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Review

Degradation of Antibiotics via UV-Activated Peroxodisulfate or Peroxymonosulfate: A Review

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Abstract: The ultraviolet (UV)/H_2O_2, UV/O_3, UV/peroxodisulfate (PDS) and UV/peroxymonosulfate (PMS) methods are called UV-based advanced oxidation processes. In the UV/H_2O_2 and UV/O_3 processes, the free radicals generated are hydroxyl radicals (•OH), while in the UV/PDS and UV/PMS processes, sulfate radicals ($SO_4^{\bullet-}$) predominate, accompanied by •OH. $SO_4^{\bullet-}$ are considered to be more advantageous than •OH in degrading organic substances, so the researches on activation of PDS and PMS have become a hot spot in recent years. Especially the utilization of UV-activated PDS and PMS in removing antibiotics in water has received much attention. Some influencing factors and mechanisms are constantly investigated and discussed in the UV/PDS and UV/PMS systems toward antibiotics degradation. However, a systematic review about UV/PDS and UV/PMS in eliminating antibiotics is lacking up to now. Therefore, this review is intended to present the properties of UV sources, antibiotics, and PDS (PMS), to discuss the application of UV/PDS (PMS) in degrading antibiotics from the aspects of effect, influencing factors and mechanism, and to analyze and propose future research directions.

Keywords: ultraviolet radiation; peroxodisulfate; peroxymonosulfate; antibiotics; sulfate radical; hydroxyl radical

Citation: Song, T.; Li, G.; Hu, R.; Liu, Y.; Liu, H.; Gao, Y. Degradation of Antibiotics via UV-Activated Peroxodisulfate or Peroxymonosulfate: A Review. *Catalysts* **2022**, *12*, 1025. https://doi.org/10.3390/catal12091025

Academic Editor: Wenhui Wang

Received: 24 August 2022
Accepted: 7 September 2022
Published: 9 September 2022

1. Introduction

In recent years, multiple antibiotics have been detected gradually in surface water due to the abuse of antibiotics and the unintentionally discharge of effluents from wastewater treatment plants (WWTPs), pharmaceutical factories, hospitals and livestock farms [1]. Although the conventional secondary biological treatment processes in the WWTPs can remove part of antibiotics, the concentration of antibiotics in the secondary treated effluents remains in the range of 10–1000 ng L^{-1} [2]. Continuous discharge of antibiotics into the receiving water can promote the propagation of resistant bacteria and pose a potential threat to human health through drinking water and the food chain [3]. Since antibiotics are difficult to be biodegraded, it is urgent to use more efficient methods than biological methods to degrade antibiotics in water.

Advanced oxidation processes (AOPs) based on hydroxyl radicals (•OH) and sulfate radicals ($SO_4^{\bullet-}$) are currently considered as effective methods to deal with refractory antibiotics [4]. Furthermore, $SO_4^{\bullet-}$ has shown excellent ability for the degradation of antibiotics since $SO_4^{\bullet-}$ has a higher oxidation potential (E^0 = 2.5–3.1 V) and a longer lifetime (t = 30–40 μs) than that of •OH (E^0 = 2.8 V, t = 0.02 μs) [5]. The oxidant persulfate, including peroxodisulfate (PDS, $S_2O_8^{2-}$) and peroxymonosulfate (PMS, HSO_5^-), can be employed to generate $SO_4^{\bullet-}$ in water under the presence of activators that may be ultraviolet (UV), ultrasound (US), heat, microwave (MW), transition metals (Fe^{2+}, Cu^{2+}, Co^{2+}), and carbon materials (activated carbon, biochar) [6]. The corresponding activation mechanism is depicted

in Figure 1. The chemical reactions involved in these activation processes are described in Equations (1)–(6). The principles of UV, US, MW and traditional heat activation of PDS or PMS are consistent. During these activation processes, external energy exceeding the bond energy of peroxy bonds (140–213.3 kJ/mol) [6] is applied to break the peroxy bond of PDS or PMS, thereby generating sulfate radicals or hydroxyl radicals (Equations (1) and (2)) [7]. The activation of transition metal ions for PDS or PMS is based on the reducibility of metals that reduce PDS or PMS to sulfate radicals and byproducts, while the valence state of the metal ions increased (Equations (3) and (4)) [8]. For the activation of PDS and PMS via carbon materials, the mechanism is related to electron transfer. Both PDS and PMS gain electrons to generate sulfate radicals (Equations (5) and (6)) [9]. Among these methods of activating PDS (PMS), UV radiation is considered an effective and pollution-free approach for PDS (PS) activation. Scholars have conducted studies on UV-activated PDS (PMS) to treat some antibiotics in water, and investigated the influencing factors, removal effect and reaction mechanism in UV/PDS (PMS) systems. There are several reviews on UV-generated •OH to degrade organics [10–13]. In addition, Pirsaheb et al. [14] summarized the UV/PDS in degrading antibiotics in water. However, there is no systematic review on UV-activated PMS and PDS toward antibiotics degradation in water.

$$S_2O_8^{2-} \xrightarrow{\text{UV, US, MW, Heat}} 2SO_4^{\bullet-} \quad (1)$$

$$HSO_5^- \xrightarrow{\text{UV, US, MW, Heat}} SO_4^{\bullet-} + \bullet OH \quad (2)$$

$$S_2O_8^{2-} + M^n \rightarrow M^{n+1} + SO_4^{\bullet-} + SO_4^{2-} \quad (3)$$

$$HSO_5^- + M^n \rightarrow M^{n+1} + SO_4^{\bullet-} + OH^- \quad (4)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} \quad (5)$$

$$e^- + HSO_5^- \rightarrow SO_4^{\bullet-} + OH^- \text{ or } \bullet OH + SO_4^{2-} \quad (6)$$

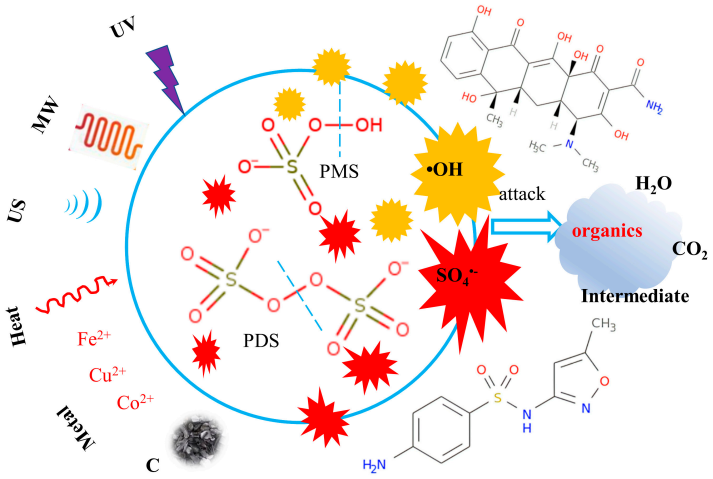


Figure 1. Various activation methods for PDS and PMS.

In this review, we summarized the types and characteristics of UV light sources (natural source and artificial sources), expounded the classes and chemical structures of common antibiotics in water, analyzed the mechanism of UV-activated PDS(PMS) on the degradation of various antibiotics, and explored several influencing factors (reactor, UV intensity, oxidant concentration, solution pH, anions) in UV/PDS(PMS) systems toward antibiotics removal. Finally, we conducted a deep analysis of the current problems and future research in order to promote the application of UV/PDS(PMS) systems in the treatment of antibiotic-contaminated wastewater.

2. Sources of UV

2.1. The Solar Radiation

Sunlight broadly refers to the electromagnetic radiation from all spectrums of the sun. The spectrum of solar radiation is divided into ultraviolet rays (UV, 100–400 nm), visible light (400–700 nm) and infrared radiation (700–10^6 nm) according to the wavelength [15]. UV rays only make up about 5% of terrestrial sunlight. Sunlight is an inexpensive source of UV rays, and the use of UV to drive advanced oxidation reactions for the purification of contaminants in water is an active area of research. However, there are disadvantages of complicated equipment and insufficient light energy in utilizing the natural UV rays. Therefore, the use of visible light-responsive catalysts to treat organic matter in water has also received more attention. For instance, photocatalysts V_2O_5, $LaVO_4$, $BiVO_4$, Bi_2MoO_6, Bi_2WO_6, $MoS_2/MoO_3/TiO_2$, and Ag_3VO_4 are very effective in dealing with some refractory organic matters under visible light irradiation [16–20]. However, PDS and PMS can be activated by UV instead of visible light without photocatalysts. Another way to utilize visible light is to combine visible light catalysis with sulfate radical advanced oxidation.

2.2. Artificial UV Sources

Compared with the natural UV source, the advantage of the artificial UV sources is that the parameters of UV light, such as wavelength and radiation dose, can be adjusted according to the needs of the reaction. The UV spectrum can be divided into three different spectral regions based on the wavelength: UVC (100–280 nm), UVB (280–315 nm) and UVA (315–400 nm) in water treatment process. UVC spectrum has been employed extensively for UV range of water disinfection since microbial cells are more likely to absorb UVC photons. Some UVC light sources are also used for wastewater treatment, such as low-pressure mercury vapor lamps (LPUV), medium-pressure mercury vapor lamps (MPUV), high-pressure mercury vapor lamps (HPUV), UV light-emitting diodes (UV-LED), and far-UVC radiating excimer lamps [15,21]. The properties of these artificial UV light sources are described in Table 1 [22,23]. The main UV sources for current UV assist systems in water treatment are LPUV and MPUV. However, there are also problems in the application of mercury lamp. On the one hand, the mercury lamp is fragile, and the mercury in it leaks into the environment, which is difficult to dispose of. On the other hand, mercury lamp needs high power input and short service life [15,23]. As a new UV light source, UV-LED has received much attention. LED lamps use the p-n junction formed by holes and electrons of semiconductor materials to emit UV radiation. Different semiconductor materials emit different wavelengths. The commonly used semiconductor materials include gallium nitride (GaN, 365 nm), aluminum nitride (AlN, 210 nm) and aluminum nitride (AlGaN, 210–365 nm) [23,24]. LEDs have the advantages of variable radiation wavelength, firm lamp, low energy consumption, long service life, fast start and frequent opening and closing [24]. The optically filtered xenon arc lamp is a classic solar simulator, and has a smooth continuous spectrum in the UV, visible and infrared region. Optical filters and dichroic mirrors are used to shape the unwanted spectrum. The xenon lamp can produce pulsed UV, which has more instantaneous energy than continuous UV. The irradiation field of xenon arc lamp is limited to less than 15 cm × 15 cm. When the field is increased, the irradiance will be insufficient for application [25]. A far-UVC light (200–230 nm) is generated by fltered excimer lamps such as krypton chloride (KrCl) excimer lamps [26]. This Far-UVC lamp filtered to minimize ultraviolet emissions at wavelengths longer than 230 nm, is less harmful to human skin and eyes than traditional ultraviolet lamp (254 nm) [27,28].

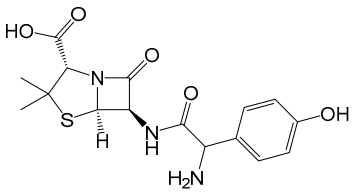
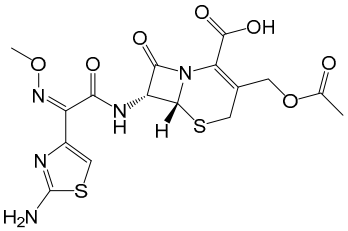
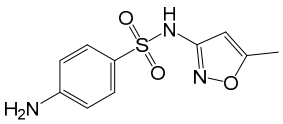
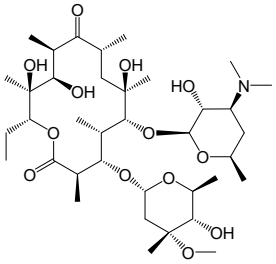
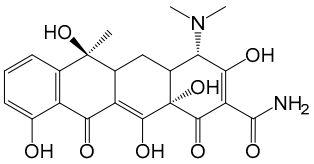
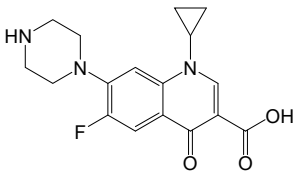
Table 1. Artificial UV sources and their properties.

UV Sources	Pressure (Pa)	Wavelength (nm)	Wall Plug Efficiency (%)	Life Time(h)	Electrical Input(W)	Operating Temperature (°C)
LPUV	1–10	Monochromatic 254	35–38	8000–10,000	8–100	40
MPUV	10–100	Polychromatic 200–500	10–20	4000–8000	100–60,000	600–900
HPUV	100–10^5	315–450	-	1000	100–25,000	-
UV-LED	-	Any from 240	75	100,000	Up to 1	Same as process water
Xenon lamps	19,000–26,600	Pulsed UV, 100–1000	-	1000	75–6000	-
Far-UVC excimer lamps	-	200–230	-	3000–10,000	20	-

3. Characteristics of Antibiotics

Antibiotics in the water environment come from the discharge of WWTPs, agricultural livestock and poultry farming wastewater. Antibiotics degrade slowly in the aquatic environment, can be adsorbed by soil and sediments in the water, and exist in the form of particles and colloids that might enter the water purification plant as a component of water source [29]. Therefore, antibiotics pose a greater risk to human health if they are present in aquatic environment with high concentration. Antibiotics produce antibacterial effects by interfering with the physiological and biochemical metabolic processes of pathogenic microorganisms. According to chemical structures, antibiotics are divided into the following categories: β-lactams, sulfonamides, monobactams, carbapenems, aminoglycosides, glycopeptides, lincomycin, macrolides, polypeptides, polyenes, rifamycin, tetracyclines, chloramphenicol, quinolones and fluoroquinolones [30,31]. Due to the large population in China, the use of antibiotics is very considerable. β-lactams (β-Ls), macrolides (MLs), sulfonamides (SAs), quinolones (QNs) and tetracyclines (TCs) are the most frequently used antibiotic compounds for human and veterinary treatments in China [32]. Table 2 gives details of these antibiotics. It can be seen that these antibiotics all contain complex groups, thus it is difficult for them to be degraded by some conventional treatment processes (biological treatment, adsorption, filtration, etc.). Advanced oxidation has a suitable degradation effect on these different types of antibiotics. Through the attack of free radicals, these antibiotics are opened, chain-broken, and turned into medium and small molecules of organic matter, which can finally be converted into CO_2 and H_2O. Since various antibiotics have different molecular weights and molecular structures, the optimal operating parameters required in advanced oxidation processed to achieve complete mineralization are necessarily different. These parameters mainly include the concentration of the oxidants, the amount of the activators, the environmental conditions of the water (pH value, ion concentrations, temperature), and the oxidation time. Therefore, the regulation of reaction parameters is crucial for the mineralization of antibiotics.

Table 2. Common antibiotics in water and their chemical structures.

Antibiotics (Representative Drugs)	Structural Features	Chemical Structures of Representative Drugs
β-Ls (penicillins: penicillin G, penicillin V, amoxicillin, ampicillin. cephalosporins: cefotaxime, ceftizoxime, ceftriaxone, ceftazidime, cefpirome, cefazolam)	Of the β-Ls antibiotics that are currently available, all feature the reactive β-lactam ring system, a highly strained and reactive cyclic amide [33]. Penicillins possess a basic bicyclic structure, 6-aminopenicillanic acid or 6-APA. The β-lactam ring of cephalosporins is fused to a seven-membered ring (7-aminocephalosporanic acid or 7-ACA).	 Amoxicillin  Cefotaxime
SAs (sulfamethoxazole, sulfamethazine, sulfadiazine, sulfadimethoxine, sulfamethoxypyridazine, sulfapyridine, sulfadiazine)	SAs contain a 4-aminobenzene sulfonamide core and differ from each other in theN-substituent of the sulfonamide linkage [34].	 Sulfamethoxazole
MLs (clarithromycin, erythromycin, roxithromycin, spiramycin, tylosin)	MLs have various amino sugars attached to one macrolide ring, which can be classified according to the number of carbon atoms in the macrocycle, such as 14-, 15- and 16-membered-ring compounds [35].	 Erythromycin
TCs (tetracycline, chlortetracycline, doxycycline, oxytetracycline)	TCs all contain a tetraphenyl skeleton.	 Tetracycline
QNs (ofloxacin, ciprofloxacin, norfloxacin)	The basic structure of QNs is a quinolone ring to which fluorine and other substituents are added to produce fluoroquinolones [36].	 Ciprofloxacin

4. Mechanisms of Activated PDS (PMS) with UV

PDS or PMS is the precursor of $SO_4^{\bullet -}$. PDS has a symmetric structure, while PMS has an asymmetric structure (Figure 2). PDS includes three salts, potassium PDS, sodium PDS and ammonia PDS. Among them, potassium PDS and sodium PDS are often used for advanced oxidation processes, while ammonium PDS is not commonly used due to the pollution of water by ammonium ions [6]. The PMS commercially available is Oxone,

which is cheap and stable in chemical properties [37]. The properties of PDS and PMS are shown in Table 3.

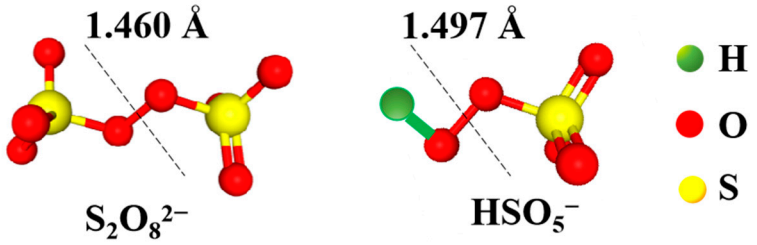


Figure 2. Chemical structures of $S_2O_8^{2-}$ and HSO_5^-.

Table 3. Properties of PDS and PMS.

Chemical Name	CAS Number	Formula	Molecular Weight ($g \cdot mol^{-1}$)	O-O Bond Dissociation Energy ($kJ \cdot mol^{-1}$)	Color	Solubility (20 °C) ($g\ L^{-1}$)	Redox Potential (V)
Sodium PS	7775-27-1	$Na_2S_2O_8$	238.10	92	White to yellow	550	2.01
Potassium PS	7727-21-1	$K_2S_2O_8$	270.32	92	White	520	2.01
ammonium PS	7727-54-0	$(NH_4)_2S_2O_8$	228.20	92	White to yellow	582	2.01
PMS (Oxone)	37222-66-5	$H_3K_5O_{18}S_4$	614.74	377	White	>250	1.82

UV radiation is considered to be a green and efficient way for activating PDS and PMS to generate free radicals in degrading organic pollutants in water. Several mechanisms can explain the activation of PDS and PMS by UV. One is the splitting O-O bond of PMS or PDS based on the energy input by the UV, resulting in the generation of $SO_4^{\bullet -}$ and •OH (Equations (7) and (8)) [38,39]. The second is that UV can excite water molecules to produce electrons (Equation (9)), which activate PDS or PMS to generate sulfate radical through electron conduction [14,37,40,41]. In addition, H_2O can also be directly decomposed into •OH by UV photolysis (Equation (10)) [41]. Therefore, UV/PMS or UV/PDS process can degrade organic compounds either by photolysis directly or by $SO_4^{\bullet -}$ and •OH indirectly (Equation (11)) [37].

$$S_2O_8^{2-} \xrightarrow{UV} 2SO_4^{\bullet -} \quad (7)$$

$$HSO_5^- \xrightarrow{UV} SO_4^{\bullet -} + \bullet OH \quad (8)$$

$$H_2O \xrightarrow{UV} \bullet OH + H^+ + e^- \quad (9)$$

$$H_2O \xrightarrow{UV} \bullet OH + H^{\bullet} \quad (10)$$

$$SO_4^{\bullet -} + \bullet OH + \text{organics} \rightarrow \text{by-products} + SO_4^{2-} + H_2O + CO_2 \quad (11)$$

5. Application of UV/PDS (PMS) in Degradation of Antibiotics

5.1. Reactors for UV-Activated PDS (PMS) Systems

Since the studies on UV-activated PDS (PMS) to degrade antibiotics are still limited to the experimental stage, the experimental devices currently used are mainly batch reactors. Three types of batch reactors are summarized in Figure 3. The containers for the water samples in Figure 3a [42] can be three beakers (for parallel samples) or self-made containers with certain volumes. The containers are placed on magnetic stirrers, and the reactions were carried out at a certain speed. The UV lamps are suspended a few centimeters above beakers, and the radiation intensity and time are adjusted according to the needs of the reaction. This kind of reactor is simple, convenient for dosing and sampling, and suitable for the treatment of a small amount of antibiotic solution. The reactor [43] similar to

Figure 3a was used in the UV-LED/PMS/chloramphenicol system, and the operation processes were not much different. The reactor of Figure 3b [44] is slightly improved on the basis of Figure 3a, that is, the UV lamps are immersed into water to carry out the reaction. A quartz protective cover on the outside of the lamp tube was used to prevent the inner lamp from being damaged by water. The advantage of this arrangement is that the UV light can radiate water samples at close range, and the radiation intensity of the lamp is relatively uniform. Malakootian and Asadzadeh [45] carried out tetracycline degradation via this kind of reactor in UV/PDS system. Lin and Wu [46] utilized similar reactor in removing ciprofloxacin by UV/PDS process, and nitrogen protection was carried out during the reaction. The reaction apparatus of Figure 3c [47] is a little more complicated than that of Figure 3a,b. This kind of reactor adopts double walls, the outer space is used as a channel for cooling water, and the inner space is used for chemical reaction. The purpose of cooling is to maintain the reaction temperature constant at preset temperature (such as 20 °C). Without cooling control, the aqueous solution may heat up to a certain extent with the increase in UV irradiation time, which may affect the accuracy of the experiment. Similar reactors with cooling devices were utilized in the studies of treatment chloramphenicol [48], penicillin G [49], and ciprofloxacin [50] by UV/PDS system. Although the above-mentioned three reactors can meet the needs of small-scale water treatment in the laboratory, continuous flow reactors also need to be developed to move the UV/PDS (PMS) process toward large-scale applications. UV-LED lamps are easy to assemble, and the radiation area of the lamps can be controlled according to the amount of water, which may be comparable to mercury types in the future.

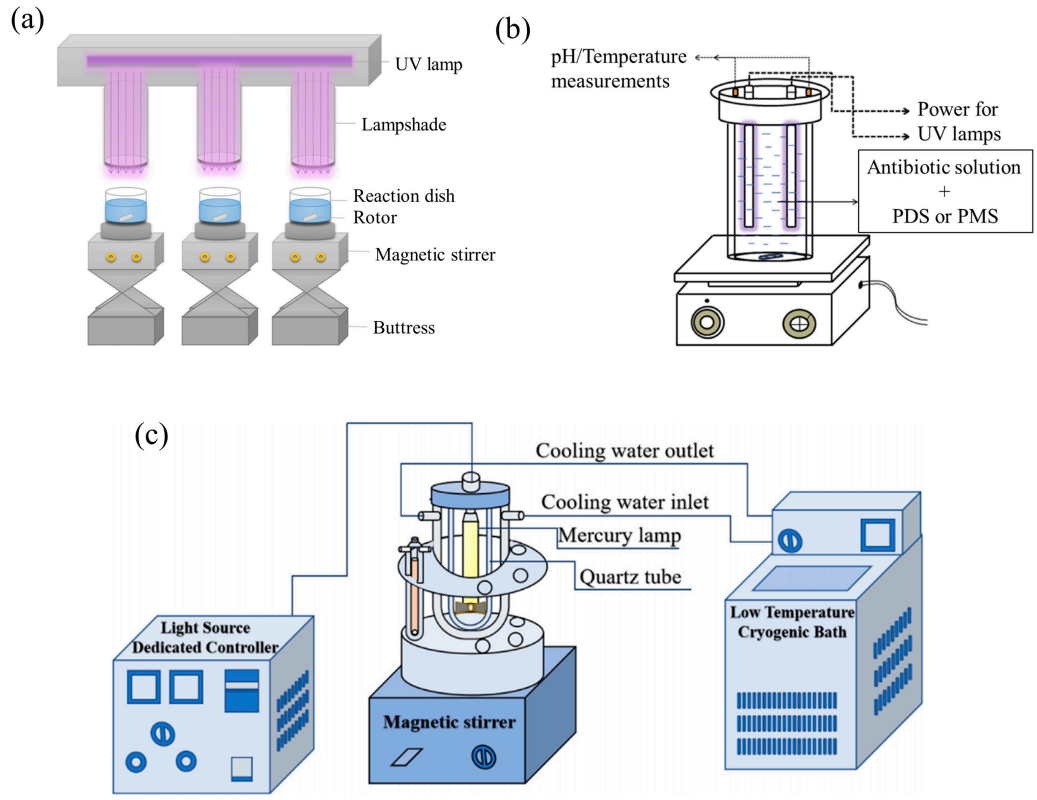


Figure 3. Several reactors for UV/PDS(PMS) in degrading antibiotics. (**a**) horizontal lamps [42]. Copyright (2020), with permission. From Elsevier. (**b**) vertical immersion [44]. Copyright (2018), with permission from Elsevier. (**c**) cooling double walls [47]. Copyright (2020), with permission from Elsevier.

5.2. Comparison of UV/PDS and UV/PMS Treatment Effects

There is no doubt that UV can activate PDS and PMS. However, UV-activated PDS can produce $SO_4^{\bullet-}$, while UV-activated PMS can produce both $SO_4^{\bullet-}$ and •OH. The difference in the free radicals generated determines the difference in the efficiency of

UV/PDS and UV/PMS in treating antibiotics, even under the same reaction conditions. Mahdi-Ahmed and Chiron [51] compared the degradation effect of ciprofloxacin (CIP) in distilled water and wastewater by UV/PDS and UV/PMS treatment under the conditions of [PDS] = [PMS] = 1.0 mM, [CIP] = 50 μm, pH = 7.0. The results showed that all kinetics were in agreement with first-order kinetic models, and the effect of PDS on CIP degradation (apparent kinetic rate constant k_{app} = 12.60 × 10^{-2} min^{-1}) in distilled water was better than that of PMS (k_{app} = 5.62 × 10^{-2} min^{-1}), while the effect in wastewater was opposite (for PMS, k_{app} = 5.64 × 10^{-2} min^{-1}; for PDS k_{app} = 2.62 × 10^{-2} min^{-1}). This showed that in the treatment of actual wastewater (from WWTP effluent: [TOC] = 50 mg/L, [NO_3^-] = 7.1 mg/L, [Cl^-] = 71 mg/L, [HCO_3^-] = 22 mg/L, conductivity= 919 μS cm^{-1}, [Fe] = 193.1 μg/L, [Cu] = 3.8 μg/L, [Zn] = 16.2 μg/L, [Co] = 0.4 μg/L), PMS was less affected by water quality conditions than PDS in removing CIP by UV irradiation. This may be due to the fact that the actual water quality conditions are more complex, which have different effects on the degradation of CIP by PMS and PDS with different physicochemical properties under UV irradiation. PMS with an asymmetric structure may be more susceptible to the auxiliary activation of some ions with certain concentrations (Cl^-, NO_3^-, Fe^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}) in wastewater than PDS with a symmetrical structure, thereby promoting the generation of free radicals. The effects of some ion species and concentrations on the degradation of antibiotics by UV/PDS and UV/PMS systems will be discussed in detail in Section 5.6. Ao and Liu [52] studied the effects of using MPUV to activate PMS and PDS to degrade sulfamethoxazole (SMX) on a batch scale experiment, and found that under the same reaction conditions ([SMX] = 23.69 μM; [PMS] = [PDS] = 1 mM; no pH adjustment), the degradation rates of SMX by UV, UV/PS, and UV/PMS were 89.0%, 97.5%, and 96.9%, respectively. Although SMX could be removed through direct photolysis, the addition of PDS and PMS further improved the removal rate of SMX. In this study, there was no significant difference in the removal rate of SMX between UV/PDS and UV/PMS. The research of Hu et al. [53] showed that based on the same reaction conditions ([tetracycline] = 9 mg/L; [PMS] = [PDS] = 0.5 mM; pH = 3.5; 25 W LPUV), the degradation effects of PMS, UV/PMS, PDS, and UV/PDS on tetracycline (TC) were 49.3%, 71.8%, 17.1%, and 40.7%, respectively. This result indicated that the effect of PMS on direct oxidation of TC was 32.2% higher than that of PDS, and the effect of UV/PMS on TC degradation was 31.1% higher than that of UV/PDS. From the above studies, it can be seen that the efficiency of UV/PDS and UV/PMS in removing antibiotics had a great relationship with the reaction conditions in the water. Different reaction conditions generate different free radicals and have different influencing factors to stimulate or inhibit the reaction.

5.3. Effect of UV Intensity

UV activation of PDS or PMS is an energy-based process where the activation effect is affected by the applied UV intensity via the reactor. Power-based unit mW·cm^{-2} for irradiance or energy-based unit J·cm^{-2} for dose have been employed in most publications to express UV intensity. The irradiance of the UV lamps can be monitored using a radiometer with a calibrated UV detector. The relationship between exposure time, dose, and irradiance is shown in Equation (12) [54]. The increase in UV dose was found to accelerate the degradation rate of antibiotics (chloramphenicol, sulfamethoxazole, sulfasalazine) in the UV/PDS systems [48,52,55]. Ghauch et al. [48] investigated chloramphenicol (CAP) degradation via UV/PDS system provided by an HPUV (254 nm) with an irradiance of 2.43 mW·cm^{-2} at a radial distance of 3.00 cm. When radiation energy increased from E10 (165 J) to E50 (874 J), the removal of CAP increased rapidly, and it reached complete degradation within 40 min under E50 energy (Figure 4a). When other conditions of the light source remain unchanged, the change of the lamp power can also be used to measure the change of the light intensity, and there is a positive correlation between them. Milh et al. [56] used LPUV lamps with different power (5, 9, 18 W) to investigate the influence of the UV intensity on the CIP degradation in a UV/PS process. They observed a steep increase in k_{obs} from 0.2051 min^{-1} at 5 W to 0.752 min^{-1} at 18 W. Zhang et al. [57]

found that the rate constant increased from 0.246 min^{-1} to 0.524 min^{-1} when the UV light power was increased from 220 W to 300 W in UV/PDS toward SMX removal (Figure 4b). Because the increased UV power enhanced the number of photons, more PDS was activated by light energy to produce free radicals to degrade antibiotics, as shown in Equation (7).

$$\text{Exposure time} = \frac{1000 \times \text{dose } (\text{J}\cdot\text{cm}^{-2})}{60 \times \text{irradiance } (\text{mW}\cdot\text{cm}^{-2})} \quad (12)$$

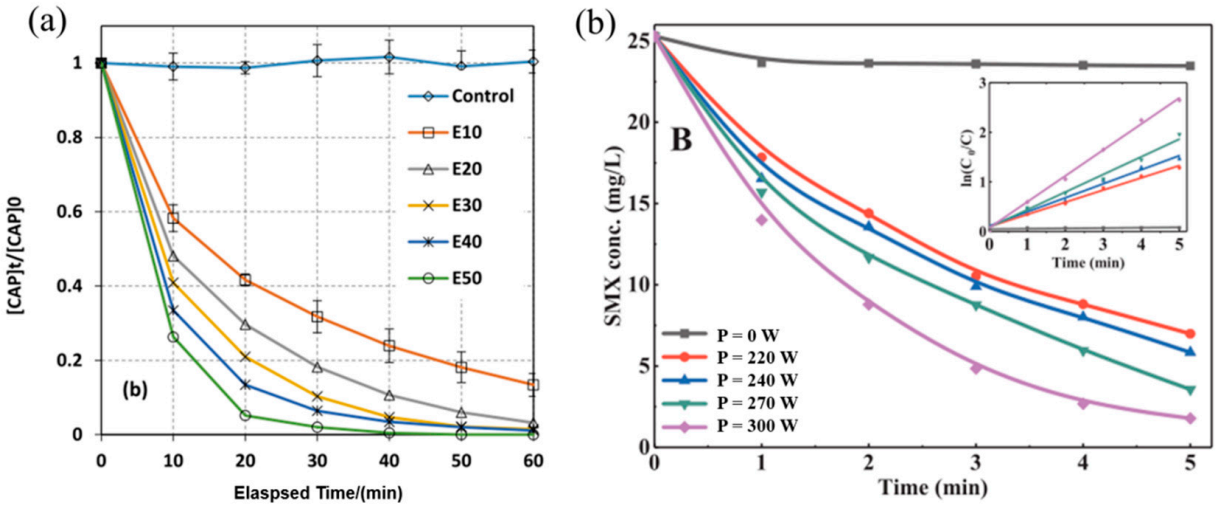


Figure 4. Effect of UV energy on the degradation of CAP and SMX (**a**) [CAP] = 31 μm; [PDS] = 0.25 mM [48]. (**b**) [PDS] = 2 mM; [SMX] = 0.1 mM; pH = 7.0 [57]. Copyright (2020), with permission from Elsevier.

It was reported that in the experiments of UV-activated PMS and PDS to degrade sulfamethoxazole (SMX), the increasing UV dose (from 0 to 200 mJ/cm^2) was positively correlated with the removal of SMX [52]. In addition, 97.5% and 96.9% of SMX were removed at the UV dose of 200 mJ/cm^2 in UV/PMS and UV/PDS, respectively. According to a previous study [6], the bond energy (O–O bond) of PDS is 140.0 kJ/mol, while the O–O bond energy of PMS is in the range of 140–213.3 kJ/mol. Therefore, at the same UV dose, PMS obtained a higher SMX removal rate than that of PDS, indicating that another factor than bond energy was responsible for this result. It is speculated that this is related to the initial pH value of the oxidant solutions and the hydrolysis conditions of SMX. In this study [52], the initial pH of PMS and PDS solution was 3.06 and 5.85, respectively. SMX possesses two pK_a values: pK_{a1} = 1.6 and pK_{a2} = 5.7. When pH values were between 1.6 and 5.7, most SMX was in a neutral molecular state, and its light-responsive ability was the strongest at this time [58]. The pH of the PMS solution was just in this range, thus providing a favorable condition for SMX. However, in the PDS solution (pH = 5.85), SMX was negatively charged, and the light absorption property became weaker at this time. This result also indicated that the effect of UV dose was closely related to the properties of antibiotics when UV-activated PMS and PDS degrade antibiotics.

5.4. Effect of PDS (PMS) Concentration on Antibiotics Degradation

The concentration of PDS (PMS) is an important parameter that determines the generation of free radicals in the reaction system. Zhang et al. [57] reported that an increase in PDS concentration obviously accelerated the removal of SMX in a UV/PDS system (Figure 5a). Other studies [46,59–61] also concluded that increasing the amount of PDS promoted the degradation of antibiotics under UV radiation. These results indicated that more PDS added to the UV/PDS system resulted in forming more sulfate radicals, which can effectively degrade antibiotics. Whereas Zarei et al. [62] found further increased PDS concentration from 1.0 g/L to 2.0 g/L, the degradation rate of metronidazole (MNZ) decreased slightly (Figure 5b). Liu et al. [63] also confirmed that too high PDS concentration

did not significantly improve the degradation of ofloxacin (OFLO) and levofloxacin (LEV) via the UV/PDS process. It is concluded that higher levels of PDS concentration would lead to an excess of oxidants that quench free radicals, as described in Equation (13) [38]. Moreover, a merger reaction could also occur between excessive free radicals, reducing the oxidative capacity (Equation (14)) [51]. Qu et al. [43] investigated the effect of PMS concentration on the degradation of CAP using the UV/PMS process. When PMS concentration increased from 0.5 mM to 1.0 mM k_{obs} of CAP degradation increased from 0.0522 min^{-1} to 0.0705 min^{-1}. This was due to the increase in the oxidant PMS resulting in the generation of more free radicals ($SO_4^{\bullet -}$, •OH) under UV radiation. By contrast, when continuing to increase the PMS concentration to 2.0 mM k_{obs} showed a downward trend. This indicated that there was a certain saturation concentration of PMS in removal antibiotics. Above this concentration, PMS will quench free radicals and inhibit the reaction (Equations (15) and (16)) [64]. Shad et al. [65], Hu et al. [53], and Ao and Liu [52] investigated the effect of PMS concentration on the degradation of antibiotics in the UV/PMS system and also achieved similar results to Qu et al. [43]. However, the studies [66,67] did not find that PMS had an inhibitory effect on the degradation of antibiotics, which might be due to the PMS concentration used in their experiments below the inhibitory concentration.

$$SO_4^{\bullet -} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet -} + SO_4^{2-} \quad (13)$$

$$SO_4^{\bullet -} + SO_4^{\bullet -} \rightarrow S_2O_8^{2-} \quad (14)$$

$$SO_4^{\bullet -} + HSO_5^{-} \rightarrow HSO_4^{-} + SO_5^{\bullet -} \quad (15)$$

$$\bullet OH + HSO_5^{-} \rightarrow H_2O + SO_5^{\bullet -} \quad (16)$$

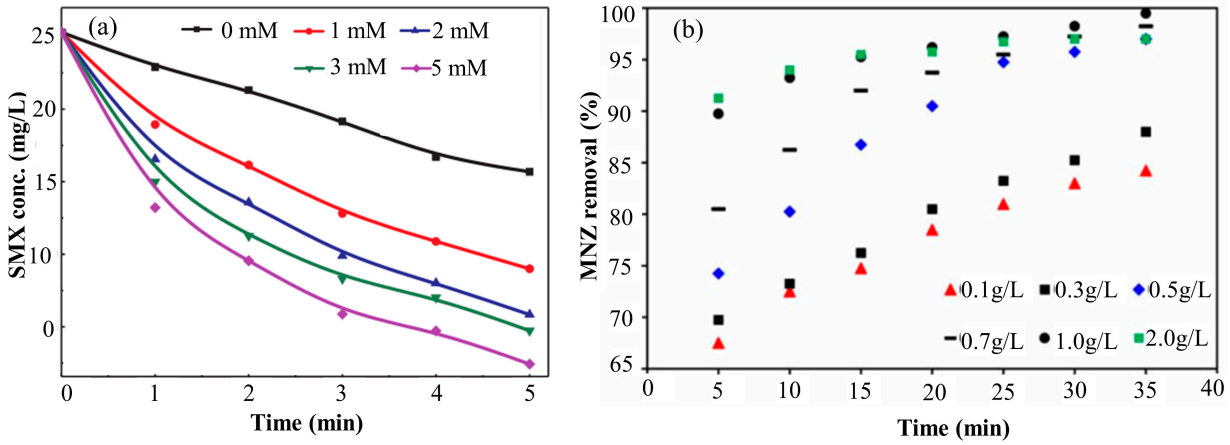


Figure 5. Effect of PDS concentration. (**a**) UV intensity 240 W, [SMX] = 0.1 mM, [PDS] = (0, 1, 2, 3, 5) mM [57]. Copyright (2020), with permission from Elsevier. (**b**) pH = 5, [MNZ] = 40 mg/L, [PDS] = (0.1, 0.3, 0.5, 0.7, 1.0, 2.0) g/L [62].

5.5. Effect of pH on Antibiotics Degradation

The initial pH of the solution plays a key role in the degradation of antibiotics in the UV/PMS (PDS) system because it can influence the predominant radical species as well as the speciation of target organic pollutants. In the studies of Ao and Liu [52], Ao et al. [66], and Ao et al. [68], the degradation rates of three antibiotics, SMX, CIP, and TC, were improved noticeably as pH rising from 5.0 to 11.0 in different UV/PMS systems. When pH was 3.0–5.0, an obvious blue shift limited the UV absorption was observed, resulting in declining antibiotics removal rates. Different from the above results, Qi et al. [67] concluded that acidic pH would facilitate the flumequine (FLU) elimination, while alkaline conditions had an inhibitory effect on FLU degradation in a UV/PMS system. According to Equation (2), two types of free radicals, $SO_4^{\bullet -}$ and •OH, were generated by UV activation in the presence of PMS. $SO_4^{\bullet -}$ was dominant under acidic conditions, while $SO_4^{\bullet -}$ was converted into

•OH under alkaline conditions [39,69], thus reducing the degradation efficiency of FLU. Additionally, the dissociation species of FLU in water had an impact on its degradation performance at different pH values. FLU is an amphoteric compound with both amino and carboxyl groups, and its dissociation forms are related to the pH of the solution. Under acidic conditions, protonation on the zwitterionic functional group can make the piperazine ring positively charged. Due to the electrostatic attraction between positively charged FLU and negatively charged $SO_4^{\bullet-}$, FLU is more easily oxidized by $SO_4^{\bullet-}$ under acidic conditions. However, at higher pH, the FLU carries more negative charges, and the repelling effect on $SO_4^{\bullet-}$ is enhanced so that the degradation efficiency of FLU decreases.

Some conclusions were also obtained regarding the effect of pH on UV/PDS degradation of antibiotics. Tan et al. [70], Chen et al. [71], Frontistis [72], and Gao et al. [73] used the different UV/PDS systems to degrade antibiotics CAP, acetamiprid (ACE), piroxicam (PIR), and sulfamethoxypyridazine (SMP), respectively, and all obtained the conclusion that the acidic conditions were optimal. As the hydrolysis process of AZA and ACE are rather time-consuming, their hydrolysis was negligible, and their degradation was mainly affected by free radicals generated at different pHs. The degradation of SMP in the UV/PDS system [73] was similar to the degradation of FLU in the UV/PMS system under acidic conditions [67]. Similar to FLU, SMP is an amphoteric compound whose hydrolysate promotes the oxidation of $SO_4^{\bullet-}$. Based on the study of Zhang et al. [74], the maximum degradation rate of carbamazepine (CBZ) in the UV/PDS system was observed at pH 2.0, which was due to the catalysis of the acid leading to more $SO_4^{\bullet-}$ generated, as shown in Equations (17) and (18) [52,74]. Different from the above results, Bu et al. [75] and Guo et al. [76] found that alkaline conditions (pH = 9.0–11.0) were beneficial for the degradation of antibiotics oxcarbazepine (OCBZ), norfloxacin (NOR), and enrofloxacin (ENR) in the UV/PDS systems. One possible reason was that the base played an auxiliary role in the activation of PDS, as shown in Equation (19) [52,77], and a large number of $SO_4^{\bullet-}$ are generated in the solution to enhance the degradation of antibiotics. Another reason was that the hydrolysis products of these antibiotics under alkaline conditions are conducive to the oxidation of free radicals in the solution. Gao et al. [78] studied the removal efficiency and mineralization efficiency of sulfamethazine (SMT) by UV/PDS process at different initial solution pH (3.0–11.0) and found that the highest SMT removal rate occurred in neutral conditions with a pH of 6.5, while the highest mineralization rate occurred at pH 11.0. This finding showed that SMT was easily oxidized by $SO_4^{\bullet-}$ at pH 6.5, and its intermediate products were recalcitrant to $SO_4^{\bullet-}$ at the same pH. Therefore, it was also inferred that there were more •OH in the solution at pH 11.0, which can effectively oxidize the intermediate products of SMT degradation. Sadeghi et al. [79] found that azithromycin (AZM) could achieve a better degradation effect in a wider pH range of 5.0–9.0 by UV/PDS process, and there was no obvious difference in AZM removal rate within this range. Therefore, it was determined that a pH of 7.0 was the best and most economical level due to no acid or alkali regulator required.

$$H^+ + S_2O_8^{2-} \rightarrow HS_2O_8^- \quad (17)$$

$$HS_2O_8^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+ \quad (18)$$

$$S_2O_8^{2-} + H_2O \xrightarrow{\text{alkaline}} SO_4^{\bullet-} + SO_4^{2-} + H^+ + \bullet OH + O_2^{\bullet-} \quad (19)$$

5.6. Effect of Anions on Antibiotics Degradation

There are some anions with various concentrations in natural waters, such as Cl^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, NO_2^-, and NO_3^-. These anions can affect the removal efficiency of targeted pollutants by reacting with free radicals or other substances in water. Table 4 summarizes the effect of some anions on the degradation of some antibiotics by UV/PDS (PMS) processes.

Table 4. Effects of different ions on antibiotics degradation in PDS/PMS systems.

Anion	Oxidation System	Parameter	Impact	Reference
Cl^-	UV/PDS/CAP	[CAP] = 0.03 mM, [PDS] = 1 mM.	[Cl^-] = 1–5 mM: Accelerated CAP degradation.	[70]
Cl^-	UV/PDS/ACE	[ACE] = 90 μM, [PDS] = 1.5 mM, pH = 7, T = 25 °C.	[Cl^-] = 5–15 mM: Inhibited ACE degradation.	[71]
Cl^-	UV/PDS/PIR	[PIR] = 1000 μg/L, [SPS] = 5 mg/L, ultrapure water, inherent pH.	[Cl^-] = 100–250 mg/L: No significant effect on PIR degradation.	[72]
Cl^-	UV/PDS/CBZ	-	[Cl^-] = 0.1–2.0 mM: No significant effect on CBA degradation. [Cl^-] = 2.0–10 mM: CBA degradation rate was inhibited.	[74]
Cl^-	UV/PMS/SMX	-	[Cl^-] = 0.6–30 mM: The SMX degradation rate increased.	[52]
Cl^-	UV/PMS/CIP	[CIP] = 3.02 μM, [PMS] = 0.2 mM.	[Cl^-] = 0.1–0.5 mM: No significant effect on CIP degradation. [Cl^-] = 2.0–10.0 mM: CIP degradation rate was obviously improved.	[66]
Cl^-	UV/PMS/TC	[TC] = 11.25 μM, [PMS] = 0.2 mM, no pH adjustment.	[Cl^-] = 0.1–0.5 mM: TC degradation rate changed a little. [Cl^-] = 2.0–5.0 mM: TC degradation rate was visibly improved.	[68]
HCO_3^-	UV/PMS/FLU	[FLU] = 76.0 μM, [PMS]: [FLU] = 1:1, pH = 7.0 ± 0.1, T = 25 ± 2 °C.	[HCO_3^-] = 0.5–5.0 mM: Decreased the degradation efficiency of FLU.	[67]
CO_3^{2-}	UV/PMS/SMX	[SMX] = 23.69 μ M; [PMS] = 1 mM; 2.8 kW MPUV.	[CO_3^{2-}] = 0.6 mM: Slightly inhibited the degradation of SMX. [CO_3^{2-}] = 3–30 mM: Improved the degradation of SMX.	[52]
CO_3^{2-}	UV/PMS/CIP	[CIP] = 3.02 μM, [PMS] = 0.2 mM.	[CO_3^{2-}] = 0.1–10 mM: Accelerated the degradation of CIP.	[66]
NO_3^-	UV/PMS/SMX	[SMX] = 23.69 μ M, [PMS] = 1 mM, 2.8 kW MPUV.	[NO_3^-] = 0.6–30 mM: Increased the degradation of PRO.	[52]
NO_3^-	UV/PDS/CAP	[CAP] = 0.03 mM, [PDS] = 1 mM.	[NO_3^-] = 1–10 mM: Slightly enhanced CAP removal.	[70]
NO_3^-	UV/PDS/CBZ	-	[NO_3^-] = 0.1–10 mM: No significant effect on CBZ degradation. [NO_3^-] = 20 mM: Inhibited the degradation of CBZ.	[74]

It was found that the influence of Cl^- on the removal of antibiotics in UV/PDS processes could be divided into three situations. The first case is that the appearance of Cl^- with relatively low concentrations was beneficial in promoting the degradation of antibiotics. Tan et al. [70] came to similar findings. Based on Equation (20) [64], $SO_4^{\bullet-}$ reacts with Cl^- to form SO_4^{2-} and $Cl^\bullet$, which is more selective in targeting pollutants with the electron-rich sites compared with $SO_4^{\bullet-}$. In addition, $Cl^\bullet$ could also promote the conversion of $S_2O_8^{2-}$ to $SO_4^{\bullet-}$ (Equation (21)) [64], resulting in a promotion of pollutants removal [50]. The second situation is that relatively high Cl^- appear in water could inhibit the degradation of antibiotics. It was observed that as the Cl^- concentration increased, the degradation efficiency of antibiotics decreased in the UV/PDS processes [57,70,71,74]. When the Cl^- concentration is relatively high, surplus Cl^- will combine with $Cl^\bullet$ to form $Cl_2^{\bullet-}$ (Equation (22)) [41,64]. Since the oxidation ability of $Cl_2^{\bullet-}$ to organics was lower than that of $SO_4^{\bullet-}$ and $Cl^\bullet$, the degradation rates of antibiotics were reduced. The last case is that the presence of a certain amount of Cl^- in water has no significant effect on the degradation of antibiotics. Zhang et al. [74] found that a Cl^- concentration of 0.1–2.0 mM had no effect on the degradation of CBZ. Frontistis [72] observed that the effect of Cl^- concentration on UV/PDS in degrading piroxicam (PIR) was basically negligible. Several studies have investigated the effect of the presence of Cl^- on the degradation of antibiotics via UV/PMS systems [52,66,68]. In these studies, Cl^- was found to have the effect of accelerating the degradation of antibiotics in UV/PMS systems. Based on Equations (23) and (24) [52,64], Cl^- can react with HSO_5^- to form HClO or Cl_2, and HClO/Cl_2 species

prefer to selectively react with the electron-rich sites of organic pollutants, such as CBZ, CIP, and TC.

$$SO_4^{\bullet -} + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet} \quad (20)$$

$$2Cl^{\bullet} + S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -} + 2Cl^- \quad (21)$$

$$Cl^{\bullet} + Cl^- \rightarrow SO_4^{2-} + 2Cl_2^{\bullet -} \quad (22)$$

$$Cl^- + HSO_5^- \rightarrow SO_4^{2-} + HOCl \quad (23)$$

$$2Cl^- + HSO_5^- + H^+ \rightarrow SO_4^{2-} + Cl_2 + H_2O \quad (24)$$

When the HCO_3^- was added to the reaction system, the HCO_3^--CO_3^{2-} system would be formed due to the hydrolysis of HCO_3^- as shown in Equations (25) and (26) [41,52]. When the HCO_3^- was relatively low, the degradation of antibiotics in the UV/PDS system was promoted, which was mostly attributed to the formation of $HCO_3^{\bullet}$ and $CO_3^{\bullet -}$ in catalyzing the propagation reactions (Equations (27) and (28)) [39,52]. However, at a higher HCO_3^- level in the UV/PDS system, $HCO_3^{\bullet}$ and $CO_3^{\bullet -}$ showed more quenching effect on $SO_4^{\bullet -}$, leading to the removal of antibiotics reducing. Qi et al. [67] found that HCO_3^- decreased the removal rate of FLU via the UV/PMS system due to the scavenging of reactive free radicals by HCO_3^-. As adding CO_3^{2-} into the UV/PMS system, CO_3^{2-} will hydrolyze, forming an equilibration of CO_3^{2-}-HCO_3^- system (Equation (29)) [66]. Therefore, the effect of CO_3^{2-} on antibiotics degradation was equivalent to that of HCO_3^- [52].

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad (25)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad (26)$$

$$SO_4^{\bullet -} + HCO_3^- \rightarrow SO_4^{2-} + HCO_3^{\bullet} \quad (27)$$

$$SO_4^{\bullet -} + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^{\bullet -} \quad (28)$$

$$CO_3^{2-} + H_2O \rightarrow OH^- + HCO_3^- \quad (29)$$

It was found that a small amount of NO_3^- had little effect on CBZ degradation in UV/PDS system, and abundant NO_3^- would inhibit CBZ degradation [74]. As shown in Equation (30) [41,67], the appearance of surplus NO_3^- made $SO_4^{\bullet -}$ quenched and replaced by the $NO_3^{\bullet}$ with weak oxidizing ability, thus inhibiting the degradation rate. In contrast, Tan et al. [70] found that NO_3^- (0–10 mM) promoted the degradation of CAP in the UV/PS system. The irradiation of NO_3^- by UV led to the generation of •OH with strong oxidative power (Equation (31)) [67], which explained this phenomenon. Ao and Liu [52] also came to a similar conclusion in removing SMX by UV/PMS system, that NO_3^- promoted the degradation of SMX. The reason for this could also be explained by (Equation (32)) [67].

$$SO_4^{\bullet -} + NO_3^- \rightarrow SO_4^{2-} + NO_3^{\bullet} \quad (30)$$

$$NO_3^- + hv \rightarrow O^{\bullet -} + NO_2^{\bullet} \quad (31)$$

$$O^{\bullet -} + H_2O \rightarrow \bullet OH + OH^- \quad (32)$$

6. Conclusions and Outlook

Due to the large-scale usage and improper discharge of antibiotics, there is much antibiotic pollution in surface waters around the world, which can cause bacteria to develop drug resistance and endanger human beings through drinking water. Antibiotics have complex chemical structures and are difficult to biodegrade. The advanced oxidation method of UV-activated PDS(PMS) has a significant mineralization effect on antibiotics due to the generation of active free radicals, so some scholars have devoted themselves to the research of this method. This persuaded us to go for a comprehensive review on the application of UV/PDS(PMS) as a potential approach to eliminating antibiotics.

At present, the research on UV/PDS(PMS) treatment of antibiotics is still in the stage of small batch experiments in the laboratory. The experimental device is relatively simple, and the influencing factors are limited to a single factor, such as oxidant concentration, pH value, VU dosage, ions and organic matter in water, etc. The mineralization process of antibiotics and the removal of resistance genes have not been thoroughly studied. Moreover, the design of the experimental device, the determination of the production and operation parameters, and the operating costs should also be considered in practical application. Although the practical application of the process faces some challenges, taking effective measures can advance its application.

(1) The actual mechanism of the UV-activated PDS (PMS) reaction is relatively complex, and the occurrence of the reaction is closely related to water environment conditions. The free radicals generated in the reaction process have chain transfer reactions, so the contribution and mechanism of various types of free radicals to the degradation of antibiotics should be continuously explored.
(2) In small-scale experiments, the effect of various composite water quality parameters on the effect of antibiotic treatment needs to be studied in detail. A continuous flow experiment simulating antibiotic wastewater needs to be performed to obtain optimal operating conditions such as hydraulic load and residence time. On this basis, the treatment of the actual wastewater containing antibiotics needs to be carried out, and the removal efficiency of antibiotics, the degree of mineralization, and the removal ability of resistant groups need more attention.
(3) The enlarged design of the reactor depends on the mode used for disinfection and water treatment, which is a relatively mature technology, but the advent of more energy-saving and environmentally friendly UV-LED lamps makes it possible for us to find more optimized light sources. However, there is no ularization and integration of the light source. The mature industrialization standard of mercury lamps also provides a powerful reference for the standardized application of UV-LED lamps. Moreover, the integration of lamps, the design of reactors, and the evaluation of operating costs and energy consumption need to be continuously improved.
(4) The pollutants in the actual sewage are complex, containing not only antibiotics but also other organic substances. Therefore, a single UV/PDS(PMS) process may not produce suitable results under complex water quality conditions. Combining the UV/PDS(PMS) process with other processes (such as biological treatment, adsorption, photocatalytic oxidation) is a better option. In particular, the photocatalytic oxidation method is essentially an advanced oxidation method, which mainly degrades organic substances by generating hydroxyl radicals. The current continuous development of visible light catalysts provides a new composite direction for PDS(PMS)-based advanced oxidation. The visible light catalyst combined with PDS(PMS) can reduce the consumption of ultraviolet light energy, which is expected to treat antibiotic-containing wastewater efficiently and economically.

Author Contributions: Conceptualization, T.S. and Y.G.; methodology, G.L.; software, R.H., Y.L. and H.L.; validation, H.L.; resources, Y.G.; datacuration, G.L.; writing—original draft preparation, Y.G.; writing—review and editing, T.S., R.H. and Y.L.; supervision, T.S.; project administration, R.H. and Y.L.; funding acquisition, T.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Jilin Provincial Department of Science and Technology of China, no. YDZJ202201ZYTS681 and no. YDZJ202201ZYTS630.

Data Availability Statement: All relevant data are included in the paper.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

ACE	Acetamiprid	NOR	Norfloxacin
AMX	Amoxicillin	OCBZ	Oxcarbazepine
AOPs	Advanced oxidation processes	OFLO	Ofloxacin
AZM	Azithromycin	PDS	Peroxodisulfate
CAP	Chloramphenicol	PG	Penicillin G
CBZ	Carbamazepine	PIR	Piroxicam
CIP	Ciprofloxacin	PMS	Peroxymonosulfate
ENR	Enrofloxacin	SMP	Sulfamethoxypyridazine
FLU	Flumequine	SMT	Sulfamethazine
HPUV	High-pressure mercury vapor lamps	SMX	Sulfamethoxazole
LEV	Levofloxacin	TC	Tetracycline
LPUV	Low-pressure mercury vapor lamps	UV	Ultraviolet
MNZ	Metronidazole	UV-LED	UV light-emitting diodes
MPUV	Medium-pressure mercury vapor lamps	WWTPs	Wastewater treatment plants

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