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Review

Performance of Traditional and Emerging Water-Treatment Technologies in the Removal of Tetracycline Antibiotics

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Abstract: Tetracycline antibiotics are widely used in human medical treatment, control of animal disease, and agricultural feed because of their broad spectrum of action, high efficiency, and low cost. The excessive use of antibiotics and arbitrary discharge of antibiotic wastewater have become increasingly serious problems, and the current sewage-treatment process is not ideal for treating water contaminated with tetracycline antibiotics, leading to increasingly prominent antibiotic pollution in water and the imminent need for its removal. In order to understand the necessity of removing tetracycline antibiotics from the water environment, this paper first expounds on their source, harms, and pollution status in oceans and in surface water, groundwater, wastewater, and drinking water. It next introduces the research status of conventional treatment methods such as adsorption methods, biological methods, and physical and chemical methods, then introduces new treatment methods such as advanced oxidation methods and comprehensive treatment technology in sewage plants. The degradation effects, mechanisms of action, and challenges of these methods were summarized. The advantages and disadvantages of each treatment technology are compared. Finally, potential future processing technologies are discussed.

Keywords: tetracycline antibiotics; environment; wastewater; pollution; treatment technology

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1. Introduction

Antibiotics are chemical substances that can interfere with the growth of other living cells and inhibit the growth of or kill some pathogenic microorganisms. They are widely used in human and animal medical treatment and in aquaculture [1]. With the continuous development of low-income countries, the demand for antibiotics is increasing. From 2000 to 2015, the global human consumption of antibiotics increased by 65% and the rate of antibiotic consumption increased by 39% [2]. It is reported that tetracycline antibiotics are the second most widely used antibiotics in the world [3]. Tetracycline antibiotics at high concentrations can inhibit the synthesis of microbial proteins and kill a variety of atypical organisms, such as Gram-positive bacteria, Gram-negative bacteria, protozoan parasites, mycoplasma, chlamydia, Rickettsia, etc. [4]. Aureomycin, oxytetracycline, and tetracycline, as well as tetracycline's semi-synthetic derivatives, such as metheomycin, doxycycline, and minocycline, are common tetracycline antibiotics that are mainly used to treat acne, trachoma, and other diseases [5,6]. However, only a small amount of antibiotics can be metabolized or absorbed by organisms, and most antibiotics are discharged into the water environment through various routes [7]. This discharge has seriously polluted the environment and destroyed ecological diversity.

Tetracycline antibiotics, although they are a new environmental pollutant, are ubiquitous in oceans and in surface water, groundwater, wastewater, and drinking water because of their persistence. It is necessary to understand the hazards associated with tetracycline antibiotics in the water environment and the methods used for their removal. This paper expounds on the sources, hazards, and pollution status of tetracycline antibiotics, introduces treatment/removal technologies and their mechanisms of action, and compares and analyzes the advantages and disadvantages of each treatment technology so as to provide a reference for the future treatment of tetracycline antibiotics, which may involve combining technologies or developing new technologies.

2. Harm of Tetracycline Antibiotic Residues in Water

Tetracycline antibiotic residues in water mainly come from two types of sources: domestic and industrial. Tetracycline-like antibiotics are difficult for organisms (humans and animals) to completely digest and absorb, and about 50–80% of antibiotics are converted into more toxic metabolites [3]. These metabolites are mainly excreted through feces and urine, which inevitably leads to antibiotics existing in urban and rural domestic sewage. Pharmaceutical wastewater contains more antibiotics than does urban domestic wastewater, showing that existing sewage treatment plants are not able to effectively remove them [8]. The wastewater produced in the pharmaceutical manufacturing process and tetracycline antibiotics that are not used by organisms enter sewage treatment plants and landfills as raw medicines and incomplete metabolites, thus polluting the water and soil and destroying the ecological balance. To understand the hazards posed by tetracycline antibiotic residues in the water environment, ECOSAR software (Ecosar.v.2.2-application) was used to predict the acute and chronic toxicity of tetracycline antibiotics and their metabolites and degradation products in the water environment, as shown in Table 1, where P1–P4 are typical photolysis products [9] and P5–P11 are typical degradation products [10].

Table 1. ECOSAR software predicts the acute and chronic toxicity of some tetracycline antibiotics and their metabolites and degradation products in the water environment (extremely toxic chemicals are shown in red, poisonous in yellow, harmful in black, and non-poisonous in green.).

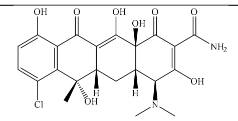
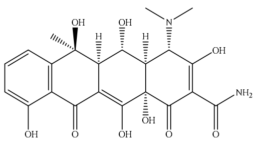
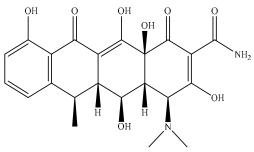
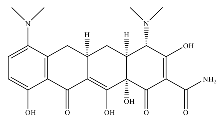
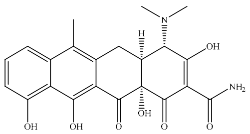
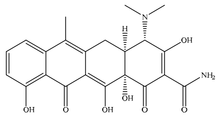
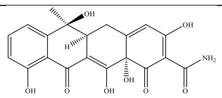
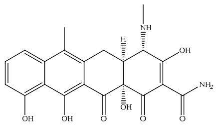
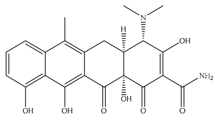
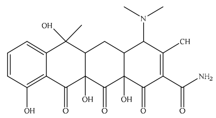
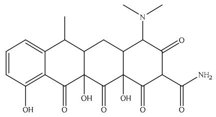
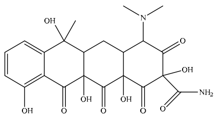
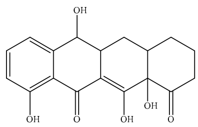
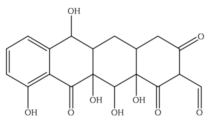
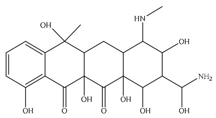
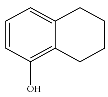
Name	Formula	Acute Toxicity (mg/L)			Chronic Toxicity (mg/L)		
		Fish (96 h-LC_{50})	Daphnia (48 h-LC_{50})	Green Alga (96 h-EC_{50})	Fish (ChV)	Daphnia (ChV)	Green Alga (ChV)
Aureomycin		4.58×10^3	590	5.22×10^3	345	40.4	408
Oxytetracycline		1.39×10^5	6.70×10^3	1.47×10^5	8.41×10^3	314	6.80×10^3
Doxycycline		1.25×10^4	1.18×10^3	1.39×10^4	877	71.9	921
Minocycline		2.86×10^3	416	3.30×10^3	222	29.9	275
Tetracycline		1.18×10^4	1.13×10^3	1.31×10^4	831	69.5	879
P1		151	49.9	187	14.1	4.91	23.9

Table 1. *Cont.*

Name	Formula	Acute Toxicity (mg/L)			Chronic Toxicity (mg/L)		
		Fish (96 h-LC_{50})	Daphnia (48 h-LC_{50})	Green Alga (96 h-EC_{50})	Fish (ChV)	Daphnia (ChV)	Green Alga (ChV)
P2		3.07×10^3	421	3.52×10^3	234	29.5	284
P3		36.2	2.22	5.34	0.301	0.477	0.861
P4		149	2.01×10^3	25.9	101	817	2.83
P5		587	134	703	50.4	11.5	74.3
P6		28.6	15.4	36.8	2.98	1.83	6.10
P7		39.4	19.7	50.3	4.03	2.27	8.03
P8		274	70.8	331	24.1	6.36	37.3
P9		7.89×10^3	821	8.84×10^3	566	51.8	617
P10		5.14×10^4	3.27×10^3	5.53×10^4	3.30×10^3	170	2.97×10^3
P11		1.95	1.64	2.60	0.224	0.233	0.547
		Extremely toxic	Poisonous		Harmful	Non-poisonous	

Tetracycline antibiotics have stable properties and can accumulate in feces, soil, the water environment, and the atmosphere, where they can persist for a long time. The concentration level of tetracycline antibiotics in the water environment is mostly measured in $\mu g \cdot L^{-1}$, a level that inhibits the growth of bacteria and the survival of organisms. These chemicals accumulate in the human body through the food chain and food web, threatening human health. Tetracycline antibiotics have been detected in most of the foods we eat [11]. In the long run, this exposure will slow down the metabolism of the human body; prevent the synthesis of proteins in lymphocytes; inhibit the immune system [12]; cause risk of superinfection [13]; have teratogenic [14], carcinogenic, and mutagenic effects [15]; and lead to to joint diseases, nephropathy, central nervous system defects, endocrine disorders, and other diseases [16].

3. Pollution Status of Tetracycline Antibiotics in Water

The use of antibiotics in China accounts for about half of the antibiotic use in the world [17]. Tetracycline antibiotics are widely used because of their broad spectrum of action, high efficiency, and low cost. Because of the abuse of antibiotics by human beings, antibiotics are discharged into the environment in the form of medicines and metabolites. Tetracycline antibiotics are ubiquitous in the water environment because of their strong hydrophilicity and low steam pressure, and they are easily soluble in water. Figure 1 shows the sources of tetracycline antibiotics in the water environment.

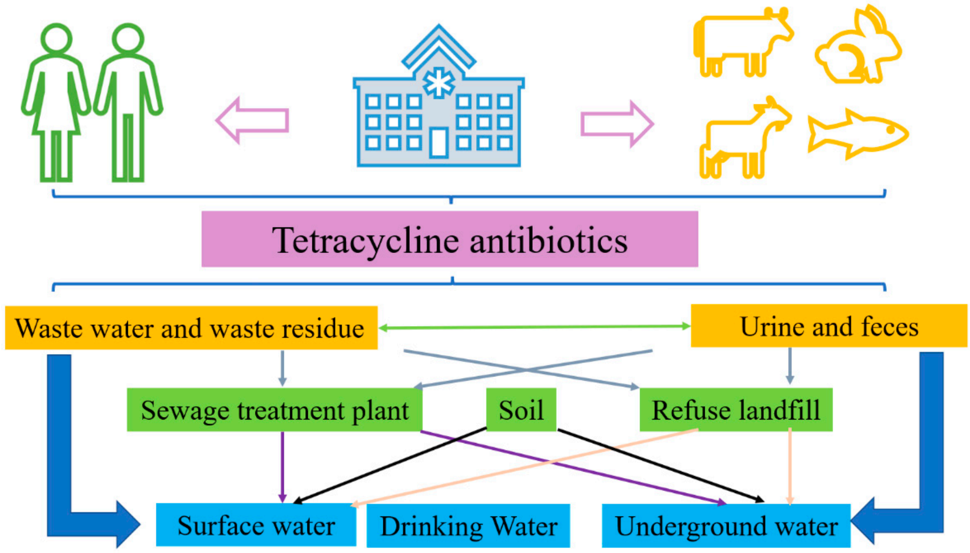


Figure 1. Sources of tetracycline antibiotics in the water environment.

In recent years, with increasing awareness of environmental protection, more and more attention has been paid to the problem of antibiotic residues in the water environment. A large number of studies at home and abroad have reported antibiotic residues in the water environment (oceans, surface water, groundwater, wastewater, drinking water). Table 2 lists the reports on the mass concentrations of tetracycline antibiotics in the water environment.

Table 2. Mass concentrations of tetracycline antibiotics in water environments.

Antibiotic Source	Region	Mass Concentration 1)	Reference
Ocean	Bohai Gulf	16 ng·L^{-1} TC, 93 ng·L^{-1} OTC	[18]
	Iran Persian Gulf	4.0~71 ng·L^{-1} TET	[19]
	Costa Rica	74~73,722 ng·L^{-1} DOX	[20]
Surface water	Jiangxi Jinjiang	ND~86.1 ng·L^{-1} OTC, ND~5.92 ng·L^{-1} DOC, ND~5.92 ng·L^{-1} TC	[21]
	Nanjing	ND~160 ng·L^{-1} DOX	[22]
	Tianjin	0~9.74 ng·L^{-1} TET, 0~34.5 ng·L^{-1} OTC 0~3.74 ng·L^{-1} DOX CTC	[23]
	Huangpu River	15.07~113.89 ng·L^{-1} TC	[24]
Underground water	Jiangxi Jinjiang	ND~4.18 ng·L^{-1} CTC, ND~2.65 ng·L^{-1} OTC, ND~1.56 ng·L^{-1} DOC	[21]
	Harbin	0.35~3.91 ng·L^{-1} DOX	[25]
waste water	Jiangxi Jinjiang	ND~58.6 ng·L^{-1} CTC, 54.0~2.72 × 10^3 ng·L^{-1} OTC, 10.9~49.3 ng·L^{-1} DOC, ND~27.4 ng·L^{-1} TC	[21]
Drinking Water	Huaihe river basin (wet season)	Mengxian 3.38 ng·L^{-1} TCs, Yingdong 4.73 ng·L^{-1} TCs, Yongqiao 5.99 ng·L^{-1} TCs, Lingbi 8.60 ng·L^{-1} TCs, Shouxian 2.02 ng·L^{-1} TCs, Hexian 3.28 ng·L^{-1} TCs	[26]

Note: 1) ND stands for not detected.

4. Research Status of Treatment Technology Used for the Removal of Tetracycline Antibiotics from Water Environments

Tetracycline antibiotics migrate and transform in the environment and eventually affect the atmosphere, water, and soil. With people paying more and more attention to the ecological environment, research on tetracycline antibiotics is growing at home and abroad. The epimers and dehydrated bodies of tetracycline antibiotics may appear at pH 3.0–6.5, and the epimerization may occur at pH 6.5–9.0 [27]. To remove pollutants more effectively, it is very important to understand both the methods currently used for removal and their mechanisms of action.

In the water environment, the treatment technologies used to remove tetracycline antibiotics include adsorption; biological, physical and chemical methods; advanced oxidation; and the comprehensive treatment technologies used in sewage plants.

4.1. Adsorption Method

Adsorption removes tetracycline antibiotics by transferring them to the adsorbent by π-interactions [28], electrostatic interactions [29], and hydrogen bonding [30]. The adsorbent surface forms a zone with low potential energy and high molecular density near the surface [31,32]. There are four steps in the adsorption of tetracycline antibiotics: transport through the stagnant membrane near the adsorbent, diffusion across the membrane, diffusion through the pores, and adsorption [33,34]. The mechanism by which adsorption removes tetracycline antibiotics is shown in Figure 2.

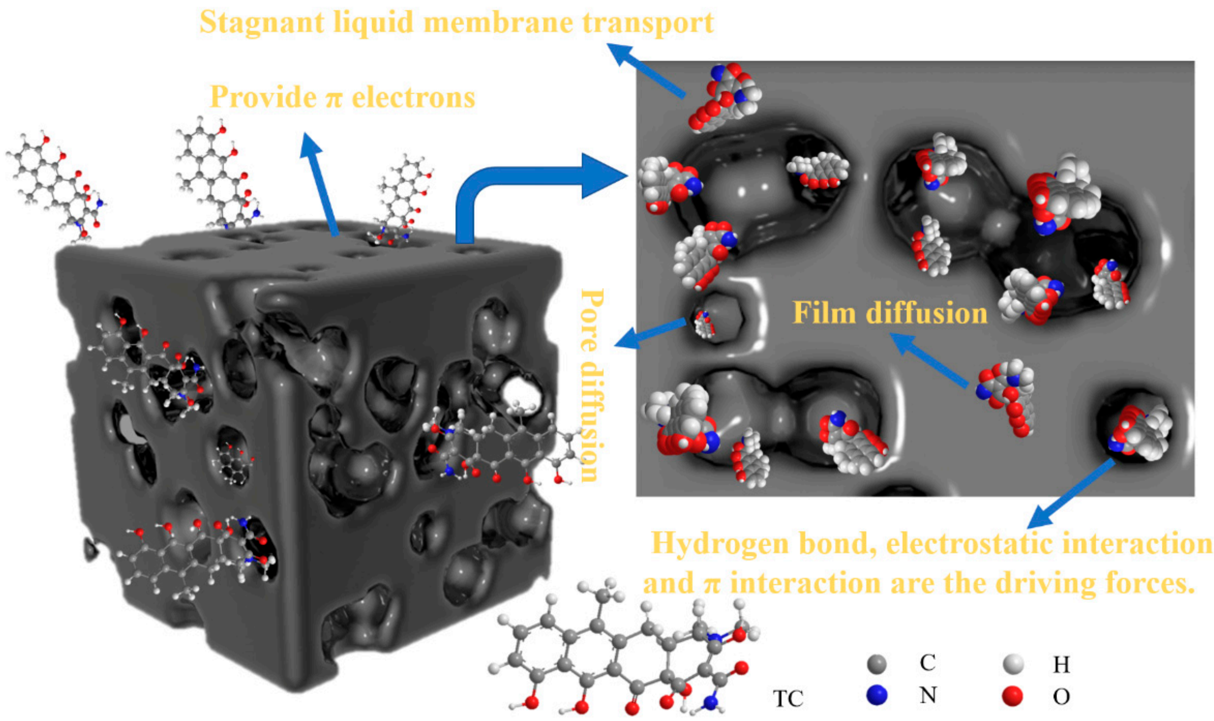


Figure 2. Diagram of the mechanism of tetracycline antibiotic removal by adsorption.

Nanoparticles produced by microorganisms in sewage treatment plants are natural adsorption materials that can be combined with tetracycline antibiotics in the water environment. Yu et al. [35] used asymmetric flow field-flow separation and multi-angle static light scattering to separate nanoparticles with different particle sizes produced by microorganisms from sewage treatment plant wastewater. These nanoparticles have a strong capacity for adsorption of tetracycline. If the adsorbate of nanoparticles and antibiotics is not properly treated, the adsorbate will further migrate and transform in the water environment, posing a great threat. Carbon materials [36], biochar [37], mineral materials [38], metal skeleton materials [39], nano-materials [40], and other new materials can be used as adsorption materials. Qiao et al. [41] developed Mn (II)-coated mesoporous silica nanoparticles to effectively remove tetracycline from an aqueous solution. It was found that Mn–O complexation was the dominant mechanism of tetracycline absorption. Electrostatic attraction and cation–π interactions also contributed to the absorption of tetracycline. Liang et al. [42] used poly-dopamine-polystyrene nanofibers to adsorb tetracycline antibiotics in water. The adsorption of this material reached equilibrium within 5 min, and the removal rate was greater than 85%. This method does not require pretreatment of water samples, but the adsorption process is most efficient at high concentrations and the residual concentration in water environment is low, so it has certain limitations. In evaluating adsorption, we should also consider whether the adsorption material can be easily separated from the water body to avoid secondary pollution. Wang et al. [43] used magnetic ion exchange resin (MIEX) to remove tetracycline from water. With this approach, the separation speed of tetracycline is fast, the reusability is high, and the capacity and rate of adsorption are high.

Adsorption collects pollutants, but it only changes their form and cannot remove them completely. Some adsorbents with small particle sizes are difficult to separate from water bodies, and it is easy for subsequent treatment to cause secondary pollution. At present, there is little research on the toxicity of adsorption materials. Therefore, the development of low-toxicity adsorption materials with high specific surface area and high adsorption capacity represents the future of tetracycline antibiotic removal by adsorption.

4.2. Biological Method

The biological method is the mainstream technology used to remove tetracycline antibiotics and mainly includes the microbial method and the plant method.

In the microbial method, tetracycline antibiotics are decomposed into small molecular substances via the action of microorganisms [44]. The activated-sludge method is a representative example of a method involving the microbial degradation of tetracycline antibiotics. It uses microorganisms, mainly bacterial micelles, to adsorb and degrade antibiotics, and this method is characterized by high adsorption and low degradation [45]. Liu et al. [46] used a method that involved adding exogenous surfactant and in-situ biosurfactant to cultivate microorganisms that could be used to remove tetracycline antibiotics. The method converts antibiotics instead of absorbing them and thus significantly reduces the toxicity of antibiotics. M.de Cazes et al. [47] successfully removed tetracycline antibiotics in an aqueous solution by immobilizing laccase at room temperature, with results showing good reactivity and stability. The use of a membrane bioreactor improves the reaction rate of activated sludge, reduces the amount of excess sludge, and results in good treatment of tetracycline antibiotic wastewater. However, membrane pollution and high energy consumption have always been the aspects of membrane bioreactors that need to be improved. Microbial degradation is the most widely used method for the removal of antibiotics, but the molecular mechanism of microbial decomposition and transformation of tetracycline antibiotics under different nutritional conditions is still unclear [48–50]. Shao et al. [51] proposed one route for the biotransformation of tetracycline (removal of methyl, carbonyl, and amine groups). Qi [52] proposed that the degradation paths of oxytetracycline are hydrolysis and biodegradation, respectively. Through dehydration, demethylation, decarbonylation, esterification, deamination, enol ketone isomerization, and enzymatic activity, oxytetracycline is degraded; the degradation process is shown in Figure 3.

The plant method uses a combination of plants and microorganisms to achieve pollution control and has the advantages of low treatment cost and environmental friendliness. Gujarathi et al. [53] used sunflower cultures to treat tetracycline and oxytetracycline, and the treatment effect decreased as the antibiotic concentration increased. Chen et al. [54] cultivated Dapiao and Eichhornia crassipes by hydroponics, with a good effect on the removal rate of tetracycline hydrochloride. Plant degradation involves high environmental requirements, and at present, there are few studies on how antibiotics enter plants and the mode of transportation, so it is still necessary to further research the plant-based degradation of tetracycline antibiotics.

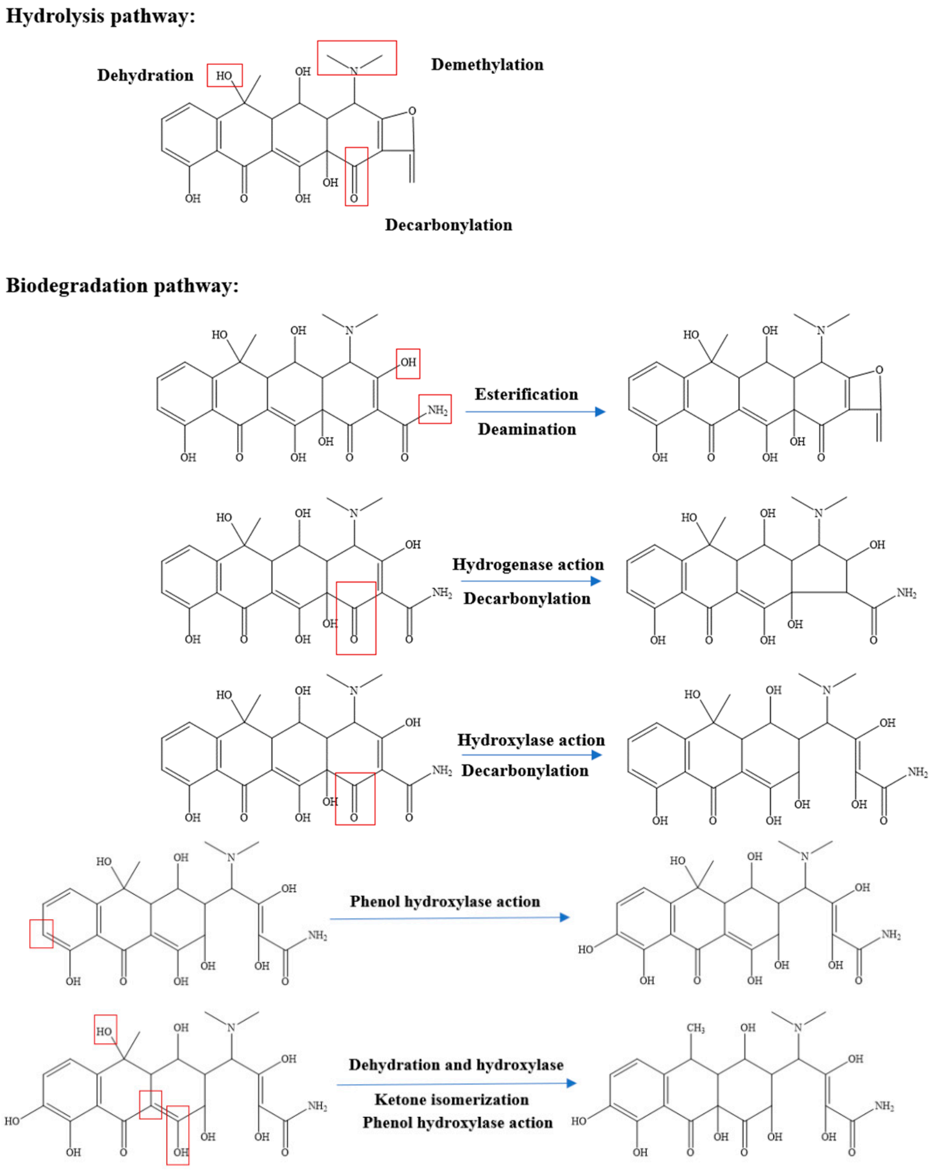


Figure 3. Mechanisms of biological treatment of tetracycline antibiotics [52].

4.3. Physical and Chemical Method

Water contaminated with tetracycline antibiotics is difficult to treat directly by biological methods because of the antibiotics' high biological toxicity. Physical and chemical methods are usually used as pretreatment, with advanced treatment methods mainly including coagulation, sedimentation, air flotation, reverse osmosis, ultrafiltration, and membrane filtration. Wojnárovits et al. [55] found that radiation therapy can make these non-biodegradable antibiotic-containing matrices biodegradable, reducing their toxicity and eliminating their antimicrobial activity, and found that the reduction of the technical parameters (COD, TOC) demonstrates the applicability of radiation technology for the degradation of recalcitrant compounds even in highly complex aqueous matrices. Zhang et al. [56] used reverse osmosis and ultrafiltration to treat tetracycline production-waste liquid, with remarkable effectiveness. Gholam Hossein Safari et al. [57] showed that RSM was a suitable method by which to optimize the operating conditions for maximum TC degradation. Under optimum conditions, the TC degradation, COD and TOC removal were 95.01%, 72.8%, and 59.7%, respectively. The US/$S_2O_8^{2-}$ process was found to be a feasible technology for TC degradation in aqueous solution. Saitoh et al. [58] used the coagulation–flotation method to quickly remove tetracycline antibiotics from water. In the presence of Al(III) ions, tetracycline in water was collected in the coagulum as hydrophobic ion pairs (m/z = 736) between Al(III) chelate and dodecyl sulfate ions. Tetracycline was completely removed from the water within 5 min. Liang et al. [59] used integrated membrane-filtration technology, including ultrafiltration and two-stage reverse osmosis, to treat pig wastewater and found that these methods could remove bacteria and 99.79% of antibiotic-resistance genes. This method is effective for the removal of antibiotics, but both water quality and membrane properties will affect the effectiveness. Membrane fouling and the existence of high concentration retentate after treatment are the main problems in the application of this technology.

The physicochemical method is simple and easy to implement and can be used as both pretreatment and advanced treatment. In the future, the physicochemical method will be used to develop a treatment method for water contaminated with tetracycline antibiotics with reduced operation complexity and operation costs, high development efficiency, and environmentally friendly qualities.

4.4. Advanced Oxidation Processes

The advanced oxidation method is being widely studied by researchers because of its advanced technology [60]. There are two main common features of advanced oxidation methods. First, the hydroxyl radicals generated by the reaction will effectively decompose the toxic organic pollutants that are difficult to degrade until they are completely converted into harmless inorganic substances, such as CO_2, N_2, SO_2^{4-}, PO_3^{4-}, O_2, H_2O, etc., without secondary pollution, which is difficult to achieve by other oxidation methods. Second, the reaction time is short, the reaction speed is fast, and the process is controllable and non-selective and can thus degrade all kinds of organic pollutants. According to the different reaction conditions used, it can be divided into ozone oxidation, Fenton oxidation, photocatalysis, electrocatalysis, and so on.

4.4.1. Ozone Oxidation Method

The ozonation method produces strong oxidizing free radicals (such as ·OH, etc.) through indirect oxidation reactions between ozone molecules and antibiotics or via decomposition reactions in water that can be used to mineralize them [61,62]. O_3 has a strong oxidizing ability and can form carboxylic acids with tetracycline antibiotics, thus improving the biodegradability of wastewater [63]. The mechanism by which ozone oxidation can be used to degrade tetracycline antibiotics is shown in Figure 4.

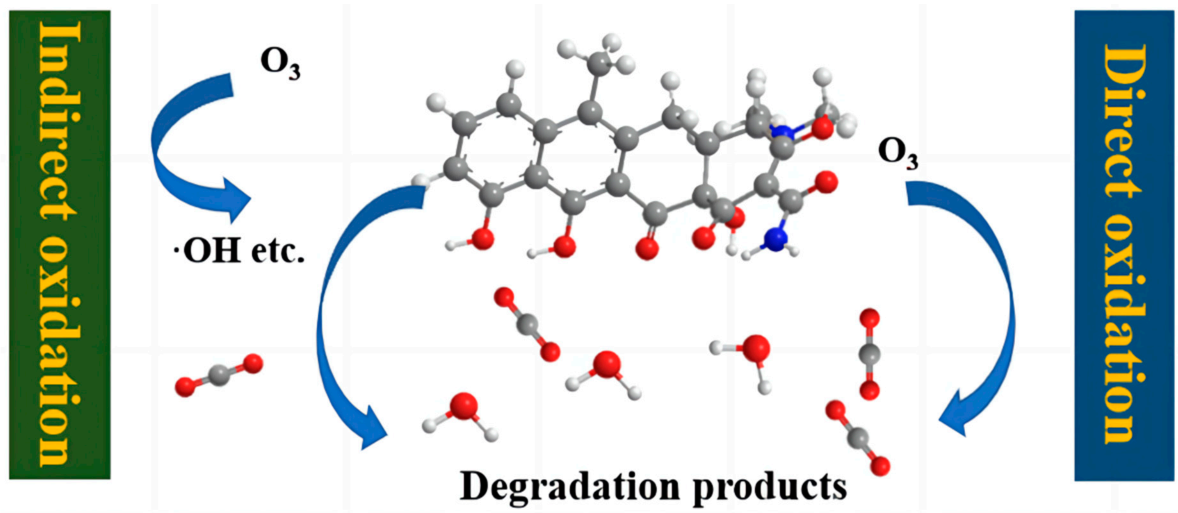


Figure 4. Mechanism of ozone oxidation degradation of tetracycline antibiotics.

Ozone is highly oxidizing and has a good effect on the degradation of organic matter. The treatment effect of ozone oxidation alone is not impressive, and catalytic ozone oxidation is often used. Luu et al. [64] used O_3, H_2O_2, and ultraviolet (UV) to degrade tetracycline. After 5 days of treatment, the biodegradability of wastewater was improved. Li et al. [65] used the combined process of denitrification biofilter + ozone + biological aeration filtration to produce reclaimed water. The combination process shows good removal performance of conventional pollutants, which meets the local discharge standards and the purpose of water reuse. The ozone method has the characteristics of quick reaction, simple process, and environmental friendliness. Developing catalysts with good catalytic effects and low cost represents the future of research on ozone oxidation.

4.4.2. Fenton Oxidation Method

Tetracycline antibiotics have strong biological toxicity, and the biodegradability of wastewater is low. Free radicals and other active oxygen substances produced by the Fenton oxidation process are effective in treatment. Hydrogen peroxide and Fe^{2+} generate OH at pH 2–5 and gradually produce other reactive oxygen species and reaction intermediates, thus contributing to the degradation of tetracycline antibiotics [66]. The reaction mechanism is as follows [67]:

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2\cdot \quad (2)$$

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

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

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2\cdot \quad (5)$$

$$Fe^{2+} + HO_2\cdot \rightarrow Fe^{3+} + HO^{2-} \quad (6)$$

$$RH + \cdot OH \rightarrow R\cdot + H_2O \quad (7)$$

$$R\cdot + Fe^{3+} \rightarrow \cdot R^+ + Fe^{2+} \quad (8)$$

$$R\cdot + H_2O_2 \rightarrow OH + \cdot OH \quad (9)$$

Fenton oxidation can be used as a pretreatment process and advanced treatment process. Bai [68] used the Fenton oxidation method to treat antibiotic wastewater in the pharmaceutical industry and achieved a good removal effect. Wu et al. [66] treated SBR effluent by the Fenton oxidation method, and the removal rate of COD reached 77.8%. Shao et al. [69] introduced nitrogen vacancies and potassium atoms into g-C_3N_4, and these molecules were then combined with FeOCl to fabricate the Z-type heterojunction catalyst FeOCl/NvCN, which was used to remove 95.74% of tetracycline (TC) within 60 min. The Fenton oxidation process can significantly improve the biodegradability of tetracycline antibiotic wastewater in the practice of systematic treatment. The Fenton oxidation process can significantly improve the biodegradability of tetracycline antibiotic wastewater in the practice of systematic treatment. However, the amount of Fe^{2+} and H_2O_2 used in the treatment process is large, and a large amount of acid and alkali are used in the pH-adjustment process, which undoubtedly increases the cost of wastewater treatment. Making catalysts with high effectiveness and low cost, exploring the best amounts to use, improving the methods, and treating large-scale wastewater are the future directions of research involving Fenton oxidation.

4.4.3. Photocatalytic Method

In the photocatalytic method, under specific light conditions, the catalyst generates electron–hole pairs, which react with H_2O and other molecules to generate ·OH, which oxidizes and decomposes tetracycline antibiotics and mineralizes them [70,71]. The ·OH acts on the double bond, keto group, amino group, and keto-enol group of tetracycline antibiotics, and the mechanism is shown in Figure 5.

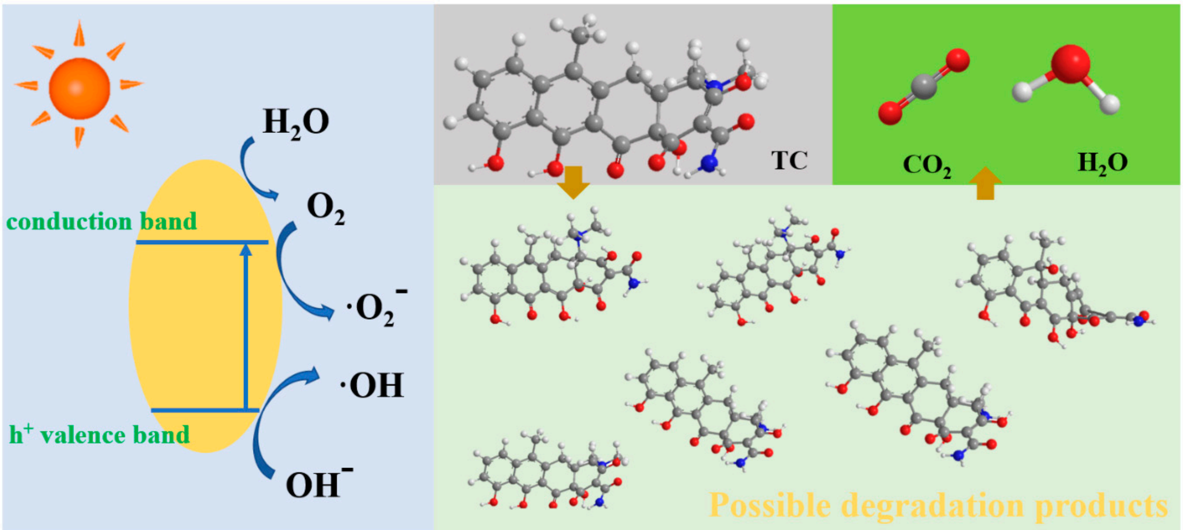


Figure 5. Mechanism of photocatalytic treatment of tetracycline antibiotics [9].

The recovery of the catalyst and the study of its stability have always been the focus of research on the photocatalytic treatment of tetracycline antibiotics. C. Reyes et al. [72] used a TiO_2 aqueous suspension to irradiate a tetracycline solution with three different light sources (an ultraviolet lamp, a sunbathing device and a UV-A lamp). The results showed that tetracycline was clearly mineralized under the action of the ultraviolet lamp and the solarium. Das et al. [73] synthesized semiconducting CdS nanorods using a hydrothermal procedure with ethylenediamine as a ligand and found higher catalytic efficiency in the presence of blue-light as compared to white-light irradiation and demonstrated that the photodegradation process did not require any supplemental oxygen source. Nagamine et al. [74] successfully synthesized cadmium sulfide semiconductor nanoparticles by a simple coprecipitation method, and these nanoparticles were used to degrade tetracycline. After exposure for 1 h, the photocatalytic efficiency reached nearly 80% for TC degradation. Zhang et al. [75] prepared TiC-SOH/g-CN (TiCSOHCN) composite photocatalysts by acid etching and sonochemistry, and the removal of TC reached 75.42% within 2 h. Ma et al. [76] prepared La/Co@TiO_2 nanospheres by co-impregnation and increased the oxygen vacancies on the catalyst surface by photocatalytic activation of molecular oxygen to accelerate the photogenerated electron-hole separation and charge transfer at the interface. The photocatalytic degradation experiments using 3 wt% La/Co@TiO_2 nanospheres showed that the efficiency of tetracycline (TC) degradation was 100% under visible light. Tang et al. [77] designed a novel p-n heterostructure visible-light photocatalyst by anchoring p-type Bi_2O_3 on n-type Ti^{3+}-TiO_2 porous material by a simple photodeposition method with subsequent calcination. Complete removal of tetracycline from various aqueous matrices under visible light was realized. Li et al. [78] successfully synthesized a novel direct Z-type SnS_2@$ZnIn_2S_4$@kaolinite heterostructured photocatalyst by a hydrothermal method. Under visible-light irradiation, in an experiment carried out in parallel with SnS_2 and $ZnIn_2S_4$, the as-obtained heterostructure displayed greatly improved photocatalytic degradation of TCH, with an apparent reaction rate of 0.0231 min^{-1}, which is 20.81 times and 2.31 times higher than those of SnS_2 and $ZnIn_2S_4$, respectively. Zong et al. [79] achieved efficient degradation of tetracycline by combining TiO_2 fragmented shells (TFNs) catalysts with convergent pulsed ultrasound in a customized ultrasonic reactor. TFNs were rapidly removed from solutions with low concentrations of tetracycline in as little as 6 min at low power input (21 W). Photocatalysis has the advantages of simple operation and mild reaction conditions, but the utilization rate of light energy is low, the cost is high, and the chromaticity of wastewater will also affect the efficiency of treatment of water contaminated with tetracycline antibiotics by light.

4.4.4. Electrocatalytic Method

In the electrocatalytic method, under the action of an electric field, ·OH radicals attack the double bonds, phenolic groups, and amine groups of tetracycline antibiotics and mineralize them [80–82]. There are four ways to treat tetracycline antibiotics by electrocatalysis, namely, direct oxidation, direct reduction, indirect oxidation, and indirect reduction. The mechanism is shown in Figure 6.

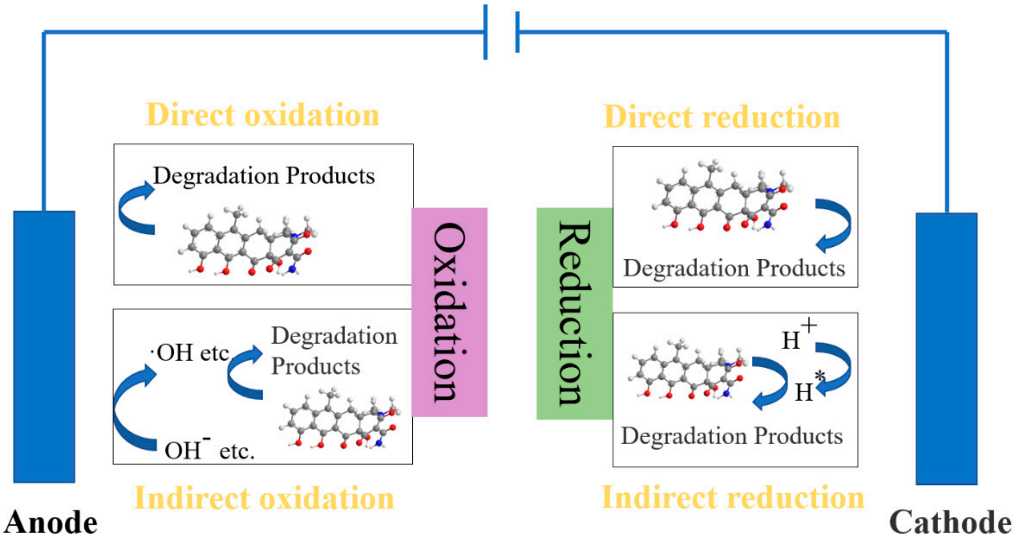


Figure 6. Mechanism of electrocatalytic treatment of tetracycline antibiotics (Which H* show Atom H) [83].

Electrocatalysis is a method with a wide application range and simple operation. Ni et al. [81] used FeNi/NF system to treat aquaculture wastewater discharged into seawater, and after 2% NaCl was added, 99.8% tetracycline could be treated in 30 min. The choice of the electrode is closely related to the effectiveness of antibiotic degradation. Oturan et al. [84] found that the process with a BDD anode showed excellent oxidation/mineralization ability. Li et al. [85] used electrocatalysis to pretreat antibiotic wastewater with salt content, and the treatment effect was good. Sun et al. [86] prepared an efficient Bi-Sn-Sb/γ-Al_2O_3 particle electrode for the degradation of tetracycline. Lu et al. [87] utilized a Pd/Ru/MXene/NF electrode for the electrocatalytic treatment of tetracycline hydrochloride wastewater, achieving a degradation rate exceeding 91% within 60 min. Shao et al. [88] loaded agarose (AG) onto ITO using the dipping method and deposited Pd onto the AG/ITO electrode through electrodeposition to prepare a Pd/AG/ITO composite electrode. The TC degradation efficiency of the AG/ITO composite electrode reached 85.21% within 120 min. It was found that the electrode has excellent electrocatalytic activity. Although the electrocatalysis method has advantages, there is little research on the treatment of pharmaceutical intermediates produced by antibiotics over different time frames, and ogoing effort is thus still needed from researchers.

4.5. Comprehensive Treatment Technology of Sewage Plant

Traditional sewage treatment plants cannot completely remove antibiotics from sewage by biodegradation or adsorption, which leads to environmental pollution and a high risk associated with the water [89]. Most sewage treatment plants are not designed to remove antibiotics themselves. Because of the limitations of individual water treatment methods, they cannot completely treat water contaminated with antibiotics. Usually, such water is treated by a combination of various methods [90,91]. Xu et al. [92] used UVC/persulfate processes to treat antibiotic wastewater, and TC was removed by hydroxylation, demethylation, decarbonylation, photochemistry, and dehydration.

The SWOT method was used to analyze the adsorption method, the biological method, the physical and chemical methods, the advanced oxidation method, and the comprehensive treatment technology used in sewage plants, as shown in Table 3.

Table 3. SWOT analysis of tetracycline antibiotics treatment technology in water environment.

Technology	Treatment Efficiency	Cost	Advantage	Disadvantage
Adsorption method	High	Low	Multifunctional, low energy consumption, easy operation and no by-products	Easily causes secondary pollution
Biological method	Low	Low	Low cost and mature technology	Unsafe
Materialization method	Low	High	Simple operation	General effect
Advanced oxidation processes	High	High	High degree of mineralization of pollutants and stable effects	Pharmaceutical intermediate
Comprehensive treatment technology used in sewage plants	High	Low	Mature technology, simple operation, etc.	Sludge treatment is difficult

5. Conclusions and Future Perspectives

Tetracycline antibiotics exist in various water environments (oceans, surface water, groundwater, wastewater, drinking water) due to the difficultly of their degradation and thus pose a threat to human health and the ecological environment. At present, the sources and distribution of tetracycline antibiotics in water resources are still unclear, so it is necessary to further monitor tetracycline antibiotics in water environments to determine the extent of this pollution and design treatment approaches.

At present, research on the degradation of tetracycline antibiotics in water environment has not been widely carried out at home and abroad. Adsorption can only concentrate pollutants, not remove them, and thus may cause secondary pollution in the process of adsorbent regeneration. The biological method is widely used and has low treatment costs and mature technology, but it is still necessary to consider the generation of medicines-resistant superbacteria in the treatment process; Antibiotics cannot be completely degraded/removed by a single method, so combined treatment methods are widely used. The physicochemical method, advanced oxidation technology and the comprehensive treatment technology used in sewage plants all have their own advantages. The physicochemical method can be used as a pretreatment technology or as advanced treatment technology. Advanced oxidation technology is efficient and easy to operate, but the research on the toxicity of pharmaceutical intermediates and their complex environmental behaviors should also be strengthened. In the comprehensive treatment of sewage, several technologies are often used to remove pollutants, with good effectiveness. In summary, in the context of aiming to improve existing technologies, future developments will involve combining technologies or developing new technologies to remove tetracycline antibiotics from water environments, thus protecting human health and helping to maintain a good ecological environment.

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References

1. Shao, S.; Hu, Y.; Cheng, J.; Chen, Y. Research Progress on Distribution, Migration, Transformation of Antibiotics and Antibiotic Resistance Genes (ARGs) in Aquatic Environment. *Crit. Rev. Biotechnol.* **2018**, *38*, 1195–1208. [CrossRef] [PubMed]
2. Klein, E.Y.; Boeckel, T.V.; Martinez, E.M.; Pant, S.; Gandra, S.; Levin, S.; Goossens, H.; Laxminarayan, R. Global Increase and Geographic Convergence in Antibiotic Consumption between 2000 and 2015. *Proc. Natl. Acad. Sci. USA* **2018**, *115*, E3463–E3470. [CrossRef] [PubMed]
3. Jandira, L.; Yasmin, V.; Nicoly, W.; Siara, S.; Guilherme, L.D.; Elvis, C. A Review of the Occurrence, Disposal, Determination, Toxicity and Remediation Technologies of the Tetracycline Antibiotic. *Process Saf. Environ. Prot.* **2022**, *160*, 25–40.
4. Haiyin, Z.; Qixing, Z. Research Progress on Treatment Technology of Tetracycline Antibiotics Pollution in the Environment. *J. Environ. Eng. Technol.* **2021**, *11*, 571–581.
5. Chopra, I.; Roberts, M.C. Tetracycline Antibiotics: Mode of Action, Applications, Molecular Biology, and Epidemiology of Bacterial Resistance. *Microbiol. Mol. Biol. Rev.* **2001**, *65*, 232–260. [CrossRef] [PubMed]

6. Chopra, I. New Developments in Tetracycline Antibiotics: Glycylcyclines and Tetracycline Efflux Pump Inhibitors. *Med. Resist. Updates* **2002**, *5*, 119–125. [CrossRef] [PubMed]
7. Bilal, M.; Mehmood, S.; Rasheed, T.; Iqbal, H.N. Antibiotics Traces in the Aquatic Environment: Persistence and Adverse Environmental Impact. *Curr. Opin. Environ. Sci. Health* **2020**, *13*, 68–74. [CrossRef]
8. Xinyan, G.; Zheng, Y.; Yi, Z.; Weili, X.; Deyang, K.; Zhengjun, S.; Na, W. Behavior of Antibiotic Resistance Genes under Extremely High-Level Antibiotic Selection Pressures in Pharmaceutical Wastewater Treatment Plants. *Sci. Total Environ.* **2018**, *612*, 119–128.
9. Krakkó, D.; Heieren, B.T.; Illés, Á.; Kvamme, K.; Dóbé, S.; Záray, G. (V) UV Degradation of the Antibiotic Tetracycline: Kinetics, Transformation Products and Pathway. *Process Saf. Environ. Prot.* **2022**, *163*, 395–404. [CrossRef]
10. Zhang, H.; Bian, J.; Yang, C.; Hu, Z.; Liu, F.; Zhang, C. Removal of Tetracycline from Livestock Wastewater by Positive Single Pulse Current Electrocoagulation: Mechanism, Toxicity Assessment and Cost Evaluation. *Sci. Total Environ.* **2022**, *810*, 151955. [CrossRef]
11. Li, Y.X.; Zhang, X.L.; Li, W.; Lu, X.F.; Liu, B.; Wang, J. The Residues and Environmental Risks of Multiple Veterinary Antibiotics in Animal Faeces. *Environ. Monit. Assess.* **2013**, *185*, 2211–2220. [CrossRef] [PubMed]
12. Lindberg, R.H.; Björklund, K.; Rendahl, P.; Johansson, M.I.; Tysklind, M.; Andersson, B.V. Environmental Risk Assessment of Antibiotics in the Swedish Environment with Emphasis on Sewage Treatment Plants. *Water Res.* **2007**, *41*, 613–619. [CrossRef] [PubMed]
13. Wang, J.; Chu, L.; Wojnárovits, L.; Takács, E. Occurrence and Fate of Antibiotics, Antibiotic Resistant Genes (ARGs) and Antibiotic Resistant Bacteria (ARB) in Municipal Wastewater Treatment Plant: An Overview. *Sci. Total Environ.* **2020**, *744*, 140997. [CrossRef] [PubMed]
14. Beyene, T. Veterinary Medicines Residues in Food-Animal Products: Its Risk Factors and Potential Effects on Public Health. *J. Vet. Sci. Technol.* **2016**, *7*, 285.
15. Klimek, L.; Aderhold, C.; Sperl, A.; Trautmann, A. Allergic Reactions to Antibiotics—Two Sides of the Same Coin: Clearly Diagnose or Reliably Rule Out. *Allergo J. Int.* **2017**, *26*, 212–218. [CrossRef]
16. Tadesse, T. Public Health Impacts of Antibiotic Residues in Foods of Animal Origin: A Review. *Public Policy Adm. Res.* **2017**, *7*, 6–11.
17. Shao, Y.; Wang, Y.; Yuan, Y.; Xie, Y. A systematic review on antibiotics misuse in livestock and aquaculture and regulation implications in China. *Sci. Total Environ.* **2021**, *798*, 149205. [CrossRef] [PubMed]
18. Zou, S.; Xu, W.; Zhang, R.; Tang, J.; Chen, Y.; Zhang, G. Occurrence and Distribution of Antibiotics in Coastal Water of the Bohai Bay, China: Impacts of River Discharge and Aquaculture Activities. *Environ. Pollut.* **2011**, *159*, 2913–2920. [CrossRef] [PubMed]
19. Raheleh, K.; Fatemeh, P.; Mohammad, S.; Sahebi, S.; Tahmasebi, R.; Ahmadi, M.; Sorial, G.; Asgari, G.; Ramavandi, B. Occurrence, Distribution, and Potential Sources of Antibiotics Pollution in the Water-Sediment of the Northern Coastline of the Persian Gulf, Iran. *Sci. Total Environ.* **2018**, *627*, 703–712.
20. Spongberg, A.L.; Witter, J.D.; Acuña, J.; Vargas, J.; Murillo, M.; Umaña, G.; Gómez, E.; Perez, G. Reconnaissance of Selected PPCP Compounds in Costa Rican Surface Waters. *Water Res.* **2011**, *45*, 6709–6717. [CrossRef]
21. Li, J.L.; Wang, M.; Hu, F.W.; Dong, Y.H.; Sun, Z.X.; Wang, Y. Antibiotic Pollution Characteristics and Ecological Risk Assessment in Jinjiang River Basin, Jiangxi Province. *Environ. Sci.* **2022**, *43*, 4064–4073.
22. Li, H.; Chen, Y.; Feng, M.J.; Wang, B.; Bu, Y.Q.; Zhang, S.H. Pollution characteristics and risk assessment of antibiotics in Nanjing drinking water sources. *Acta Sci. Circumstantiae* **2020**, *40*, 1269–1277.
23. Yin, C.N.; Xie, P.; Jiao, M.; Guo, B.Y.; Yu, C.H. Distribution characteristics of 54 kinds of PPCPs in surface water in Tianjin. *Environ. Chem.* **2021**, *40*, 2820–2831.
24. Lei, J.; Hu, X.; Yin, D.; Zhang, H.; Yu, Z. Occurrence, Distribution and Seasonal Variation of Antibiotics in the Huangpu River, Shanghai, China. *Chemosphere* **2011**, *82*, 822–828.
25. Ma, J.S.; Wang, Z.; Zhang, Z.Y.; Liu, Q.; Li, L.J. Distribution Characteristics of 29 Antibiotics in Groundwater in Harbin. *Rock Miner. Anal.* **2021**, *40*, 944–953.
26. Zhou, P.P. Investigation of Pollution and Health Risk Assessment on Tetracyclines in Drinking Water and Animal Derived Food of Anhui. Master's Thesis, Anhui Medical University, Hefei, China, 2019.
27. Turan, B.; Sarigol, G.; Demircivi, P. Adsorption of Tetracycline Antibiotics Using Metal and Clay Embedded Cross-Linked Chitosan. *Mater. Chem. Phys.* **2022**, *279*, 125781. [CrossRef]
28. Ai, Y.; Liu, Y.; Huo, Y.; Zhao, C.; Sun, L.; Han, B.; Cao, X.; Wang, X. Insights into the Adsorption Mechanism and Dynamic Behavior of Tetracycline Antibiotics on Reduced Graphene Oxide (RGO) and Graphene Oxide (GO) Materials. *Environ. Sci. Nano* **2019**, *6*, 3336–3348. [CrossRef]
29. Shen, Q.; Wang, Z.; Yu, Q.; Cheng, Y.; Liu, Z.; Zhang, T.; Zhou, S. Removal of Tetracycline from an Aqueous Solution Using Manganese Dioxide Modified Biochar Derived from Chinese Herbal Medicines Residues. *Environ. Res. Lett.* **2020**, *183*, 109195. [CrossRef] [PubMed]
30. Jang, H.M.; Yoo, S.; Choi, Y.-K.; Park, S.; Kan, E. Adsorption Isotherm, Kinetic Modeling and Mechanism of Tetracycline on Pinus Taeda-Derived Activated Biochar. *Bioresour. Technol.* **2018**, *259*, 24–31. [CrossRef]
31. Van Der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A.; Berendsen, H.C. Gromacs: Fast, Flexible, and Free. *J. Comput. Chem.* **2005**, *26*, 1701–1718. [CrossRef]
32. Rostamian, R.; Amiri, N.; Behnejad, H. How Does Graphene Nanosheet Affect the Pharmaceutical Adsorption? A Comprehensive Insight from Molecular Dynamics Simulation, Quantum Mechanics and Experimental Study. *J. Mol. Liq.* **2018**, *269*, 29–37. [CrossRef]

33. Ninwiwek, N.; Hongsawat, P.; Punyapalakul, P.; Prarat, P. Removal of the Antibiotic Sulfamethoxazole from Environmental Water by Mesoporous Silica-Magnetic Graphene Oxide Nanocomposite Technology: Adsorption Characteristics, Coadsorption and Uptake Mechanism. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *580*, 123716. [CrossRef]
34. Prarat, P.; Hongsawat, P.; Punyapalakul, P. Amino-Functionalized Mesoporous Silica-Magnetic Graphene Oxide Nanocomposites as Water-Dispersible Adsorbents for the Removal of the Oxytetracycline Antibiotic from Aqueous Solutions: Adsorption Performance, Effects of Coexisting Ions, and Natural Organic Matter. *Environ. Sci. Pollut. Res.* **2020**, *27*, 6560–6576.
35. Yu, K.; Sun, C.; Zhang, B.; Hassan, M.; He, Y. Size-Dependent Adsorption of Antibiotics onto Nanoparticles in a Field-Scale Wastewater Treatment Plant. *Environ. Pollut.* **2019**, *248*, 1079–1087. [CrossRef] [PubMed]
36. Ahmed, M.B.; Zhou, J.L.; Ngo, H.H.; Guo, W. Adsorptive Removal of Antibiotics from Water and Wastewater: Progress and Challenges. *Sci. Total Environ.* **2015**, *532*, 112–126. [CrossRef] [PubMed]
37. Qiu, B.; Shao, Q.; Shi, J.; Yang, C.; Chu, H. Application of Biochar for the Adsorption of Organic Pollutants from Wastewater: Modification Strategies, Mechanisms and Challenges. *Sep. Purif. Technol.* **2022**, *300*, 121925. [CrossRef]
38. Hu, Y.; Chen, C.; Yang, L.; Cui, J.; Hao, Q.; Sun, D. Handy Purifier Based on Bacterial Cellulose and Ca-Montmorillonite Composites for Efficient Removal of Dyes and Antibiotics. *Carbohydr. Polym.* **2019**, *222*, 115017. [CrossRef]
39. Yu, L.-L.; Cao, W.; Wu, S.-C.; Yang, C.; Cheng, J.-H. Removal of Tetracycline from Aqueous Solution by MOF/Graphite Oxide Pellets: Preparation, Characteristic, Adsorption Performance and Mechanism. *Ecotoxicol. Environ. Saf.* **2018**, *164*, 289–296. [CrossRef]
40. Huang, B.; Liu, Y.; Li, B.; Liu, S.; Zeng, G.; Zeng, Z.; Wang, X.; Ning, Q.; Zheng, B.; Yang, C. Effect of Cu (II) Ions on the Enhancement of Tetracycline Adsorption by Fe_3O_4@ SiO_2-Chitosan/Graphene Oxide Nanocomposite. *Carbohydr. Polym.* **2017**, *157*, 576–585. [CrossRef]
41. Qiao, H.; Wang, X.; Liao, P.; Zhang, C.; Liu, C. Enhanced Sequestration of Tetracycline by Mn(II) Encapsulated Mesoporous Silica Nanoparticles: Synergistic Sorption and Mechanism. *Chemosphere* **2021**, *284*, 131334. [CrossRef]
42. Liang, S.; Zhang, H.; Dai, H.; Wan, X.; Zhu, F.; Xu, Q.; Ji, W. Efficient, rapid and simple adsorption method by polydopamine polystyrene nanofibers mat for removal of multi-class antibiotic residues in environmental water. *Chemosphere* **2022**, *288*, 132616. [CrossRef] [PubMed]
43. Wang, T.; Pan, X.; Ben, W.; Wang, J.; Hou, P.; Qiang, Z. Adsorptive Removal of Antibiotics from Water Using Magneticion Exchange Resin. *J. Environ. Sci.* **2017**, *52*, 111–117. [CrossRef] [PubMed]
44. Shao, S.; Wu, X. Microbial Degradation of Tetracycline in the Aquatic Environment: A Review. *Crit. Rev. Biotechnol.* **2020**, *40*, 1010–1018. [CrossRef]
45. Scaria, J.; Anupama, K.; Nidheesh, P. Tetracyclines in the Environment: An Overview on the Occurrence, Fate, Toxicity, Detection, Removal Methods, and Sludge Management. *Sci. Total Environ.* **2021**, *771*, 145291. [CrossRef]
46. Liu, C.-X.; Xu, Q.-M.; Yu, S.-C.; Cheng, J.-S.; Yuan, Y.-J. Bio-Removal of Tetracycline Antibiotics under the Consortium with Probiotics Bacillus Clausii T and Bacillus Amyloliquefaciens Producing Biosurfactants. *Sci. Total Environ.* **2020**, *710*, 136329. [CrossRef]
47. De Cazes, M.; Belleville, M.P.; Petit, E.; Llorca, M.; Rodríguez-Mozaz, S.; De Gunzburg, J. Design and Optimization of an Enzymatic Membrane Reactor for Tetracycline Degradation. *Catal. Today* **2014**, *236*, 146–152. [CrossRef]
48. Zhang, X.; Yajuan, W.; Hong, T.; Zhang, R.; Ma, Z. Screened and Degradation Characteristics of a Four Tetracycline Antibiotics Degrading Bacterium. *Environ. Chem.* **2022**, *41*, 2761–2770.
49. Liao, Q.; Rong, H.; Zhao, M.; Luo, H.; Chu, Z.; Wang, R. Interaction between Tetracycline and Microorganisms During Wastewater Treatment: A Review. *Sci. Total Environ.* **2021**, *757*, 143981. [CrossRef] [PubMed]
50. Leng, Y.; Bao, J.; Xiao, H.; Song, D.; Du, J.; Mohapatra, S.; Werner, D.; Wang, J. Transformation Mechanisms of Tetracycline by Horseradish Peroxidase with/without Redox Mediator Abts for Variable Water Chemistry. *Chemosphere* **2020**, *258*, 127306. [CrossRef] [PubMed]
51. Shao, S.; Hu, Y.; Cheng, J.; Chen, Y. Biodegradation Mechanism of Tetracycline (TEC) by Strain Klebsiella sp. SQY5 as Revealed through Products Analysis and Genomics. *Ecotoxicol. Environ. Saf.* **2019**, *185*, 109676. [CrossRef]
52. Qi, W.-N. Microbial Degradation Mechanism of Tetracycline Antibiotics. Master's Thesis, Guizhou Normal University, Guiyang, China, 2019.
53. Gujarathi, N.P.; Haney, B.J.; Park, H.J.; Wickramasinghe, S.R.; Linden, J.C. Hairy Roots of Helianthus Annuus: A Model System to Study Phytoremediation of Tetracycline and Oxytetracycline. *Biotechnol. Prog.* **2010**, *21*, 775–780. [CrossRef] [PubMed]
54. Chen, X.J.; Li, F.Y.; Hao, Y.B. The Preliminary Exploration of Remediation the Antibiotics Polluted Water by Two Hydrophytes. *Subtrop. Plant Sci.* **2012**, *41*, 1–7.
55. Wojnárovits, L.; Wang, J.-L.; Chu, L.-B.; Tóth, T.; Kovács, K.; Bezsenyi, A.; Szabó, L.; Homlok, R.; Takács, E. Matrix effect in the hydroxyl radical induced degradation of β-lactam and tetracycline type antibiotics. *Radiat. Phys. Chem.* **2022**, *193*, 109980. [CrossRef]
56. Zhang, J.; Giorno, L.; Drioli, E. Study of a Hybrid Process Combining PACs and Membrane Operations for Antibiotic Wastewater Treatment. *Desalination* **2005**, *194*, 101–107. [CrossRef]
57. Safari, G.H.; Nasseri, S.; Mahvi, A.H.; Yaghmaeian, K.; Nabizadeh, R.; Alimohammadi, M. Optimization of sonochemical degradation of tetracycline in aqueous solution using sono-activated persulfate process. *J. Environ. Health Sci. Eng.* **2015**, *13*, 76. [CrossRef] [PubMed]

58. Saitoh, T.; Shibata, K.; Fujimori, K.; Ohtani, Y. Rapid Removal of Tetracycline Antibiotics from Water by Coagulation-Flotation of Sodium Dodecyl Sulfate and Poly(Allylamine Hydrochloride) in the Presence of Al(III) Ions. *Sep. Purif. Technol.* **2017**, *187*, 76–83. [CrossRef]
59. Liang, C.; Wei, D.; Zhang, S.; Ren, Q.; Shi, J.; Liu, L. Removal of Antibiotic Resistance Genes from Swine Wastewater by Membrane Filtration Treatment. *Ecotoxicol. Environ. Saf.* **2021**, *210*, 111885. [CrossRef] [PubMed]
60. Xujian, Q.I.; Fanhao, W.E.I.; Jiawei, F.A.N. Research progress on treatment of antibiotics and their resistance genes by advanced oxidation technologies. *Ind. Water Treat.* **2022**, *42*, 55–64.
61. Lopez Penalver, J.J.; Gomez Pacheco, C.V.; Sanchez Polo, M.; Rivera Utrilla, J. Degradation of Tetracyclines in Different Water Matrices by Advanced Oxidation/Reduction Processes Based on Gamma Radiation. *J. Chem. Technol. Biotechnol. Adv.* **2013**, *88*, 1096–1108. [CrossRef]
62. Wang, J.-S.; Yi, X.-H.; Xu, X.; Ji, H.; Alanazi, A.M.; Wang, C.-C.; Zhao, C.; Kaneti, Y.V.; Wang, P.; Liu, W.; et al. Eliminating Tetracycline Antibiotics Matrix Via Photoactivated Sulfate Radical-Based Advanced Oxidation Process over the Immobilized MIL-88A: Batch and Continuous Experiments. *Chem. Eng. J.* **2022**, *431*, 133213. [CrossRef]
63. Zhi, D.; Wang, J.; Zhou, Y.; Luo, Z.; Sun, Y.; Wan, Z.; Luo, L.; Tsang, D.W.; Dionysiou, D. Development of Ozonation and Reactive Electrochemical Membrane Coupled Process: Enhanced Tetracycline Mineralization and Toxicity Reduction. *Chem. Eng. J.* **2020**, *383*, 123149. [CrossRef]
64. Luu, H.T.; Lee, K. Degradation and Changes in Toxicity and Biodegradability of Tetracycline During Ozone/Ultraviolet-Based Advanced Oxidation. *Water Sci. Technol.* **2014**, *70*, 1229–1235. [CrossRef] [PubMed]
65. Li, X.; Shi, H.; Li, K.; Zhang, L. Combined Process of Biofiltration and Ozone Oxidation as an Advanced Treatment Process for Wastewater Reuse. *Front. Environ. Sci. Eng.* **2015**, *9*, 1076–1083. [CrossRef]
66. Wu, X.F.; Yang, K. Experimental study on advanced treatment of antibiotic wastewater by Fenton process. *Straits Sci.* **2017**, *1*, 19–21.
67. Bishop, D.F.; Stern, G.; Fleischman, M.; Marshall, L. Hydrogen Peroxide Catalytic Oxidation of Refractory Organics in Municipal Waste Waters. *Ind. Eng. Chem. Process Des. Dev.* **1968**, *7*, 110–117. [CrossRef]
68. Bai, J.L. Study on the Application of Iron-carbon Micro-electrolysis and Fenton Oxidation in Antibiotic Wastewate Treatment. *Sichuan Nonferrous Met.* **2019**, *2*, 51–54.
69. Shao, C.; Zhang, J.; Wang, Z.; Zhang, L.; Wang, B.; Ren, J.; Zhang, X.; He, W. Photo-Fenton degradation of tetracycline on nitrogen vacancy and potassium-doped Z-scheme FeOCl/NvCN heterojunction with low H_2O_2 consumption: Activity and mechanism. *J. Alloys Compd.* **2023**, *970*, 172532. [CrossRef]
70. Lv, J.; Zhang, B.; Qi, G.H.; Yan, L.; Li, C.; Zhang, Z. Research Progress of Photocatalytic Oxidation Process to Antibiotic Wastewater Treatment with TiO_2. *Shanghai Chem. Ind.* **2014**, *39*, 7–10.
71. Xiao, M.W. A New Technology for Treatment of Antibiotic Wastewater by Photocatalytic Oxidation. Master's Thesis, Guangdong University of Technology, Guangzhou, China, 2005.
72. Reyes, C.; Fernandez, J.; Freer, J.; Mondaca, M.A.; Zaror, C.; Malato, S.; Mansilla, H.D. Degradation and Inactivation of Tetracycline by TiO_2 Photocatalysis. *J. Photochem. Photobiol. A Chem.* **2006**, *184*, 141–146. [CrossRef]
73. Das, S.; Ahn, Y.H. Synthesis and application of CdS nanorods for LED-based photocatalytic degradation of tetracycline antibiotic. *Chemosphere* **2022**, *291*, 132870. [CrossRef]
74. Nagamine, M.; Osial, M.; Jackowska, K.; Krysinski, P.; Widera-Kalinowska, J. Tetracycline Photocatalytic Degradation under CdS Treatment. *J. Mar. Sci. Eng.* **2020**, *8*, 483. [CrossRef]
75. Zhang, J.; Shao, C.; Zhen, L.; Li, Y.; Bai, H.; Zhang, L.; Ren, G.; Wang, X. Treatment of antibiotics in water by SO_3H-modified Ti_3C_2 Mxene photocatalytic collaboration with g-C_3N_4. *J. Mater. Sci. Technol.* **2024**, *194*, 124–137. [CrossRef]
76. Ma, Y.-Y.; Qi, P.; Meng, S.; Zuo, N.; Mominou, N.; Li, S.Z.; Jing, C.Y.; Wang, L. Photocatalytic oxidation degradation of tetracycline over La/Co@TiO_2 nanospheres under visible light. *Environ. Res.* **2022**, *215*, 114297. [CrossRef] [PubMed]
77. Tang, T.; Yin, Z.-L.; Chen, J.-R.; Zhang, S.; Sheng, W.-C.; Wei, W.-X.; Xiao, Y.-G.; Shi, Q.-Y.; Cao, S.-S. Novel p-n heterojunction Bi_2O_3/Ti^{3+}-TiO_2 photocatalyst enables the complete removal of tetracyclines under visible light. *Chem. Eng. J.* **2020**, *417*, 128058. [CrossRef]
78. Li, Y.-C.; Yu, B.; Hu, Z.-Q.; Wang, H. Construction of direct Z-scheme SnS_2@$ZnIn_2S_4$@kaolinite heterostructure photocatalyst for efficient photocatalytic degradation of tetracycline hydrochloride. *Chem. Eng. J.* **2022**, *429*, 132105. [CrossRef]
79. Zong, Z.-Y.; Gilbert, E.; Wong, C.Y.; Usadi, L.; Qin, Y.; Huang, Y.-H.; Raymond, J.; Hankins, N.; Kwan, J. Efficient sonochemical catalytic degradation of tetracycline using TiO_2 fractured nanoshells. *Ultrason. Sonochem.* **2023**, *101*, 106669. [CrossRef] [PubMed]
80. Liu, Z.; Zhu, M.; Wang, Z.; Wang, H.; Deng, C.; Li, K. Effective Degradation of Aqueous Tetracycline Using a Nano-TiO_2/Carbon Electrocatalytic Membrane. *Materials* **2016**, *9*, 364. [CrossRef] [PubMed]
81. Ni, T.; Feng, H.; Tang, J.; Wang, J.; Yu, J.; Yi, Y.; Wu, Y.; Guo, Y.; Tang, L. A Novel Electrocatalytic System with High Reactive Chlorine Species Utilization Capacity to Degrade Tetracycline in Marine Aquaculture Wastewater. *Chemosphere* **2022**, *300*, 134449. [CrossRef] [PubMed]
82. Xie, W.; Shi, Y.; Wang, Y.; Zheng, Y.; Liu, H.; Hu, Q.; Wei, S.-Y.; Gu, H.-B.; Guo, Z.-H. Electrospun Iron/Cobalt Alloy Nanoparticles on Carbon Nanofibers Towards Exhaustive Electrocatalytic Degradation of Tetracycline in Wastewater. *Chem. Eng. J.* **2021**, *405*, 126585. [CrossRef]

83. Wu, S.; Hu, Y.H. A Comprehensive Review on Catalysts for Electrocatalytic and Photoelectrocatalytic Degradation of Antibiotics. *Chem. Eng. J.* **2021**, *409*, 127739. [CrossRef]
84. Oturan, N.; Wu, J.; Zhang, H.; Sharma, V.K.; Oturan, M.A. Electrocatalytic Destruction of the Antibiotic Tetracycline in Aqueous Medium by Electrochemical Advanced Oxidation Processes: Effect of Electrode Materials. *Appl. Catal. B Environ.* **2013**, *140–141*, 92–97. [CrossRef]
85. Li, Z.P.; Xu, G.H.; Cao, H.; Dai, X. On the Anaerobic Treatment Technology of Antibiotic Wastewater by Three Dimensional Electro Catalytic Coupling. *Value Eng.* **2014**, *33*, 305–306.
86. Sun, W.; Sun, Y.; Shah, K.J.; Chiang, P.-C.; Zheng, H. Electrocatalytic Oxidation of Tetracycline by Bi-Sn-Sb/γ-Al_2O_3 Three-Dimensional Particle Electrode. *J. Hazard. Mater.* **2019**, *370*, 24–32. [CrossRef]
87. Lu, M.; Sun, J.; Cui, B.; Zhang, J.; Ren, J.; Li, R. Pd, Ru/2D MXene nanosheets/3D self-supporting nickel foam composite electrode and its electrocatalytic synergistic degradation of antibiotics. *Sep. Purif. Technol.* **2024**, *340*, 126736. [CrossRef]
88. Shao, C.; Zhang, J.; Liu, Y.; Jiang, Y.T.; Jia, Y.P.; Li, G.M.; Sun, Z. Effective degradation of tetracycline by Pd/AG/ITO electrode: Electrode preparation, characterization, kinetics, degradation mechanism and toxicity assessment. *J. Environ. Chem. Eng.* **2023**, *11*, 110344. [CrossRef]
89. Jing, H.; Juan, Z.; Pan, W.; Tsang, Y.F. Occurrence and Fate of Antibiotics in a Wastewater Treatment Plant and Their Biological Effects on Receiving Waters in Guizhou. *Process Saf. Environ. Prot.* **2018**, *113*, 483–490.
90. Chen, J.; Liang, J.; Li, C.; Dai, J.; Mai, W.; Wei, Y. An Enriched Ammonia-Oxidizing Microbiota Enables High Removal Efficiency of Ammonia in Antibiotic Production Wastewater. *Chemosphere* **2023**, *310*, 136854. [CrossRef] [PubMed]
91. Pei, M.; Zhang, B.; He, Y.; Su, J.; Gin, K.; Lev, O.; Shen, G.; Hu, S. State of the Art of Tertiary Treatment Technologies for Controlling Antibiotic Resistance in Wastewater Treatment Plants. *Environ. Int.* **2019**, *131*, 105026. [CrossRef] [PubMed]
92. Xu, M.; Deng, J.; Cai, A.; Ma, X.; Li, J.; Li, Q.; Li, X. Comparison of UVC and UVC/Persulfate Processes for Tetracycline Removal in Water. *Chem. Eng. J.* **2020**, *384*, 123320. [CrossRef]