

Mini Review

Technologies for the Removal of Antibiotics in the Environment: a Review

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In recent years, China has consumed between 150,000 and 200,000 tons of antibiotics per year, accounting for half of global consumption. However, the effective utilization rate is relatively low. Most of them remain in the environment and potential health threats. Therefore, how to effectively remove the residual antibiotics in the environment has become a hot issue in recent years. In this paper, the common techniques for removing antibiotics from the environment, such as adsorption, chemical and physical methods, were reviewed, and the removal mechanism was discussed in detail. The effectiveness, advantages and disadvantages of different electrochemical oxidation methods and different membrane materials for the removal of antibiotics were reviewed in depth. Recently, the representative membrane biological method has been highlighted for its excellent potential. Finally, the remaining obstacles and prospects are discussed in order to develop techniques for removing antibiotics from the environment efficiently.

Keywords: residual antibiotics; membrane; soil; water

1. INTRODUCTION

Antibiotics are used in a wide range of medical applications, agriculture, industry and other fields because of their bactericidal, inhibiting microbial growth or reproduction characteristics. The discovery of antibiotics is very important in terms of disease prevention and control of human diseases, effectively improving the survival rate of human beings. However the improper or excessive use of antibiotics caused potential risks to human health. According to statistics, the proportion of patients using antibiotics in China has reached 70%, but less than 20% really need to be used [1]. There is a flood of antibiotics in varying degrees. The abuse of antibiotics not only led to the emergence of some superbacteria, but

also led to the pollution of groundwater and surface water. They will also enrich through the food chain and eventually cause greater harm to humans, animals and plants [1]. Therefore, it is urgent to study the methods of removing antibiotics from the environment and reducing the pollution of the environment by antibiotics. In this paper, the current situation of antibiotic pollution and the progress of membrane treatment of antibiotics were reviewed, which provided some research directions for the further study of membrane treatment of antibiotics.

2. CURRENT SITUATION OF ANTIBIOTIC POLLUTION IN ENVIRONMENT

2.1 Antibiotics Contamination in Water Environment

Antibiotics can only be found in trace amounts in nature, generally in the level of the trace. Different researchers had studied the residues of antibiotics in water environment. Tian et al. found that the pollution of antibiotics in the water environment was shown to be higher than in other environmental media. After antibiotics entered the human body or animals, 30%~90% of the drugs were still not absorbed by the organism and discharged with the excretion. They remained in the water environment and continued to cause water pollution [2]. Li et al. (2018) analyzed the residues of 94 antibiotics in four major sea areas and seven major rivers in China from 2005 to 2016. Among them, 12 kinds of common antibiotics were found, including 3 kinds of SAs, 2 kinds of TCs, 4 kinds of FQs and 3 kinds of MLs [3]. Guo et al. (2019) investigated the levels of eight common antibiotics in the surface waters and sediments of the Yangtze River estuary's nearshore zone and estuarine channels. The results showed that the antibiotics in surface water were mainly sulfonamides and tetracyclines, and the antibiotics in the sediments were mainly tetracyclines and fluoroquinolones [4].

2.2 Antibiotics Contamination in soil

In recent years, antibiotics play an important role in animal husbandry, but these antibiotics entering animals can not be fully absorbed. Unabsorbed antibiotics are directly applied to the soil as organic fertilizer with animal manure, resulting in soil pollution. Many scholars had detected antibiotics with different degrees of pollution in soil. Huang et al. (2013) looked at six antibiotics in farming soil in four Fujian coastal cities. The maximum concentrations of oxytetracycline, enrofloxacin, ciprofloxacin, Chlorotetracycline, ofloxacin, and tetracycline were 613.2, 637.3, 237.3, 2668.9, 205.7, and 189.8 $\mu\text{g}/\text{kg}$, respectively [5]. Wu et al. (2013) tested antibiotics contained in 3 types of land: asparagus land, vineyard and mustard land in suburban Hangzhou, Zhejiang, East China, and found that oxytetracycline and doxycycline were dominant in asparagus production soil [6]. The results showed that oxytetracycline and doxycycline were dominant in asparagus production soil, mainly oxytetracycline in vineyards and aureomycin in mustard soil [6]. Zhang et al. (2021) used HPLC to detect 43 soil surface samples collected from Yinchuan farmland. It was found that the antibiotic detected in all soil samples was tetracycline with concentrations ranging from 40.68 to 1074.42 $\mu\text{g}/\text{kg}$ with a mean concentration of 462.24 $\mu\text{g}/\text{kg}$ [7].

3. TREATMENT TECHNOLOGY OF ANTIBIOTICS

The dangers of antibiotic residues in the environment have been well known, so the research on antibiotic removal had received more and more attention. In recent 10 years, there were more than 10,000 literatures on the elimination of antibiotics. The methods of removing antibiotics mainly include adsorption, chemical, physical, biological method, membrane method.

3.1 Adsorption

Adsorption method has the advantages of wide range of adaptation, good treatment effect, simple operation, no toxic substances and reusable adsorbent. However, when antibiotics are removed by adsorption, antibiotics are not eliminated fundamentally, but transferred to the adsorbent, and the adsorption capacity is easily affected by the specific surface area, porosity and other competitive adsorption factors. Recent years, the adsorption materials widely applied in the treatment of residual antibiotics in the environment include activated carbon, biochar, graphene, zeolite and montmorillonite.

Adsorption methods include: physical adsorption, chemisorption and exchange adsorption method. The main influencing factors of physical adsorption are the specific surface area and pore distribution of the adsorbent; the main influencing factors of chemical adsorption are the surface chemical properties of adsorbent and the chemical properties of adsorbate; the main influencing factors of exchange adsorption method are ion charge number and hydration radius.

The eliminating effect and quantum chemistry of antibiotics by different adsorption materials are shown in table 1.

Table 1. The eliminating effect and quantum chemistry of antibiotics by different adsorption materials

Adsorbing Material	Specific Surface area (m ² /g)	Adsorbed Antibiotics Type	Reaction Equilibrium Time (h)	Maximum Adsorption Capacity (mg/g)	Adsorption Isotherm Model	Adsorption Kinetics	Adsorption Mechanism	References
Activated Carbon	NAC: 1029	AMX	6	437.00	Langmuir Model	pseudo-second order kinetic model	electrostatic adsorption	[8] Moussavi et al., 2013
	Zn-AC: 224	TC	2	282.06	Redlich-Peterson Model	general order kinetic model	Non-electrostatic π - π bond dispersion、hydrophobic interaction	[9] Afshin et al., 2017
	Fe/Zn+H ₃ PO ₄ -SBC: 39.1	SDZ NOR OFX TC	6	83.70 39.30 25.40 128.10	Freundlich Model	pseudo-second order kinetic model	physical interaction and chemical action	[10] Ma et al., 2020
Biochar	seaweed—SBC600: 10.68	CAZ	10	61.70	Langmuir Model	pseudo-second order kinetic model	Coulomb interactions π - π electron-donor-acceptor interaction	[11] Song et al., 2019
	HAB: 26.28	CIP NOR ENR	10	3.76 3.94 4.03	Langmuir Model and Freundlich Model	pseudo-second order kinetic model	Electrostatic, hydrophobic, hydrogen bond and π - π bond interaction	[12] Zhao et al., 2019
	ZnO-BC-2-650:915	CIP	4	449.40	Temkin Model		π - π stacking interaction、electrostatic	[13] Hu et al., 2019

						pseudo-second-order kinetic model	interaction, cation exchange	
Graphene	TiO ₂ -GS:67.2	TC	48	1,805.00	Temkin Model	pseudo-second order kinetic model	electrostatic interaction	[14] Zhao et al., 2015
	MGO:141.2	TC OXY CTE	10	141.44 289.86 303.95	Freundlich Model	pseudo-second-order kinetic model	physical interaction and chemical action	[15] Miao et al., 2019
Zeolite	La-Z:10.267	CTC	10	127.55	Langmuir Model	pseudo-second order kinetic	physical interaction	[16] Yu et al., 2020
Montmorillonite	magnetic montmorillonite-biochar composites	OXY	8	58.85	Langmuir Model	pseudo-second-order kinetic model	hydrogen bonding and π-π interaction, cation exchange	[17] Liang et al., 2019
	magnetic montmorillonite:51.574	TC CIP	6	240.91 330.00	Langmuir-Freundlich Model	pseudo-second order kinetic model	physical interaction	[18] Zhang, 2019

3.2 Chemical Method

In the past decade, chemical methods have been widely used in the study of antibiotic removal by scholars in China and abroad. Chemical method has the advantages of rapid reaction and high removal efficiency. Chemical methods widely used in antibiotic removal include chlorine oxidation, ozone oxidation, Fenton oxidation, photocatalytic oxidation and electrochemical oxidation.

Ben et al. (2017) used ClO₂ oxidation method to remove sulfa antibiotics, and the removal rate was 99.975%. The removal mechanism was the fracture of SAs bond and CAS bond in SMX molecule and hydroxylation of aniline group [19]. Ling (2021) and others used A-Mn/CeO-γAl₂O₃ as catalyst for catalytic ozonation to remove tetracycline from simulated marine aquaculture effluent. The removal efficiency was 71.6%, and the removal mechanism was electrophilic substitution reaction [20]. Katia (2019) used high-frequency homogeneous ultrasound-Fenton oxidation to remove ciprofloxacin, and the removal efficiency was 60%. The removal mechanism was the interaction between hydroxyl and organic matter [21]. Serna-Galvis et al. (2017) used TiO₂ photocatalytic oxidation to remove o-chloropenicillin, and the removal efficiency was 85%. The removal mechanism was the combined action of holes and adsorbed hydroxyl radicals [22]. Serna-Galvis (2017) used NaCl electro-catalytic oxidation to remove o-chloropenicillin, and the removal efficiency was 100%. The removal mechanism was NaClO oxidation [22].

The advantages and disadvantages of each chemical treatment of antibiotics are shown in table 2.

Table 2. Advantages and disadvantages of chemical treatment of antibiotics

Handling Method	Antibiotics Removal Type	Removal Efficiency (%)	Removal Mechanism	Advantages	Limitations	References
chlorine oxidation method	SAs	99.975	The breaking of SAN and CAS bonds and hydroxylation of	mature process equipment, simple and mature operation, high oxidation rate, a wide range of uses	the treatment cost is high, the reaction is not complete, easy to cause secondary pollution, chlorine oxidizer transportation and use has a certain degree of danger	[19] Ben et al., 2017

			aniline groups in SMX			
catalytic ozonation	TC	71.6	electrophilic substitution reaction	good degradation effect, rapid reaction, simple process, no secondary pollution problem	O ₃ preparation technology is not mature, high cost, low utilization rate	[20] Ling et al., 2021
High frequency homogeneous ultrasound-Fenton oxidation process	CIP	60	hydroxyl groups interact with organic matter	short reaction time, high degradation efficiency and simple operation	high cost, large sludge output, equipment is easy to be corroded	[21] Katia, 2019
TiO ₂ photocatalytic oxidation	BRL	85	the hole interacts with the hydroxyl radical adsorbed	mild reaction conditions, strong oxidation capacity, wide range of application, high treatment efficiency, high utilization efficiency of oxidizer, treatment process without other impurities	Uv generating equipment is required, which requires disassembly, poor reaction selectivity, and the photodecomposition of wastewater organic compounds is often interfered by other competitive reactions, which may produce more toxic by-products	[22] Serna-Galvis et al., 2017
NaCl electrocatalytic oxidation	BRL	100	NaClO oxidative	strong oxidation, small footprint of equipment, simple operation, high efficiency, environmental friendly	electrode materials are expensive, easy to lose, high cost and low current efficiency	

3.3 Electrochemical Oxidation Process

Electrochemical oxidation is increasingly being used for the removal of antibiotics from the water environment because of its mild reaction conditions, controllability, cost-effectiveness, power, flexibility of treatment, and lack of secondary pollution. The working mechanism of electrochemical oxidation was shown in Figure 1. In the study of the use of electrochemical oxidation for the removal of antibiotics, on the one hand, there was a single electrochemical oxidation method; on the other hand, there was a bioelectrochemical system, which combined electrochemical oxidation with biodegradation to remove antibiotics from the aqueous environment.

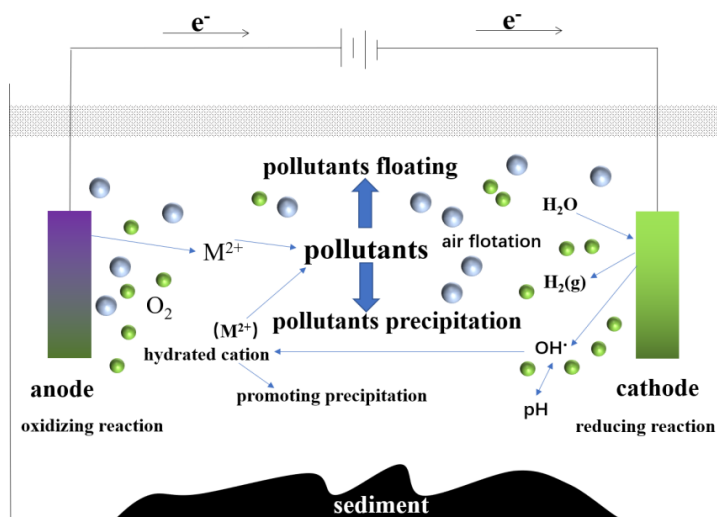


Figure 1 Working mechanism of electrochemical oxidation method

(1) Single electrochemical oxidation method

A large part of the efficiency of electrochemical oxidation techniques depends on the catalytic activity and stability of the electrode materials (mainly anode materials). Therefore, in order to improve the reaction efficiency, new electrode materials with low resistance, high current efficiency, and low cost can be used. Haidar et al. (2021) used platinum or thin film boron-doped diamond (BDD) as the anode and carbon felt as the cathode for electrochemical oxidation to remove sulfachloropyridazine (SCP) from synthetic aqueous solutions with a removal efficiency efficiency of more than 95% [23]. The degradation of SCP by BDD anode was very rapid, which was beneficial to the application of this technology in the purification of antibiotic SCP wastewater [23]. Teng et al. (2020) used titanium suboxide mesh (TiSOM) as the anode material for the electrochemical oxidation of heavy sulfadiazine (SDZ) from pharmaceutical wastewater, and the results showed that SDZ was completely removed [24]. The reticulated TiSOM anode achieved a large chemically active area (ECSA) and improved mass transfer from the bulk electrolyte to the anode under flow-through operation, and TiSOM as an anode material provided an effective method for electrochemical treatment of pharmaceutical wastewater [24]. Li et al. (2018) used RuO₂-TiO₂/Nano-G as an electrode material for electrochemical oxidation to remove ceftriaxone sodium (CAS) from wastewater with a removal efficiency higher than 97.3% [25]. This anode material (RuO₂-TiO₂) was characterized by a large specific surface area, strong electrochemical oxidation activity, low charge transfer resistance, and a low preparation cost, so it could be used as a cheap, feasible, and promising electrode for effective electrochemical removal of antibiotics from wastewater for future practical applications [59]. Wang et al. (2016) used SnO₂-Sb/Ti as an electrode material for electrochemical oxidation of ciprofloxacin in aqueous solution with 99.5% removal rate [26]. Liu et al. (2015) used carbon nanotube (CNT) electrochemical filters for the removal of tetracycline (TC) from wastewater treatment plants and the results were all removed [27]. Miyata et al. (2011) used Ti/IrO₂ as an electrode material to electrochemically oxidize tetracycline antibiotics (TCs) in livestock wastewater, and the removal rates of tetracycline (TC) and oxytetracycline (OTC) were as high as 99.4% and 99.3%, respectively, and the removal rates of doxycycline (DOY) and chrysomycin (CTC) were both higher than 99% [28]. Dirany et al. (2010) used platinum or thin film boron-doped diamond (BDD) as the anode and carbon felt as the cathode for electrochemical oxidation of sulfamethoxazole (SMX) from aqueous solutions at pH 3. The results showed that SMX was completely removed by oxidation [29]. Studies on the removal of antibiotics from aqueous environments by electrochemical oxidation with different electrode materials are shown in Table 3.

Table 3 Electrochemical oxidation of antibiotics in environment with different electrode materials

Electrode Material	Antibiotic Type	Removal Efficiency (%)	Removal Mechanism	Reaction Kinetics	Influencing Factor	References
BDD/Carbon	SCP	>95	oxidation of hydroxyl radical	quasi first order dynamics	pH, current intensity, anode material	[23] Haidar et al., 2021
TiSOM	SDZ	100	oxidation of hydroxyl radical	quasi first order dynamics	hydrodynamic properties of anode surface, electrolyte, pH value, current density and energy consumption	[24] Teng et al., 2020

RuO ₂ -TiO ₂ /Nano-graphite composites	CAS	>97.3	Synergistic effect between RuO ₂ , TiO ₂ and Nano-G	quasi first order dynamics	electronic conductivity, specific surface area, electrolysis time of electrode	[25] Li et al., 2018
SnO ₂ -Sb/Ti	CIP	99.5	oxidation of the piperazine ring, hydroxylation of the quinolone moiety, and defluorination (OH/F substitution)	first-order kinetics	pH, current density, initial CIP concentration	[26] Wang et al., 2016
Carbon nanotube	TC	100	CNT mass transfer, physical adsorption, electron transfer and desorption of oxidation products	oxidation kinetics	battery potential, hydraulic retention time, NMO concentration and TC oxidation flux in water	[27] Liu et al., 2015
Ti/IrO ₂	TC	99.4	oxidation of hydroxyl radical	quasi first order dynamics	anode material, electrolyte, power consumption, electrolyte	[28] Miyata et al., 2011
	OTC	99.3				
BDD/Carbon	DOY	>99	oxidation and electron transfer of hydroxyl radical	quasi first order dynamics	current intensity, electrolysis time	[29] Dirany et al., 2010
	CTC	>99				
SMX		100				

(2) Bioelectrochemical system

Electrochemical technology was combined with biodegradation to form a bioelectrochemical system, which was a novel technology that mainly used the function of microorganisms to cathodically reduce pollutants or anodically oxidize them [30]. In recent years, more and more researchers have applied this technology to the removal of antibiotics in the aqueous environment. Xu et al. (2022) used 'electro-Fenton+bioelectrochemistry' to treat tetrahydrofuran in pharmaceutical wastewater with a removal rate of 97.65% [31]. Li et al. (2021) constructed a novel electrochemical membrane bioreactor (EMbFR) for the removal of sulfadiazine (SDZ), while inhibiting the production of antibiotic resistance genes (ARG), and the results showed that the EMbFR achieved 94.9% removal of SDZ [32]. Hua et al. (2020) used an upflow anaerobic bioelectrochemical system (UBES) to treat sulfamethoxazole (SMX) in antibiotic wastewater and showed that the closed-circuit UBES exhibited good SMX removal performance with 73.7±2.0% removal [33]. Kong et al. (2014) used a biocathodic bioelectrochemical system to remove chloramphenicol from wastewater with a removal efficiency of 99% [34]. Saidi et al. (2013) used an electrochemical process coupled with biological treatment to degrade the biodegradable sulfadimethoxazole (SDZ) with a degradation efficiency of over 90% [35]. Song et al. (2013) used a two-chamber microbial fuel cell to remove metronidazole (MNZ) from water and achieved 85.4% removal of metronidazole in MFCs within 24 h, compared to only 35.2% in the open-circuit condition [36]. Studies on the removal of antibiotics from the aqueous environment by different coupled electrochemical and biodegradation processes are shown in Table 4.

Table 4. Studies on the removal of antibiotics in environment by different electrochemical and biodegradation coupling processes

Electrode material	Antibiotic Type	Removal Efficiency (%)	Removal Mechanism	Reaction Kinetics	References
ElectroFenton+ Bioelectrochemistry	THF	97.65	electrochemical oxidation, biodegradation	influent COD concentration, temperature, voltage, pH	[31] Xu et al., 2022
EMbFR	SDZ	94.9	integrated synergy between EAOP and MBfR	battery voltage, influent COD concentration, electrode material	[32] Li et al., 2021

UBES	SMX	73.7±2.0	anaerobic biodegradation, bioelectrochemical degradation	time, temperature, circuit voltage, influent COD concentration, loading rate, influent SMX concentration	[33] Hua et al., 2020
Biocathode Bioelectrochemical System Coupling	CAP	99	biocatalysis, biodegradation, electron transfer	temperature, potential, pH	[34] Kong et al., 2014
electrochemical process with biological treatment	SDZ	>90	electrochemical oxidation, biodegradation	current velocity, applied potential	[35] Saidi et al., 2013
Two-chamber microbial fuel cell	MNZ	85.4	electrochemical oxidation, biodegradation	initial concentration of metronidazole fil	[36] Song et al., 2013

3.4 Physical Method

Physical method used natural forces such as van der Waals force, electric gravity, and physical barriers to achieve antibiotics removal [37]. Physical method is usually used as a pretreatment method of biological method or an auxiliary method of advanced treatment, which generally has the advantages of simple process and low energy consumption. The physical methods widely used in removing residual antibiotics in water environment mainly include coagulation method, precipitation and air flotation method. In recent years, air flotation has been widely used in the removal of antibiotics residues in the environment, such as gentamicin, oxytetracycline, midecamycin and other antibiotics wastewater treatment.

The advantages and disadvantages of various physical methods in the treatment of antibiotics are shown in table 5.

Table 5. Advantages and Disadvantages of Various Physical Methods in the Treatment of Antibiotics

Handling Method	Antibiotics Removal Type	Advantages	Limitations	References
coagulation method	TC	significantly reducing the concentration of suspended solids in wastewater can also reduce the concentration of COD in wastewater to a certain extent	risk of secondary pollution; the type and amount of coagulant are affected by water quality. the operation is time-consuming and laborious.	[38] He et al., 2021
precipitation	TC	simple equipment, low cost, easy access to raw materials, convenient for small batch production	The resulting precipitate may contain a variety of substances, or contain a large amount of salts, or be wrapped with solvents, and the purity of the product is often lower than that of the crystallization method, and the filtration is also more difficult.	[39] Su et al., 2021
air flotation	ASP	equipment occupies less space, higher efficiency, convenient operation; the sludge produced is dry and not easy to decay; the amount of oxygen in the water increases	high energy consumption; easy to block, maintenance and management workload is large; scum exposed to water, susceptible to wind, rain and other weather factors	[40] Wang et al., 2009

3.5 Summary

When the antibiotics in the environment are treated by adsorption method, the antibiotics are not fundamentally eliminated, but transferred to the adsorbent. The adsorption capacity is easily affected by the specific surface area, porosity and competitive adsorption of other substances of the adsorbent.

Chemical treatment of antibiotics in the environment requires the addition of chemicals in the treatment process, which is easy to cause secondary pollution of the environment, and the transportation and use of many chemicals are dangerous and expensive. When removing antibiotic pollution in water by physical method, the pollutant concentration should not be too high and the treatment efficiency is low, so it is not suitable for large-scale industrial treatment.

When using a single electrochemical oxidation method, the removal of antibiotics by electrochemical oxidation with novel materials as electrodes was very effective. When the bioelectrochemical system was used, the removal effect of antibiotics was obvious, and the synergistic effect of electrochemical oxidation and biodegradation was one of the main reasons for improving the removal efficiency of antibiotics in water environment. The oxidation mechanism of single electrochemical oxidation is mainly through the generation of superoxide radicals ($\cdot\text{O}_2$), hydrogen peroxide (H_2O_2) and hydroxyl radicals ($\cdot\text{OH}$) by electrode materials, operating conditions (current density, electrode spacing), medium conditions (electrolyte concentration, pH, other ions) and other factors. The reaction mechanism of a bioelectrochemical system is that at least one of the anode and cathode of the system undergoes a microbially catalysed oxidation/reduction reaction, where an electron transfer process involving microorganisms or microbial metabolites takes place at the electrode. The influencing factors of bioelectrochemical systems are electrode materials, operating conditions (current density, electrode spacing), medium conditions (influent COD concentration, pH value, temperature), microbial activity.

Although numerous studies have been done on electrochemistry, it still suffers from high energy consumption, rapid electrode consumption and high operating costs. Therefore, the development of new electrode materials (low resistance, high current efficiency, and low cost) and the coupling of electrochemical oxidation technology with biodegradation technology will be important future directions in the study of the use of electrochemical oxidation for the removal of antibiotics from the aqueous environment.

Membranes have many advantages: high separation accuracy, up to nano level; Normal temperature operation, no phase change; no need to add chemicals, no secondary pollution. The equipment can be flexibly configured according to the processing capacity, with small floor area; Strong adaptability and stable operation. In particular, membrane biological method has the advantages of stable operation, strong impact load resistance, more economic and energy saving, no sludge bulking and so on. Therefore, Membrane method has become a hot spot of antibiotics removal research because of its irreplaceable advantages in the removal of antibiotics.

4. REMOVAL OF ANTIBIOTICS CONTAMINATION BY MEMBRANES

4.1 Several commonly used membranes

Membrane is a material with selective separation function. Membrane separation is a physical process. Membrane separation technology can be targeted to the solid waste, liquid waste and gaseous

waste for effective separation and treatment, and make it meet the specified standards for discharge, but also through a certain technical method to recycle materials. The process route of membrane treatment of antibiotics is shown in figure 2.

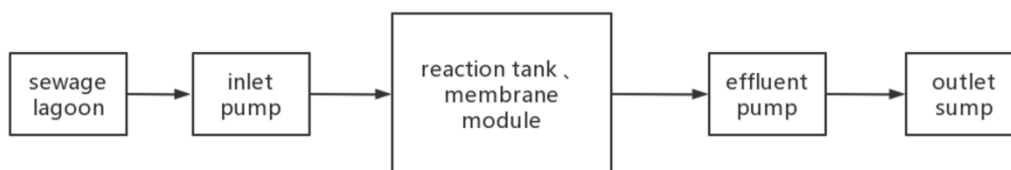


Figure 2. Process route of membrane treatment of antibiotics.

Membrane materials widely used in the removal of residual antibiotics in the environment mainly include microfiltration (MF) membrane, nanofiltration (NF) membrane, ultrafiltration (UF) membrane, reverse osmosis membrane and so on.

Microfiltration (MF) membrane. Microfiltration membrane began in the early 19th century. With the static pressure difference as the driving force, the membrane process is separated by the screening effect of membrane. The separation mechanism is similar to that of ordinary filtration, but the filtration accuracy is high, and the particles or organic macromolecules between 0.1~1.0 μm can be intercepted, so it is also called precision filtration. There are two modes of microfiltration: dead end filtration and cross flow filtration. The membrane structure of microfiltration membrane is shown in figure 3.

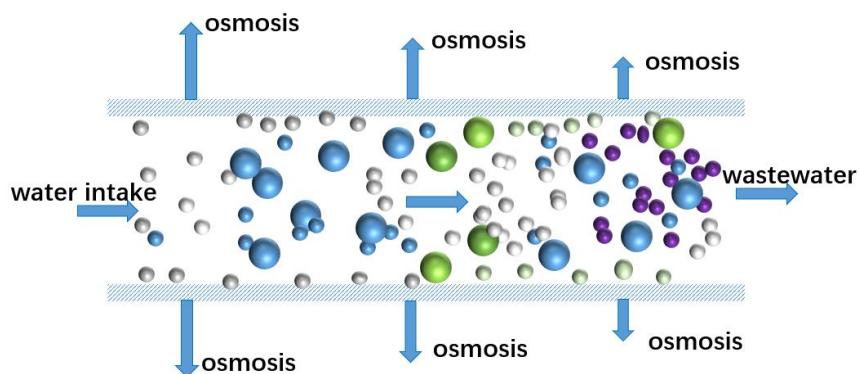


Figure 3. Membrane structure of microfiltration membrane

Nanofiltration (NF) membrane. Nanofiltration membrane began in the 1980s. Nanofiltration membrane is between ultrafiltration and reverse osmosis. Its retained molecular weight is in the range of 80~1000 and its pore size is several nanometers, so it is called nanofiltration. The forms of membrane modules include hollow fiber, spiral-wound type, plate-frame type and tube type. Hollow fiber or spiral-wound membrane modules are mostly used in nanofiltration system. The working principle of the nanofiltration membrane is shown in Figure 4.

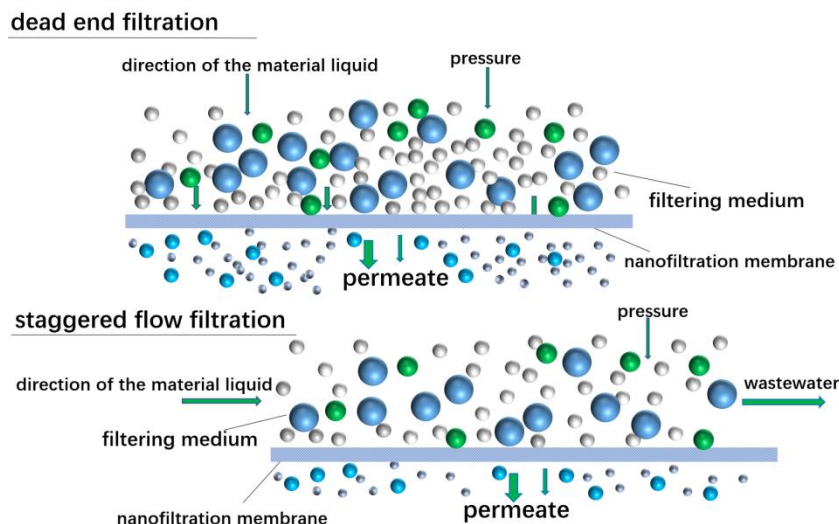


Figure 4. Schematic diagram of working principle of nanofiltration membrane

Ultrafiltration (UF) membrane. The ultrafiltration membrane began in the 1970s. With the pressure difference of 0.1~0.5 MPa as the driving force, the material particles with different sizes in the solution are separated by physical interception. Ultrafiltration has a good effect on the removal of particles, colloids, bacteria, pyrogens and various organic substances in water. The working principle of ultrafiltration membrane is shown in figure. 5.

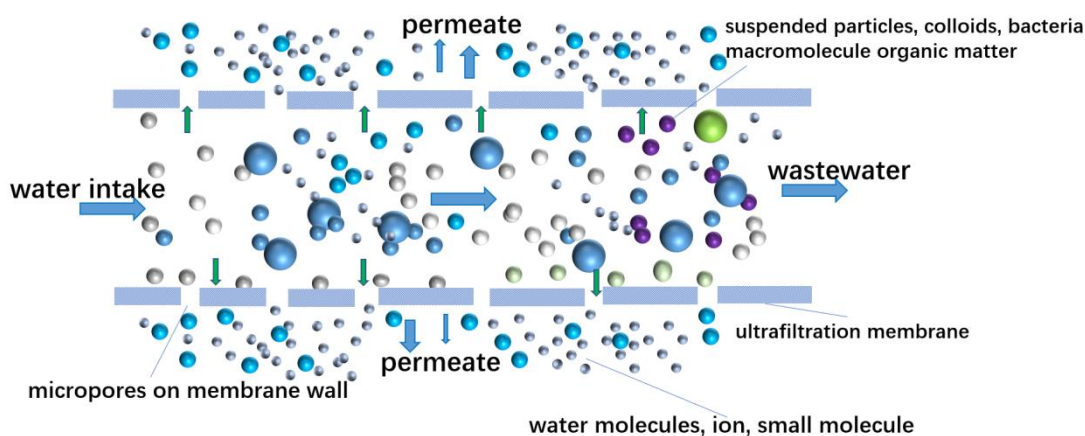


Figure 5. Schematic diagram of working principle of ultrafiltration membrane

Reverse osmosis (RO) membrane. Reverse osmosis membrane began in 1960. Reverse osmosis technology is powered by pressure difference, which is higher than the osmotic pressure of the solution, and leaves these substances and water based on the nature that other substances cannot pass through the semi-permeable membrane. Reverse osmosis membrane can effectively remove dissolved salts, colloids, microorganisms, organic matter and other substances from water because of its very small membrane pore size. It has the advantages of low energy consumption, no pollution, simple process and easy

operation. The membrane structure of reverse osmosis is shown in figure. 6.

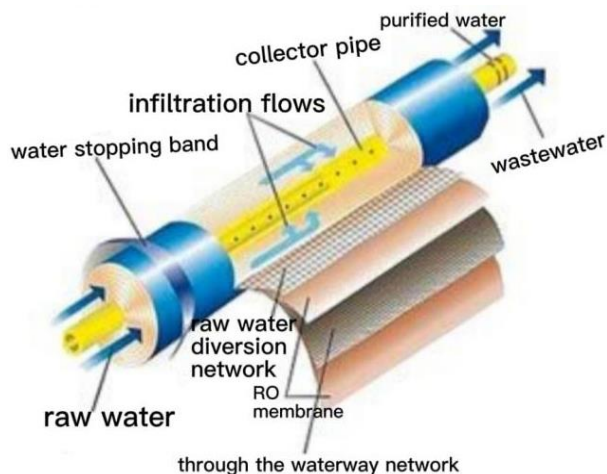


Figure 6. Membrane structure of reverse osmosis

The advantages and disadvantages of each membrane to treat environmental pollution are shown in table 6.

Table 6. Advantages and disadvantages of each membrane for environmental pollution treatment

Membranes	Advantages	Disadvantages	References
MF	low cost, high filtration accuracy, strong reliability, not easy to produce secondary pollution, good treatment effect	small particle discharge volume and short cleaning cycle; Pre-filtration is required	[41] Chen et al., 2020 [42] Meng et al., 2016 [43] Zhan, 2019
NF	high processing output, low loss, compact structure, small footprint, low energy consumption, recycling, simple operation, can realize automatic operation, good stability, convenient maintenance	chlorine cannot be removed and requires pre-treatment and periodic replacement and cleaning of the membrane assembly	[44] Nuray et al., 2018
UF	small footprint, high efficiency, convenient operation; the sludge produced by air float is dry and not easy to decay. the amount of oxygen in the water increases	high energy consumption; easy to plug, equipment maintenance management workload is large; scum exposed to water, susceptible to wind, rain and other weather factors	[45] Santra et al., 2020 [46] Shaik et al., 2021 [43] Zhan, 2019
RO	no phase change, normal temperature operation, simple equipment, high efficiency, less occupation, convenient operation, less energy consumption, wide range of adaptation, high degree of automation and good effluent quality	membrane easy oxidation pollution, membrane separation performance	[47] Pei et al., 2019

4.2 The treatment of Residual Antibiotics in Environment by Membrane bioreactor

Membrane bioreactor began in the 1920s and 1930s. It combined biological reaction with membrane separation. Under the condition of sufficient oxygen supply, it used microorganisms such as bacteria, protozoa, and epigenetic animals attached to the filler or carrier to remove organic substances in wastewater. Membrane separation was used as a medium to replace the conventional gravity precipitation solid-liquid separation to obtain the effluent, so as to purify the wastewater. At present, it has been widely used in various fields of wastewater treatment. The schematic diagram of biofilm treatment of wastewater is shown in Figure 7.

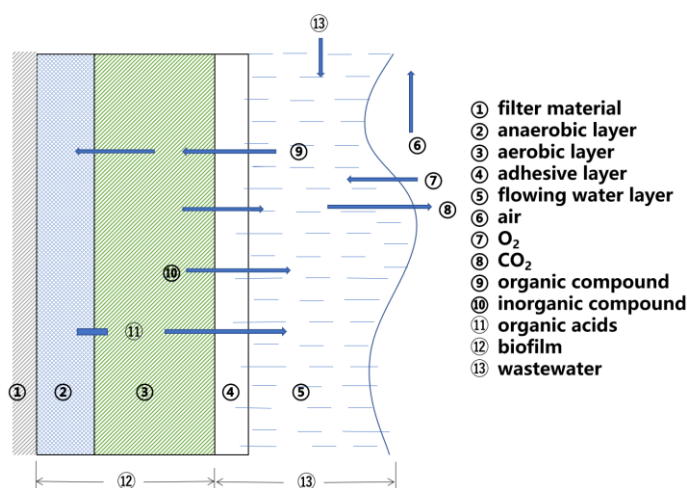


Figure 7. Principle diagram of biofilm treatment of wastewater

Compared with other membrane methods, membrane bioreactor has become a research hotspot in the removal of residual antibiotics in the environment because of its advantages of stable operation, strong impact load resistance, economy and energy saving, less residual sludge and simple equipment upgrading. When it is used to remove residual antibiotics in the environment, membrane bioreactor is often used in combination with other removal methods.

(1) Removal of tetracycline by MBR. Taskan (2016) et al. used a hydrogen-based membrane biofilm reactor method to achieve 80% to 98% removal at an HRT of 10 h and H₂ gas pressure of 6 psi (0.41 atm), with removal dominated by biodegradation [48]; Nguyen et al. used hollow fiber (HF) sponge MBR and flat plate (FS) sponge MBR. The removal efficiency of the two processing processes was about 100%, but compared with flat plate (FS) sponge MBR, hF-sponge MBR had lower pollution. The removal of tetracycline by both processes was mainly sludge adsorption and biodegradation [49]; Song et al. used the biofilm-membrane bioreactor (BF-MBR) to achieve the highest removal efficiency of 81.7% when the system was run twice on the 106th day, which was higher than that of traditional MBR. According to the survey that the BF-MBR method was based on biofilm adsorption and biodegradation for antibiotic removal [50]. The consequence display that the eliminating of antibiotics by BF-MBR was mainly by biofilm adsorption and biodegradation [50]; Raghavan et al. used a permeable membrane bioreactor method with a maximum efficiency of 99%, and the removal mechanism was biodegradation

[51]; Taskan et al. used the membrane aeration biofilm reactor (MABR) method with a maximum TC removal rate of 63% at an HRT of 18 h and 0.41 bar air pressure, and removing mechanism was biodegradation [52]; Xu et al. used sequencing batch membrane bioreactor (SMBR), and the removal efficiency was higher than 90%. The removal mechanism was biodegradation, sludge adsorption and membrane retention [53]; Wang et al. used UCPS-TiO₂ composite biofilm method, and the removal rate of tetracycline reached 82% under visible light. The removal mechanism was membrane adsorption, biodegradation and TiO₂ oxidation [54]; It can be seen that membrane bioreactors and different process combinations showed high removal rates of tetracycline, with hollow fiber (HF) sponge MBR method and flat plate (FS) sponge MBR method being the most effective. In these processes, biodegradation plays a key role, while membrane interception and sludge adsorption also to be pivotal in the removal of tetracycline. The elimination factor and mechanism of residual tetracycline in the environment by MBR are shown in table 7.

Table 7. The elimination factor and mechanism of residual tetracycline in the environment by MBR

Handling Method	Detection of Antibiotics Types	Maximum Removal Efficiency (%)	Removal Mechanism	References	
HBMBR	TC	80~98	biodegradation	[48] Taskan et al., 2016	
HFSMBR		100	sludge adsorption、biodegradation	[49] Nguyen et al., 2017	
FSSMBR					
BF-MBR		81.7	membrane adsorption、biodegradation	[50] Song et al., 2017	
Osmotic membrane bioreactor		99	biodegradation	[51] Raghavan et al., 2018	
MABR		63	biodegradation	[52] Taskan et al., 2019	
SMBR		90	biodegradation、sludge adsorption、Membrane interception	[53] Xu et al., 2019	
UCPS-TiO ₂ composite biofilm		82	membrane adsorption、biodegradation、TiO ₂ oxidation	[54] Wang et al., 2020	

(2) Removal of ciprofloxacin by MBR. Gustavo et al. used MBR to remove ciprofloxacin,, and the removal efficiency was 88.7%, and the removal mechanism was biodegradation [55]. Nguyen et al. used hollow fiber (HF) sponge MBR and flat plate (FS) sponge MBR respectively. The removal efficiencies of the two processes were 76%~93% and 54%~70%, respectively. However, HF-sponge MBR had lower membrane fouling and the removal mechanisms were sludge adsorption and biodegradation [56]. Raghavan et al. used the osmotic membrane bioreactor for removal, and the maximum removal efficiency was 99.9%. The removal mechanism was spatial steric hindrance, electrostatic interaction and hydrophobic interaction between compounds and membranes [57]. Vo et al used ozone coupled sponge-membrane bioreactor, and the removal rate was greater than 80%, and the removal mechanism was membrane adsorption, biodegradation and ozone oxidation [58]. Mai et al. used anaerobic membrane bioreactor (AnMBR), when the concentration of CIP was 0.5~1.5 mg/L, CIP elimination factor was 50%~76%, CIP removal was mainly dependent on biodegradation [59]. The

combination of membrane bioreactors to remove CIP played a dominant role in biodegradation, as did tetracycline elimination. However, it was found that steric hindrance, electrostatic interaction and hydrophobic interaction between compounds and membranes also played a role. The elimination factor and mechanism of residual ciprofloxacin in the environment treated by MBR are shown in table 8.

Table 8. Elimination Factor and mechanism of residual ciprofloxacin in the environment by MBR

Handling Method	Detection of Antibiotics Types	Maximum Removal Efficiency (%)	Removal Mechanism	References
MBR		88.7	biodegradation	[55] Gustavo et al., 2017
HFSMBR		76~93	sludge adsorption, biodegradation	[56] Nguyen et al., 2017
FSSMBR		54~70		
Osmotic membrane bioreactor	CIP	99.9	steric hindrance, electrostatic interaction, hydrophobic interaction between compound and membrane	[57] Raghavan et al., 2018
Process of sponge-membrane bioreactor combined with ozone oxidation		>80	membrane adsorption, biodegradation, O ₃ oxidation	[58] Vo et al., 2019
AnMBR		50~76	biodegradation	[59] Mai et al., 2019

(3) Sulfadiazine removal studies were mainly focused on, Song et al. used the biofilm-membrane bioreactor (BF-MBR) to remove sulfadiazine, and the maximum removal efficiency was 94.9% when the biofilm-membrane bioreactor (BF-MBR) was run twice on the 106th day, higher than the conventional MBR [50]. The consequence showed that the BF-MBR was mainly used for antibiotics removal by biofilm adsorption and biodegradation [50]; Yu et al. removed sulfadiazine using a novel sponge plastic biological carrier (SPSMBR) aerobic sink membrane bioreactor method with 91% removal efficiency and the removal mechanism was biodegradation [60]; Xu et al. used sequencing batch membrane bioreactor (SMBR), and the removal efficiency was greater than 90% and the removal mechanism was biodegradation, sludge adsorption and membrane retention [61]; Peng et al. used a novel microalgae biofilm-membrane photobioreactor (BF-MPBR) method to remove sulfonamide antibiotics from mariculture wastewater with 61.0%~79.2% removal efficiency, and the removal mechanism was biodegradation [62]; Arlen et al. used membrane bioreactor-ozone oxidation (MBR-O₃), and the removal efficiency was 100%. The removal mechanism was biodegradation and ozone oxidation [63]. Zhang et al. used the moving bed biofilm reactor-membrane bioreactor (MBBRMBR) system, under the conditions of SDZ concentration of 0.5 mg/L and high carbon nitrogen ratio of 9, the removal efficiency of SDZ was 75% [64]; Li et al. adopted a novel electrochemical membrane biofilm reactor (EMBFR) method, and the elimination efficiency was 94.9% [65]. The removal mechanism was the synergistic effect of electrochemical process and biological process [65]. It can be seen that the membrane bioreactor combined with different processes has a high removal rate of sulfadiazine, and the membrane bioreactor-

ozonation method has the most obvious effect. Biodegradation plays a critical role in these processes, and sludge adsorption, membrane interception and ozone oxidation also play a certain role in the removal of sulfadiazine. The elimination factor and mechanism of sulfadiazine residues in the environment by MBR are shown in table 9.

Table 9. Elimination Factor and mechanism of sulfadiazine residues in the environment by MBR

Handling Method	Detection of Antibiotics Types	Maximum Removal Efficiency (%)	Removal Mechanism	References
BF-MBR		94.9	membrane adsorption, biodegradation	[50] Song et al., 2017
SPSMBR		91	biodegradation	[60] Yu et al., 2018
SMBR		>90	Biodegradationm, membrane interception	[61] Xu et al., 2019
BF-MPBR	SDZ	61.0~79.2	biodegradation	[62] Peng et al., 2020
MBR-O ₃		100	Biodegradation, Ozonation	[63] Arlen et al., 2020
MBBRMBR		75	biodegradation	[64] Zhang et al., 2020
EMBFR		94.9	synergistic effects of electrochemical, biological processes	[65] Li et al., 2021

5. CONCLUSIONS AND PERSPECTIVES

5.1. Conclusions

Antibiotics have been detected in a variety of environmental media. The environmental pollution and human life and health problems caused by antibiotics can't be ignored. Therefore, the removal of antibiotics is urgent. Advanced oxidation methods in chemical methods have the advantages of rapid reaction and high removal efficiency, which are of great advantage in the removal of antibiotics. Among them, the single electrochemical oxidation method with new materials as electrodes and the coupling of electrochemical oxidation and biodegradation techniques to obtain the process are significant for the removal of antibiotics. The membrane method has the advantages of high separation efficiency, single equipment cylinder, easy operation, no phase change, and energy saving. It has irreplaceable advantages in the removal of antibiotics. One of them is membrane bioreactor, a new and efficient wastewater treatment technology that can effectively treat residual antibiotics in the environment and has a very important role in the green and sustainable development of society.

5.2. Perspectives

Although there have been many studies on electrochemical and membrane methods, the chemical method still suffers from high energy consumption, rapid electrode consumption, and high operating costs, and the membrane method still suffers from membrane contamination, expensive membrane module materials, and high treatment costs. Therefore, in the research of using electrochemical methods to remove antibiotics from water environment, the development of new electrode materials with low resistance, high current efficiency, and low cost and the process of coupling electrochemical oxidation technology with biodegradation technology will be the direction of effort for removing antibiotics from the environment by the electrochemical oxidation method in the future. The development of cheap, anti-pollution membrane materials and high efficiency, low energy consumption, high life and intelligent membrane combined processes will be an important research direction for the membrane treatment of residual antibiotics in the environment.

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