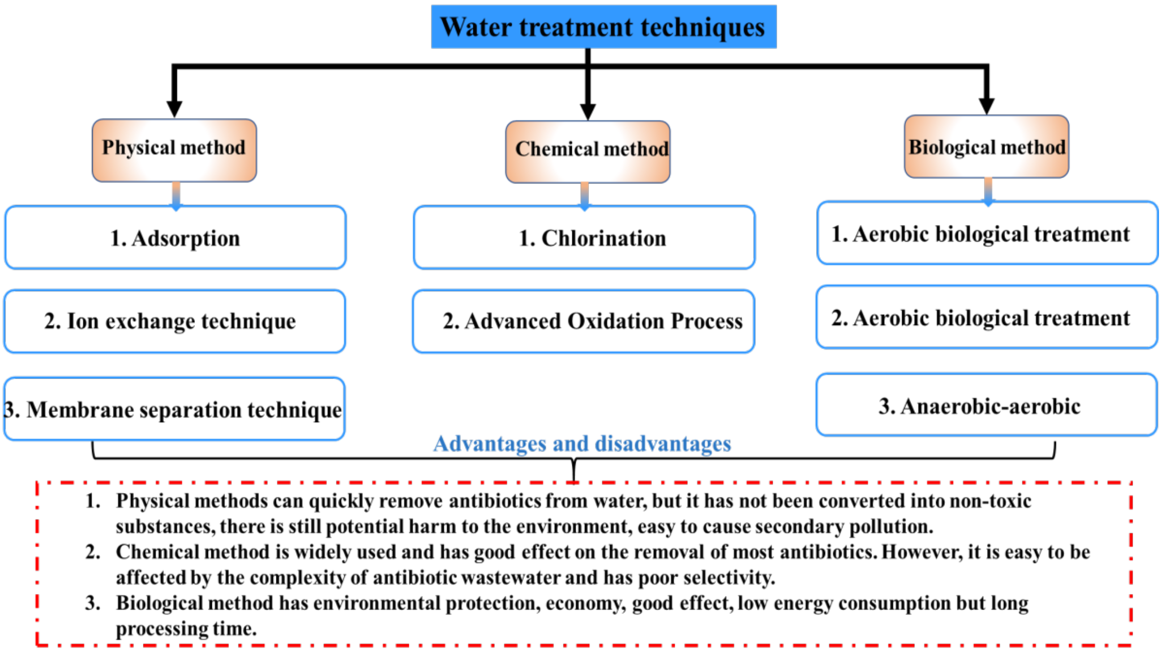

Fig. 1. Conventional treatment techniques of antibiotics.

performance of the adsorbent with the allocation coefficient. For instance, the adsorption and removal of fluoroquinolone compounds by carbon-based adsorbents mainly depend on the surface porosity of the adsorbents and the adjustable chemical properties of the functional groups on the adsorbents as well as the specific surface area and the dosage of the adsorbents.

The most common and effective adsorbent is activated carbon (AC). AC is widely used in applications including water and wastewater treatment. It has an amorphous structure, highly porous interior and a large surface area. The pore structure of activated carbon can be adjusted by various surface modifications, which is the reason why activated carbon is widely used in the treatment of antibiotics in wastewater. The surface of AC contains carboxylic acid functional groups, which are negatively charged at pH > pHPZC, so the cationic antibiotics portion can be easily adsorbed to the negatively charged AC. The chemisorption interaction with antibiotics was demonstrated by AC and PAC to adsorb experiments of 28 antibiotics in deionized water and surface water was also investigated [6]. When the dosage of PAC was 20 mg/L and the contact time was 120 min. The removal rate of antibiotics in deionized water and surface water reached 99.9 % and 99.6 %, respectively (Figure 2).

For most adsorbents used for antibiotics adsorption, over a limited solution pH range, the adsorption affinity is good and/or the adsorption capacity decreases with the increase of the negative surface of the adsorbent due to the pH increases. These shortcomings can be addressed by using biochar as a multifunctional adsorbent. Ideally, biochar has different adsorption capacities for organic pollutants due to the heterogeneity of its surface functional groups. The adsorption capacity of norfloxacin is 325 mg·g−1 and the PC value is 11.61 L·g−1 due to the multi-layer electrostatic adsorption of hematite BC composite.

2.1.2. Ion exchange technique

Ion exchange technology primarily uses ion exchange resin to exchange the target ions in the water with the ions on the exchange resin, so as to dispose of the pollutants in the water. Magnetic ion exchange resin (MIEX) is a strongly alkaline anion exchange resin that

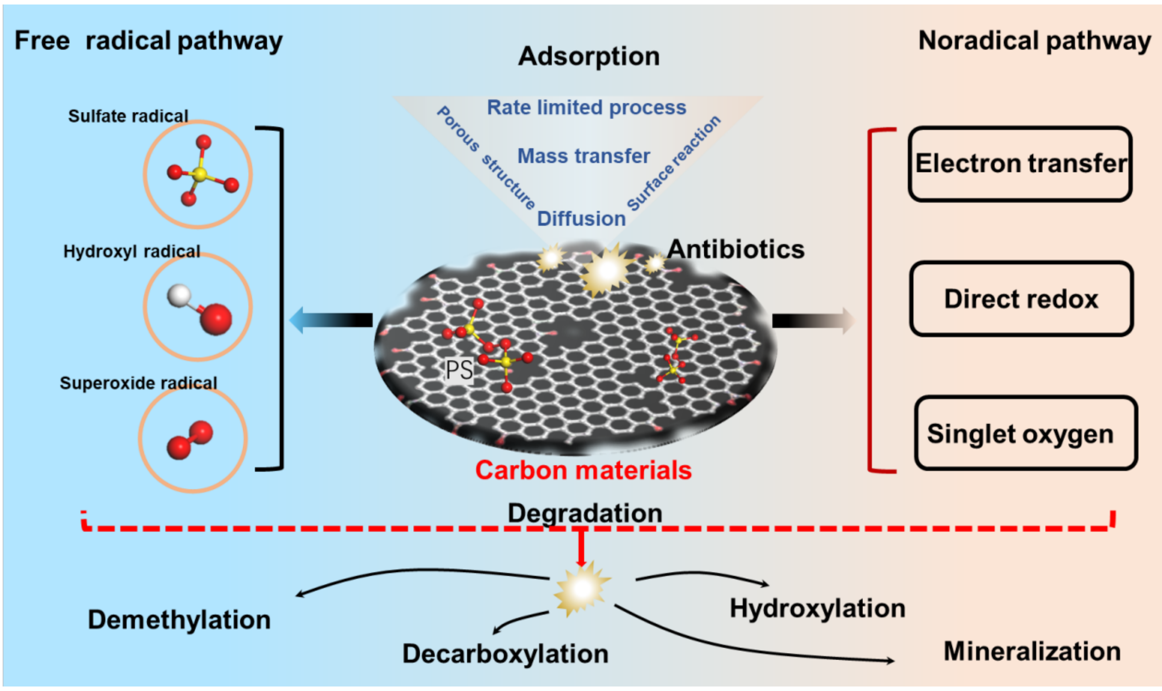

Fig. 2. Degradation mechanism and interaction of antibiotic pollutants via carbon materials.

integrates iron oxide into a macroporous polyacrylic acid matrix and is commonly used with chloride ions as an exchange ion. Compared to traditional anion exchange resins, MIEX resins have a larger surface area due to the very small resin bead size. The average diameter of the MIEX resin is 150 to 180 μm (2 to 5 times smaller than conventional resins), which may result in rapid adsorption of contaminants on the surface of the MIEX resin Wang et al. prepared a magnetic ion exchange resin for the simulated wastewater removal experiments of sulfamethoxazole (SMX), tetracycline (TCN) and amoxicillin (AMX). The results showed that the maximum adsorption capacity of SMX, TCN and AMX was 789,32, 443.18, 155.15 mg /L, respectively. Importantly, the resin is renewable and still maintain a high adsorption removal rate. Humbert et al evaluated the use of a series of strong anion exchange resins to remove two pesticides (namely atrazine and isopropyron) from surface water. The results showed that the removal rates of atrazine and isoprolon were 7% and 5% at 8 mL/L of MIEX resin, respectively.

2.1.3. Membrane separation technique

Membrane separation technology mainly uses the pore size of membrane to intercept antibiotics and to screen out macromolecules of antibiotics. According to the different pore size, it can be divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and so on. Nanofiltration is an attractive pressure-driven membrane separation technique. Because of its high retention rate for polyvalent ions and hundreds of molecular weight organic compounds under low operating pressure, it has been widely used in drinking water quality control, wastewater treatment and industrial applications. (Murthy and Chaudhari 2009) The separation mechanism of NF includes size exclusion and Donnan effect (electrostatic interaction). Although size exclusion is the key mechanism for retaining neutral molecules, which both are important for the separation of ion species. Antibiotics usually have positive and negative functional groups. When charged nanofiltration membranes are applied, the size repulsion and charge interaction between antibiotic molecules and the membrane surface have significant effects on antibiotic retention.(Ajwa et al. 2007) Using polyethylenimine modified NF membrane to filter the simulated wastewater of cephalospore hydrobenzyl (CFR) and Enrofloxacin (ENR), when the transmembrane pressure difference is at 38 MPa, the interception rate of CFR was 72 % (pH 10) and that of ENR was 85 % ~ 93 % (pH 3 ~ 5) [6].

2.2. Chemical method

2.2.1. Method of chloride

Chlorination is the most popular water disinfection method at present, which chiefly involves liquid chlorine, sodium hypochlorite, chlorine dioxide and other chemical reactions with contaminated water bodies, thereby to achieve the removal and disinfection effect. Chlorine dioxide ($ClO2$) is a commonly used water disinfectant. Compared with free chlorine, it has high disinfection efficiency, low pH dependence and less disinfection byproduct formation. It has been simulated that Chlorine dioxide ($ClO2$) could oxidize wastewater containing 6 sulfonamides, and the rate constant was 3.85×103–2.59×104 mol/(L·s), this rate can predict the destination of sulfa antibiotics in the oxidation of $ClO2$ in surface water and the effective removal of sulfa antibiotics by $ClO2$ under actual water treatment conditions. Chlorination of simulated wastewater containing chloramphenicol, ciprofloxacin and sulfadiazine by chlorine gas was found to have a certain removal effect, but the chlorination process formed trihalomethanes, haloacetic acid, haloacetonitrile and other disinfection byproducts [7].

2.2.2. Advanced Oxidation Process (AOP)

Advanced oxidation processes (AOPs) are techniques for treating toxic pollutants that were developed in the 1980s. AOPs takes advantage of the strong oxidation ability of hydroxyl radical (·OH) to oxidize and degrade macromolecular substances into smaller molecules in wastewater through chain reactions, and even further decompose into $H2O$ and $CO2$. It has recently been found that sulfates (·SO4−) and superoxide radicals (·O2−) have strong oxidation capacity and can degrade organic pollutants.(Sg et al. 2020; Wang et al. 2020) They are also an important part of AOP. It has been demonstrated that there are three key types of reactions in the degradation of organic compounds by free radicals, namely addition, hydrogen capture, and electron transfer. ·OH is prone to hydrogen addition and capture reactions, and ·SO4 − is prone to electron transfer reaction [8].

Fenton oxidation process is a traditional and efficient method, which is widely used in water treatment. The principle is that $H2O2$ decomposes to produce ·OH under the catalytic action of Fe2+. With the continuous development of technology, researchers have developed a variety of Fenton technologies based on traditional Fenton, such as ultrasound-Fenton, electro-Fenton, UV-Fenton, microwave-Fenton and so on.

Photocatalytic oxidation is the use of photocatalyst, under the action of light radiation to produce highly active ·OH, and to degrade all pollutants. Commonly used photocatalysts are titanium oxide $TiO2$ and zinc oxide ZnO. (Makropoulou et al. 2020) Under the condition of different pH values, the oxidation mechanism of ozonation method is different: pH < 4, mainly direct oxidation, can react with antibiotics directly; pH value ≥10, indirect oxidation with antibiotics through the decomposition of ·OH. Electrochemical oxidation method is to change the structure of some electrochemical active functional groups through the forced action of electric field, so as to change the chemical properties of organic matter, weaken or eliminate its toxicity. Ultrasonic cavitation technology is a new advanced oxidation technology. The principle is that the tiny bubble core in the liquid vibrates under the action of ultrasonic wave. When the sound pressure exceeds the limit value, the bubble will collapse and close rapidly. In this process, high energy will be generated to break the chemical bond and generate ·OH [8].

2.3. Biological method

2.3.1. Aerobic biological treatment

Aerobic biological treatment is in the condition of oxygen, the use of aerobic microorganisms (including facultative microorganisms) biological metabolism, so as to achieve the purpose of degrading organic matter. The common aerobic biological treatment methods include activated sludge, biological contact oxidation, SBR process and so on. When the activated sludge reactor was operated with a retention time of 24 h, the degradation rate of β-lactam antibiotics was close to 99 %, and the removal rates of COD and BOD were 88,4 % and 94,8 % respectively. The cephalosporin wastewater was treated by biological contact oxidation process. Under the optimal experimental conditions (the biofilm hanging days of biological contact oxidation tank was 20 days, pH value was 7.0−8.0, dissolved oxygen was 3.0 mg/L, hydraulic retention time of the first and second contact oxidation tanks was 24 h and 15 h, respectively), the total removal rate of ammonia nitrogen and CODCr was about 90 %.

2.3.2. Aerobic biological treatment

Anaerobic biological treatment method is in anaerobic conditions, the use of obligate anaerobic microorganisms and facultative anaerobic microbial metabolism, degradation of organic matter. Common anaerobic biological treatment methods include upflow anaerobic sludge bed (UASB), anaerobic compound bed (UBF), hydrolysis acidification method, etc. Anaerobic sludge reactor was used to treat synthetic wastewater containing tetracyclines and sulfonamides. The results showed that the removal rate of tetracyclines was almost all, and the removal rate of sulfonamides was 84,2 % ~ 91,0 %. It was also found that tetracyclines were removed by anaerobic sludge adsorption, while sulfonamides were removed by biodegradation. (Cheng et al. 2019) A two-stage UASB reactor was used to treat fermentation antibiotic wastewater. The influent COD of the first stage was 11,88~14,60 g/L (pH 5). The influent COD of the second stage is 4,450–6,267 g/L, and the pH value is 6–7, thus the COD removal rate of the first stage is 61 %–72 %, the COD removal rate of the second stage is 46 %–64 %, and the final effluent COD is ≤ 2.5 g/L.

2.3.3. Anaerobic-aerobic biome method

Single aerobic or anaerobic biological treatment of antibiotic wastewater has certain limitation and the combination of anaerobic and aerobic biological treatment has gradually become the mainstream technology. An anaerobic digestion-sequencing batch reactor (AD-SBR) process was used to treat piggery wastewater containing 19 antibiotics. The total removal efficiencies of COD and antibiotics were 95 % and 92 % respectively at a hydraulic retention time of as low as 3,3 days. The effluent of the AD-SBR process contained enough nutrients to be used for irrigation. Multi-stage A/O process was used to treat piggery wastewater containing antibiotics. The results showed that the process could remove all the target antibiotics in different degrees, and the removal rate of tylosin could reach 93,92 %. Hydrolytic acidification-biological contact oxidation process was used to treat biopharmaceutical wastewater. The results of orthogonal experiment showed that when the hydraulic retention time (HRT) was 12 h, the reactor operated in the best state. Under the optimal conditions, the removal rate of CODCr was close to 96 % and the removal rate of ammonia nitrogen was 90 % [9].

3. Comparison between treatment technologies

Comparison between treatment technologies were discussed according to the current research on antibiotic wastewater treatment methods. Although the physical method can quickly remove antibiotics from water, it only separates antibiotics from water, and does not convert them into nontoxic substances, still exists in the environment in the form of antibiotics or their derivatives, thus it still has potential harm to the environment, and improper treatment is easy to cause secondary pollution [10]. Chemical method is widely used and has good removal effect on most antibiotics, it is easily affected by the complexity of antibiotic wastewater quality and has poor selectivity. Biological method has the advantages of environmental protection, economy, good effect and low energy consumption, which deserves attention of researcher and in-depth investigation.

The characteristics of each treatment method are as follows: 1) Adsorption; It has good adsorption performance, simple operation and can be reused, but the adsorption effect is affected by many factors such as pore structure, surface chemical properties, adsorbate properties and so on. 2) Ion exchange technology; the resin has good removal performance and stable property, but that cost of the resin is high, and microorganism are easy to proliferate on the surface after bee used for a long time. 3) Membrane separation technique; no phase change, no need to add chemicals, and no secondary pollution, but the membrane is easy to plug, process of application is easily limited by water quality conditions. 4) Chlorination method; high reaction speed and wide application range, and most antibiotic can be directly chlorinated, but that reaction is not complete and by-product are easy to generate. 5) Fenton oxidation method; The method has the advantages of simple process, high reaction rate and low energy consumption, but needs some external aids (ultrasound, electricity, UV, microwave and the like) to obtain better effects. 6) Photocatalytic oxidation. the reaction condition is mild, that effect is thorough, no secondary pollution is cause, but the treatment object is single, and the utilization rate of the light energy of the catalyst is low. 7) Ozone oxidation; The characteristics include strong oxidation capacity, simple equipment, no secondary pollution, but the production of ozone power consumption is high, the technology is not advanced enough to large-scale application. 8) Electrochemical oxidation method; the advantages include wide adaptability, strong controllability and convenient operation, but the disadvantages, including large energy consumption and high cost and incomplete decomposition of organic matters, were elucidated. 9) Ultrasonic cavitation technology; It could effectively improve biodegradability of the waste water and is beneficial to the subsequent treatment, but the single use of the technology has long time consumption and high economic cost. 10) Aerobic biological treatment; The treatment period is short, the speed is fast, the pollution is less, but the effect is difficult to reach the expectation due to the limitation of water body. 11) Anaerobic biological treatment; No oxygen and low energy consumption can produce clean energy such as biogas, but the residence time is long, the treatment effect of toxic substances is not satisfactory. 12) Anaerobic-aerobic biological combination method; It combines the advantages of aerobic and anaerobic treatment methods, and obviously improves the treatment efficiency.

4. Conclusions

At present, pollutants in water bodies are increasingly complicated, and a plurality of antibiotics and other pollutants often exist in the water bodies, so that a single treatment technology is not enough to efficiently remove the antibiotics in the water bodies. Each treatment method has its advantages and disadvantages, so it is necessary to consider the combination of various technologies to achieve better treatment effect. Although the treatment process of the combination of multiple technologies is complicated and the operation cost is high, the combination of multiple technologies is the best means for treating antibiotic wastewater from the perspective of practical and efficient analysis, which can achieve the effect of complementary advantages and has a broader application prospect.

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