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Review

The Effect Review of Various Biological, Physical and Chemical Methods on the Removal of Antibiotics

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Abstract: Antibiotics are highly effective bactericidal drugs that are widely used in human medicine, aquaculture and animal husbandry. Antibiotics enter the aquatic environment through various routes due to low metabolic levels and increased use. Not only are antibiotics inherently toxic, but the spread of potential drug resistance introduced has been identified by the World Health Organization as one of the major threats and risks to global public health security. Therefore, how to efficiently remove antibiotics from water and eliminate the ecological safety hazards caused by antibiotics has been a hot topic in recent years. There are various research methods for decontaminating water with antibiotics. This paper reviews the research and application of various biological, physical, chemical methods and combined processes in antibiotic pollution control. Moreover, this paper describes the degradation mechanism, removal efficiency, influencing factors and technical characteristics of different antibiotics by various methods in detail. Finally, an outlook on future research in antibiotic removal is provided to help promote the development of antibiotic removal technology.

Keywords: antibiotics; combined processes; biological method; physical method; chemical method

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1. Introduction

Antibiotics are generally secondary metabolites produced by microorganisms (e.g., bacteria, fungi, actinomycetes) or certain higher plants and animals in the course of their life activities or compounds synthesized by humans [1]. Antibiotics specifically interfere with the structure, function and metabolic activity of bacterial cells, depriving them of their normal ability to grow and reproduce, thereby inhibiting or killing them. [2]. Therefore, antibiotics are widely used in human medicine, aquaculture and animal husbandry production and other industries for antibacterial treatment and prevention [3]. Antibiotic use is reported to have increased by 65% from 2000 to 2015 [4]. It is estimated that global antibiotic use is expected to reach 106,000 tons by 2030 [5].

Because most of the antibiotics ingested in the organism are water-soluble and not easily absorbed by the intestine, 30% to 90% of the antibiotics are usually discharged in the form of metabolic waste (such as feces and urine) [6]. However, as shown in Figure 1, antibiotics can enter the water environment through various forms, such as surface runoff, rainwater flushing and sewage discharge [7]. Therefore, the water environment has become an important receiver system for antibiotics residues. At present, there are two characteristics of antibiotics in the water environment: variety and wide distribution. According to the different chemical structures and properties of antibiotics, they can be divided into six categories, including common sulfonamides, tetracyclines, fluoroquinolones, macrolides, β-lactams, aminoglycosides, etc. [8]. In addition, antibiotics are distributed in a variety of aqueous environmental media such as surface water [9], groundwater [10], and drinking water [11]. However, antibiotics were identified as a trace amount of persistent organic

pollutants, due to their special chemical structure [12]. Studies have reported that antibiotics in the water environment have certain toxicological effects, and once they enter the human body, they can easily cause an imbalance in the human intestinal flora, which can lead to a series of diseases [13]. In addition to the toxicity of antibiotics themselves to the environment, the long-term existence of antibiotics can also cause antibiotic-resistant bacteria (ARB) and antibiotic-resistant genes (ARGs), which will accelerate the spread of antibiotic resistance [14]. Moreover, the potential spread of drug resistance caused by the use of antibiotics has also been identified by the World Health Organization (WHO) as one of the major threats and risks to the future security of global public health [15].

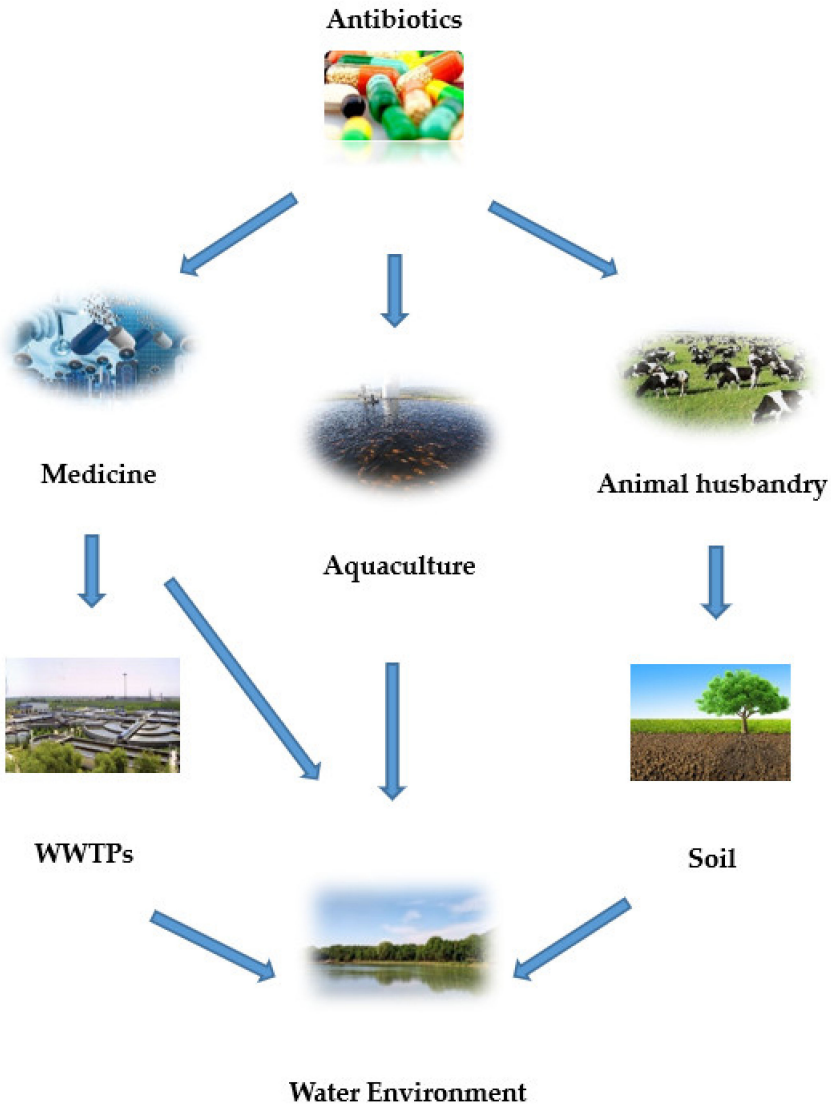

Figure 1. Sources of antibiotics in the water environment.

Due to the serious contamination of antibiotics, which threatens human health and safety, research on their contamination control has received widespread attention. In recent years, the research on the technology of removing antibiotics in the water environment has been mainly based on biological treatment methods, physical treatment methods and chemical oxidation methods [16]. Therefore, the review systematically summarized discusses various techniques for removing antibiotics from water, including biological methods (activated sludge treatment, membrane bioreactor) [17,18], physical methods (adsorption, membrane filtration and ion resin treatment) [19–21] and chemical methods (strong oxidant oxidation method and advanced oxidation method) [22,23]. The degradation mechanism, removal efficiency, influencing factors and technical characteristics of various treatment

methods for antibiotics are described and analyzed. Furthermore, the advantages and disadvantages of various treatment methods in the process of controlling antibiotic pollution in the water environment have been analyzed, and the problems in the application of various treatment methods have been put forward. This paper can further provide a reference for the improvement and joint application of various processing technologies.

2. Mechanism of Different Methods

2.1. Biological Treatment Method

Biological treatment is an artificial enhanced biological treatment technology based on environmental self-purification, which uses the metabolic action of microorganisms in the environment to oxidize and decompose organic pollutants in water and convert them into stable and harmless inorganic substances. As shown in Figure 2, the main mechanisms for the removal of antibiotics from water by biological treatment are based on two pathways: biodegradation and biosorption [24]. Biodegradation includes microbial co-metabolism and microbial metabolism. The former antibiotics can be degraded under the action of corresponding enzymes secreted by the microbial community, and the latter microorganisms can use antibiotics as carbon sources and energy substrates for their growth. Therefore, the microorganisms can decompose and transform antibiotics by themselves [25]. He et al. [26] found that the removal rate of tetracycline by 0.2 μM Tet(X) could reach about 80.5% within 15 min. Jiang et al. [27] studied the degradation and metabolic pathway of sulfamethoxazole by Pseudomonas psychrophilic HA-4 and found that Pseudomonas can use the antibiotic sulfamethoxazole as the sole carbon source and energy source to degrade sulfamethoxazole. Compared with biodegradation, the adsorption and removal of antibiotics are based on hydrophobic and electrostatic interactions. Generally, aliphatic and aromatic antibiotic compounds have a hydrophobic effect. In addition, electrostatic interactions occur between positively charged antibiotic contaminants and negatively charged microorganisms or sludge. Chen et al. [28] found that biological methods have better adsorption effects on antibiotics such as erythromycin, clarithromycin and azithromycin, mainly through electrostatic and hydrophobic interaction mechanisms.

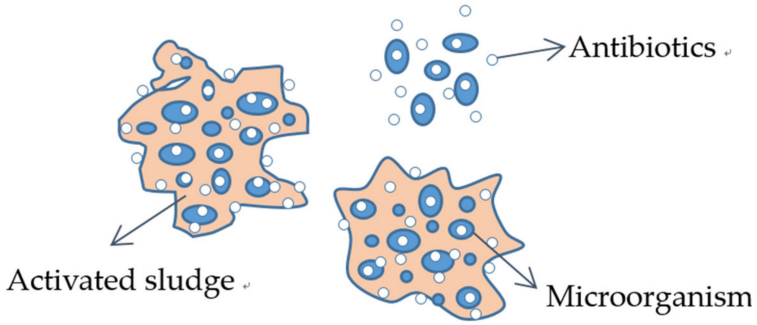

Figure 2. The main mechanism of action of antibiotic biological treatment.

2.2. Physical Treatment Method

Common physical treatment methods for antibiotics include: adsorption, ionic resin and membrane filtration [25]. Adsorption methods are mainly based on physical and chemical adsorption between substances. Physical adsorption is mainly caused by van der Waals forces, Π–Π interactions, hydrophobic interactions and hydrogen bonds between adsorbate and adsorbent molecules. Chemical adsorption is due to the transfer, exchange or sharing of electrons between adsorbate molecules and adsorbent surface atoms (or molecules) to form adsorption chemical bonds (such as ion exchange). Sharma et al. [29] found that the adsorption of two antibiotics, norfloxacin and ofloxacin by the integrated adsorption-membrane process mainly involved a combined mechanism of electrostatic interaction, anion exchange and hydrophobic interaction. The ionic resin method is mainly based on the functional groups and magnetic structure of the magnetic ionic resins. On the

basis of adsorption, the removal of pollutants can be further enhanced by the ion exchange route. Choi et al. [30] used ion exchange resin to remove sulfonamide and tetracycline antibiotics and found that ion exchange resin was effective for the removal of antibiotics, and the antibiotics that existed in the form of ions under neutral pH conditions could be removed by ion exchange. Compared to adsorption, membrane filtration not only has an adsorption effect but also uses a membrane structure with selective permeation, high permeation flux and strong rejection properties for the filter medium [31]. J. Jaime et al. [32] used reverse osmosis to study the removal of ciprofloxacin in seawater and found that the removal rate of ciprofloxacin in seawater by reverse osmosis membrane module (RO) was greater than 90%.

2.3. Chemical Treatment Method

For a long time, the chemical treatment of antibiotics can be divided into strong oxidant oxidation and advanced oxidation according to the mode of action. Strong oxidant oxidation is mainly based on the strong oxidizing properties of the oxidant itself, which readily reacts with pollutants in a redox manner. The addition of strong oxidants generally uses chemicals with high redox potential or strong oxidizing properties (such as chlorine (E_h = 1.36 V), and ferrate (E_h = 2.20 V)). During the chlorination process, redox reactions usually occur between free chlorine, hypochlorous acid and hypochlorite radicals and pollutants. Compared with chlorine, ferrate (Fe(VI)) shows better application potential. Fe(VI) is an environmentally friendly chemical agent for water treatment, which has the functions of oxidation, sterilization, disinfection and flocculation. Fe(VI) can generate Fe(V) or Fe(IV) with a stronger oxidizing ability through single-electron or double-electron transfer, and self-decompose to generate reactive oxygen species O^{2-} or H_2O_2 to achieve rapid degradation of pollutants [33]. A. Acosta et al. [22] found that ferrate has a good removal effect on sulfonamide antibiotics. When pH = 3, Fe(VI): SNs = 6:1, 100% degradation of sulfonamide antibiotics can be achieved within 5 min, and the byproducts after oxidation are relatively less toxic. However, the advanced oxidation treatment processes [34] are mainly based on various reactive free radicals with stronger oxidizing properties that are generated in the reaction system, such as hydroxyl radicals, peroxy radicals, sulfate radicals, etc. Active free radicals can undergo chemical reactions such as dehydrogenation reaction, electrophilic addition reaction and electron transfer with antibiotics in water, which can realize the mineralization and removal of antibiotics or convert them into non-toxic and degradable small molecules. Von Sonntag et al. [23] found that the removal of pollutants by ozone-catalyzed oxidation includes two pathways: the direct reaction of ozone molecules and the indirect reaction of the decomposition of ozone molecules to generate hydroxyl radicals. Compared with physical methods, chemical methods can destroy the chemical structure of antibiotics and convert them into non-toxic, harmless or less toxic low-molecular-weight substances.

3. Application of Different Methods in the Removal of Antibiotic

3.1. Antibiotic Biological Treatment

Biological treatment is mostly used in the treatment of antibiotic sewage. Commonly used biological treatment methods are activated sludge method and membrane bioreactor. This section provides an overview of the application of different biological treatment processes for the degradation of antibiotics, including removal efficiencies, mechanisms and influencing factors.

3.1.1. Activated Sludge Process

The activated sludge process, also known as the aerobic biological treatment process, can remove antibiotics from water through biodegradation and sludge adsorption [25]. Biodegradation mainly achieves the removal of antibiotics through two metabolic actions of microorganisms (Section 2.1 for details). However, the adsorption is mainly based on the fact that activated sludge is a porous flocculated microbial community and a combination of attached organic and inorganic substances, which has a large specific surface area and

can be used as an adsorption carrier for pollutants. Some antibiotics can be adsorbed on the adsorption sites on the surface of sludge particles through intermolecular forces, such as electrostatic interactions, hydrophobic interactions and hydrogen bonds. Commonly used activated sludge methods are: conventional activated sludge (CAS) and sequencing batch reactor (SBR).

Although activated sludge processes have been widely used in wastewater treatment plants, studies have found that adsorption is the most dominant way to remove most antibiotics compared to biodegradation in the treatment of antibiotic wastewater. Prado et al. [17] found that the biodegradation rate of tetracycline by CAS was up to 35%, and the adsorption and removal capacity of tetracycline was up to 60%, and the adsorption effect was stronger than the biodegradation effect. Similarly, Peng et al. [35] found that the removal of seven antibiotics by CAS includes three types of sludge adsorption, autotrophic biodegradation and heterotrophic biodegradation, in which sludge adsorption shows the strongest effect. Compared with CAS, SBR has the advantages of a simple process structure, small footprint, low operating cost and good treatment effect in antibiotic wastewater treatment. Zhao et al. [36] studied the degradation of sulfonamides in an anaerobic sequencing batch reactor and found that the removal mechanism of sulfadiazine (SDZ) included adsorption and biodegradation, while sulfamethoxazole (SMX) was mainly through biodegradation. Similarly, Lu et al. [37] found that the adsorption and biodegradation removal rates of fluoroquinolone antibiotics by SBR were 78–91% and 9–22%, respectively, indicating that the main way of removing fluoroquinolone antibiotics by SBR is adsorption. The reason why activated sludge adsorption is stronger than biodegradation may be the continuous generation and renewal of activated sludge flocs during process operation, which can provide more adsorption sites for antibiotics in water, resulting in more antibiotics being adsorbed on the surface of sludge flocs.

In addition, the performance of the activated sludge process in removing antibiotics is influenced by the chemical structure of the antibiotics, the nature of the sludge and the operating conditions of the biological treatment process. The adsorption performance of the activated sludge process for different antibiotics was different, which was affected by the adsorption coefficient (Kd) value, the octanol–water partition coefficient (log Kow) value and the acid dissociation constant (pKa) value. Generally, the larger the adsorption coefficient Kd value, the stronger the adsorption performance. The Kd value of the adsorption coefficient of activated sludge for sulfonamide antibiotics is in the range of 3.8–100.5 L/kg, while the Kd value of the adsorption coefficient for tetracycline antibiotics is in the range of 999–22,170 L/kg, and the Kd value of the latter adsorption coefficient is much higher than that of sulfonamide antibiotics [38]. This also confirmed that the removal of tetracycline by the activated sludge method was mainly adsorption, while the removal of sulfonamide antibiotics was mainly biodegradation. However, the octanol-water partition coefficient (log Kow) value is often used to represent the hydrophobicity of antibiotics and their ability to adsorb from the liquid phase to the solid phase. Rogers [39] proposed to use the Kow value to evaluate the size of the adsorption capacity. When log Kow < 2.5 represents low adsorption potential, 2.5 < log Kow < 4.0 represents medium adsorption potential, and log Kow > 4.0 represents high adsorption potential. Tran et al. [28] found that the adsorption of erythromycin, clarithromycin and azithromycin by biological methods was mainly based on electrostatic interaction and hydrophobic interaction, among which relatively high log Kow (3.06–4.02) can be representative of hydrophobic interactions. The acid dissociation constant (pKa) is used to describe the polarity parameter of antibiotics with a certain degree of dissociation in solution. Since some antibiotics contain alcohol (–OH), amine ($–NR^{3+}$), the carboxylic acid (–COOH) and other functional groups, acidolysis will occur in different pH environments, resulting in antibiotic molecules in the form of anions, neutrals and cations present [40]. Therefore, the pH value of the solution will affect the electrostatic interaction between antibiotics and activated sludge or microorganisms, which will affect the adsorption and removal of antibiotics. Yang et al. [41] found that the removal rate of sulfadiazine and sulfamethazine was 24% (pKa = 6.3) and 9% (pKa = 5.7)

by activated sludge process at pH 7.0, respectively. Similarly, Song et al. [42] found that the removal of oxytetracycline(OTC) by the activated sludge process was mainly based on electrostatic interaction, and the adsorption capacity and adsorption affinity of activated sludge to oxytetracycline were highly dependent on pH value. In addition, the properties of activated sludge (such as suspended sludge and biofilm) also affect the mass transfer between antibiotics and microorganisms, which in turn affects the adsorption and removal of antibiotics. For example, Torresi et al. [43] found that the adsorption coefficient of macrolide antibiotics in biofilm is higher than that of sludge in CAS, which is due to the increase in sludge adsorption with the increase in biofilm thickness and biofilm porosity. Finally, the operating parameters hydraulic retention time (HRT) and solids retention time (SRT) are also important factors for the removal of antibiotics by activated sludge process. Huang et al. [44] studied the removal of sulfamethazine by aerobic sequencing batch reactor and found that the removal rate of sulfamethazine increased from 45% to 80% when HRT was extended from 5 days to 25 days. Neyestani et al. [45] investigated the effect of SRT on trimethoprim removal and found that increasing SRT from 2 days to 20 days increased TMP removal from 19% to 71%. This is due to the fact that with the increase in HRT or SRT, not only the abundance of slow-growing bacteria (such as nitrifying bacteria) and bio-associations can be improved, but also, the floc particle properties of the outer polymer coating containing polysaccharides and proteins can be affected, thereby affecting the sludge adsorption and biodegradation removal of antibiotics.

3.1.2. Membrane Bioreactor

Membrane bioreactor (MBR) is a treatment process based on CAS combined with membrane separation, combining the three functions of biosorption, biodegradation and membrane separation [46]. Compared with the activated sludge process, the MBR has the characteristics of long sludge residence time SRT, low sludge volume and high suspended solids concentration. Although some membrane structures cannot effectively remove antibiotics (such as microfiltration membranes and ultrafiltration membranes), they can intercept toxic substances in water, improve a good environment for the growth of microorganisms and maintain a high biomass concentration. Therefore, the biodegradation in the membrane bioreactor is enhanced. Dutta et al. [47] used a two-stage anaerobic fluidized membrane bioreactor to remove a variety of antibiotics and found that under the combined action of biodegradation, sludge adsorption and membrane filtration, the removal rate of antibiotics was as high as 86–100%. Xiao et al.[18] conducted an experimental study on 5 drugs using an anaerobic membrane bioreactor and found that biodegradation was the main removal mechanism for trimethoprim and sulfamethoxazole, with removal rates of 93.3 $\pm$ 5.7% and 76.7 $\pm$ 14.6%, respectively.

In addition, the removal effect of MBR on antibiotics is affected by the type of antibiotics, initial concentration of antibiotics, membrane structure and process operating parameters. Divya et al. [48] found that the biodegradation and removal rates of sulfathiazole, enrofloxacin and chlortetracycline were the highest in an osmotic membrane bioreactor, which were 94.4%, 90.2% and 78.9%, respectively, followed by trimethoprim (68.2%), lomefloxacin (57.1%) and norfloxacin (53.2%), which may be related to the nature of antibiotics. Ali et al. [49] found that the removal rate of sulfamethoxazole and erythromycin by an anaerobic membrane bioreactor was related to the initial concentration compared with ampicillin. When the initial antibiotic concentration was increased from 50 to 250 μg/L, the removal rates of sulfamethoxazole and erythromycin decreased from 82% to 72.9% and from 81.0% to 74.0%, respectively, while the removal rate of ampicillin stabilized at about 98%, indicating that the degradation and removal rate of antibiotics is affected by the type and initial concentration of antibiotics. Similarly, Harb et al. [50] also found that the degradation and removal rate of antibiotics sulfamethoxazole and erythromycin by an anaerobic membrane bioreactor (AnMBR) was affected by the initial concentration. In addition, hydraulic retention time (HRT) is also an important factor affecting the removal efficiency of antibiotics, and the prolongation of HRT is beneficial

to the removal of antibiotics. Liu et al. [51] found that the removal rate of tetracycline, oxytetracycline and chlortetracycline by submerged membrane bioreactor was affected by hydraulic retention time (HRT). When HRT was shortened from 8–12 d to 2.7 d, tetracycline (TC), the removal rates of oxytetracycline and CTC decreased from 94.0%, 92.3% and 78.6% to 78.6%, 47.6% and 61.8%, respectively. Similarly, Song et al. [52] found that when the hydraulic retention time (HRT) was 5–4 d, the removal rate of MBR for 11 antibiotics was 83.8%, while when the HRT was shortened to 3–2 d and 1 d, the removal rate was reduced to 57.0% and 25.5%. It shows that HRT values are also an important factor in the removal of antibiotics. The effect of hydraulic retention time (HRT) may be attributed to the fact that longer HRT favors the enrichment of slow-growing bacteria (such as digesting bacteria), increased microbial diversity, and domestication of microbial populations, thereby enhancing MBR biodegradation [38]. Table 1 shows the application of different membrane bioreactors for antibiotic removal.

Table 1. The performance of antibiotics removal by using different membrane bioreactors.

Membrane Bioreactor (MBR)	Antibiotics	Removal Rate	Mechanisms	References
Sequencing-batch membrane bioreactor (SMBR)	Tetracycline Oxytetracycline Chlortetracycline	>90%	Biodegradation/ biotransformation	[53]
Anaerobic membrane bioreactor (AnMBR)	Amoxicillin Ceftriaxone Cefoperazone	73.2 ± 4.3% 47.7 ± 2.2% 79.4 ± 4.1%	Biodegradation	[54]
Hollow-fibre MBR	Norfloxacin Ofloxacin Ciprofloxacin Tetracycline	62–86% 68–93% 54–70% 100%	Biodegradation	[55]
Anoxic—aerobic MBR (2S-MBR)	Ciprofloxacin	58%	Biodegradation	[56]
Anaerobic membrane bioreactor(AnMBR-UF)	Sulfamethoxazole	>88%	Biodegradation	[57]
Ultrafiltration membrane bioreactor (MBR-UF)	Triclosan Carbamazepine	89.7 ± 8.3% 36.2 ± 6.8%	Biodegradation	[58]
Submerged membrane bioreactor (SMBR)	Triclosan	98.20%	Biodegradation	[59]
Anaerobic/anoxic/oxic-membrane bioreactor (A_1/A_2/O-MBR)	Sulfonamides	93.9–97.5%	Biodegradation	[60]
Aerobic submerged membrane bioreactor	Sulfadiazine Sulfamethoxazole	91% 88%	Biodegradation	[61]

3.2. Antibiotic Physical Treatment

Physical treatment is a method of water purification based on the enrichment and transfer of pollutants by physical action. This section reviews the research applications of three different methods, adsorption, membrane filtration and ionic resins, for the removal of antibiotics from water, including treatment efficiency, removal mechanisms and influencing factors.

3.2.1. Adsorption Method

In the study of physical removal of antibiotics, adsorption methods based on the properties of adsorbent materials have been widely studied and applied. Adsorbent materials are fast, efficient and economical in the treatment of antibiotics. Due to the unique and superior physical properties of most adsorbent materials, such as larger specific surface area and higher porosity, they can provide more active adsorption sites for adsorbates, combined with van der Waals forces between adsorbents and adsorbates, electrostatic, hydrogen bonding, Π–Π and hydrophobic forces, which can efficiently adsorb and remove pollutants in water [62]. Therefore, most of the current research on antibiotic adsorption is based on carbon-based materials. Mohamed et al. [19] found that single-walled carbon

nanotubes have a larger specific surface area and higher porosity than double-walled and multi-walled carbon nanotubes. The adsorption capacity of single-walled carbon nanotubes for ciprofloxacin and oxytetracycline was as high as 520 mg/L and 375 mg/L, respectively, and the removal of antibiotics was mainly through hydrophobic interaction and electrostatic interaction. Hala et al. [63] found that hydrogen bonding, π–π interactions, hydrophobic and electrostatic interactions were the main mechanisms for the adsorption of ciprofloxacin on nanostructured activated biochar and the adsorption capacity was 142.86 mg/g. Similarly, Fu et al. [64] also found that activated carbon could remove quinolone antibiotics by adsorption, and the adsorption mechanism is mainly through hydrophobic interaction and electrostatic interaction. In addition to carbon-based materials, the adsorption research of composite materials as adsorbents has also attracted extensive attention in recent years. Composite materials are generally composed of two or more monomer materials. The combined monomer materials can complement each other in performance and produce a synergistic effect so that the comprehensive performance of the composite material is better than that of the raw material, and it has a better application effect. Bao et al. [65] found that the removal rate of five sulfonamide antibiotics by carbon-coated magnetic nanocomposites (Fe_3O_4@C) was 74–96% under optimal conditions by electrostatic interaction and hydrogen bonding. Similarly, Ke et al. [66] found that N-doped graphitic carbon nanofiber composites have good adsorption properties for tetracycline hydrochloride and ciprofloxacin, with adsorption amounts of 546.5 mg/g and 549.6 mg/g, respectively, and the adsorption mechanism is Hydrogen Bonding and Π–Π Interactions. Table 2 shows the adsorption performance of different adsorbents for antibiotics.

Table 2. The performance of antibiotics adsorption with different carbon-based adsorbent.

Absorbent Material	Antibiotics	Removal Rate or Sorption Capacity	Mechanisms	References
Carbon nanotubes	Sulfamerazine	——	Hydrogen bonding	[67]
Graphene oxide	Sulfamethoxazole Ciprofloxacin	379 mg/g 240 mg/g	π–π electron donor-acceptor interaction Electrostatic attractions	[68]
Multiwalled carbon nanotubes	Sulfamethoxazole	——	Hydrophobic and π–π interactions	[69]
Carbon dot-modified magnetic carbon nanotubes	Carbamazepine	80% (65 mg/g)	π–π interactions	[70]
MWCNT/NH_2-MIL-53(Fe)	Tetracycline Chlortetracycline	368.49 mg/g 254.04 mg/g	π–π interactions	[71]
Co@CoO/NC	Tetracycline	385.60 mg/g	Hydrogen bonding and π–π EDA interaction	[72]
Multiwall carbon nanotube	Ciprofloxacin hydrochloride	88%	Electrostatic attractions	[73]
Zn-MOFs derived nanoporous carbons	Carbamazepine	663.7 mg/g	Hydrophobic interaction	[74]
N-doped regular octahedron MOF-199 derived porous carbon	Oxytetracycline	1280.422 mg/g	The electrostatic force, hydrogen bonding and π–π interaction	[75]

The adsorption performance of the adsorbent not only related to the performance of the adsorbent itself, but also influenced by the pH. The pH value can affect the surface charge characteristics of the adsorbent and the protonated form of the antibiotic (i.e., cation, zwitterion, anion), thereby affecting the adsorption effect of antibiotics. Muthanna et al. [76] studied the adsorption effect of ciprofloxacin and norfloxacin by preparing biochar from Albizia japonica seed pod biomass and found that when the pH value increased from 2 to 9, the removal rate of ciprofloxacin increased by 6.52%, and when the pH value increased from 2 to 5, the removal rate of norfloxacin increased by 3.34%. However, the presence of coexisting cations may compete with positively charged antibiotic molecules, resulting in the shielding effect of charges on the surface of the adsorbent, thereby affecting the adsorption effect of antibiotics. Zhao et al. [77] studied the effect of Na+ concentration on the adsorption of antibiotics sulfamethoxazole and ibuprofen on multi-walled carbon nanotubes and found that the adsorption capacity of the adsorbent for antibiotics decreased with the increase in Na^+

concentration. Similarly, Luo et al. [78] also found that when the Na^+ concentration increased from 0 to 0.01 mol/L, the adsorption capacity of sulfamethoxazole on wood-based granular activated carbon decreased from 233.9 to 212.6 mg/g, and the increase in cation concentration is not conducive to the removal of antibiotics.

3.2.2. Membrane Filtration Method

Membrane filtration is a green, harmless and efficient treatment method, which is widely used in the research field of zero-emission and no harmful additives. The membrane filtration method has the advantages of high separation efficiency, wide range of application and simple operation. Common membrane treatment processes include microfiltration membranes, ultrafiltration membranes, nanofiltration membranes and reverse osmosis membranes. However, compared with microfiltration and ultrafiltration membranes, nanofiltration membranes and reverse osmosis membranes have smaller pore sizes and molecular weight cut-off (MWCO) of 0.001–0.008 μm and less than 0.001 μm, respectively, which can intercept and remove water pollutants more efficiently, so common antibiotic treatment is also mostly based on reverse osmosis membrane and nanofiltration membrane research. Dolar et al. [79] found that the removal rate of the antibiotic enrofloxacin by the loose nanofiltration membrane was greater than 92%, while the removal rate of the antibiotic enrofloxacin by the reverse osmosis membrane and the tight nanofiltration membrane was as high as 99%. Cheng et al. [80] found that the separation of the antibiotic tobramycin by the polyamide nanofiltration membrane was based on the high permeation flux of the membrane structure and the rejection of positively charged antibiotics, and the retention rate of antibiotics was as high as 96% under optimal conditions.

Although membrane filtration is effective in retaining antibiotics, the retention efficiency is dependent on the type of antibiotic and the pH of the solution. Changes in pH can affect the degree of protonation of amine groups and antibiotics, the strength of the membrane surface charge and the presence of antibiotics. Zhao et al. [81] found that the polyethyleneimine cross-linked nanofiltration membrane can achieve the retention of more than 90% of enrofloxacin molecules through electrostatic repulsion under the condition of pH 3–4, and with the increase in pH value, antibiotics enrofloxacin retention was reduced. This is mainly because the increase in pH value will lead to the decrease of the positive charge intensity on the membrane surface, the enrofloxacin molecules gradually turn from positively charged to neutral, and the repulsion between the nanofiltration membrane and the antibiotic molecules gradually decreases. Reza et al. [82] found that with the increase in pH from 6.3 to 8.3, the retention rate of amoxicillin by high-permeability polysulfide nanofiltration membrane increased by 35%, and the improvement of retention efficiency was related to the nature of the antibiotic itself. The physicochemical properties of antibiotic amoxicillin and enrofloxacin are different, and the degree of protonation of amoxicillin increases with the increase in pH value.

3.2.3. Ion Resin Method

The bound antibiotics also exist in the form of ions, and the research on magnetic ion exchange resins has also begun to be used. The magnetic ion exchange resin structure contains polyacrylic acid matrix, quaternary amine functional group and magnetization components, which can act as a weak magnet [83]. Compared with traditional ion exchange resins, magnetic ion exchange resins have smaller particle sizes and larger specific surface areas, which can quickly adsorb pollutants. Miao et al. [21] found that the adsorption of ibuprofen by magnetic anion resin originated from electrostatic interaction, hydrogen bonding, van der Waals interaction and π–π interaction, while the adsorption of sulfadiazine was mainly attributed to functional groups and effective adsorption sites of resin anion exchange. Li et al. [84] found that magnetic cationic resin can effectively adsorb and remove coexisting copper ions and tetracycline at the same time, and the adsorption effect is 5.5–13.5 times that of monomer adsorption. Similarly, Wang et al. [85] found that compared with powdered activated carbon, magnetic ion exchange resin has a better adsorption effect on antibiotics, and

the adsorption effect of sulfamethoxazole, tetracycline and amoxicillin at 25 °C is 2–7 times that of powdered activated carbon. In addition, it is pointed out that anion exchange is the main mechanism for the adsorption of antibiotics on the anion resin, and the hydrogen bond formed between the antibiotics and the resin also enhances the adsorption.

In addition, the removal performance of the magnetic ion resin for antibiotics is also related to factors such as pH value and coexisting anions. The effect of pH value is mainly based on the different degrees of protonation of antibiotics under different pH conditions, which will affect the ion exchange with ion resin. Miao et al. [21] found that when the pH value increased from 4 to 7, the ionization degree of sulfadiazine increased, and it began to change from neutral form to anion form, thereby enhancing the ion exchange with ion resin, and the removal rate of sulfadiazine increased. The effect of coexisting ions is mainly based on the competition of ion exchange between coexisting inorganic anions and anionic antibiotics, thereby affecting the ion exchange interaction between antibiotics and ion resins. Wang et al. [86] found that coexisting anions can compete with ibuprofen through the ion exchange pathway, which affects the adsorption capacity of ibuprofen by magnetic ion resin. Although magnetic ion resin has good adsorption, it is greatly affected by coexisting ions and pH value in antibiotic treatment, which further hinders its application.

3.3. Antibiotics Chemical Treatment

The chemical treatment method is based on the chemical reaction between chemical oxidizing agents or reactive oxides generated in the reaction process and pollutants, thereby destroying the chemical molecular structure of pollutants, further converting pollutants into non-toxic and harmless small molecular substances or realizing complete mineralization and removal, and finally, achieving the purpose of pollutant degradation or harmless treatment. Common chemical treatment methods include strong oxidant oxidation and advanced oxidation. This section summarizes the research and application of two different chemical treatment methods in the removal of antibiotics from water, including treatment efficiency, removal mechanism and influencing factors.

3.3.1. Strong Oxidant Oxidation Method

The strong oxidant oxidation method mainly relies on the strong oxidizing property of the oxidant itself to attack the electrophilic group structure in the antibiotic, destroy the chemical structure of the antibiotic and realize the oxidative degradation of the antibiotic. Common strong oxidants include chlorination and ferrate oxidation. In addition to water disinfection, chlorination has also been used in the study of antibiotic degradation. Wang et al. [87] found that HClO easily reacts with electrophilic active groups of antibiotics and can react rapidly with oxytetracycline and chlortetracycline. Angie V. et al. [88] found that electrically generated active chlorine was effective in removing cefadroxil and reducing antibiotic activity. Similarly, Efraim et al. [89] found that electrogenerated active chlorine had a better removal effect on antibiotics; the removal rate of ciprofloxacin and norfloxacin was close to 100%, and the removal rate of levofloxacin was about 75%. Although the chlorination method has a better removal effect on antibiotics, the byproducts generated by the chlorination method are often more toxic, which further limits the research and application of the chlorination method [90]. For example, He et al. [91] found that the antibiotic fleroxacin forms halogenated disinfection byproducts during the chlorination degradation process, and the oxidative degradation products have higher biological toxicity. Similarly, Zhu et al. [92] found that when bromide and iodide ions are present in the solution, brominated and iodized disinfection byproducts are generated during the chlorination degradation of sulfamethoxazole, which is more toxic than the parent compound. In addition, pH is an important factor influencing the chlorinated removal of antibiotics. PH can indirectly affect the removal of antibiotics by affecting the presence of oxidants and protonation of antibiotics. Gui et al. [93] found that the degradation and removal rate of fleroxacin by chlorine and chlorine dioxide increased first and then decreased with pH from 6.5 to 9.0. This is because the degree of deprotonation of fleroxacin increases with the

increase in pH value; the protonation of fleroxacin is more susceptible to affinity attack, and the removal rate increases. However, when the pH value increases to a certain value, the active form of chlorine begins to change from HClO to oxidation OCl^- with low capacity, thus resulting in lower removal of fleroxacin. This suggests that pH affects not only the degree of ionization and deprotonation of antibiotics but also the form of oxidant present during chlorination.

In addition to the chlorination method, the green water treatment agent ferrate has also been proved to be prone to chemical reactions (such as cleavage and hydroxylation) with some antibiotics containing electron-rich organic groups, which are used for the degradation of antibiotics and product toxicity assessment studies [94]. Ferrate is a positive hexavalent iron salt, with high oxidation potential, strong oxidation performance and wide application pH range, and the reduction product is a trivalent iron salt. Ferrate has a good degradation effect in antibiotic treatment applications. Ma et al. [95] found that under the condition of Fe(VI): TC = 1:10, the degradation rate of TC reached more than 98.6% within the 60 s. Zhou et al. [96] found that the removal rate of ciprofloxacin was higher than 90% at a material ratio of 10:1 between Fe(VI) and ciprofloxacin and a pH of 6–9, with the removal rate mechanism of ciprofloxacin piperazine ring cutting or hydroxylation. Compared with chlorination, ferrate oxidation can not only reduce the toxicity of reactants but also control the generation of chlorination disinfection byproducts. For example, Pavla et al. [97] studied the removal performance and toxicity evaluation of antibiotics by ferrate and found that antibiotics could not only be effectively oxidized and degraded but also reduce the toxicity of ofloxacin, ciprofloxacin and oxytetracycline after oxidation. Similarly, Zhang et al. [98] found that ferrate not only effectively degrades sulfamethazine (SMZ) and sulfadiazine (SDZ) but also controls the generation of chlorinated disinfection byproducts. In addition, pH value is also an important factor affecting the degradation of antibiotics by ferrate, and the oxidative degradation pathways of ferrate to antibiotics are different at different pH values. A. Acosta et al. [22] found that the degradation pathway of sulfa antibiotics by ferrate is related to pH. At acidic pH, ferrate can cleave the C-S and S-N bonds of antibiotics, and at neutral pH, antibiotics can be converted into nitro and nitroso derivatives, while at alkaline pH, hydroxylation is the main reaction. The changes of antibiotic degradation pathways are related to the existing forms of ferrate under different pH conditions. Wang et al. [99] studied the effect of pH on the oxidation of fluoroquinolone antibiotics by ferrate and found that pH affected the protonated form of ferrate. At the same time, compared with basic conditions, the active species under acidic conditions had a small amount of hydroxyl radicals in addition to Fe(VI), Fe(V) and Fe(IV). Although ferrate has a good treatment effect on antibiotic removal, the poor stability and low yield of ferrate further limit its practical application. Currently, most applications of ferrate are based on experimental studies.

3.3.2. Advanced Oxidation Method

Compared with the strong oxidant oxidation method, the advanced oxidation method can generate more active strong oxidizing free radicals (such as hydroxyl radicals, sulfate radicals, superoxide radicals, etc.) to achieve the degradation of pollutants and the improvement of biodegradability. Advanced oxidation methods can be divided into Fenton oxidation, ozone catalytic oxidation and photocatalytic oxidation according to how active free radicals are generated.

Fenton Oxidation

Among the many advanced oxidation methods, Fenton oxidation has been widely studied for the removal of antibiotics. Fenton oxidation includes both conventional Fenton oxidation and oxidation-like methods. The Fenton reaction is mainly based on the rapid reaction of Fe^{2+} with hydrogen peroxide under acidic conditions to generate hydroxyl radicals [100] (Equation (1)). A hydroxyl radical has a high redox potential of 2.8 V, which can degrade antibiotic through H atom substitution reaction, electron transfer or electrophilic

addition [101]. The Fenton oxidation method can effectively remove antibiotics, reduce product toxicity and improve the biodegradability of reaction products and has good application prospects. Gupta et al. [102] found that the removal rate of ciprofloxacin by Fenton oxidation could reach 70%, and the toxicity of the oxidation product was reduced. However, due to the shortcomings of the traditional Fenton method, which is influenced by pH, low H_2O_2 utilization efficiency and the tendency to produce iron sludge, most antibiotics research in recent years has been based on the application of Fenton-like oxidation. Fenton-like oxidation methods include homogeneous Fenton (such as optical Fenton and electric Fenton) and heterogeneous Fenton [103]. Wang et al. [104] found that electro-Fenton oxidation could completely remove the β-lactam antibiotic cefoperazone within 120 min, and the biodegradability was also improved. Similarly, Marjan et al. [105] found that homogeneous Fenton oxidation not only had a high removal rate for the antibiotic ciprofloxacin but also improved the biodegradability of the reaction product. Therefore, the Fenton reaction is one of the effective means to remove antibiotics. Table 3 summarizes the application of Fenton-like oxidation for antibiotic removal.

Table 3. The performance of antibiotics removal by using different Fenton-like processes.

Fenton Oxidation	Antibiotics	Operating Conditions	Removal Rate	References
Photo-Fenton	Tylosin	$[Tylosin]_{sample}$ = 15 mg/L $[H_2O_2]$ = 20 mg/L $[Fe^{2+}]$ = 5 mg/L pH = 2.6 UV light lamp	97.1%	[106]
Heterogeneous Fenton-like	Ofloxacin (OFL)	$[OFL]_{sample}$ = 30 mg/L Catalyst: Fe-Cu@MPSi = 1 g/L $[H_2O_2]$ = 2000 mg/L pH = 9	85%	[107]
Photo-Fenton	Tetracycline (TC) Oxytetracycline (OTC)	$[TC]_{sample}$ = 100 mg/L $[OTC]_{sample}$ = 100 mg/L $[H_2O_2]$ = 20 mg/L $[Fe^{2+}]$ = 5 mg/L pH = 5.5 4 W Hg UV lamps	94.2% 94.8%	[108]
Electro-Fenton	Ciprofloxacin (CIP)	[CIP] = 0.2 mM $[Fe^{2+}]$ = 2 mM Current = 200 mA $[Na_2SO_4]$ = 0.05 M pH = 3–9	88.11%	[109]
Heterogeneous electro-Fenton	Tetracycline (TC)	$[TC]_{sample}$ = 20 mg/L Catalyst: Cu-doped Fe@Fe_2O_3 $[Na_2SO_4]$ = 0.02 M Current =40 mA pH = 3	98.1%	[110]
Heterogeneous photo-Fenton	Sulfamethoxazole (SMX)	$[SMX]_{sample}$ = 5 mg/L $[H_2O_2]$ = 9.79 mM Catalyst: Fe_3S_4 = 0.3 g/L pH = 5 10 W LED	100%	[111]
Heterogeneous Fenton	Ciprofloxacin (CIP)	$[CIP]_{sample}$ = 10 mg/L Catalyst: Fe_3O_4 = 1.75 g/L $[H_2O_2]$ = 12 mg/L pH = 3	89%	[112]

Table 3. *Cont.*

Fenton Oxidation	Antibiotics	Operating Conditions	Removal Rate	References
Heterogeneous Fenton	Tetracycline (TC)	[TC] = 100 mg/L Catalyst: Fe^0/CeO_2 = 1 g/L $[H_2O_2]$ = 100 mmol/L pH = 5.8	93%	[113]
Fenton-like	Sulfamethoxazole (SMX)	$[SMX]_{sample}$ = 20 mg/L Catalyst: Fe@MesoC = 0.2 g/L $[H_2O_2]$ = 3 mM pH = 4	100%	[114]
Heterogeneous Fenton	Sulfamethoxazole (SMX) Carbamazepine (CBZ) Ciprofloxacin (CIP)	$[SMX]_{sample}$ = 20 mg/L Catalyst: CoFe50@C = 0.1 g/L $[H_2O_2]$ = 15 mM Ph = 3	98% 90% 84%	[115]
Electro-Fenton	Oxytetracycline (OTC)	$[OTC]_{sample}$ = 0.2 Mm Current = 5.17 mA $[Na_2SO_4]$ = 0.05 M pH = 3	83.75%	[116]
Electro-Fenton	Ciprofloxacin (CIP)	[CIP] = 50 mg/L Current = 400 Ma $[Na_2SO_4]$ = 0.05 M Catalyst: Mn^{2+} /Fe^{2+} = 2:1 pH = 3	94%	[117]

Although Fenton oxidation has the advantages of simple operation, low cost and fast degradation efficiency, it is easily affected by pH, Fe^{2+} and H_2O_2 concentration. Fenton oxidation mainly catalyzes H_2O_2 to generate ·OH and ·OH2 through the cyclic conversion of Fe^{2+}/Fe^{3+} (Equations (1)–(4)). However, when the pH increases to a certain value, Fe^{2+} exists in the form of iron hydroxide, resulting in a decrease in the concentration of Fe^{2+} catalyst in the reaction system, thereby inhibiting the Fenton reaction and reducing the ability of pollutant degradation [118]. Mohamed et al. [119] found that when the pH increased from 3 to 10, the photo-Fenton oxidative degradation rate of amoxicillin decreased from 100% to 62%, indicating that the effect of pH on antibiotics cannot be ignored. In addition, the concentration of H_2O_2 and Fe^{2+} as reaction substrates directly affects the degradation effect of the Fenton reaction on antibiotics. The formation of hydroxyl radicals during the reaction is related to the concentration of H_2O_2. When the concentration of the reaction substrate H_2O_2 is low, the generation of hydroxyl radicals is less, which reduces the degradation efficiency of pollutants. However, when the concentration of the reaction substrate H_2O_2 is high, the excess H_2O_2 reacts with the generated hydroxyl radicals to generate peroxy radicals with weak oxidation performance (Equation (2)), which will not only reduce the degradation effect but also increase the processing fee [120]. Hou et al. [121] found that the degradation of pollutants by Fenton oxidation was not positively correlated with H_2O_2 concentration. When the concentration of H_2O_2 increased from 10 mM to 150 mM, the removal rate of tetracycline increased from 62% to 93.6%. However, when the concentration of H_2O_2 increased from 150 mM to 250 mM, the tetracycline removal rate of 93.7% did not change, which further indicated that appropriate dosage of H_2O_2 could improve the removal of antibiotics, and excessive dosage would lead to an increase in treatment costs. Qi et al. [122] studied the degradation of metacycline by heterogeneous Fenton and found that the removal rates of metacycline were 43.6%, 54.3%, and 95.1% when H_2O_2 was added at 100, 300, and 500 µL, respectively. Similarly, Fe^{2+} as a reaction catalyst affects the production of hydroxyl radicals. The increase in Fe^{2+} concentration can promote the generation of hydroxyl radicals, but when excessive, it reacts with the generated hydroxyl radicals, hindering the degradation and removal of pollutants [123] (Equation (5)). Cyrine et al. [124] studied the degradation and removal of the antibiotic enoxacin by electro-Fenton and found that when the Fe^{2+} concentration increased from 0.1 mM to 0.2 mM, the degradation removal rate increased from 93% to 97%, and when

the Fe^{2+} concentration increased from 0.2 mM to 0.5 mM, the degradation removal rate decreased from 93% to 87%.

It can be seen from Table 3 that the Fenton-like oxidation method has shown a good application effect in removing antibiotics, but there are still deficiencies in practical therapeutic applications [125]. The advantages and disadvantages of Fenton-like reactions are shown in Table 4.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (1)$$

$$\bullet OH + H_2O_2 \rightarrow \bullet HO_2 + H_2O \quad (2)$$

$$2\bullet OH \rightarrow H_2O_2 \quad (3)$$

$$Fe^{3+} + \bullet HO_2 \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \quad (5)$$

Table 4. The advantages and disadvantages of Fenton-like reactions.

Fenton-like	Advantages	Disadvantages
Electro-Fenton	H_2O_2 can be generated in situ, avoiding the cost and risk of H_2O_2 transportation and storage; Fe^{3+} can be reduced to Fe^{2+} at the cathode, to realize the regeneration of Fe^{2+}; the low iron sludge production.	The low concentration of H_2O_2 yield; the low current efficiency; the low unit cell body throughput;
Photo-Fenton	Light energy promotes cycling between Fe^{3+} and Fe^{2+}; the low initial Fe^{2+} concentration; the low iron sludge production.	The low utilization rate of light energy; the high operation costs;
Heterogeneous Fenton	With the wide range of pH; the catalyst is stable and reusable; the low iron sludge production.	The catalyst preparation cost is high; the catalyst preparation process is complicated.

Ozone or Ozone Catalytic Oxidation

Compared with Fenton oxidation, ozone or ozone catalytic oxidation is an environmentally friendly and efficient treatment method without secondary pollution [126]. Ozone is a strong oxidizing agent with a redox potential of 2.07 V and can react directly with organic pollutants in redox reactions. In addition, ozone molecules can also be used to mineralize organic compounds by reacting chemically with water molecules or catalysts to produce hydroxyl radicals with greater oxidizing properties (Equations (6)–(8)) [127]. Therefore, in the process of ozone or ozone catalytic oxidation, the degradation and removal mechanisms of pollutants include direct oxidation of ozone molecules and indirect oxidation of hydroxyl radicals generated as products (Figure 3). Wang et al. [128] found that the degradation of ofloxacin, trimethoprim, norfloxacin and ciprofloxacin by ozone could be rapidly degraded and removed within 10 s. In addition, it was also pointed out that the high removal rate is mainly based on the fact that the electron-rich groups in the antibiotic structure can directly react with ozone molecules for rapid oxidation. Similarly, M.Gorito et al. [129] also found that ozone can achieve complete removal of oxytetracycline and sulfamethazine within 30 min, and the removal mechanism is mainly through the direct oxidation of ozone molecules. Compared with ozone oxidation alone, the application of catalysts can stimulate ozone molecules to form hydroxyl radicals, especially catalysts containing transition metal ions (such as Fe^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} Cr^{2+}, etc.) [130]. Catalytic ozonation is based on the cyclic conversion of metal ions in different valence states, which can react with ozone molecules to generate more hydroxyl radicals, thereby improving the mineralization and degradation of pollutants [131]. Omid et al. [132] used γ-Al_2O_3 as an ozone catalyst to study the effect of ciprofloxacin on the degradation and removal of ciprofloxacin and found that the removal rate of antibiotics by ozone catalytic oxidation was higher than that of ozone treatment under any parameter study conditions. Huang et al. [133] studied the degradation of ibuprofen by ferrosilicon catalytic ozonation and found that catalytic ozonation had a better degradation effect than ozonation alone, with removal rates of 75% and 37% for ibuprofen, respectively. The increase in degradation

and removal rates is attributed to the fact that ozonolysis produces more active hydroxyl radicals in the presence of a catalyst. Similarly, Hai et al. [134] found that although the removal rate of sulfamethazine by catalytic ozonation was similar to that of ozonation alone, the mineralization efficiency was 3 times higher than that of ozonation alone. The increase in mineralization rates is attributed to the catalyst $NiCo_2O_4$, which can promote the generation of hydroxyl radicals, thereby enhancing the mineralization removal of antibiotics. Table 5 summarizes the application of ozone or ozone-catalyzed oxidation to the degradation of antibiotics. In addition, pH value is also an important factor affecting the removal efficiency of antibiotics by ozonation or catalytic ozonation. It has been found that the decomposition of ozone and the formation of free radicals are related to the pH of the reaction system [135]. Under acidic conditions, ozone molecules are relatively stable, and the degradation of pollutants is mainly through direct oxidation of ozone molecules. However, under alkaline conditions, ozone molecules are less stable and more likely to react to generate hydroxyl radicals, resulting in the degradation of pollutants mainly through direct oxidation of ozone molecules and indirect oxidation of hydroxyl radicals.

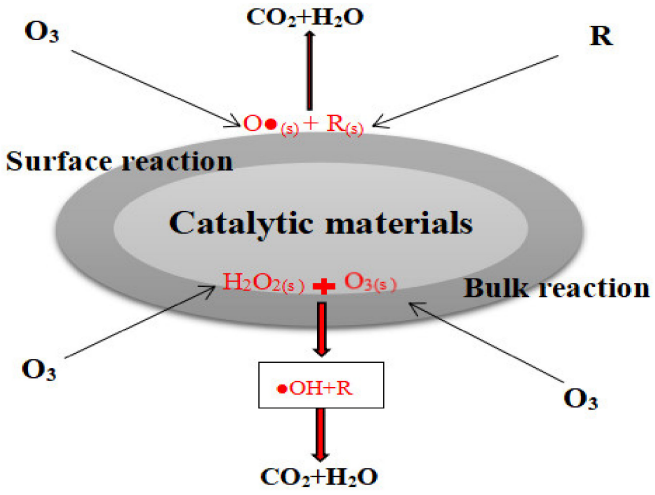

Figure 3. The main reaction pathway for the removal of pollutants by ozone oxidation (R, compound; R(s), adsorbed compound).

It is worth noting that ozone tends to produce toxic substances such as bromate when treating aqueous solutions containing bromide [135]. Yang et al. [136] found that bromate can be generated by ozone oxidation and catalytic ozonation in the treatment of bromide-containing antibiotic-contaminated water, and the influence of hydroxyl radicals is smaller than that of ozone molecules, indicating that the generation of bromate is mainly related to ozone dose. Similarly, Lu et al. [137] studied the oxidative properties of ozone on ciprofloxacin in the presence of bromide and found that the presence of bromide enhanced the reaction and also produced more toxic Br-TPs. Therefore, the application of ozonation and catalytic ozonation in the application of antibiotics to pollute water should consider bromide and its concentration [138]. At the same time, how to control the formation of bromate in the process of ozone oxidation is also the focus of research.

$$O_3 + H_2O \rightarrow 2\bullet OH + O_2 \quad (6)$$

$$O_3 + \bullet OH \rightarrow O_2 + HO_2\bullet \quad (7)$$

$$O_3 + HO_2\bullet \rightarrow 2O_2 + \bullet OH \quad (8)$$

$$O_3 + \bullet OH \rightarrow O_2 + HO_2 \quad (9)$$

$$2HO_2\bullet \rightarrow O_2 + H_2O_2 \quad (10)$$

Table 5. The performance of antibiotics removal by using ozone or ozone catalytic process.

Antibiotics	Operating Conditions	Removal Rate	References
Sulfamethazine (SMT)	Catalyst: MnxOy/γ-Fe_2O_3 = 0.3 g/L $[SMT]_{sample}$ = 20 mg/L $[O_3]$ = 6 mg/L pH = 7	100%	[139]
Sulfamethoxazole (SMX)	$[SMX]_{sample}$ = 20 mg/L $[O_3]$ = 4.5 mg/min pH = 5.2	100%	[140]
Oxytetracycline (OTC) Sulfadimethoxine (SDM) Sulfamethoxazole (SMX) Trimethoprim (TMP)	$[OTC]_{sample}$ = 100 ng/L $[SDM]_{sample}$ = 100 ng/L $[SMX]_{sample}$ =100 ng/L $[TMP]_{sample}$ =100 g/L $[O_3]$ = 1.5 mg/L pH = 8	>98%	[129]
Ciprofloxacin (CIP)	Catalyst: Mn-CeOx@γ-Al_2O_3/O_3 = 0.3 g/L $[CIP]_{sample}$ = 50 mg/L $[O_3]$ = 14 mg/L pH = 8.5	100%	[141]
Sulfamerazine (SMZ)	Catalyst: $Mn_xFe_yO_z$/AC = 0.05 g/L $[SMZ]_{sample}$ = 10 mg/L $[O_3]$ = 50 mL/min pH = 6.1	90.5%	[142]
Ibuprofen (IBU)	Catalyst: $FeSi_2$ = 1.0 g/L $[IBU]_{sample}$ = 10 mg/L $[O_3]$ = 9 mg/L pH = 8	75%	[133]
Sulfamethazine (SMT)	Catalyst: $NiCo_2O_4$ = 0.05 g/L $[SMT]_{sample}$ = 20 mg/L $[O_3]$ = 4.5 mg/min pH = 5.2	100%	[134]
Norfloxacin (NOF)	Catalyst: Co_3O_4/C = 0.05 g/L $[NOF]_{sample}$ = 20 mg/L $[O_3]$ = 15 mg/L pH = 6.7	100%	[143]
Metoprolol (MET)Ibuprofen (IBU)	Catalyst: α-MnO_2 = 0.1 g $[MET]_{sample}$ = 20 mg/L $[IBU]_{sample}$ = 20 mg/L $[O_3]$ = 1 mg/min pH = 7	100%	[144]
Metronidazole (MNZ)	Catalyst: Fe_3O_4@$Mg(OH)_2$ = 0.05 mol/L $[MNZ]_{sample}$ = 20 mg/L $[O_3]$ = 1 mg/min pH = 6.8	81.3%	[145]

Photocatalytic Oxidation

Photocatalytic oxidation technology is a green, low-cost treatment technology. Photocatalytic reactions use semiconductors (S) as catalysts to remove organic and inorganic pollutants from water by causing an oxidation-reduction reaction through photoexcitation. Figure 4 shows the free radical generation mechanism of the photocatalytic reaction. The photocatalytic mechanism is based on the fact that when sunlight is irradiated on a semiconductor catalyst, electrons (e-) in the valence band (VB) of the catalyst are excited to the conduction band (CB), resulting in the generation of positively charged holes (h+) in the valence band, and negatively charged energetic electrons are generated in the conduction band (Equation (11)). However, positively charged holes (h+) generated in the valence band can further split water molecules to generate highly reactive hydroxyl radicals (Equation (12)). In addition, the negatively charged high-energy electrons generated in the conduction band can also be captured by oxygen molecules to generate superoxide radicals (Equation (13)). In addition, the free radicals generated in the reaction can generate more hydroxyl radicals through other pathways [146] (Equations (14)–(16)). The degradation of

target pollutants by photocatalytic oxidation is mainly based on the strong oxidative and highly reactive hydroxyl radicals generated during the catalytic reaction. Based on the mild photocatalytic oxidation reaction conditions and strong oxidation performance, it is also used for the degradation of pollutant antibiotics. Joao et al. [147] found that the removal of antibiotics oxalic acid and tetracycline by TiO_2 photocatalytic oxidation is mainly due to the action of active oxidant hydroxyl radicals, and the catalytic oxidation system not only has a good removal effect on antibiotics but also has high mineralization efficiency. Similarly, Thanh et al. [148] studied the effect of ZnO-modified TiO_2 nanocomposites on the heterogeneous photocatalytic degradation of amoxicillin and found that the degradation and mineralization rates of amoxicillin were improved. To improve photocatalytic efficiency, a variety of catalytic materials have been used in photocatalytic research, including metal oxides and sulfides (TiO_2, SnO_2 and CdS), metal semiconductors (BiOBr, BiOCl, $BiVO_4$ and $GdVO_4$) [149–152] and non-metallic semiconductors (gC3N4) [153]. However, among many catalysts, TiO2 and $BiVO_4$ are widely used in the removal of various antibiotics, such as tetracycline [154], ciprofloxacin [155,156], penicillin [157], norfloxacin [158], sulfamethoxazole [159], oxytetracycline [160], etc.

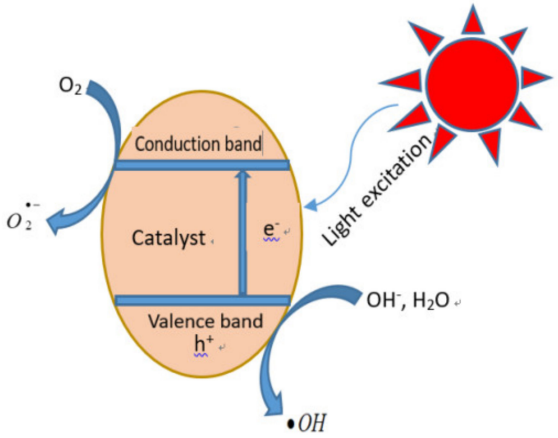

Figure 4. Generation of free radicals during photocatalytic reactions.

In addition, catalyst dosage and pH value are also important factors for the degradation of antibiotics. The amount of catalyst affects the photocatalytic intensity. When the amount of catalyst is appropriately increased, it provides more active sites for pollutants, increases the contact between catalyst and pollutant, and improves the degradation and mineralization rate of pollutants. On the contrary, when the catalyst is in excess, light scattering and shielding effects occur, which is not conducive to the degradation of pollutant antibiotics. Azimi et al. [161] found that when the number of photocatalyst PbS-CdS increased from 0.25 g/L to 1.5 g/L, the degradation rate of tetracycline gradually increased, and when it was further increased to 2.5 g/L, the degradation rate of tetracycline did not change. In addition, Ahmadi et al. [162] used (MWCNT/TiO_2) as a photocatalyst to degrade tetracycline and also came to the same conclusion that the degradation and removal rate of antibiotics does not increase with the increase in catalyst dosage. However, pH affects not only the ionization and protonation of antibiotics but also the charged properties and ionization state of the catalyst surface, which in turn affects the degradation and adsorption of antibiotics [163]. Zhu et al. [164] studied the photocatalytic degradation of tetracycline by nano-TiO_2 and found that when the pH value increased from 3 to 9, the TC removal rate increased continuously, which was mainly due to the dependence of the surface properties of the catalyst TiO_2 and the morphology of tetracycline on the pH value.

Although photocatalytic reactions have the advantage of mild conditions and high oxidation capacity, they still suffer from low light energy utilization and difficulties in preparing fine particles of catalytic materials and are not suitable for water environments

with poor light transmission. Therefore, improving the utilization of light and developing efficient catalytic materials remains the main direction of photocatalytic research.

$$S + h\nu \rightarrow S(h)^{+}_{VB} + e^{-}_{CB} \quad (11)$$

$$S(h)^{+}_{VB} + H_2O \rightarrow S + H^{+} + \bullet OH \quad (12)$$

$$e^{-}_{CB} + O_2 \rightarrow O_2^{\bullet -} \quad (13)$$

$$O_2^{\bullet -} + H^{+} \rightarrow HO_2^{\bullet} \quad (14)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (15)$$

$$H_2O_2 \rightarrow 2 \bullet OH \quad (16)$$

3.4. Combination Method

The single treatment technology has a poor removal effect on some antibiotics, especially the application of biological treatment has the disadvantage of generating resistance genes. To further enhance the degradation and removal of pollutants, the combination of physical, chemical and biological methods has been widely studied, including the combination of biological methods and physical methods, the combination of biological methods and chemical methods, and the combination of physical methods and chemical methods. The combined treatment process makes up for the deficiency of the separate treatment process, combines the complementary advantages of the two technologies and has a better effect on the degradation of antibiotics. The application research of the combined process is shown in Table 6.

Table 6. The performance of antibiotics removal by using combination process.

Types of Antibiotics	Combined Process	Removal Rate	References
Sulfadiazine	Light-Fenton Ceramic Membrane Filtration	100%	[165]
Sulfamethoxazole, erythromycin, clarithromycin	Optical Fenton—Membrane Bioreactor	100% 100% 85%	[166]
Salt tetracycline	Photocatalysis-Activated Sludge Process	87.4%	[167]
Tetracycline	Photocatalytic film (DPMR)	79.6%	[168]
Sulfadiazine	Ultrafiltration Membrane—Photocatalysis	91.4%	[169]
Amoxicillin	O_3 + UV/Vis + TiO_2	100%	[170]
Amoxicillin	Aerobic biological + O_3	99%	[171]
Sulfamethoxazole Ciprofloxacin Amoxicillin	Multi-walled carbon nanotube-based electrochemical membrane.	90% 76% 99%	[172]
Amoxicillin	Combination of Fenton and nanofiltration processes (NF/FT)	92.3%	[173]
Ibuprofen Sulfamethoxazole	Staged anaerobic fluidized bed membrane bioreactor + granular activated carbon (SAF-MBR + GAC)	100% 100%	[174]
Sulfamethoxazole Triclosan	Anaerobic membrane bioreactor + powdered activated carbon(AnMBR + PAC)	95.5 ± 4.6% 93.2 ± 6.6%	[18]
Ofloxacin	Ozone + Fenton	96.7%	[175]
Tetracycline	Photocatalytic + ozonation	85%	[176]

4. Advantages and Disadvantages of Treatment Methods

In the treatment of antibiotic pollutants, the application of biological, physical and chemical methods has different advantages and disadvantages. To give full play to the application of each treatment method and improve its shortcomings, the advantages and existing problems of each treatment method should be fully understood. The advantages and disadvantages of the three treatment methods are shown in Table 7.

Table 7. The advantages and disadvantages of the three treatment methods.

Methods	Advantages	Disadvantages
Biological	The biological method is suitable for the treatment of high-concentration antibiotic wastewater, such as medical and aquaculture wastewater. It has the advantages of strong load tolerance, mature technology, simple process and low operating cost. In the biological treatment process, there are many species and a high abundance of microorganisms, which can use a variety of antibiotic pollutants as carbon sources addition and completely remove antibiotics through their metabolism.	Due to the bactericidal effect of antibiotics, antibiotic wastewater needs to be pretreated before biological treatment. The effectiveness of biological treatment of antibiotics is influenced by the type of biological treatment process (e.g., aerobic, anoxic or anaerobic biological treatment) and process operating parameters (e.g., sludge retention time, dissolved oxygen, physicochemical properties, pH and temperature). In addition, the biological treatment method takes a long time to degrade antibiotics and easily leads to the production of antibiotic-resistant bacteria and drug-resistant genes, which poses a potential threat to ecological security.
Physical	The physical treatment method has the advantages of low operating cost, simple operation, wide source of raw materials, and no introduction of new pollutants.	The physical method is not degradable or destructive to the antibiotics; the enriched antibiotics are prone to secondary pollution and other problems, and secondary advanced treatment is required.
Chemical	The chemical method has the advantages of high treatment efficiency, short time, complete removal of pollutants and no sludge generation. Chemical treatment methods rely on the strong oxidizing properties of strong oxidizing agents or advanced oxidation methods that produce highly reactive hydroxyl radicals that undergo redox reactions with antibiotics, thereby destroying the molecular structure of the antibiotic or being mineralized by the hydroxyl radicals.	The application of chemical methods suffers from the difficulty of controlling the amount of chemical reagents and the high cost of advanced oxidation processes. A number of factors including temperature, pH, catalyst, dosage and co-existing organic matter influences chemical oxidation. In addition, chemical methods are also prone to secondary pollution.

5. Future Perspective

As one of the emerging micro-pollutants, antibiotics are not only widely used, but their use is increasing every year. Although the environmental hazards of antibiotics are receiving increasing attention, the lack of corresponding regulations on the production, use and disposal of pollutants discharged from antibiotics has led to increasing antibiotic pollution. Therefore, it is very important to formulate corresponding management, application and discharge systems to control the sources of antibiotic pollution. In addition, current research on antibiotic contamination is mostly laboratory-based, with relatively homogeneous research conditions and relatively little research on the coexistence of many different types of antibiotics. Considering the many factors that influence the effectiveness of treatment, further research on actual antibiotic-contaminated water bodies needs to be strengthened. In addition to being harmful to antibiotics themselves, the persistence of antibiotics will further lead to the generation of drug-resistant genes and bacteria. Therefore, there is a need for further research into the changing patterns and efficient control of drug-resistant genes and drug-resistant bacteria.

Antibiotic treatment methods can be divided into biological, physical and chemical treatments. The removal performance of antibiotics is not only related to the physicochemical properties of the antibiotics themselves, but the condition parameters have a huge impact on the treatment results. Although biological treatment methods can effectively remove antibiotics from water through biodegradation and adsorption, there are few studies on the contribution rate of biodegradation and adsorption to pollutant removal. In addition, the generation of resistance genes and drug-resistant bacteria during biological treatment has not been studied. Therefore, the biological treatment method has potential risks to biological safety to a certain extent, and further research is needed. Compared with the biological treatment method, the physical treatment method realizes the enrichment

or interception and removal of antibiotics in water by means of adsorption, membrane filtration and ion exchange, which is simple in operation and low in cost. Although the physical treatment method does not generate new pollutants and cause biosafety problems, the physical method fails to destroy the chemical structure of antibiotics, and there is a lack of research on the advanced treatment of enriched high-concentration antibiotics. Compared with the former two, the chemical method can achieve the degradation and mineralization removal of antibiotics by a redox reaction with antibiotics, which has the advantages of fast and high efficiency. However, the effect of chemical oxidation treatment is affected by a variety of factors, and its adaptability and practicability are poor. Therefore, it is necessary to further strengthen the research and application to actual polluted water bodies. In addition, combined with the complexity of the actual antibiotic water composition and the difficulty of treatment, a single treatment method can hardly meet the discharge requirements, so the in-depth study of the combined process has a good development trend.

6. Conclusions

This paper reviews the research and application of biological, physical and chemical methods in antibiotic pollution control, including the degradation efficiency, removal mechanism, influencing factors, advantages, disadvantages and research prospects of treatment methods. The removal of antibiotics by biological treatment is based on two mechanisms: adsorption and biodegradation, and different types of antibiotics have different removal pathways. For example, fluoroquinolones and tetracyclines are mainly removed by adsorption, while sulfonamide antibiotics are mainly removed by biodegradation. The removal rate of antibiotics by biological methods not only related to the properties of the antibiotics and the structure of the functional groups but also has a huge impact on the process parameters, such as pH, water retention time and so on. The physical method can realize the adsorption, retention, or enrichment of antibiotics in water through adsorption, membrane filtration, ion exchange, etc. Although the physical method has a high removal rate for some antibiotics, it cannot completely degrade and remove the antibiotics, which easily cause secondary pollution and require further advanced treatment. Compared with the former two, the chemical method can use the strong oxidizing property of the oxidant or the redox reaction between the highly reactive free radicals generated and the antibiotic to destroy the molecular structure of the antibiotic and realize the complete removal of the antibiotic. Although chemical methods are effective in treating antibiotics and have high removal rates, they have poor selective oxidation of pollutants and are easily affected by water conditions. How to achieve the oxidative removal of targeted pollutants needs further in-depth study. In addition, based on the drawbacks of each separate treatment process, the combined process treatment can promote strengths and avoid weaknesses and has a good development trend, especially under conditions of complex and difficult water quality, the combined treatment process can show strong adaptability.

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