

Activated persulfate and peroxymonosulfate based advanced oxidation processes (AOPs) for antibiotics degradation – A review

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ABSTRACT

Sulfate radical AOPs (SR-AOP) were successfully utilized in degradation of antibiotics in water and wastewater treatment. The review discusses details on SR-AOPs mechanisms and applications for antibiotics degradation. The progress in this field was discussed, highlighting the most promising developments and remaining challenges. The applicability of SR-AOPs was summarized revealing the most susceptible and persistent to oxidation groups of pharmaceuticals. Highest effectiveness was reported for degradation of pharmaceuticals on ppb level. Systems revealed a scavenging effect in case of oxidant dose 0.7 mM of the PS and 2 mM of PMS. Future development demands simple persulfates activation systems for real matrix treatment.

1. Introduction

Antibiotics as compounds having antibacterial, antiviral, and antifungal activity are widely used in eradicating and preventing the growth of microorganisms in medicine and veterinary [1]. They are entered the environment through a variety of sources, such as the pharmaceutical industry, hospital sewage and disposal of human and animal wastes [2]. Approximately 30–90% of antibiotics remain active and non-metabolized, and are disposed to the environment through urine and feces [3,4]. The inability of conventional

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wastewater treatment processes to remove antibiotics and their discharge into the environment can result in adverse effects on the ecosystem and human. There is strong evidence for the presence of antibiotics in aqueous solutions at the level of nano and micrograms per liter [5,6] which can lead to the development of antibiotic-resistant pathogens that potentially threaten the ecosystem and human health [7,8].

Conventional wastewater treatment processes are known to be non-effective for the removal or degradation of several organic chemicals especially pharmaceuticals. These compounds, due to their high toxicity, in particular to the bacterial community, can cease the biological process of wastewater treatment [9,10]. Various methods have been used to remove pharmaceutical compounds but the best method for removing these compounds is advanced oxidation processes (AOPs) which were first introduced by Glaze in 1987 for water and wastewater treatment [11].

AOPs are the most effective method for treatment of highly polluted industrial, toxic, hazardous, resistant and non-biodegradable organic pollutants in aqueous solutions, which has gained an important place in water and wastewater treatment [12,13].

Today, the best way to degrade more effectively the pollutants present in aquatic and soil environments is to apply the AOPs without the formation of hazardous and intermediate substances [14–16]. AOPs fundamentally are the methods that produce strong oxidizing agents such as OH^\bullet , $\text{SO}_4^{\bullet-}$, Cl^- and some oxidizers that allow direct electron transfer [17,18]. The oxidation potential of some common oxidants is shown in Table 1 [19].

The two types of radicals OH^\bullet and $\text{SO}_4^{\bullet-}$ are strong oxidizing radicals with redox potentials (E°) 2.8V and 2.5–3.1V, respectively, which can rapidly and non-selectively oxidize and decompose most organic compounds in water and wastewater [20,21]. Today, AOPs based on $\text{SO}_4^{\bullet-}$ have received high attention due to some unique features. AOPs can be classified according to the type of produced radicals. The AOPs based on the production of OH^\bullet and $\text{SO}_4^{\bullet-}$ are called HR-AOP and SR-AOP, respectively [22,23]. AOPs are used to achieve the oxidation and decomposition of pollutants into neutral and low-risk products [9].

The advantages of AOPs are complete mineralization of organic matter, the low production of residual materials and the ability to combine with biological systems [24,25].

The aim of this review study is to evaluate the effect and mechanism of persulfate (PS) and peroxymonosulfate (PMS) activated by different methods to remove antibiotics from aqueous solutions. This study also investigated the impact of scavengers, by-products formation and assessment of toxicity of treated effluents.

2. Idea of persulfates application for AOPs

2.1. Properties of persulfate

Persulfate (PS, $\text{S}_2\text{O}_8^{2-}$) is a one of two most popular chemicals used in this field its properties were already well summarized in respect S-AOPs [26]. Briefly it was compiled in Supp. Info. section S1 (Supporting information).

2.1.1. Activation methods

2.1.1.1. *Persulfate activated by UV.* Several papers proved possibility of PS activation by UV (Table 2). Explanation of mechanism and main achievements are summarized in Supp. Info. section S2.

It is clear that excess of oxidant, calculated as the molar ratio of oxidant to pollutant (i.e., rox) is needed. Reasonable performance well obtained for rox between 8 and 10. In other cases much higher rox as 40 or even 150 was used. Because in most of the studies the authors do not focus on the rox, defining the concentration of oxidant as molar concentration and pollutant in mg/L, this relation is not directly visible. Although in some cases, high effectiveness was obtained, the 40 or 150 M excess of oxidant seems to be out of scope and real sense in relation to the possible implementation of such process in the real scenario. PS has high molecular mass; thus, such molar excess means high mass dose of oxidant, which is relatively expensive.

In the chloramphenicol degradation process, the addition of $\text{Cl}^- = 1 \text{ mM}$, $\text{SO}_4^{2-} = 0.5 \text{ mM}$ and $\text{NO}_3^- = 10 \text{ mM}$ increases the degradation efficiency. Low Cl^- concentration has a positive effect on the degradation of chloramphenicol. Two scenarios are possible through UV irradiation: first, $\text{SO}_4^{\bullet-}$ is produced for reaction with NO_3^- so that NO_3^\bullet is produced with significant oxidation power ($E_{\text{red1/2}} = 2.50\text{V}$) (Eq. (1)). Second, NO_3^- becomes a source of nitrite and oxygen radicals (Eq. (2)). O^\bullet could enhance CAP oxidation upon

Table 1
Oxidation potential of some common oxidants.

Oxidant	Standard reduction potential (E°) (V_{NHE})
Fluorine	3.0
Hydroxyl radical (HO^\bullet)	2.8
Sulfate radical ($\text{SO}_4^{\bullet-}$)	2.5-3.1
Ozone (O_3)	2.1
Persulfate ($\text{S}_2\text{O}_8^{2-}$)	2.1
Peroxymonosulfate (HSO_5^-)	1.82
Hydrogen peroxide (H_2O_2)	1.8
Permanganate (MnO_4^-)	1.68
Chlorine dioxide (ClO_2)	1.5
Chlorine (Cl_2)	1.4

Table 2
Activation of PS with UV for degradation of antibiotics.

Pollutant	matrix	Pollutant Concentration (mM)	Oxidant Concentration (mM)	Molar ratio oxidant to pollutant (r_{ox})	Wavelength [nm]	pH	Time (min)	Degradation (%)	References
Tetracycline	Deionized water	0.01	0.08	7.63	254	6.89	30	95.73	[27]
Sulfamethazine	Milli-Q water	0.02	0.2	10	254	6.5	45	90	[28]
Chloramphenicol	Deionized water	0.031	0.25	8.06	254	6.07	60	100	[29]
Sulfamethoxazole	Deionized water/surface water	0.0236	1	42.37	254	8	120	97	[30]
Oxytetracycline	Milli-Q water	0.04	1	25	254	7	360	100	[31]
Metronidazole	Deionized water	0.0584	0.7	11.98	254	9	30	98.73	[32]
Penicillin G	Deionized water	0.02	3	150	254	5	90	94.28	[20]
Ofloxacin	Deionized water	0.1106	0.967	8.75	254	6	20	94.35	[33]



reaction with water to generate HO^\bullet (Eq. (3)), responsible for more CAP degradation. Other studies proved that in the case of the presence of sulfate ions, excess energy introduced into the liquid can cause the formation of $\text{SO}_4^{\bullet-}$ [34].



A break-even point was determined for PS ($0.25 < \text{PS} < 0.5$ mM) at a fluence of 330J for 1h reaction. UV/PS system was pH independent. Full CAP degradation was reached in 1h upon increasing PS = 2.5 mM along with the UV fluence 874J. In the optimal condition [29].

The main reason for the high degradation of oxytetracycline in the UV/PS system is the presence of $\text{HCO}_3^- = 20$ mM and $\text{Cu}^{2+} = 1$ mM. Due to the reaction of Cu^{2+} with PS, the possibility of forming additional $\text{SO}_4^{\bullet-}$ increases according to Eq. (4). Also, the presence of HCO_3^- due to the production of carbonate radicals has a positive role in the degradation of OTC (Eq. (5)).



It was found that $\text{SO}_4^{\bullet-}$ was probably the predominant radical species for the degradation of OTC by UV/PS at pH = 7. The k_{obs} was the highest at near neutral conditions [31]. The degradation of OTC by UV-PS method was shown in Fig. 1.

2.1.1.2. Persulfate activated by heat. Many studies verified the activation of PS by heat (Table 3). Extra information about this method is summarized in Supp. Info. section S3.

The reason for the high degradation efficiency for Sulfamethazine (SMZ) is the presence of bicarbonate and chloride enhanced SMZ degradation. Since SMZ contains aniline moiety, the enhancement in SMZ degradation rate was likely a result of $\text{HCO}_3^-/\text{CO}_3^{\bullet-}$ reaction, which offsets the negative effect of $\text{SO}_4^{\bullet-}$ and/or HO^\bullet scavenging. The enhancement in SMZ oxidation with increasing Cl^- concentration was likely due to the contribution of reactions involving reactive chlorine species, which compensated for the depletion of $\text{SO}_4^{\bullet-}$ and/or HO^\bullet due to Cl^- scavenging. In this study, heat/PS oxidation of SMZ in the aqueous solution was systematically investigated. It was shown that increasing the temperature and PS dosage significantly enhanced the removal rate of SMZ. SMZ could be degraded efficiently at the pH ranged from 7.0 to 9.0, but higher and lower pH showed inhibitory effects [40]. Fig. 2 demonstrate the degradation of SMZ by heat activated PS (see also Fig. 3).

Under the optimal condition, Tetracycline (TTC) degraded in 100%. The C=C double bond and phenolic moiety in TTC molecule are the reactive sites toward $\text{SO}_4^{\bullet-}$ attack. Potential reactive sites may include C2-C3 keto-enol moiety, C7, C9, and C11a-C12 double bond. Increasing the temperature and solution pH favored the removal of TTC. TTC was degraded faster in artificial surface water (ASW) than that in Milli-Q water, suggesting that the natural water constituents may facilitate the degradation of TCs by SR-AOPs. Approximately 70% TTC was degraded after 240min at 40 °C, whereas TTC was completely eliminated within 30min at 70 °C. Higher temperature promoted the activation of PS and enhanced the formation rate of SR, which favored the degradation of TTC. Furthermore, the chemical reactions initiated by the radical attack were significantly elevated at higher temperatures according to

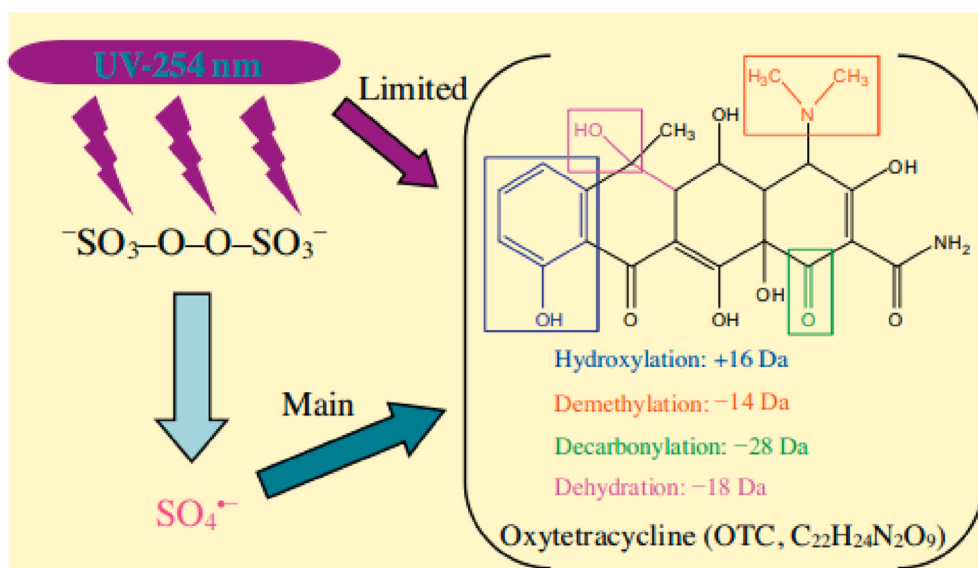


Fig. 1. Schematic illustration of OTC degradation by UV-PS system [31].

Table 3
Activation of PS by heat for degradation of antibiotics.

Pollutant	Matrix	Pollutant Concentration (mM)	Oxidant Concentration (mM)	Molar ratio oxidant to pollutant (r_{ox})	Temperature (°C)	pH	Time (min)	Degradation (%)	References
Oxytetracycline	Deionized water	0.04	8.9	222.5	72	8.9	26.5	89.7	[35]
Chloramphenicol	Deionized water	0.2	16	80	70	5.4	120	96.3	[36]
Penicillin G	Deionized water	0.02	0.5	25	80	5	72	98	[37]
Fluconazole	Ultrapure water	0.0326	20	613.49	60	3	240	87	[38]
Enrofloxacin	Reverse osmosis water	0.013	1.04	80	50	4	120	77.5	[39]
Ciprofloxacin	Reverse osmosis water	0.013	1.04	80	50	4	120	69.2	[39]
Sulfamethazine	Milli-Q water	0.03	2.0	66.6	60	7	120	100	[40]
Triclosan	Underground water	0.031	0.155	5	80	7.8	360	>90	[41]
Tetracycline	Artificial surface water	0.03	2	66.6	50	7	240	100	[42]



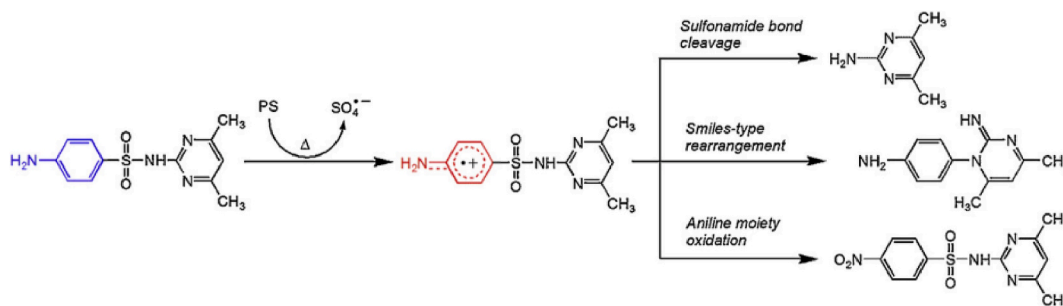


Fig. 2. Degradation of SMZ by heat activated PS system [40].

thermodynamic law. The degradation of TTC showed a pH dependence, and k_{obs} increased with increasing the pH. Since TTC has three pKa, this result suggests that the deprotonated, non-dissociated TTC was more reactive for SR attack. The phenolate form of phenolicdiketone group and the unprotonated dimethylamine moiety were more reactive, most likely due to the higher electron densities of these moieties which favored the electrophilic attack of SR [42].

2.1.1.3. Persulfate activated by transition metals. Various studies have used the transition metals method to activate the PS (Table 4), which is given in Supp. Info. section S4.

Application of magnetic particles makes their isolation from the reaction system after the process easier by means of the magnetic field. In all cases studied, the pH was acidic, due to the needed form of metal cations activating PS. In many cases the time needed to obtain satisfactory results was less than 1hr in almost a half of studies, only 30min of treatment was needed to obtain quantitative degradation.

The cause of high degradation Sulfamonomethoxine (SMM) is Fe_3O_4 MNPs activate PS, yield $\text{SO}_4^{\bullet-}$ species, and then accelerate the decomposition of SMM [43]. The degradation efficiencies of the Ag/AgCl-various weight percentage of zero-valent iron particles (NZVI) modified zeolite X catalysts (Ag/AgCl/(x)FeX) for total Tetracycline removal were high due to the enhanced adsorptive capacity of (x)FeX (the x denotes the weight percentage of NZVI), the extended absorbance in the visible-light region and improved space separation of photo-induced charge carriers [45].

2.1.1.4. Persulfate activated by ultrasound irradiation. Some researchers have proved the ability of US for activation of PS (Table 5). The additional information is summarized in Supp. Info. section S5.

The reason for the high efficiency of tetracycline hydrochloride degradation in US/PS method was to increase the intensity of ultrasound by 500W. It is clear that the increase of ultrasound intensity to a specific high level promoted the decomposition of $\text{S}_2\text{O}_8^{2-}$ and generation of reactive species and consequently increased the rate of tetracycline hydrochloride degradation. In addition, the increase of the power intensity leads to a significant increase of the number of cavitation bubbles. The degradation efficiency of Tetracycline hydrochloride under optimal condition was 88.51% [55].

2.1.1.5. Persulfate activated by carbon materials. Another method of PS activation is based on application of carbon-based materials. Activated carbon (AC), biochar (BC), carbon nanotubes (CNT) and graphene as carbon-based materials are widely used as adsorbents and catalysts. High specific surface area, high pore volume, and affordability are their main advantages [56–58].

2.1.1.5.1. Activated carbon. One of the most widely used non-metallic catalysts for the activation of persulfate is activated carbon (AC). Among its advantages, can be mentioned the developed porous structure, large specific surface area, abundant functional groups, and cost-effectiveness. surface functional groups, delocalized π electrons, sp^2 hybrid carbon at defect edges and oxygen-containing functional groups ($-\text{COOH}$, $\text{C}-\text{OH}$, $\text{C}-\text{O}$) are among the active sites of AC for persulfate activation [59,60]. These sites react with persulfate and produce hydroxyl and sulfate radicals in order to remove pollutants [61]. There are different types of activated carbon, including powdered activated carbon (PAC), granular activated carbon (GAC) and activated carbon fiber (ACF). In addition to the mentioned advantages, the main problem of activated carbon is the poor mass transfer of pollutant molecules due to the size of micropores, which limits the rate of degradation, because catalytic reactions occur only on the surface of the carbon or the adjacent boundary layers, thus causing weak AC performance. But this problem can be solved by changing the porous structure to mesoporous or hierarchical pores by soft/hard mold method [62]. The mechanisms of pollutant degradation by persulfate activated with carbon can be summarized in three aspects: adsorption, free radical pathway and nonradical pathway. The non-radical path can be divided into singlet oxygen, electron transfer, and direct oxidation. These persulfate activation mechanisms can occur simultaneously in one reaction [63,64]. Various factors such as surface functional groups, surface electrochemical impedance, graphitization degree and porous structure, which are related to the raw materials, preparation strategies, and modification methods can affect the activation of persulfate by carbon materials [65,66]. According to Eqs. (6)–(8), persulfate produces sulfate and hydroxyl radicals through the interaction with the surface of activated carbon (AC) through the electron transfer mechanism, and finally, these generated radicals decompose organic pollutants into inorganic compounds and organic intermediates [67].



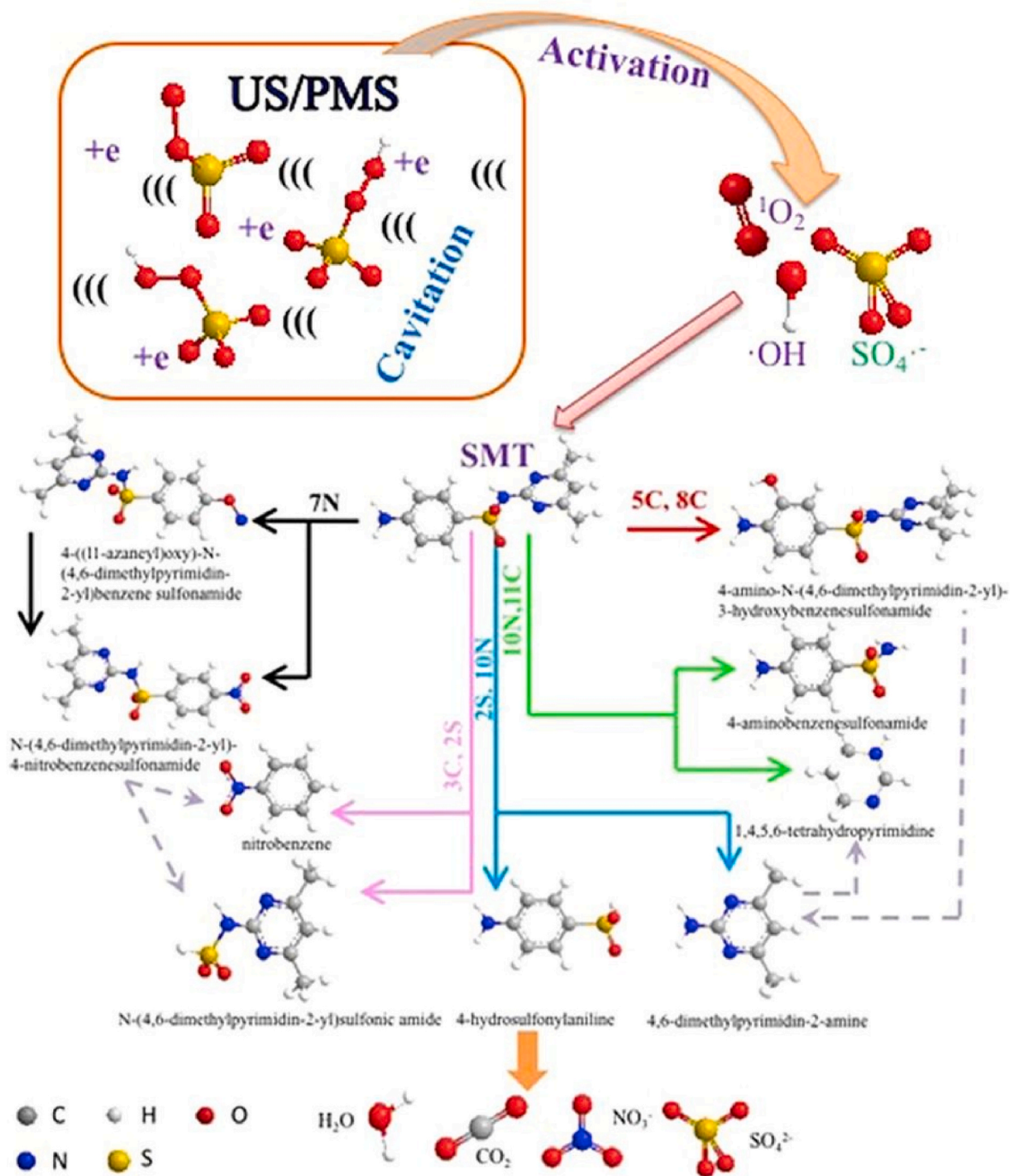


Fig. 3. The mechanism of activation PMS by US for degradation of sulfamethazine [55].



Table 6 shows some research on the activation of persulfate by activated carbon in order to remove antibiotics. Generally, application of AC allows effective activation of persulfates providing close to 90% degradation effectiveness of studied antibiotics.

Table 4
Transition metals activation of PS for degradation of antibiotics.

Pollutant	matrix	Pollutant concentration (mM)	Oxidant concentration (mM)	Molar ratio oxidant to pollutant (r_{ox})	Metal oxide	pH	Time (min)	Degradation (%)	Reference
Sulfamonomethoxine	Deionized water	0.06	1.2	20	Fe ₃ O ₄ 2.4 mM	6.4	15	100	[43]
Tetracycline	Deionized water	0.18	30	166.6	AC@Fe ₃ O ₄ 0.4gL ⁻¹	3	240	99.8	[44]
Tetracycline	Milli-Q water	0.022	5	22.72	Ag/AgCl/(0.05)FeX 1gL ⁻¹	3.5	120	100	[45]
Norfloxacin	Milli-Q water	0.015	1	66.66	Magnetite nanoparticle 0.3gL ⁻¹	4	60	90	[46]
ciprofloxacin	Milli-Q and river water	0.03	0.6	20	Fe ²⁺	6	30	95.6	[47]
Ciprofloxacin	Deionized water	0.15	3.62	24	nZVI 120mgL ⁻¹	4.5	60	94	[48]
Metronidazole	Deionized water	0.14	1.85	13.21	nZVI 0.5gL ⁻¹	3	30	90.3	[49]
Ciprofloxacin	Deionized water	0.03	0.09	3	Fe(VI)0.09 mM	4	60	91.5	[50]



Table 5
US activation of PS for degradation of antibiotics.

Pollutant	Matrix	Pollutant Concentration (mM)	Oxidant Concentration (mM)	Molar ratio oxidant to pollutant (r_{ox})	Ultrasonic system	pH	Time (min)	Degradation (%)	Reference
Sulfadiazine	Deionized water	0.07	1.84	26.28	20 kHz, 40W	5	60	13.7	[51]
Tetracycline hydrochloride	Milli-Q water	0.112	4.0	35.71	35 kHz, 500W	10	120	96.5	[52]
Tetracycline	Deionized water	0.02	4	200	35 kHz, 500W	10	120	>20	[53]
Tetracycline	Deionized water	0.06	4	66.66	35 kHz, 500W	10	120	95.01	[54]



Table 6
Degradation of antibiotic by persulfate activated with activated carbon.

Pollutant	Matrix	Pollutant Concentration (mM)	Oxidant Concentration (mM)	Molar ratio oxidant to pollutant (rox)	Carbon materials	Carbon dosage (g/L)	pH	Doping Elements	Reactive oxygen species	Degradation (%)	References
Sulfamethoxazole	Deionized water	0.0019	0.5	263.15	Activated carbon	0.1	7.2	–	SO ₄ ^{•-} , OH [•]	91.2	[68]
Metronidazole	Deionized water	0.58	58	100	Activated carbon	5	3.9	N	SO ₄ ^{•-} , OH [•]	87	[69]
Chlortetracycline	Deionized water	0.1	11.48	114.87	Activated carbon	0.2	5	Fe ⁰	SO ₄ ^{•-} , O ₂ ^{•-}	88	[60]
Sulfamethoxazole	Ultrapure water	0.019	4	210.52	Activated carbon	–	–	–	SO ₄ ^{•-} , OH [•] , Electron transfer	95	[70]



Table 7
Degradation of antibiotic by persulfate activated with biochar.

Pollutant	Matrix	Pollutant Concentration (mM)	Oxidant Concentration (mM)	Molar ratio oxidant to pollutant (rox)	Carbon materials	Carbon dosage (g/L)	pH	Doping Elements	Reactive oxygen species	Degradation (%)	References
Sulfamethoxazole	deionized water, tap water and surface water	0.019	4	210.52	Biochar	0.05	6	N	SO ₄ ^{•-} , OH [•] , ¹ O ₂ Electron transfer	100	[65]
Norfloxacin	Deionized water	0.031	3.72	120	Biochar	0.8	6.5	N	SO ₄ ^{•-} , OH [•]	90	[78]
Tetracycline	Deionized water	0.02	2	100	Biochar	0.4	3	N, S	¹ O ₂ Electron transfer	100	[79]
Tetracycline	Deionized water	0.045	10	222.22	Biochar	0.4	3	Fe ₃ O ₄	SO ₄ ^{•-} , OH [•] , O ₂ ^{•-}	92.3	[80]
Tetracycline	Deionized water	0.045	0.5	11.11	Biochar	0.2	7	N, Cu	SO ₄ ^{•-} , OH [•] Electron transfer	100	[81]



Table 8
Degradation of antibiotic by persulfate activated with graphene.

Pollutant	Matrix	Pollutant Concentration (mM)	Oxidant Concentration (mM)	Molar ratio oxidant to pollutant (rox)	Carbon materials	Carbon dosage (g/L)	pH	Doping Elements	Reactive oxygen species	Degradation (%)	References
Cephalexin	Deionized water	0.014	1	71.42	carbon nanotubes	0.5	7	N, Ni	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	100	[83]
Sulfamethoxazole	Deionized water	0.019	1	52.63	carbon nanotubes	0.1	7	Fe_3C	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	100	[84]
Sulfamethoxazole	Deionized water	0.04	0.8	20	N-doped graphene	0.5	3.4	N	Electron transfer	91.7	[85]
Amoxicillin	Deionized water	–	10	–	C_3N_4 /graphene	1	–	MnFe_2O_4	$\text{SO}_4^{\bullet-}$, h^+ , $\text{O}_2^{\bullet-}$, HO^{\bullet}	65	[86]
Norfloxacin	Deionized water	0.06	10	166.6	Graphene	0.1	6.6	N, Fe_3O_4	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	100	[87]



However, at least 100 time molar excess of oxidant in respect to pollutant (r_{ox}) is needed to obtain such results, which seems to be a high value, especially in respect to costs of treatment process. Future studies should focus on PS/AC systems in real case scenario, i.e. to treat real effluents, instead of studies performed in ideal (deionized water) environment.

2.1.1.5.2. Biochar. Biochar (BC) is produced from biomass waste by pyrolysis process (no oxygen or limited oxygen and temperature 800-300 °C) [61,71]. Common types of biochars can be mentioned to the wood-based biochar [72], algae-based biochar [65], sludge-based biochar [73], straw-based biochar [74] and shell-based biochar [75]. Since biochar is produced by pyrolysis of biomass waste without adding any chemical or physical activating agents (KOH, H_3PO_4 , $ZnCl_2$, CO_2 and steam), it has a lower specific surface area (<500 m^2/g) than AC [61] but due to its low cost and having many functional groups, it is used as a catalyst for persulfate activation. Oxygen functional groups and stable free radicals on BC surface activate persulfate [76].

Wang et al. proposed a possible activation mechanism of persulfate by BC. They found that the activation of persulfate depends on the formed defective structures and stable free radicals in BC, including semiquinones and phenoxyls, and also the activation of persulfate can be enhanced due to the high degree of graphitization and aromatic conjugated π electrons in BC [77]. According to data compiled in (Table 7), application of biochar allows to obtain above 90% degradation of studied antibiotics. Typically, reported r_{ox} still mostly exceeded value of 100, however in one study (34), a 100% degradation of tetracycline was possible by PS activated with biochar at r_{ox} of 11. This approach seems to be reasonable in respect to application in real case scenario.

2.1.1.5.3. Carbon nanotubes. Good conductivity, high mobility of electrons on the surface and low mass transfer resistance have caused the high reactive activity of carbon nanotubes (CNT) [82]. Different dimensions and surface chemistry of CNT are responsible for different catalytic performance compared to other carbon materials. The catalytic reaction of CNT is related to the defect level and electronic state, which can be changed by increasing wall layers and doping heteroatoms [59,83]. CNT can be divided into two groups: single-walled CNT (SWCNT) and multi-walled CNT (MWCNT). The surface of MWCNT is much more active than SWCNT due to the presence of a large number of surface functional groups such as $-COOH$, $-C-O$ and $-OH$. Some researchers showed that by doping nitrogen to CNT enclosed with Fe_3C , it can be used to activate persulfate through hydroxylation, oxidation, ring opening, bond cleavage and sulfonation in order to degrade sulfamethoxazole, and as a result, they found that the catalytic performance of persulfate by CNT doped with nitrogen increases due to higher absorption and faster charge transfer [84].

Shang et al., shown that a 100% degradation of sulfamethoxazole was obtained with PS/nitrogen-doped carbon nanotubes with encapsulated Fe_3C nanoparticles. During this process the Fe_3C encapsulated NCNTs were beneficial both for the electron transfer and to avoid the Fe_3C from dissolving in the solution. EPR spectra revealed that the $SO_4^{\bullet-}$, HO^{\bullet} and 1O_2 contributed to the degradation of sulfamethoxazole [84]. Also, few other studies (Table 8) confirmed the activation of PS by carbon nanotubes. In this case r_{ox} between 50 and 70 revealed to be effective for 100% antibiotics removal.

2.1.1.5.4. Graphene. Graphene is a thin carbon sheet with a six-membered carbon ring as the core structure and various types of edge defects. Graphene has various functional groups including hydroxyl ($-OH$), carboxyl ($-COOH$), carbonyl ($-C-O$) and epoxy groups ($C-O-C$) [88]. Graphene can be divided into reduced graphene oxide (rGO), graphene oxide (GO) and pristine graphene based on the degree of surface oxidation. GO/rGO have an acidic surface and as a result, they need a basic surface to activate persulfate. Modified graphene is a suitable option for persulfate activation due to its higher specific surface area for adsorption and catalysis compared to CNT and BC, as well as good electrical conductivity and electron mobility for the redox reaction of sp^2 electrons [89]. Also, removing oxygen-containing groups on rGO surface by thermal method can improve the integrity of the π -conjugated structure and surface hydrophobicity [90]. Nucleophilic ketone and quinoid functional groups can act as active sites for redox reactions and persulfate activation due to having many electrons [91]. But the most important disadvantages of using graphene for persulfate activation relates to being expensive compared to other carbon materials and using dangerous oxidizing materials (H_2SO_4 , HNO_3 , and $KMnO_4$) in the classical Hummers synthesis method for GO [61].

Peng et al., applied N-RGO/ Fe_3O_4 to activate PS in order to degrade norfloxacin. Incorporation of N-RGO with Fe_3O_4 nanoparticles improved the catalytic efficiency - in 210 min it caused complete removal of norfloxacin. Also, based on the ESR spectrum, it was determined that both sulfate and hydroxyl radicals are produced during the activation.

Some researches proved the possibility of PS activation by carbon nanotube and graphene for degradation of antibiotics (Table 8).

In summary, it can be concluded that carbon-based catalysts are effective activators of persulfates for antibiotics activation. It is possible to obtain a 100% degradation of antibiotics using relatively low amounts of catalyst – 0.1–0.5 gL^{-1} . However, in some studies load above $1gL^{-1}$ also was reported as optimal, which seems to be not reasonable amount for real – large scale applications. In few studies it was proved that effective degradation can be obtained with minimized consumption of oxidant resulting in r_{ox} values of 10–20. Unfortunately, in many studies much higher load of oxidant (r_{ox} exceeding 100) was reported. Such a high values of oxidant dose could be typical for direct oxidation, but cannot be named as acceptable for advanced catalytic systems. Thus, in future studies a “milestone” optimal parameter should be oriented on the best reported values.

2.2. -Properties of peroxymonosulfate

Peroxymonosulfate (HSO_5^-), also known as PMS and Oxone, is another popular oxidant that used for degradation of pollutants [26]. Briefly it was compiled in Supp. Info. section S6.

2.2.1. Activation methods

2.2.1.1. Peroxymonosulfate activated by UV. Many literatures are explained the use of UV for activation of PMS (Table 9). More

Table 9
UV activation of PMS for degradation of antibiotics.

Pollutant	Matrix	Pollutant concentration (mM)	Oxidant Concentration (mM)	Molar ratio oxidant to pollutant (r_{ox})	Wavelength (nm)	pH	Time (min)	Degradation (%)	References
sulfamethazine	Drinking water	0.0062	0.0088	1.40	254	7.5	5	100	[92]
Sulfamethoxazole	Milli-Q water	0.02369	1	42.21	254	6.24	na.	97	[93]
Ciprofloxacin	Domestic wastewater	0.125	2.5	20	278	7	60	100	[94]
Cefexime	Deionized water	0.0011	1.37	124.54	254	7.5	30	93.18	
Tetracycline	Milli-Q water	0.01125	0.2	17.77	254	11	na.	82	[95]



information is given in Supp. Info. section S7.

The performance of UV, PMS, and UV/PMS used for degradation Sulfamethazine was compared. UV/PMS provided more thorough degradation of Sulfamethazine, as demonstrated by the complete degradation of $0.2\mu\text{gL}^{-1}$ of Sulfamethazine within 5min at an initial PMS = 1mgL^{-1} , pH = 7.5, UV = 254 nm, rox = 1.4. UV promoted Sulfamethazine degradation by PMS resulting in a higher effectiveness of the combined process comparing to the sole use of UV photolysis or PMS. PMS decomposes with UV by cleavage of its peroxide bond, which produces $\text{SO}_4^{\bullet-}$ and HO^{\bullet} [92]. The pyrimidine ring structure of sulfamethazine is resistant to oxidation by $\text{SO}_4^{\bullet-}$. Thus, their rapid degradation is attributed to oxidation of the aniline moiety and cleavage of the sulfonamide bond by $\text{SO}_4^{\bullet-}$ or HO^{\bullet} .

A study on degradation of Ciprofloxacin demonstrated the effectiveness of S-AOPs for treatment of domestic wastewater containing this pharmaceutical by comparing three UV-254nm based AOPs: UV/PS, UV/PMS and UV/H₂O₂. In distilled water, the order of degradation efficiency was UV/PS > UV/PMS > UV/H₂O₂, while in wastewater, the most efficient process was UV/PMS > UV/PS > UV/H₂O₂ mainly because PMS decomposition into sulfate radical anion was activated by bicarbonate ions. UV/PMS has demonstrated better kinetic performances over UV/H₂O₂ system for CIP removal wastewater treatment plant effluents mainly because bicarbonate ions are able to activate PMS decomposition into SRA and due to the higher selectivity in reactivity of SRA with respect to HR in organic-rich matrices. CIP was completely degraded in wastewater at the optimized parameters. The disadvantage of PMS applied as Oxone is the triple salt form, which results in high mass dose of Oxone needed to obtain desired rox. The price of chemical is related to its mass not moles, thus PMS processes with comparable rox to PS will be much more expensive. Sulfate radical anion attacks prompted transformations at the piperazinyl ring through the one electron oxidation mechanism as a major pathway while OH^{\bullet} attacks were mainly responsible for quinolone moiety transformations as a minor pathway. Sulfate radical anion generation has made UV/PMS a kinetically effective process in degradation CIP from wastewater [94].

2.2.1.2. Peroxymonosulfate activated by graphene oxide, transition metals, nanoscale magnetic and $\alpha\text{-MnO}_2$. Multiple studies have been confirming the activation of PMS by transition metals, nanoscale magnetic and $\alpha\text{-MnO}_2$, and graphene oxide. the information about these methods exists in Supp. Info. section S8.

Babayi et al. shown the performance of graphene-based CoFe_2O_4 in the activation of PMS and amoxicillin removal from aqueous solutions. In optimum condition, the amoxicillin, COD and TOC removal efficiency was 99.27%, 83.1%, and 61.11%, respectively, showing that despite high degradation efficiency of the amoxicillin, it was not fully mineralized [96]. Almost 40% of the remaining TOC, indicates the by-products of degradation were not effectively degraded. In such cases, an evaluation of by-products toxicity is a must to fully present the advantages of the developed process. Many by-products of pharmaceuticals degradation can be much more toxic comparing to primary form. Thus, there is a risk that biotoxicity of the treated effluent could significantly increase.

They used pH = 3–9 and concluded that AOPs based on Co/PMS have better performance in neutral and alkaline pH. The best process efficiency was achieved in the removal of amoxicillin in pH 6. However, the optimal performance of the system in pH 4 to 7 does not differ much from each other, but in pH < 4 and pH > 7, the efficiency of the system significantly decreases. The reason for this decrease in acidic pH is the lack of effective activation of PMS according to Eq. (9).



The reason for the decrease in efficiency in alkaline pH > 7 is the reaction of free $\text{SO}_4^{\bullet-}$ with hydroxyl ions and the production of sulfate ions and free OH^{\bullet} . This free OH^{\bullet} is rapidly converted to free radical hydrogen, which is much weaker than $\text{SO}_4^{\bullet-}$. Another important parameter in G/CoFe₂O₄/PMS process is the catalyst concentration, which plays a significant role in the removal of amoxicillin. In this experiment, the optimum concentration of catalyst was obtained 0.5gL^{-1} . The removal efficiency of amoxicillin increases to a concentration of 0.5gL^{-1} from the catalyst, but there was no significant difference from 0.5 to 1.25gL^{-1} . As the dose of catalyst increases, the efficiency of removal increases, which is due to the increase in active sites available for PMS decomposition and the production of more free $\text{SO}_4^{\bullet-}$ [96]. In this study, the rox = 150 which means the authors do not focus on the rox, defining the concentration of oxidant as molar concentration and pollutant in mgL^{-1} , this relation is not directly visible.

The antibiotic removal with transition metals/PMS was shown in Table 10.

Feng et al. used $\alpha\text{-Fe}_2\text{O}_3$ as the activator of PMS for degradation of sulfamethoxazole (SMX). The weight ratio between Cu₂O and

Table 10
Transition metals activation of PMS for degradation of antibiotics.

Pollutant	Matrix	Pollutant Concentration (mM)	Oxidant Concentration (mM)	Molar ratio oxidant to pollutant (r_{ox})	Activator	pH	Time (min)	Degradation (%)	References
Sulfamethoxazole	Ultrapure water	0.0063	0.1575	25	$\alpha\text{-Fe}_2\text{O}_3$ 0.4gL^{-1}	6.8	180	100	[97]
Chloramphenicol	Milli-Q water	0.03	1	33.33	$\text{Co}_3\text{O}_4\text{KIT}$ 0.1gL^{-1}	7	60	100	[98]
Sulfadiazine	Purified water	0.008	0.033	4.125	CuFeO_2 RCs 0.1gL^{-1}	8.5	24	100	[99]
fluoroquinolones	Deionized water	0.03	10	333.3	Fe(VI) 0.15 mM	7	30	100	[100]
Sulfamethoxazole	Deionized water	0.1	0.5	5	Fe(VI) 0.05 mM	5.2	30	30	[101]

α -Fe₂O₃ influenced the degradation of SMX and the optimal ratio depended on the dosage of PMS and catalyst. With 40mgL⁻¹ PMS and 0.6gL⁻¹ catalyst, a pseudo-first-order constant of $\sim 0.019\text{min}^{-1}$ was achieved for CT2.5%Cu₂O, whereas only 0.004min⁻¹ was realized for α -Fe₂O₃. Nearly complete degradation of the sulfamethoxazole was achieved within 180min under the conditions of 40mgL⁻¹ PMS, 0.4gL⁻¹, CT2.5%Cu₂O, and pH 6.8. The CT2.5%Cu₂O had efficient reactivity for SMX degradation and the highest stoichiometric efficiency value after a reaction time of 60min. The reactivity of the CT2.5%Cu₂O was highly dependent on its contact time with the PMS [97].

Deng et al. by survey of some conditions such as catalyst = 0.02–0.4gL⁻¹, pH = 3–11 and PMS = 0.2–4 mM, for decomposition of chloramphenicol by PMS activated with Co₃O₄ are concluded that, by optimum conditions pH = 7, catalyst dosage = 0.1gL⁻¹ and PMS = 1 mM, chloramphenicol degraded completely. The superior catalytic performance of Co₃O₄-KIT6 was ascribed to the combination of multiple unique characteristics, including the large specific surface area, high pore volume, high Co²⁺ content and high density of surface-active sites. Higher catalyst dosage, higher PMS concentration, neutral pH and higher reaction temperature favored the removal. The balance among Co²⁺/Co³⁺, O₂/O₂ and PMS decomposed in solution ensured the continuous generation of OH[•] and SO₄^{•-}, and the latter made the predominant contribution for the CAP degradation. Considering its outstanding catalytic activity, excellent reusability and long-term stability, mesoporous Co₃O₄ are other advantages of that [98].

Zhang et al. used CuBi₂O₄/MnO₂/PMS to degrade ceftiofur (CEF). The authors concluded that by the optimization of selected parameters such as mass ratio of CuBi₂O₄ to MnO₂ = 1:5, CEF = 5mgL⁻¹, PMS = 0.4gL⁻¹ and pH = 11, it was possible to obtain a CEF degradation reaching 93.6%. The degradation of CEF was tested in the pH range of 3–11. It could be noticed that the degradation efficiency of CEF increased from 83.3% to 93.6% with the pH increasing from 3 to 11. The increase of solution pH helped the formation of hydroxyl groups on the surface of CuBi₂O₄/MnO₂ composite, which could be served as the active site for the electron transfer to improve the activation of PMS. Also, by increasing PMS concentration from 0 to 0.5gL⁻¹ the degradation rate was increased. The higher PMS concentrations could lead to higher catalytic performance. Corresponding, the k_{app} of CEF removal was increased from 0.00772min⁻¹ to 0.05624min⁻¹ as the concentration of PMS increased from 0 to 0.5gL⁻¹, indicating the accelerated reaction rates. Probably, it follows from the fact, that more SO₄^{•-} would be produced with the increase of PMS concentration, resulting in the enhancement of CEF degradation efficiency. However, when the PMS concentration was continuously increased from 0.4gL⁻¹ to 0.5gL⁻¹, a limited increase was clearly observed, which might be due to the reaction between excess PMS and active species (a self-scavenging effect), thus inhibited degradation of the CEF [102].

Deng et al. revealed under optimal parameters the degradation of ciprofloxacin was obtained 93.6%. Nanoscale α -MnO₂ with different morphologies (nanoparticles, nanoflowers and nanorods) were synthesized via a facile hydrothermal method and tested in PMS activation for CIP degradation. The catalytic activity of α -MnO₂ mainly relied on the specific surface area and crystallinity, and followed the order of α -MnO₂ nanoflowers > α -MnO₂ nanorods > α -MnO₂ nanoparticles > commercial MnO₂. The removal efficiency decreased from 93.68% to 83.81% as solution pH increased from 3 to 7, suggesting that acidic conditions were more favorable to the degradation than neutral condition. Without MnO₂ catalysts, only 16.99% CIP was removed by PMS alone, indicating that PMS was not effective as an oxidant to directly degrade this pollutant. In the absence of PMS, MnO₂ caused a slight reduction of CIP (less than 7%) which was primarily attributed to the adsorption of CIP on the catalyst surface. Among the four MnO₂ samples, α -MnO₂ nanoflowers presented the highest efficiency in CIP adsorption which resulted from its highest BET surface area. When PMS and MnO₂ were simultaneously introduced into the solution, the CIP removal was evidently enhanced, because of the involvement of SO₄^{•-} and HO[•] which originated from the decomposition of PMS caused by the electron exchange between Mn³⁺ and Mn⁴⁺ in MnO₂. The removal efficiencies of CIP with α -MnO₂ nanoflowers, nanorods, nanoparticles and commercial MnO₂ as PMS initiators were 93.68, 71.33, 61.97 and 22.94%, respectively [103].

2.2.1.3. Peroxymonosulfate activated by heat. Using heat to activate PMS is also used to degrade pollutants in water and wastewater. Elevated temperatures are needed to activate PMS, and on the other hand, its not high efficiency makes this activation method not practical for large scales. The exemption are process effluents that due to previous stages of operation initially could have temperatures exceeding 40 °C. On the other hand, comparing to other activation methods, the use of heat allows to shorten the required reaction time and activation energy [104]. In the heat-activated PS oxidation process, only SO₄^{•-} radicals are formed while from the activation of PMS with heat, both sulfate and hydroxyl radicals are produced (Eq. (10)) The activation mechanism of PMS with heat is to cleave the O–O bond and produce sulfate radicals. Compared to the thermal activation of PS, fewer studies were conducted on the thermal activation of PMS. Yang et al. showed that heat activation is effective for PS while not for PMS [105]. Therefore, more studies should be done on the mechanism of PMS activation by heat. So far, this method rarely has been used to activate PMS for the degradation of antibiotics and studies in this field are scarce [35].



Only a few studies have been conducted to remove antibiotics using heat-activated peroxymonosulfate. Ulucan-Altuntas et al., used PMS activated by heat for degradation of oxytetracycline. In this method, they shown that optimal conditions are obtained at temperature of 75 °C, allowing to obtain 84% degradation in 20 min of treatment [35]. In another study Milh et al., revealed that PMS/heat process under optimum conditions at 70 °C allowed to obtain 94% degradation of sulfamethoxazole in 60 min [106].

2.2.1.4. Peroxymonosulfate and persulfate activated by gamma radiation. The use of gamma radiation in wastewater and water treatment to remove toxic pollutants is a relatively new technology. With gamma radiation, hydroxyl radicals, hydrated electrons, and hydrogen radicals are produced [107]. These active species, through the oxidation of hydroxyl radicals and the reduction of hydrated

electrons, can cause the decomposition of pollutants and also cause the activation of PS and PMS. In addition, due to the high energy of the gamma-ray, it can activate PS and PMS by cleavage of O–O bond. Although gamma rays have a high penetration comparing to UV, the cost of making gamma-ray equipment is much higher than UV equipment, for this reason, applications of this method are not common [35,108].

According to Eqs. (1), (11)–(13) kGy irradiated dose of radiation produces 10^{-5} mol eq $^{-1}$ and H $^{\bullet}$ which can theoretically convert 10^{-5} mol/sulfate to SO $_4^{\bullet-}$ [109].



When the eqq-are produced from gamma radiation, they react with PMS and can produce OH $^{\bullet}$ and SO $_4^{\bullet-}$ (Eqs. (14) and (15)) [35].



Some papers investigated the possibility of activation of PS and PMS by gamma radiation for the degradation of antibiotics (Table 11). Importantly, in all studies a r_{ox} values below 100 were reported. It follows from high effectiveness of this method of activation, however with high energy costs. A variety of reported effectiveness (also in respect to same pollutant, see carbamazepine), confirms that this type of activation demands standardization of experimental conditions and validation of performance to allow real comparison of results. According to already published data, this method has high potential for future studies.

3. Effect of operation parameters for antibiotics degradation

3.1. Effect of pH

The pH is one of the most important and influential parameters on the amount and type of radicals formed under AOPs and as well as the efficacy of antibiotics. In most chemical and electrochemical processes pH of solution is one of the most important factors in the management and process efficiency. This factor can affect process efficiency by affecting the pollutant properties and used methods. Therefore, the main factor in determining the dominant radical in the process is completely influenced by the pH of solution [33]. PS in different pHs of the solution is stable, while PMS can be affected by different pH. PMS is stable in pH < 6 or pH = 12. When pH = 9, it showed the poorest stability where half of HSO $_5^-$ decomposes to SO $_5^{\bullet-}$ [112]. Under alkaline conditions, PS can be decomposed to SO $_4^{\bullet-}$. Sulfate radicals can further transform into OH $^{\bullet}$. Thus, SO $_4^{\bullet-}$ play a major role in degrading the organic compounds under alkaline conditions. While SO $_4^{\bullet-}$ are the primary reactive species at acid conditions. Under neutral conditions, both OH $^{\bullet}$ and SO $_4^{\bullet-}$ contributed to the degradation of organic pollutants [113]. As mentioned above, PS presented stability in the solution at different pH, while the existing form of PMS was significantly influenced by the solution of pH. Alkaline conditions can activate both PS and PMS. In pH < 5, hydrogen ion acts as the scavenger of SO $_4^{\bullet-}$ and OH $^{\bullet}$ (J [114]. In general, PS and PMS have a wide pH range of application, although their oxidation potential changes with the pH. The appropriate pH should be adjusted based on PS and PMS activation methods [115].

3.1.1. Effect of pH on activation method by UV

The best pH for activating PS and PMS to produce SO $_4^{\bullet-}$ is in the range of 5 and 7. In both UV/PS and UV/PMS systems at pH < 7, especially 3 to 5 the superiority is with SO $_4^{\bullet-}$ generation. According to Eq. (16), when the pH is between 7 and 9, SO $_4^{\bullet-}$ and OH $^{\bullet}$ are present in the system and in alkaline conditions, especially pH = 12, SO $_4^{\bullet-}$ react with hydroxyl ions and generate OH $^{\bullet}$ (Eq. (17)). Therefore, the presence of SO $_4^{\bullet-}$ will be superior, and in alkaline conditions the potential of OH $^{\bullet}$ oxidation will be greatly reduced [116].

Also at higher pHs, SO $_4^{\bullet-}$ and OH $^{\bullet}$ react with each other according to Eq. (18), which the process efficiency is significantly reduced so that the oxidation system becomes vacant of radicals [117].

Table 11

Activation of PS and PMS with gamma radiation for degradation of antibiotics.

Pollutant	matrix	Pollutant Concentration (mM)	Kind of oxidant	Oxidant Concentration (mM)	Molar ratio oxidant to pollutant (r_{ox})	Irradiated dose [Gy]	pH	Degradation (%)	References
Triclosan	Milli-Q water	0.026	PS	1.5	57.69	300	6.5	100	[108]
Trimethoprim	Deionized water	0.068	PS	2	29.41	1000	6.5	34	[109]
Carbamazepine	Deionized water	0.042	PS	2	47.61	200	6.5	80.9	[110]
Carbamazepine	Deionized water	0.04	PMS	0.8	20	300	3	100	[111]



In the process of activating PS and PMS with UV, some studies reported data also confirming this statement. Similarly to these studies, it was shown that the highest degradation efficiency of Sulfamethazine [28], Ciprofloxacin [118], Chloramphenicol [29], Sulfamethoxazole [93,119], Oxytetracycline [31], Penicillin G [20], Ofloxacin [33] and Cefexime [120] were obtained at pH = 5.8–7 with PS/UVC.

However, some studies present in the literature are in contrast with this theory. In these cases, the highest degradation efficiency was obtained for pH > 7. For example, the highest degradation efficiency of Sulfamethoxazole [93], metronidazole [32], Sulfamerazine, Sulfamethizole, Sulfachloropyridazine [92] and Tetracycline [95] were obtained at pH between 7.5 and 11. They have a different result in comparison with previous studies. From these studies, it appears that each system based on UV/PS has different performance at different pHs and it has been proved that the characteristics of the pollutant and its decomposition mechanism are probably responsible for this difference [115].

3.1.2. Effect of pH on activation method by heat

In this method, the optimal pH is between 5 and 7. Because at pH < 7, the activation is focused on formation of $\text{SO}_4^{\bullet-}$. It should be noted that at certain temperatures, pH also affects the conversion of $\text{SO}_4^{\bullet-}$ to OH^{\bullet} . It has been reported that $\text{SO}_4^{\bullet-}$ at pH < 7, $\text{SO}_4^{\bullet-}$ and OH^{\bullet} at pH = 9 and OH^{\bullet} at pH = 12 predominate [115]. The type and rate of the produced radicals are among the important effects of pH changes on AOPs. At neutral pH, the $\text{SO}_4^{\bullet-}$ radicals are dominant, at pH = 9, both $\text{SO}_4^{\bullet-}$ and OH^{\bullet} radicals are presented, and in pH > 12, the OH^{\bullet} radical is dominant. When PS is used as an oxidizer, according to Eq. (9), in addition to $\text{SO}_4^{\bullet-}$, OH^{\bullet} radical is also generated. So, the degradation efficiency of antibiotics is reduced at high pH (Eq. (19)) due to the reaction of $\text{SO}_4^{\bullet-}$ radical by OH^{\bullet} , that conduces to higher consumption of $\text{SO}_4^{\bullet-}$ and subsequently degradation efficiency. In addition, reactions in Eqs. (20) and (21) also occur in the presence of OH^{\bullet} at pH = 9 and 11, respectively. The reaction of OH^{\bullet} with OH^{\bullet} can conduce to a quick loss of OH^{\bullet} in an alkaline solution. In alkaline conditions, the redox potential of OH^{\bullet} decreases (about 2.0V) and leading to the drop in the oxidation potential of OH^{\bullet} . So, the degradation efficiency in alkaline conditions would be less than that in acidic and neutral conditions [121].



Similar to these studies, the highest degradation efficiency of fluconazole [38], Enrofloxacin and Ciprofloxacin [39], Penicillin G [37], chloramphenicol [36], Sulfamethazin [40], tetracycline [42] and Triclosan [41] was obtained in pH 3 to 7.8 respectively.

3.1.3. Effect of pH on activation method by ultrasound

Naseeri et al. surveyed the effect of pH on degradation of tetracycline by using peroxydisulfate activated by ultrasound irradiation. The tetracycline degradation efficiencies in pH 4, 7 and 10 on batch mode by using an ultrasonic bath with ultrasound power: 500W, 35 kHz were obtained 77.35%, 62.46% and 88.51%, respectively. The pKa values of tetracycline are 3.3, 7.7 and 9.7; in addition, it is an amphoteric molecule. So, the molecules of tetracycline had a positive charge and they are neutral at pH = 4. On the other hand, at pH = 9 they had negative charge. Tetracycline molecules with negative charge cause reactive species like OH^{\bullet} due to high electrical density on the ring system that accelerated degradation of tetracycline [52].

Yin et al., used ultrasound irradiation for activation of PMS in different ranges of pH 3, 5, 7, 9 and 11 to degrade sulfamethazine. The studies revealed that at pH = 5, 7, 9 and 11 a 99% degradation was obtained, while at pH = 3 the removal efficiency was decreased to 90%. At pH lower than 5, H^+ act as a scavenger for hydroxyl and $\text{SO}_4^{\bullet-}$, which explains the reported decrease in degradation efficiency. On the other hand, in basic pH, the presence of OH^- can activate PMS and subsequently, the removal efficiency has increased [55].

3.1.4. Effect of pH on activation method by transition metals

The effect of pH on S-AOPs based on transition metals activation of PS was studied in several papers. The authors proved the importance of pH optimization. Cobalt oxide is known as an effective activator in S-AOPs. At high pH, cobalt oxides convert to cobalt hydroxide complexes which reduces its catalytic activity. In addition, pH also effects the surface charge of metal oxide which effectively affects the activation function of metal oxides (Y. [122]; Y [123]). In the process of PS activation with iron, pH has a direct effect on the type and state of iron required by the PS and it is also effective in determining the dominant type of formed radicals [117]. At pH > 4, Fe^{2+} ions are converted to Fe^{3+} , which has low ability to activate PS and generate $\text{SO}_4^{\bullet-}$. With increasing pH, the Fe^{3+} ions, are converted to ferric hydroxide which results in absence of cations as well as increases the production of sludge. Also, with increasing pH, iron precipitates as colloidal FeOH^+ according to Eq. (22) [124] that is unable to participate in the activation of PS.



By increasing pH>9, species of oxyhydroxylperic acid $\text{Fe}(\text{OH})_3^*$, $\text{Fe}(\text{OH})_4^*$, FeOH^{3+} and $\text{Fe}_2(\text{OH})_3^{4+}$ are produced. This type of iron species has very low ability to activate PS [125]. Also, by changing the pH to alkaline, the product of PS activation with Fe^{2+} , which is SO_4^* , can change and lead the reaction to the production of OH^* [116].

The reason for this decrease was that at high pH, SO_4^* and OH^* react with each other, in which case the efficiency of the process decreases so that the oxidation system becomes vacant of radicals according to Eq. (23) [49].



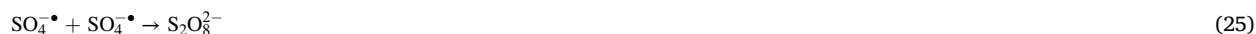
Feng et al. showed that at the optimized pH = 6.8 a total degradation of sulfamethoxazole was obtained 100% by using Cu_2O for activated PMS; while, by activated PMS by $\alpha\text{-Fe}_2\text{O}_3$ under similar conditions the removal efficiency was obtained less than 20% [97]. Deng et al. also showed that the highest (100%) degradation efficacy in respect to chloramphenicol degradation was obtained at neutral pH [98]. In another study, Feng et al. used CuFeO_2 rhombohedral crystal-catalyzed PMS for degradation of sulfadiazine, and showed the sulfadiazine degradation efficiency was obtained about 100% at pH = 8.5. On the other hand, by reducing the pH to 4 and 5 (acidic conditions) the degradation efficiency was decreased. When pH is in the range of 4–8.5, due to pKa values of PMS ($\text{pK}_{a1} < 0$ and $\text{pK}_{a2} = 9.4$); therefore, PMS is present as HSO_5^- . The inhibitory effect of H^+ could be described by the effect of stabilizing H^+ on HSO_5^- [99]. Additional information about pH effects on persulfates can be found in Supp. Info. section S9.

3.2. Effect of antibiotic concentration

The initial concentration of antibiotics also has a significant impact on the performance of AOPs with PS and PMS [17]. In all the studies, with increasing the concentration of antibiotics, the decomposition efficiency decreases because with increasing antibiotic concentration the proportion of OH^* to pollutant decreases. In addition, the tendency of intermediate compounds for consume of OH^* increases too [126]. Also, due to the short life of the produced free radicals such as SO_4^* and OH^* , which are about 4 s and 20 ns, respectively, they may react with the intermediate compounds immediately after production and before reacting with the contaminant. For this reason, lower concentrations of antibiotics lead to fewer intermediates. Hence, the removal rate increases, while the decomposition efficiency decreases with increasing antibiotic concentration where more intermediates are formed [127,128].

3.3. Effect of persulfate and peroxymonosulfate concentration

In all activation methods, by increasing the concentration of PS and PMS, the production of SO_4^* increases and leads to an increase in removal efficiency. However, as the concentration increases further, the removal efficiency is constant and sometimes decreases. This reduction in efficiency is due to the high concentration of oxidants in the environment, which acts as a radical scavenger and reduces SO_4^* and OH^* in the environment. According to Eqs. (24) and (25), high concentration of PS acts as a radical scavenger of SO_4^* and also the excessive concentration of SO_4^* can lead to SO_4^* consumption [129,130].



In the process of PS and PMS activation by UV, heat, ultrasounds and transition metals some studies reported data also confirming the scavenging effect of higher concentrations of oxidants. Similarly, to these studies, it was showed that by increasing the concentration of PS and PMS to some extent, the removal efficiency of tetracycline [52], sulfamethazine [92], ampicillin [8], penicillin G [37], cefixime [120], chloramphenicol [36] and metronidazole [32] were increased and with increasing oxidant to excessive concentration due to the production of radical scavengers the removal efficiency decreases.

Naseri et al. degraded tetracycline by using US/PMS and concluded that by increasing the concentration of $\text{S}_2\text{O}_8^{2-}$ from 1 mM to 4 mM under the optimal conditions (alkaline pH and 120min), the degradation efficiency of tetracycline increased from 55.76% to 88.51%, due to the production of more SO_4^* . But with increasing the concentration more than 4 mM the removal efficiency did not increase significantly. In this study concentrations higher than 6 mM were not investigated to determine. However, by increasing $\text{S}_2\text{O}_8^{2-}$ too much, the possibility of sulfate anions being formed without the production of SO_4^* increases [52].

Fan et al. survey the effect of heat/PS for degradation of sulfamethazine. In this study, with increasing the concentration of PS, k_{obs} of sulfamethazine increased significantly and also the half-life of sulfamethazine decreased with increasing the concentration of PS from 0.25 mM to 0.4 mM from 258 to 27min respectively. So, with increasing PS concentration the removal efficiency increases. In this study, the effect of more than 4 mM of oxidant and also its excessive effect as a radical scavenger were not investigated. Also, the effect of excessive oxidant concentration, which acts as a radical scavenger, has not been investigated [40].

Frontistis et al. investigated the degradation of antibiotic ampicillin on boron-doped diamond anode using the combined electrochemical oxidation sodium PS process and observed that by increasing the concentration of PS from 100mgL^{-1} to 500mgL^{-1} the ampicillin removal efficiency increased. According Eqs.(26)–(28), SO_4^* on the cathode can be electrogenerated, while anodic oxidation of sulfate ions produces PS. PS can also react with OH^* at the anode surface to produce excess SO_4^* [131].



Previously, some researchers suggested a non-radical pathway to increase the efficiency of combining BDD with PS. According to this method, the non-radical electro-activation of PS is similar to carbon catalysts activating PS. PS should be used with caution as it may increase treatment costs, and sulfate anions at concentrations above 250mgL^{-1} are considered as contaminants, according to the WHO [132]. Since the removal efficiency at concentrations of 250mgL^{-1} and 500mgL^{-1} was not much different, for the reason mentioned above, the optimal concentration was determined to be 250mgL^{-1} . In this study, the effect of scavengers was not investigated [8].

Norzaee et al. used heat/PS for degradation of Penicillin G, concluding that increasing the PS concentration from 0.05 mM to 0.1 mM, increased the removal efficiency of penicillin G to 97.25% in 75min. On the other hand, when the concentration was further increased above 0.1 mM, the removal efficiency was significantly decreased. PS acted as a scavenger of $\text{SO}_4^{\bullet-}$ and also it was found that excessive increase of $\text{SO}_4^{\bullet-}$ may lead to termination of other sulfate radicals' molecules. Therefore, excessive presence of PS leads to a decrease in the removal efficiency of penicillin G [121].

Khazaei et al. used the UV/PMS method to remove cefixime. In this approach, with increasing the concentration of PMS, the removal efficiency of the antibiotic increased, but with its increase to more than 1.37 mM, the removal efficiency decreased.

3.4. Effect of scavengers

There are many ions present in real conditions in aqueous media that can have different effects on $\text{SO}_4^{\bullet-}$ and OH^{\bullet} resulting from the activation of PS and PMS. Chloride ion is a major ion in water sources, experimental findings show that the presence of chloride ion can decrease or sometimes increase the removal efficiency of some contaminants. Chloride ions react with $\text{SO}_4^{\bullet-}$ to produce chloride radicals, which reduce $\text{SO}_4^{\bullet-}$. In addition, other secondary radicals such as dichloride radicals can be generated due to the reaction of the chloride radical with the chloride ion according to Eqs.(29)–(31) [133].



Carbonate, bicarbonate, sulfate, nitrate and nitrite ions have a negative effect on $\text{SO}_4^{\bullet-}$ and OH^{\bullet} . Because these ions can suppress $\text{SO}_4^{\bullet-}$ and OH^{\bullet} . Among these anions, the sulfate ion can not only suppress radicals but can also chelate metal oxide. Phosphate has a stronger inhibition effect on the removal of organic pollutants by $\text{SO}_4^{\bullet-}$ and OH^{\bullet} comparing to other anions [134].

Interestingly, chloride, bicarbonate, carbonate, and hydrogen phosphate can effectively activate PMS but not PS. In addition, the activation performance increases with increasing concentration of chloride, bicarbonate and hydrogen phosphate and decreases with increasing concentration of carbonate. Natural organic matter has been shown to have a negative effect on the removal of organic pollutants by PS and PMS activated methods. It has also been shown that the negative effect has a link with pH of the solution [135].

In the case of heterogeneous catalytic systems, at low pH the natural organic matter scavenged, the positive holes on the surface of the catalyst, while at the high pH, the natural organic compounds mainly scavenged the radicals. Some components of natural organic matter such as hydroquinones, quinones and phenols can effectively activate PMS. In general, the negative impact of wastewater compounds caused by ubiquitous anions is mainly due to the action of inhibiting anions to radicals. The positive effects of chloride, bicarbonate, carbonate and hydrogen phosphate are mainly due to the formation of chlorine and carbonate radicals [136].

In the case of chlorine, the positive effect can be explained by two reasons, one is that chlorine radicals are formed because the reaction between chlorine and $\text{SO}_4^{\bullet-}$ and OH^{\bullet} can react with pollutants. The second reason is that chlorine radicals react mainly with water to form $\text{SO}_4^{\bullet-}$ and OH^{\bullet} , which can further reduce pollutants [137].

For carbonate, a positive effect occurs only when the carbonate concentration is much higher comparing to the concentration of PS or PMS. In this case, $\text{SO}_4^{\bullet-}$ and OH^{\bullet} can be completely converted to carbonate radicals, which can further degrade some organic pollutants. It should be noted that chloride and nitrate radicals lead to the production of chlorinated by-products and nitrated by-products, which could pose a potential risk to the environment and human health [115].

Norzaee et al. used the heat/PS method for removing penicillin G and investigated the effect of chloride and carbonate as radical scavengers. The degradation efficiency of penicillin G in the presence of radical scavengers was reduced. According to the results, at 75min contact time with the addition of chloride and carbonate anions, the removal efficiency decreased from 98% to 73.40% and 60.74% respectively [37]. Possible reactions that occur in the presence of radical mineral scavengers are shown in Eq. (32), 33 [138].



According to Eqs.(29)–(31), chloride ions can form various radicals by reacting with reactive species. According to Eq. (29), low concentrations of chloride may cause reduce the recombination frequency of $\text{SO}_4^{\bullet-}$ to sulfate ions because Cl^- can consume activated $\text{SO}_4^{\bullet-}$ and thus increase the concentration of SO_4^{2-} in solution [139]. However, at very high concentrations of chloride, $\text{SO}_4^{\bullet-}$ turn into chlorine less reactive species such as $\text{Cl}_2^{\bullet-}$ and this condition reduces the decomposition efficiency. Carbonate anion can inactivate $\text{SO}_4^{\bullet-}$ and OH^{\bullet} . Carbonate anion can act as a scavenger of $\text{SO}_4^{\bullet-}$ and OH^{\bullet} and produce carbonate radicals ($\text{CO}_3^{\bullet-}$) according to Eqs. (32) and (33). So, pre-treatment of wastewater can be effective in removing or reducing radical scavengers [40].

Nasseri et al. Studied the effect of humic acid on the decomposition process of tetracycline and concluded that humic acid at low

Table 12
Effects of the water matrix on degradation efficiency of antibiotics.

Antibiotic	Oxidation system	Main mechanism	Effect of anions					Ref.
			Cl ⁻	HCO ₃ ⁻	NO ₃ ⁻	SO ₄ ²⁻	NOM	
Ciprofloxacin	magnetic γ -Fe ₂ O ₃ -MnO ₂ /PMS	SO ₄ ^{-•} , HO [•]	H (-)	H (-)	H (-)	H (-)	H (-)	[144]
Tetracycline	UV/PS	SO ₄ ^{-•} , HO [•]	High (-)	-	-	-	-	[27]
Norfloxacin	AC-based CoFe ₂ O ₄ SAC Nanocomposites/PMS	SO ₄ ^{-•} , HO [•]	L (-)	L (+)	No significant effect	-	-	[145]
Sulfamethoxazole	Heat/PS	Singlet Oxygen (¹ O ₂)	-	H (+)	-	-	L (+)	[146]
Sulfamethazine	Heat/PS	Singlet Oxygen (¹ O ₂)	H (+)	H (+)	-	-	H (-)	[147]
Tetracycline	US/PS	SO ₄ ^{-•} , HO [•]	L (-)	L (-)	-	-	L (+) H (-)	[52]
Erythromycin	Gamma/PS	SO ₄ ^{-•} , HO [•]	H (-) L (-)	H (-) L (-)	H (-) L (-)	H (+)	-	[148]
Fluconazole	Heat/PS	SO ₄ ^{-•} , HO [•]	H (-)	H (-)	-	-	H (-)	[149]
Tetracycline	UV/PMS	Singlet Oxygen (¹ O ₂)	H (+)	-	-	-	-	[95]
Sulfamethoxazole	UV/PS	Singlet Oxygen (¹ O ₂)	H (+)	-	H (+)	H (+)	-	[93]
Sulfamethoxazole	UV/PMS	Singlet Oxygen (¹ O ₂)	H (+)	-	H (+)	No significant effect	-	[93]
Penicillin G	Heat/PS	Singlet Oxygen (¹ O ₂)	H (+) L (-)	-	-	-	-	[121]
Ciprofloxacin and Sulfamethoxazole	Ferrous/PS	SO ₄ ^{-•} , HO [•]	-	No significant effect	-	-	No significant effect	[47]
Tetracycline	magnetic Ag/AgCl/modified zeolite X/ PS	SO ₄ ^{-•} , HO [•]	H (-)	-	-	-	-	[45]
Oxytetracycline	UV/PS	SO ₄ ^{-•} , HO [•]	H (-) L (-)	H (+)	No significant effect	No significant effect	H (-)	[150]
Chloramphenicol	Heat/PS	SO ₄ ^{-•} , HO [•]	H (-)	H (-)	No significant effect	-	H (-)	[151]
Chloramphenicol	UV/PS	SO ₄ ^{-•} , HO [•]	H (-) L (+)	H (-)	H (-)	H (-) L (+)	H (-)	[152]
Cefixime	UV/PMS	SO ₄ ^{-•} , HO [•]	-	-	-	L (-)	-	[153]
Sulfamethoxazole	Graphene/PMS	Singlet Oxygen (¹ O ₂)	H (+)	-	-	-	H (-)	[154]
Tetracycline	Biochar/PS	nonradical mechanism	No significant effect	No significant effect	-	-	-	[81]
Ciprofloxacin	UV/PMS	Singlet Oxygen (¹ O ₂)	H (+) L (-)	H (-)	-	-	H (-)	[155]

H – high concentration; L – low concentration; (+) – positive effect; (-) negative effect.



concentrations (5mg l^{-1}) increases the rate of tetracycline degradation while increasing the concentration of humic acid to $10\text{--}20\text{mg l}^{-1}$ has a negative effect on the decomposition of tetracycline. Addition of $10\text{--}20\text{ mg l}^{-1}$ of humic acids reduced the degradation efficiency of tetracycline from 88.51% to 78.92% and 64.65%, respectively [52]. These results indicate that humic acid consumes SO_4^\bullet and OH^\bullet faster than tetracycline. Humic acids act as a OH^\bullet at low concentrations but act as a strong radical scavenger at high concentrations while, by adding an excess of S_2O_8 the negative effect of HA was omitted [140].

Khazaee et al. reported that for UV/PMS process for degradation of cefixime scavengers have reduced the decomposition efficiency from 95% removal to 85% in case of carbonates presence, while lowest efficiency related to the presence of chloride ions (75%) was reported. Thus, luckily the effect of scavengers was not so high.

3.5. Effects of water matrix

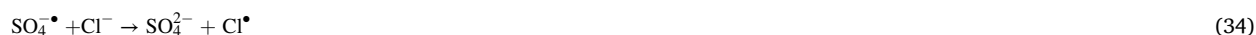
Aqueous environments contain different organic compounds as well as mineral anions, and the concentration of these compounds is different in surface and underground waters, which can interfere with S-AOPs. These matrix components can react with active species formed intentionally in treatment system to degrade target pollutant [141]. Obviously, in such cases the effectiveness of treatment process will be lowered or higher dose of oxidant will be needed. Depending on dominant mechanism of degradation process, co-existing ions and natural organic matter (NOM) have different effects on persulfate-based and peroxymonosulfate-based systems [84,142,143]. Table 12 summarizes the effects of the water matrix on the removal of antibiotics by S-AOPs, which are discussed in following paragraphs.

3.5.1. Coexisting anions

In general, on the basis of available literature it can be concluded that the coexisting anions have a stronger effect on the free radical pathway than the nonradical pathway. However, depending on applied system of persulfates activation, Cl^- , NO_3^- , HCO_3^- , SO_4^{2-} and HPO_4^{2-} can have different effects on the degradation of antibiotics in S-AOPs processes [156].

3.5.2. Effect of chloride ions

In the process of chloramphenicol degradation by persulfate/UV, increasing the chlorine ion concentration from 1 mM to 10 mM, the k_{obs} value also increased from $3.13(\pm 0.11) \times 10^{-2}$ to $4.02(\pm 0.24) \times 10^{-2} \text{ min}^{-1}$ and as a result, the removal efficiency increased due to the increase in the oxidative power of the reactive medium after producing Cl^\bullet . In another study, Tan et al. showed that in the PS/UV method of chloramphenicol decomposition, in the presence of Cl^- with a concentration of 1–10 mM, the removal efficiency increased, and on the other hand, at a concentration higher than 10 mM, the k_{obs} value decreased to $1.5(\pm 0.05) \times 10^{-2} \text{ min}^{-1}$, but increasing the chlorine ion concentration to 100 mM increased the k_{obs} value to $2.22(\pm 0.090) \times 10^{-2} \text{ min}^{-1}$, which indicates that Cl^- can play an additional role in the presence of high density of Cl^\bullet as well as Cl_2^\bullet ($E_{1/2}^{\text{red}} = 2.09 \text{ V}$) where chloramphenicol-radical reactions become more important than radical-radical quenching reactions. Comparison of $E_{1/2}^{\text{red}}$ for studied system revealed, that such conditions can have a positive effect on the PS/UV process in the degradation of antibiotics in brackish water with high Cl^- concentration (14–140 mM). On the other hand, at higher concentrations Cl^- can scavenge sulfate and hydroxyl radicals and reduce their degradation efficiency according to Eqs (34)–(39) [81].



Importantly, in case of tetracycline degradation by UV/PS, addition of Cl^- decreased only slightly from 96.06% to 95.26% (Zhang et al.). On the other hand, presence of Br^- doubled the degradation rate of tetracycline, which indicated that bromine improves the degradation of tetracycline. It was also found that in the presence of $5.8 \mu\text{M}$ of Br^- , Br^\bullet ($E_0 = 2.00 \text{ V}$) and Br_2^\bullet ($E_0 = 1.63 \text{ V}$) are produced with a concentration of 1–2 times higher than sulfate radicals, which can increase the efficiency of tetracycline [27], sulfamethoxazole [157] and ofloxacin [158] degradation in the UV/PS system. Interestingly, Frontistis et al., reported that in case of PS/transition metal system presence of chlorides up to 151 mg/L increases the degradation rate of ampicillin three times, while no significant effect was observed with the increase of chloride ion to 303 mg/L [159].

3.5.3. Effect of bicarbonates

Bicarbonates revealed to have ambivalent effect on persulfate based systems. For degradation of chloramphenicol with PS/UV with increasing the concentration of bicarbonate from 1 to 100 mM, a 50% decrease in k_{obs} was observed [152]. It follows from the fact that the reaction of sulfate and hydroxyl radicals with bicarbonate and the production of CO_3^\bullet with relatively less oxidative properties than the original radicals [156]. In contrast the positive effect of bicarbonate in degradation of sulfamethoxazole by PS/heat was also reported. With increasing bicarbonate concentration from 0 to 20 mM the degradation rate was increased. The reason is that

$\text{HCO}_3^-/\text{CO}_3^{\bullet-}$ can react with electron-rich compounds, such as anilines, with a relatively high-rate constant ($10^8 \text{ M}^{-1}\text{s}^{-1}$) and sulfamethoxazole has an aniline moiety as well.

In other study the degradation of oxytetracycline was enhanced by increasing bicarbonate from 0 to 20 mM by forming $\text{CO}_3^{\bullet-}$ according to Eq. (40) degradation of pollutants [150].



3.5.4. Effect of sulfates

Sulfate anions have generally a positive effect in persulfate-based systems. For example, degradation of chloramphenicol with UV/PS process was aided by addition of sulfates in concentration range of 12–48 mg/L, where k_{obs} rate increased by 35% and 39. Above this concentration range (96 mg/L) sulfates caused decrease of rate constant by 31%. The rate constant of the quenching reaction of $\text{SO}_4^{\bullet-}$ with $\text{S}_2\text{O}_8^{2-}$ is almost 3 orders of magnitude lower than that of $\text{SO}_4^{\bullet-}$ with an organic compounds containing atoms of low ionization energy. Accordingly, the UV/PS process can be a good method for the treatment of underground water and some special effluents contaminated with pharmaceutical substances even in the presence of nitrate (10–10 mg/L⁻¹) and sulfate (0.125–1.0 mM) in the natural concentration's range [152].

3.5.5. Effect of nitrite anions

For degradation of chloramphenicol with UV/PS process, Ghauch et al. shown that the presence of nitrite at a concentration of 0.5 mg/L⁻¹ does not have a significant effect on k_{obs} (less than 20%), small decrease is explained mostly by quenching of sulfate radicals by nitrite, which is not as strong oxidizing agent for chloramphenicol degradation ($E_{1/2}^{\text{red}} = 1.02 \text{ V}$). However, nitrate in concentrations 10 mg/L⁻¹ caused a significant improvement of k_{obs} up to 37%, but at concentrations of 2.5 and 50 mg/L, a decrease of 9% and 37% was observed in k_{obs} , respectively. A two hypotheses explaining this behavior were proposed, first that the sulfate radicals react with nitrate to produce NO_3^{\bullet} radicals with a relatively strong oxidizing potential ($E_{1/2}^{\text{red}} = 2.5 \text{ V}$). Second, that nitrate becomes a source of nitrite and oxygen radicals (Eq. (41)). Nitrite is not an oxidizer of chloramphenicol, while $\text{O}^{\bullet-}$ can increase the oxidation of chloramphenicol by reacting with water to produce HO^{\bullet} (Eq. (42)), which is responsible for further degradation of chloramphenicol [139,152].



Zhao et al., studying a PMS/magnetic $\gamma\text{-Fe}_2\text{O}_3\text{-MnO}_2$ system for the degradation of ciprofloxacin concluded that by adding Cl^- , NO_3^- , HCO_3^- , SO_4^{2-} and HPO_4^{2-} ions up to 1 mM didn't significantly lowered the degradation efficiency of ciprofloxacin. The low effect of these ions on the degradation efficiency of ciprofloxacin by the visible-light/PMS/ $\gamma\text{-Fe}_2\text{O}_3\text{-MnO}_2$ method indicates the high selectivity of the this coupled system [144]. On the other hand, it must be taken into account that this system was evaluated only under low concentration of anions conditions.

3.5.6. Natural organic matter (NOM)

Natural organic matter (NOM) contains a mixture of weak organic acids and organic compounds of unknown structure that are commonly found in water and wastewater. Humic acid (HA), formic acid (FA), and fulvic acids are important components of NOM, which make up 60% of water-soluble organic matter. HA contains a large number of carboxyl, phenolic, and hydroxyl alkyl functional groups that can interact with the functional groups of the catalyst surface or organic compounds [160]. In case of abovementioned system based on visible-light/ $\gamma\text{-Fe}_2\text{O}_3\text{-MnO}_2$ /PMS, Zhao et al. confirmed negative effect of NOM on the removal of ciprofloxacin. This system was effective (degradation >90%) for NOM concentrations up to 2 mg/L, while above this value degradation consequently decreased to 72.1% for NOM concentration of 6 mg/L. In case of sulfamethazine degradation using a simpler thermal activation of PS it was reported that NOM had inhibitive effect above 10 mg/L [147]. The decrease in ciprofloxacin removal efficiency can be explained relating to three aspects. First, the negatively charged HA binds to the positively charged ciprofloxacin and prevents it from moving towards the catalyst surface. Second, HA attenuates the light and reduces the number of photons on the catalyst surface and in the third case, HA traps oxygen-carrying radicals [144]. In another study Ghauch et al., concluded that HA in concentrations of 5 and 20 mg/L⁻¹ reduces the rate of k_{obs} to 35 and 63%, however in a low concentration (0.5 mg/L⁻¹) the effect is neglected. Importantly, it was highlighted that FA has a greater effect on reducing the rate of k_{obs} , so by increasing the concentration of FA from 12 to 582 mg/L⁻¹ the k_{obs} rate decreased from 29% to even 86% respectively. This significant decrease in k_{obs} is attributed to the smaller size of FA molecules as well as its higher oxygen content compared to HA, which makes them more effective to quenching of $\text{SO}_4^{\bullet-}$. In addition, HA and FA act as internal filter effect, which absorb well in the 254 nm range, and thus reduce the amount of sulfate radicals that are produced by UV, and on the other hand, they have electron-rich sites which are prone to absorb sulfate and hydroxyl electrophilic radicals. Therefore, in the presence of HA and FA, the efficiency of chloramphenicol degradation by UV/PS method decreases [152]. In other study, tetracycline degradation was partially inhibited in presence of HA at concentrations exceeding 10 mg/L⁻¹ [52]. Importantly, in case of oxytetracycline degradation the negative effect of HA was observed even at 3mg/L⁻¹ level [150].

In overall it can be concluded, that systems based on formation of singlet oxygen are not negatively affected by presence of inorganic anions and, what is advantageous in most of reported cases, the effect of inorganic anions was positive. Such situation was observed for Sulfamethoxazole, Sulfamethazine, Tetracycline, Penicillin G. This observation is particularly important for real case

scenarios with high salinity effluents – correct reports suggests that persulfate systems able to form singlet oxygen should be effective for treatment of this type of sewages. In case of systems based on radical degradation pathway, such a generalization is not possible. It seems that several systems are effective in case of low concentration of anions, while high concentrations strongly decrease the degradation. However, observed effects depend of type of anion. For instance, for chlorides presence a partially positive effect was reported for Norfloxacin and Chloramphenicol and for most of antibiotics effect was negative. Also, for carbonates positive effect was reported for Norfloxacin, Oxytetracycline while for most of reviewed pollutants it was negative. Different effect depending on compound was also reported for nitrates and sulfates. Reported positive effects of anions on mentioned antibiotics results from reactivity of these compounds with formed (by reaction of hydroxyl or sulfate radicals with anions) secondary radical species making their contribution in degradation process. This proved importance of studies of matrix effects on effectiveness of developed processes. On the other hand, it is known that secondary radicals despite improvement of degradation of main pollutant can cause formation of secondary pollutants (like Cl^- or NO_2^- containing derivatives) with higher toxicity than primary pollutant [34,161]. This aspect should be also considered in future studies. In respect to catalytic systems the evaluation of risks on by-product formation should include studies of sorption of these compounds on catalyst surface.

3.6. Mechanisms of degradation

Compared to conventional AOP methods that rely exclusively on hydroxyl radicals, S-AOP involves much more complex oxidation pathways, which differ depending on water compositions and types of activators used. Although sulfate and hydroxyl radicals can decompose various types of organic compounds, however the pollutant degradation mechanism is significantly different depending on the free radical and the nature of the pollutant. The mechanism of degradation of organic pollutants by sulfate radicals usually includes electron transfer, while hydroxyl radicals also include hydrogen-atom abstraction reactions in addition to electron transfer [57,162]. In the path of electron transfer, this process generally takes place through two mechanisms, the bridged and outer space mechanisms. The bridged mechanism has a slow electron transfer rate because it requires the formation of a transition bond, while no bond formation is required for the outer space mechanism [163,164]. The degradation and decomposition of organic pollutants by sulfate and hydroxyl radicals include different mechanisms. $\text{SO}_4^{\bullet-}$ participates mainly in outer space mechanism for electron transfer reaction, while OH^{\bullet} undergoes reaction via bridge mechanism (C–C, C–N, C–S addition, and H-abstraction reactions) for degradation of organic pollutants [165]. The mechanisms of antibiotic degradation are compared in Table 13.

Table 13
Degradation mechanisms of antibiotics.

Antibiotic	Method	Oxidative agent	Degradation mechanism	Ref
Carbamazepine	Gamma/PS	$\text{SO}_4^{\bullet-}$ HO^{\bullet}	electron transfer hydroxylation of the aromatic rings	[110]
Chloramphenicol	UV/PS	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	Direct photolysis Hydrogen abstraction Electron transfer	[152]
Ciprofloxacin	$\gamma\text{-Fe}_2\text{O}_3\text{-MnO}_2/\text{PMS}$	$\text{SO}_4^{\bullet-}$	Oxidation of the piperazine ring	[144]
Ciprofloxacin	Biochar/PS	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	ring-opening	[166]
Flumequine	$\text{Fe}_3\text{O}_4/\text{MWCNT}/\text{PHQ}/\text{PS}$	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	ring-opening	[167]
Oxytetracycline	UV/PS	$\text{SO}_4^{\bullet-}$	electron transfer	[150]
Sulfadiazine	US- Fe^0/PS	$\text{SO}_4^{\bullet-}$	Hydrogen abstraction Oxidation of amine group in the benzene ring Cleavage of C–N bonds in the heterocyclic ring Heterocyclic ring opening Hydroxylation Cleavage of S–N bond	[51]
Sulfadiazine	$\text{CuFeO}_2/\text{PMS}$	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	Cleavage of the C–N bond linking pyrimidine and the benzene ring	[99]
Sulfamethazine	US/PSM	$\text{SO}_4^{\bullet-}$, HO^{\bullet} , $^1\text{O}_2$	Cleavage of the 2S–10 N bond, Cleavage of the 2S–3C bond Cleavage of 10N–11C bond, Adducting on the 5C or 8C atoms, Addition of the 7 N atom on the rings	[55]
Sulfamethazine	Heat/PS	$\text{SO}_4^{\bullet-}$	sulfonamide S– N bond cleavage, aniline moiety oxidation, and Smiles-type rearrangement	[147]
Sulfamethoxazole	$\text{Fe}_3\text{O}_4/\text{PS}$	$\text{SO}_4^{\bullet-}$	electron transfer	[47]
Ciprofloxacin		$\text{SO}_4^{\bullet-}$, HO^{\bullet}	ring-opening	
Sulfamethoxazole	Graphene/PS	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	ring-opening	[65]
Sulfamonomethoxine	Fe_3O_4 MNPs/PS	$\text{SO}_4^{\bullet-}$	ring-opening	[168]
Tetracycline	UV/PS	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	ring-opening	[27]
Tetracycline	Fe_3O_4 -doped biochar/PS	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	oxidation of double bonds and aromatic ring	[80]
Tetracycline	UV/PMS	HO^{\bullet}	hydrogen abstraction, hydroxyl addition and electron transfer	[95]
Tetracycline	Heat/PS	$\text{SO}_4^{\bullet-}$	ring-opening	[169]
Tetracycline	US/PS	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	Hydrogen abstraction through HO^{\bullet} and $\text{SO}_4^{\bullet-}$ attack Loss of methyl group Loss of amine group	[52]
Triclosan	Gamma/PS	$\text{SO}_4^{\bullet-}$, HO^{\bullet} ,	electron transfer	[108]
Trimethoprim	Gamma/PS	e_{aq}^- $\text{SO}_4^{\bullet-}$	electron transfer	[109]

Table 14
The kinetic of antibiotics by activated PS and PMS.

Antibiotics	Methods	Oxidant concentration (mM)	Pollutant concentration (mM)	Molar ratio (oxidant/pollutant)	pH	Time (min)	k_{obs} (min^{-1})	Oxidative agent	Efficiency (%)	ref
Chloramphenicol	UV/PS	0.5	0.031	16.12	7	60	0.036	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	86	[152]
Chloramphenicol	Co_3O_4 -KIT6/PMS	1	0.030	33.33	7	60	0.079	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	74.85	[98]
Ciprofloxacin	magnetic $\gamma\text{-Fe}_2\text{O}_3$ - MnO_2 /PMS	1.56	0.050	31.2	4	30	0.114	$\text{SO}_4^{\bullet-}$, HO^{\bullet} , $\text{O}_2^{\bullet-}$, h^+ , e^-	98.3	[144]
Norfloxacin	magnetic CuFe_2O_4 /PMS	0.5	0.025	20	7	120	0.039	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	90	[172]
Ofloxacin	MoO_3 /g- C_3N_4 /PS	5	0.027	185.18	3	60	0.022	$\text{SO}_4^{\bullet-}$, HO^{\bullet} , $\text{O}_2^{\bullet-}$, h^+ , $^1\text{O}_2$	94.4	[173]
Ofloxacin	hierarchical Co(II)-doped TiO_2 /PMS	1	0.069	14.49	7	30	1.22	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	92.3	[174]
Sulfamethazine	US/PMS	3.1	0.170	18.23	7.5	30	0.172	$\text{SO}_4^{\bullet-}$, HO^{\bullet} , $^1\text{O}_2$	99.6	[55]
Sulfamethazine	Heat/PS	2	0.030	66.66	7	120	0.026	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	77	[147]
Tetracycline	UV/PS	0.15	0.011	14.19	6.8	30	0.10	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	95.73	[27]
Tetracycline	Cu(II) /UV/PS	0.5	0.020	25	3.5	50	0.181	$\text{SO}_4^{\bullet-}$, HO^{\bullet}	67.1	[175]
	Cu(II) /UV/PMS	0.5	0.020	25	3.5	50	0.206		93.1	
Trimethoprim	UV/PS	0.5	0.010	50	7.5	–	0,0004	$\text{SO}_4^{\bullet-}$	97	[176]



In the process of chloramphenicol (CAP) decomposition by PS/UV, Ghauch et al. proposed that chloramphenicol molecules first undergo the following processes: 1- direct photolysis, 2- abstraction of hydrogen by hydroxyl radicals that are created directly by water splitting or indirectly by the reaction of sulfate radicals with water, 3- electron abstraction, which occurs mainly on the nitrobenzene ring via sulfate radicals to produce the corresponding unstable $[CAP]^+$, and in the next step hydroxylated CAP and unstable $[CAP]^+$ undergo oxidation to produce further hydroxylated CAP and sulfonated/hydroxylated CAP. Finally, intermediates produced through direct photolysis are oxidized by sulfate or hydroxyl radicals and are converted into smaller molecules. As a result, it can be said that in this process chloramphenicol is degraded by direct photolysis, hydrogen abstraction, and electron transfer [152].

Zhang et al. showed that the main degradation pathway of tetracycline by UV/PS process was via functional group shedding and ring-opening reactions taking place sequentially by sulfate and hydroxyl radicals. In this study, the degradation of tetracycline molecules in deionized water was divided into three paths. First, $SO_4^{\bullet-}$ selectively reacted with electron-rich groups (amide group, tertiary amine group, hydroxyl group, and double bond) and OH^{\bullet} showed high activity for olefin double bond. In the first pathway, the tertiary amine groups of TC, then hydroxyl, methyl, and formamide were destroyed, and after the ring opening and substitution reactions, some intermediate products were produced. In the second pathway, the cycloaddition of OH^{\bullet} , it occurred through the loss of formamide and methyl groups, followed by a series of ring opening and replacement reactions to produce other intermediate compounds. In the third pathway, the removal of carboxamide and the third amine group from tetracycline molecules and the production of intermediate products occurred, and finally, by using cycloaddition of OH^{\bullet} and dimethylation reaction, the intermediate products were converted into small molecular products. Among the three degradation pathways, the electron withdrawing groups such as carbonyl and carboxyl were not easily directly attacked, but were continuously degraded by the gradual opening of the ring structure of tetracycline molecules [27].

In the degradation process of Sulfadiazine by US/Fe₀/PS process, two degradation pathways were proposed. In first, the sulfate radicals caused the oxidation of the amine group and produced nitro-SD derivatives, and then by attacking the nitro-SD derivatives, the ring opening of the heterocyclic ring took place. In the second path of degradation, sulfate radicals caused direct oxidative cleavage of the S-N bond. The results of the ion chromatography tests revealed that formic acid, acetic acid, and some inorganic ions were the final products of Sulfadiazine decomposition [51].

3.7. Kinetics

The oxidation process of antibiotics by PS and PMS generally follows the pseudo-first-order kinetic model [170]. Various operating factors such as pH, temperature, oxidant concentration, antibiotic concentration, and the presence of water matrix affect the rate constant [171]. For all kinetic experiments under different conditions, the degradation of antibiotics is fitted with the pseudo-first-order kinetic equation Eq. (43):

$$\ln(C_0/C_t) = k_{obs} \times t \quad (43)$$

Where, C_0 and C_t are the molar concentrations of antibiotic at the time 0 and reaction time t , respectively; k_{obs} is the pseudo-first-order constant (min^{-1}). Table 14 compare the kinetics of degradation of antibiotics with different activation methods.

Beside general conclusions pointed out at the end of this paragraph, some researchers formed useful observations. For instance, Fan et al. confirmed a general rule about positive influence of increased temperature on rate constant value. In case of sulfamethazine the degradation rate increased with increasing temperature in heat-activated PS systems, from 20% to 70% as the temperature increased from 40 °C to 60 °C, while the value of k_{obs} increased by 21 times [147]. It follows from high sensitivity to temperature of thermally activated persulfate systems, where heat as sole factor can significantly gain the performance of such systems [104].

All of the research that investigated the rate constant values of antibiotics degradation by different methods of PS and PMS activation concluded that with increasing oxidant concentration to some extent, the k_{obs} also increases. For instance, by studying the degradation of oxytetracycline by UV/PS process and investigating the reaction kinetics, Liu et al. concluded that the destruction of oxytetracycline follows pseudo-first-order kinetics. So that with the increase of persulfate concentration up to 1 mM, it seems that k_{obs} was proportional to the linear regression slope of $0.0214 \text{ cm}^2 \text{ mJ}^{-1} \text{ mM}^{-1}$ ($R^2 = 0.99$), and with the increase of PS concentration, a non-linear increase was observed, which is due to the self-scavenging effect of PS and the recombination of sulfate radicals [150].

Zhang et al., by examining the kinetics of tetracycline degradation by UV/PS method, concluded that with increasing persulfate concentration from 0 to 30 mgL^{-1} , the degradation rate constant increased from 0.008 to 0.1 min^{-1} and the removal efficiency reached 95.73%. While increasing the concentration to 40 and 50 mgL^{-1} , the degradation of tetracycline did not improve because the excess persulfate acted as a scavenger and reacted with sulfate radicals, reducing the rate constant and thus the removal efficiency [27].

In overall, according to compared results, it can be stated that rate constant (under optimized conditions) is strongly dependent of structure of target pollutant. There is no clear relation between the used excess of oxidant or type of radical species with rate constant order of magnitude [27,55,98,144,147,152,170–175]. For example, tetracycline degradation rate constant in a two strongly different oxidation systems was in the range of 0,1–0,21 min^{-1} , while for chloramphenicol it was in the range of 0,036–0,079 min^{-1} . Typically, rate constant values seem to be in range of 0,05–0,2 min^{-1} .

4. Conclusion

Because the reaction rate of PS and PMS is slow when directly reacting with the contaminants, activation of PS and PMS is essential for the treatment of organic contaminants. Different types of activation methods for PS and PMS were reviewed and compared

exclusively in terms of process pH, contact time, initial concentration of antibiotic and concentration of oxidant. This analysis revealed that the optimal pH in the S-AOP process depends on the method of activation of oxidant, so it has to be optimized for every new type of catalyst. The decomposition efficiency of antibiotics by all methods for activating PS and PMS increases with increasing contact time generally, more than 30min is required for most published processes to obtain final degradation over 90%. In all the studies, with increasing the concentration of antibiotics, the decomposition efficiency as it lowers the ratio of radical species to radical species at fixed dose of oxidant as well as due to presence of secondary pollutants also reacting with radicals. This aspect clearly shows the need of process optimization using a molar ratio of oxidant to pollutant (rox) as one of parameters. Therefore, the highest degradation efficiency of antibiotics was obtained for studies with the lowest concentration of antibiotics. In fact, these results are promising, as the presence of pharmaceuticals in the environment is mostly at ppb level, thus studies of ppm level are not proving their usefulness.

In all activation methods, by increasing the concentration of PS and PMS, the production of $\text{SO}_4^{\bullet-}$ increases and leads to improved removal efficiency. However, as the concentration increases further, the removal efficiency is constant and sometimes decreases. This reduction in efficiency is due to the high concentration of oxidants in the environment, which acts as a radical scavenger and reduces $\text{SO}_4^{\bullet-}$ and OH^{\bullet} in the environment. Typically scavenging effect was observed above 0.7 mM of the PS and 2 mM of PMS.

AOPs based on PS and PMS have been widely studied as an efficient and effective method for degrading various kinds of organic pollutants, especially antibiotics, and aid in environmental restoration. Complete degradation of organic pollutants is possible by using PS and PMS. Chloramphenicol, Oxytetracycline, Sulfamethazine, Tetracycline, Sulfamonomethoxine were effectively degraded by PS-based processes, while Sulfamethazine, Ciprofloxacin, Sulfamethoxazole, Chloramphenicol, and Sulfadiazine were completely degraded by PMS. Thus, it can be said that for certain compounds both PS and PMS were highly effective. On the other hand, the degradation efficiency of Tetracycline hydrochloride, Enrofloxacin, Fluconazole and Norfloxacin by using PS and PMS was not so effective – degradation below 90% was reported. Thus, further developments should focus on effective degradation via S-AOPs of these persistent types of molecules instead of proving effectiveness to pharmaceuticals that were already degraded via S-AOPs.

However, the optimal operating conditions for cost-effective and fast decomposition in real systems still need to be reconsidered. In addition, the presence of excess sulfate ions can have adverse effects on the environment, therefore, it is necessary to study the effects and methods of sulfate reduction. Finally, a proper activation method should be developed. Despite the scientific value of papers relating to very sophisticated catalysts, which preparation sounds more like “jewelry art”, their applicability in routine applications, seems to be very limited. It follows from several stages of preparation (often off-green chemistry approach) as well as high costs. Finally, their management at the waste stage is not addressed. On the other hand, processes developed on their basis revealed a much higher sensitivity to real matrix components (such as anions or NOM) comparing UV-based and thermally activated S-AOPs. Several attempts on the application of relatively simple catalysts based on carbon type materials, proved their effectiveness to degrade environmental pollutants via S-AOPs, thus future progress on S-AOPs should strongly focus on applications of such low-cost catalysts for pharmaceuticals degradation.

Most of the studied articles lacked many important parameters such as measuring the amount of pollutant mineralization by determining the final COD or TOC values. Most of the articles did not describe the pathway of pollutant degradation and even the intermediate products and by-products were not examined. Secondly, metals leaching from catalyst into the effluents should be always controlled. Therefore, it is not possible to decide on the safety of many already developed methods.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wri.2022.100194>.

References

- [1] I. Michael, L. Rizzo, C.S. Mcardell, C.M. Manaia, C. Merlin, T. Schwartz, C. Dagot, D. Fatta-Kassinou, Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: a review, *Water Res.* 47 (2013) 957–995.
- [2] J. Tolls, Sorption of veterinary pharmaceuticals in soils, *Environ. Sci. Technol.* 35 (2001) 3397–3406.

- [3] N. Javid, Z. Honarmandrad, M. Malakootian, Ciprofloxacin removal from aqueous solutions by ozonation with calcium peroxide, *Desalination Water Treat.* 174 (2020) 178–185.
- [4] X. Sun, J. Liu, L. Ji, G. Wang, S. Zhao, J.Y. Yoon, S. Chen, A Review on Hydrodynamic Cavitation Disinfection: the Current State of Knowledge, *Science of the Total Environment*, 2020, 139606.
- [5] B. Halling-Sorensen, S. Nielsen, P. Lanzky, F. Ingerslev, H. Lutzhoft, S. Jorgensen, Occurrence, fate and effects of pharmaceutical substances in the environment-a review, *Chemosphere* 36 (1998) 357–393.
- [6] P. Kovalakova, L. Cizmas, M. Feng, T.J. McDonald, B. Marsalek, V.K. Sharma, Oxidation of antibiotics by ferrate (VI) in water: evaluation of their removal efficiency and toxicity changes, *Chemosphere* 277 (2021), 130365.
- [7] S.D. Richardson, T.A. Ternes, Water analysis: emerging contaminants and current issues, *Anal. Chem.* 90 (2018) 398–428.
- [8] Z. Frontistis, D. Mantzavinos, S. Meric, Degradation of antibiotic ampicillin on boron-doped diamond anode using the combined electrochemical oxidation - sodium persulfate process, *J. Environ. Manag.* 223 (2018) 878–887.
- [9] J. Bacardit, V. García-Molina, B. Bayarri, J. Giménez, E. Chamorro, C. Sans, Coupled photochemical-biological system to treat biorecalcitrant wastewater, *Water Sci. Technol.* 55 (2007) 95–100.
- [10] X. Sun, W. You, X. Xuan, L. Ji, X. Xu, G. Wang, S. Zhao, G. Boczkaj, J.Y. Yoon, S. Chen, Effect of the cavitation generation unit structure on the performance of an advanced hydrodynamic cavitation reactor for process intensifications, *Chem. Eng. J.* 412 (2021), 128600.
- [11] W.H. Glaze, J.-W. Kang, D.H. Chapin, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, *Ozone Sci. Eng.* 9 (1987) 335–352.
- [12] G. Boczkaj, A. Fernandes, Wastewater treatment by means of Advanced Oxidation Processes at basic pH conditions: a review, *Chem. Eng. J.* 320 (2017).
- [13] M. Gagol, A. Przyjazny, G. Boczkaj, Wastewater treatment by means of advanced oxidation processes based on cavitation – a review, *Chem. Eng. J.* 338 (2018) 599–627.
- [14] A. Fernandes, P. Makoś, G. Boczkaj, Treatment of bitumen post oxidative effluents by sulfate radicals based advanced oxidation processes (S-AOPs) under alkaline pH conditions, *J. Clean. Prod.* 195 (2018) 374–384.
- [15] A. Fernandes, P. Makoś, J.A. Khan, G. Boczkaj, Pilot scale degradation study of 16 selected volatile organic compounds by hydroxyl and sulfate radical based advanced oxidation processes, *J. Clean. Prod.* 208 (2019) 54–64.
- [16] J.A. Khan, M. Sayed, N.S. Shah, S. Khan, Y. Zhang, G. Boczkaj, H.M. Khan, D.D. Dionysiou, Synthesis of eosin modified TiO₂ film with co-exposed {001} and {101} facets for photocatalytic degradation of para-aminobenzoic acid and solar H₂ production, *Appl. Catal. B Environ.* 265 (2020), 118557.
- [17] J.A. Khan, M. Sayed, S. Khan, N.S. Shah, D.D. Dionysiou, G. Boczkaj, Chapter 9 - advanced oxidation processes for the treatment of contaminants of emerging concern, in: A.J. HERNÁNDEZ-MALDONADO, L. BLANEY (Eds.), *Contaminants of Emerging Concern in Water and Wastewater*, Butterworth-Heinemann, 2020.
- [18] Y. Wen, C.-H. Huang, D.C. Ashley, D. Meyerstein, D.D. Dionysiou, V.K. Sharma, X. Ma, Visible light-induced catalyst-free activation of peroxydisulfate: pollutant-dependent production of reactive species, *Environ. Sci. Technol.* 56 (2022) 2626–2636.
- [19] A. Babuponnusami, K. Muthukumar, A review on Fenton and improvements to the Fenton process for wastewater treatment, *J. Environ. Chem. Eng.* 2 (2014) 557–572.
- [20] S. Norzaee, E. Bazrafshan, B. Djahed, F.K. Mostafapour, R. Khaksefidi, UV activation of persulfate for removal of penicillin G antibiotics in aqueous solution, *Hindawi Sci. World J.* (2017) 1–6.
- [21] J. Lee, U. Von Gunten, J.-H. Kim, Persulfate-based advanced oxidation: critical assessment of opportunities and roadblocks, *Environ. Sci. Technol.* 54 (2020) 3064–3081.
- [22] Y. Deng, C.M. Ezyske, Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate, *Water Res.* 45 (2011) 6189–6194.
- [23] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, *Catal. Today* 147 (2009) 1–59.
- [24] A. Fernandes, M. Gagol, P. Makoś, J. Khan, G. Boczkaj, Integrated Photocatalytic Advanced Oxidation System (TiO₂/UV/O₃/H₂O₂) for Degradation of Volatile Organic Compounds, *Separation and Purification Technology*, 2019.
- [25] A. Fernandes, P. Makoś, Z. Wang, G. Boczkaj, Synergistic effect of TiO₂ photocatalytic advanced oxidation processes in the treatment of refinery effluents, *Chem. Eng. J.* (2019), 123488.
- [26] F. Ghanbari, M. Moradi, Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants: Review, *Chem. Eng. J.* 310 (2016).
- [27] Y. Zhang, Y.-G. Zhao, Y. Hu, M. Gao, L. Guo, J. Ji, Insight in degradation of tetracycline in mariculture wastewater by ultraviolet/persulfate advanced oxidation process, *Environ. Res.* 212 (2022), 113324.
- [28] Y. Gao, N. Gao, Y. Deng, Y. Yang, Y. Ma, Ultraviolet (UV) light-activated PS oxidation of sulfamethazine in water, *Chem. Eng. J.* 195–196 (2012) 248–253.
- [29] A. Ghauch, A. Baalbaki, M. Amasha, R.E. Asmar, O. Tantawi, Contribution of PS in UV-254 nm activated systems for complete degradation of chloramphenicol antibiotic in water, *Chem. Eng. J.* 317 (2017) 1012–1025.
- [30] X. Ao, W. Liu, Degradation of sulfamethoxazole by medium pressure UV and oxidants: PMS PS, and hydrogen peroxide, *Chem. Eng. J.* 313 (2017) 629–637.
- [31] Y. Liu, X. He, Y. Fu, D.D. Dionysiou, Kinetics and mechanism investigation on the destruction of oxytetracycline by UV-254 nm activation of PS, *J. Hazard Mater.* 305 (2016) 229–239.
- [32] F. Azadbakht, A. Esrafil, M.Y. Badi, J. Sajedifar, M. Amiri, M. Gholami, Efficiency of persulfate-based advanced oxidation process (UV/Na₂S₂O₈) in removal of metronidazole from aqueous solutions, *J. Mazandaran Univ. Med. Sci.* 27 (2017) 119–129.
- [33] P. Tavassoli, E. Bazrafshan, F.K. Mostafapour, Z. Maghsoodi, D. Balarak, H. Kamani, A.A. Zarei, Efficiency of UV activated persulfate in removal of ofloxacin from aqueous solutions, *J. Mazandaran Univ. Med. Sci.* 27 (2018) 116–129.
- [34] M. Gagol, E. Cako, K. Fedorov, R.D.C. Soltani, A. Przyjazny, G. Boczkaj, Hydrodynamic cavitation based advanced oxidation processes: studies on specific effects of inorganic acids on the degradation effectiveness of organic pollutants, *J. Mol. Liq.* 307 (2020), 113002.
- [35] K. Ulucan-Altuntas, S. Yazici Guvenc, E. Can-Güven, F. İlhan, G. Varank, Degradation of oxytetracycline in aqueous solution by heat-activated peroxydisulfate and peroxymonosulfate oxidation, *Environ. Sci. Pollut. Control Ser.* 29 (2022) 9110–9123.
- [36] M. Nie, Y. Yang, Z. Zhang, C. Yan, X. Wang, H. Li, W. Dong, Degradation of chloramphenicol by thermally activated persulfate in aqueous solution, *Chem. Eng. J.* 246 (2014) 373–382.
- [37] S. Norzaee, M. Taghavi, B. Djahed, F. Kord Mostafapour, Degradation of Penicillin G by heat activated persulfate in aqueous solution, *J. Environ. Manag.* 215 (2018) 316–323.
- [38] J.-F. Yang, L. Yang, Z. Song-Bai, L. Ou, C.-B. Liu, L.-Y. Zheng, Y.-F. Yang, G.-G. Ying, S.-L. Luo, Degradation of azole fungicide fluconazole in aqueous solution by thermally activated persulfate, *Chem. Eng. J.* 321 (2017) 113–122.
- [39] H. Guo, N. Gao, Y. Yang, Y. Zhang, Kinetics and transformation pathways on oxidation of fluoroquinolones with thermally activated persulfate, *Chem. Eng. J.* 292 (2016).
- [40] Y. Fan, Y. Ji, D. Kong, J. Lu, Q. Zhou, Kinetic and mechanistic investigations of the degradation of sulfamethazine in heat-activated persulfate oxidation process, *J. Hazard Mater.* 300 (2015) 39–47.
- [41] H. Gao, J. Chen, Y. Zhang, X. Zhou, Sulfate radicals induced degradation of Triclosan in thermally activated persulfate system, *Chem. Eng. J.* 306 (2016).
- [42] Y. Ji, Y. Shi, W. Dong, X. Wen, M. Jiang, J. Lu, Thermo-activated persulfate oxidation system for tetracycline antibiotics degradation in aqueous solution, *Chem. Eng. J.* 298 (2016) 233.
- [43] J. Yan, M. Lei, L. Zhu, M. Anjum, J. Zou, H. Tang, Degradation of sulfamonomethoxine with Fe₃O₄ magnetic nanoparticles as heterogeneous activator of persulfate, *J. Hazard Mater.* 186 (2011) 1398–1404.

- [44] B. Kakavandi, Heterogeneous Fenton-like catalytic oxidation of tetracycline by AC@Fe₃O₄ as a heterogeneous PS activator: adsorption and degradation studies, *J. Ind. Eng. Chem.* (2016) 323–333.
- [45] M. Liu, L.-A. Hou, Q. Li, X. Hu, S. Yu, Heterogeneous degradation of tetracycline by magnetic Ag/AgCl/modified zeolite X–persulfate system under visible light, *RSC Adv.* 6 (2016) 35216–35227.
- [46] D. Ding, C. Liu, Y. Ji, Q. Yang, L. Chen, C. Jiang, T. Cai, Mechanism insight of degradation of norfloxacin by magnetite nanoparticles activated persulfate: identification of radicals and degradation pathway, *Chem. Eng. J.* 308 (2017) 330–339.
- [47] Y. Ji, C. Ferronato, A. Salvador, X. Yang, J.-M. Chovelon, Degradation of ciprofloxacin and sulfamethoxazole by ferrous-activated persulfate: implications for remediation of groundwater contaminated by antibiotics, *Sci. Total Environ.* 472 (2014) 800–808.
- [48] A.R. Rahmani, H. Almasi, S. Bajalan, H. Rezaei Vahidian, A. Zarei, A. Shabanloo, Optimization of ciprofloxacin antibiotic sonochemical degradation with persulfate activated by nano zero-valent iron by central composite design method, *J. Health* 8 (2017) 231–245.
- [49] A. Hamzehzadeh, M. Fazlzadeh, K. Rahmani, Efficiency of nano/Persulfate process (nZVI/PS) in removing Metronidazole from aqueous solution, *J. Environ. Health Eng.* 4 (2017) 307–320.
- [50] C. Li, H. Lin, A. Armutlulu, R. Xie, Y. Zhang, X. Meng, Hydroxylamine-assisted catalytic degradation of ciprofloxacin in ferrate/persulfate system, *Chem. Eng. J.* 360 (2019) 612–620.
- [51] X. Zou, T. Zhou, J. Mao, X. Wu, Synergistic degradation of antibiotic sulfadiazine in a heterogeneous ultrasound-enhanced Fe⁰/persulfate Fenton-like system, *Chem. Eng. J.* 257 (2014) 36–44.
- [52] S. Nasserī, A.H. Mahvi, M. Seyedsalehi, K. Yaghmaei, R. Nabizadeh, M. Alimohammadi, G.H. Safari, Degradation kinetics of tetracycline in aqueous solutions using peroxydisulfate activated by ultrasound irradiation: effect of radical scavenger and water matrix, *J. Mol. Liq.* 241 (2017) 704–714.
- [53] M. Malakootian, S.N. Asadzadeh, Removal of tetracycline from aqueous solution by ultrasound and ultraviolet enhanced persulfate oxidation, *Desalination Water Treat.* 197 (2020) 191–199.
- [54] G.H. Safari, S. Nasserī, A.H. Mahvi, K. Yaghmaei, R. Nabizadeh, M. Alimohammadi, Optimization of sonochemical degradation of tetracycline in aqueous solution using sono-activated persulfate process, *J. Environ. Health Sci. Eng.* 13 (2015) 1–15.
- [55] R. Yin, W. Guo, H. Wang, J. Du, X. Zhou, Q. Wu, H. Zheng, J. Chang, N. Ren, Enhanced peroxymonosulfate activation for sulfamethazine degradation by ultrasound irradiation: performances and mechanisms, *Chem. Eng. J.* 335 (2018) 145–153.
- [56] G. Fang, C. Liu, J. Gao, D.D. Dionysiou, D. Zhou, Manipulation of persistent free radicals in biochar to activate persulfate for contaminant degradation, *Environ. Sci. Technol.* 49 (2015) 5645–5653.
- [57] P. Devi, U. Das, A.K. Dalai, In-situ chemical oxidation: principle and applications of peroxide and persulfate treatments in wastewater systems, *Sci. Total Environ.* 571 (2016) 643–657.
- [58] Y. Zhao, H. Wang, Structure–function correlations of carbonaceous materials for persulfate-based advanced oxidation, *Langmuir* 37 (2021) 13969–13975.
- [59] D.-G. Kim, S.-O. Ko, Advanced oxidative degradation of acetaminophen by carbon catalysts: radical vs non-radical pathways, *Environ. Res.* 188 (2020), 109767.
- [60] L. An, P. Xiao, Zero-valent iron/activated carbon microelectrolysis to activate peroxydisulfate for efficient degradation of chlortetracycline in aqueous solution, *RSC Adv.* 10 (2020) 19401–19409.
- [61] U. Ushani, X. Lu, J. Wang, Z. Zhang, J. Dai, Y. Tan, S. Wang, W. Li, C. Niu, T. Cai, Sulfate radicals-based advanced oxidation technology in various environmental remediation: a state-of-the-art review, *Chem. Eng. J.* 402 (2020), 126232.
- [62] W. Tian, H. Zhang, X. Duan, H. Sun, M.O. Tade, H.M. Ang, S. Wang, Nitrogen-and sulfur-codoped hierarchically porous carbon for adsorptive and oxidative removal of pharmaceutical contaminants, *ACS Appl. Mater. Interfaces* 8 (2016) 7184–7193.
- [63] J. Lei, P. Duan, W. Liu, Z. Sun, X. Hu, Degradation of aqueous cefotaxime in electro-oxidation—electro-Fenton—persulfate system with Ti/CNT/SnO₂-Sb-Er anode and Ni@NCNT cathode, *Chemosphere* 250 (2020), 126163.
- [64] L. Feng, X. Li, X. Chen, Y. Huang, K. Peng, Y. Huang, Y. Yan, Y. Chen, Pig manure-derived nitrogen-doped mesoporous carbon for adsorption and catalytic oxidation of tetracycline, *Sci. Total Environ.* 708 (2020), 135071.
- [65] Y. Qi, B. Ge, Y. Zhang, B. Jiang, C. Wang, M. Akram, X. Xu, Three-dimensional porous graphene-like biochar derived from *Enteromorpha* as a persulfate activator for sulfamethoxazole degradation: role of graphitic N and radicals transformation, *J. Hazard Mater.* 399 (2020), 123039.
- [66] M. Kohantorabi, G. Moussavi, S. Giannakis, A review of the innovations in metal- and carbon-based catalysts explored for heterogeneous peroxymonosulfate (PMS) activation, with focus on radical vs. non-radical degradation pathways of organic contaminants, *Chem. Eng. J.* 411 (2021), 127957.
- [67] A. Rey, A. Hungria, C. Duran-Valle, M. Faraldos, A. Bahamonde, J. Casas, J. Rodriguez, On the optimization of activated carbon-supported iron catalysts in catalytic wet peroxide oxidation process, *Appl. Catal. B Environ.* 181 (2016) 249–259.
- [68] J. Liang, X. Xu, W.Q. Zaman, X. Hu, L. Zhao, H. Qiu, X. Cao, Different mechanisms between biochar and activated carbon for the persulfate catalytic degradation of sulfamethoxazole: roles of radicals in solution or solid phase, *Chem. Eng. J.* 375 (2019), 121908.
- [69] M. Forouzesah, A. Ebadi, A. Aghaeinejad-Meybodi, R. Khoshbouy, Transformation of persulfate to free sulfate radical over granular activated carbon: effect of acidic oxygen functional groups, *Chem. Eng. J.* 374 (2019) 965–974.
- [70] H. Song, L. Yan, J. Jiang, J. Ma, S. Pang, X. Zhai, W. Zhang, D. Li, Enhanced degradation of antibiotic sulfamethoxazole by electrochemical activation of PDS using carbon anodes, *Chem. Eng. J.* 344 (2018) 12–20.
- [71] W. Zhang, X. Li, Q. Yang, D. Wang, Y. Wu, X. Zhu, J. Wei, Y. Liu, L. Hou, C. Chen, Pretreatment of landfill leachate in near-neutral pH condition by persulfate activated Fe-C micro-electrolysis system, *Chemosphere* 216 (2019) 749–756.
- [72] D. Huang, Q. Zhang, C. Zhang, R. Wang, R. Deng, H. Luo, T. Li, J. Li, S. Chen, C. Liu, Mn doped magnetic biochar as persulfate activator for the degradation of tetracycline, *Chem. Eng. J.* 391 (2020), 123532.
- [73] R. Wang, X. Duan, S. Wang, N.-Q. Ren, S.-H. Ho, Production, properties, and catalytic applications of sludge derived biochar for environmental remediation, *Water Res.* 187 (2020), 116390.
- [74] R. Zhang, Y. Li, Z. Wang, Y. Tong, P. Sun, Biochar-activated peroxydisulfate as an effective process to eliminate pharmaceutical and metabolite in hydrolyzed urine, *Water Res.* 177 (2020), 115809.
- [75] Y. Zou, W. Li, L. Yang, F. Xiao, G. An, Y. Wang, D. Wang, Activation of peroxymonosulfate by sp²-hybridized microalgae-derived carbon for ciprofloxacin degradation: importance of pyrolysis temperature, *Chem. Eng. J.* 370 (2019) 1286–1297.
- [76] M. Yu, C. Sun, L. Wang, K. Zang, M. Li, L. Zhou, Y. Zheng, Semi-coke activated persulfate promotes simultaneous degradation of sulfadiazine and tetracycline in a binary mixture, *Chem. Eng. J.* 416 (2021), 129122.
- [77] J. Wang, S. Wang, Preparation, modification and environmental application of biochar: a review, *J. Clean. Prod.* 227 (2019) 1002–1022.
- [78] B. Wang, Y.-N. Li, L. Wang, Metal-free activation of persulfates by corn stalk biochar for the degradation of antibiotic norfloxacin: activation factors and degradation mechanism, *Chemosphere* 237 (2019), 124454.
- [79] X. Huo, P. Zhou, J. Zhang, Y. Liu, X. Cheng, Y. Liu, W. Li, Y. Zhang, N, S-Doped porous carbons for persulfate activation to remove tetracycline: nonradical mechanism, *J. Hazard Mater.* 391 (2020), 122055.
- [80] Z. Pi, X. Li, D. Wang, Q. Xu, Z. Tao, X. Huang, F. Yao, Y. Wu, L. He, Q. Yang, Persulfate activation by oxidation biochar supported magnetite particles for tetracycline removal: performance and degradation pathway, *J. Clean. Prod.* 235 (2019) 1103–1115.
- [81] Q. Zhong, Q. Lin, R. Huang, H. Fu, X. Zhang, H. Luo, R. Xiao, Oxidative degradation of tetracycline using persulfate activated by N and Cu codoped biochar, *Chem. Eng. J.* 380 (2020), 122608.
- [82] X. Chen, W.-D. Oh, T.-T. Lim, Graphene-and CNTs-based carbocatalysts in persulfates activation: material design and catalytic mechanisms, *Chem. Eng. J.* 354 (2018) 941–976.
- [83] P. Duan, D. Chen, X. Hu, Tin dioxide decorated on Ni-encapsulated nitrogen-doped carbon nanotubes for anodic electrolysis and persulfate activation to degrade cephalixin: mineralization and degradation pathway, *Chemosphere* 269 (2021), 128740.

- [84] Y. Shang, C. Chen, P. Zhang, Q. Yue, Y. Li, B. Gao, X. Xu, Removal of sulfamethoxazole from water via activation of persulfate by Fe₃C@ NCNTs including mechanism of radical and nonradical process, *Chem. Eng. J.* 375 (2019), 122004.
- [85] H. Chen, K.C. Carroll, Metal-free catalysis of persulfate activation and organic-pollutant degradation by nitrogen-doped graphene and aminated graphene, *Environ. Pollut.* 215 (2016) 96–102.
- [86] X. Wang, A. Wang, J. Ma, Visible-light-driven photocatalytic removal of antibiotics by newly designed C₃N₄@ MnFe₂O₄-graphene nanocomposites, *J. Hazard Mater.* 336 (2017) 81–92.
- [87] G. Peng, M. Zhang, S. Deng, D. Shan, Q. He, G. Yu, Adsorption and catalytic oxidation of pharmaceuticals by nitrogen-doped reduced graphene oxide/Fe₃O₄ nanocomposite, *Chem. Eng. J.* 341 (2018) 361–370.
- [88] P. Tang, G. Hu, M. Li, D. Ma, Graphene-based metal-free catalysts for catalytic reactions in the liquid phase, *ACS Catal.* 6 (2016) 6948–6958.
- [89] Z.-T. Hu, J. Liu, X. Yan, W.-D. Oh, T.-T. Lim, Low-temperature synthesis of graphene/Bi₂Fe₄O₉ composite for synergistic adsorption-photocatalytic degradation of hydrophobic pollutant under solar irradiation, *Chem. Eng. J.* 262 (2015) 1022–1032.
- [90] J. Sheng, H. Yin, F. Qian, H. Huang, S. Gao, J. Wang, Reduced graphene oxide-based composite membranes for in-situ catalytic oxidation of sulfamethoxazole operated in membrane filtration, *Separ. Purif. Technol.* 236 (2020), 116275.
- [91] W. Qi, D. Su, Metal-free carbon catalysts for oxidative dehydrogenation reactions, *ACS Catal.* 4 (2014) 3212–3218.
- [92] C. Cui, L. Jin, L. Jiang, Q. Han, K. Lin, S. Lu, D. Zhang, G. Cao, Removal of trace level amounts of twelve sulfonamides from drinking water by UV-activated peroxymonosulfate, *Sci. Total Environ.* 572 (2016) 244–251.
- [93] X. Ao, W. Liu, Degradation of sulfamethoxazole by medium pressure UV and oxidants: peroxymonosulfate, persulfate, and hydrogen peroxide, *Chem. Eng. J.* 313 (2017) 629–637.
- [94] M. Mahdi-Ahmed, S. Chiron, Ciprofloxacin oxidation by UV-C activated peroxymonosulfate in wastewater, *J. Hazard Mater.* 265 (2014) 41–46.
- [95] X. Ao, W. Sun, S. Li, C. Yang, C. Li, Z. Lu, Degradation of tetracycline by medium pressure UV-activated peroxymonosulfate process: influencing factors, degradation pathways, and toxicity evaluation, *Chem. Eng. J.* 361 (2019) 1053–1062.
- [96] E. Babayi Lashkariyani, R. Rezaei Kalantary, A. Jonidi Jafari, M. Gholami, Performance of graphene-based CoFe₂O₄ in activation of peroxymonosulfate and amoxicillin removal from aqueous solutions, *J. Mazandaran Univ. Med. Sci.* 28 (2018) 94–109.
- [97] Y. Feng, C. Liao, H. Li, C. Liu, K. Shih, Cu₂O-promoted degradation of sulfamethoxazole by α-Fe₂O₃-catalyzed peroxymonosulfate under circumneutral conditions: synergistic effect, Cu/Fe ratios, and mechanisms, *Environ. Technol.* 39 (2018) 1–11.
- [98] J. Deng, S. Feng, K. Zhang, J. Li, H. Wang, T. Zhang, X. Ma, Heterogeneous activation of peroxymonosulfate using ordered mesoporous Co₃O₄ for the degradation of chloramphenicol at neutral pH, *Chem. Eng. J.* 308 (2017) 505–515.
- [99] Y. Feng, D. Wu, Y. Deng, T. Zhang, K. Shih, Sulfate radical-mediated degradation of sulfadiazine by CuFe₂O₄ rhombohedral crystal-catalyzed peroxymonosulfate: synergistic effects and mechanisms, *Environ. Sci. Technol.* 50 (2016) 3119–3127.
- [100] M. Peng, L. Cizmas, Z. Wang, V.K. Sharma, Synergistic effect of aqueous removal of fluoroquinolones by a combined use of peroxymonosulfate and ferrate (VI), *Chemosphere* 177 (2017) 144–148.
- [101] H. Gong, W. Chu, K. Xu, X. Xia, H. Gong, Y. Tan, S. Pu, Efficient degradation, mineralization and toxicity reduction of sulfamethoxazole under photo-activation of peroxymonosulfate by ferrate (VI), *Chem. Eng. J.* 389 (2020), 124084.
- [102] H. Zhang, L.-C. Nengzi, X. Li, Z. Wang, B. Li, L. Liu, X. Cheng, Construction of CuBi₂O₄/MnO₂ composite as Z-scheme photoactivator of peroxymonosulfate for degradation of antibiotics, *Chem. Eng. J.* 386 (2020), 124011.
- [103] J. Deng, Y. Ge, C. Tan, H. Wang, Q. Li, S. Zhou, K. Zhang, Degradation of ciprofloxacin using α-MnO₂ activated peroxymonosulfate process: effect of water constituents, degradation intermediates and toxicity evaluation, *Chem. Eng. J.* 330 (2017) 1390–1400.
- [104] S. Sonawane, M.P. Rayaroth, V.K. Landge, K. Fedorov, G. Boczkaj, Thermally activated persulfate-based Advanced Oxidation Processes — recent progress and challenges in mineralization of persistent organic chemicals: a review, *Curr. Opin. Chem. Eng.* 37 (2022), 100839.
- [105] S. Yang, P. Wang, X. Yang, L. Shan, W. Zhang, X. Shao, R. Niu, Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants: persulfate, peroxymonosulfate and hydrogen peroxide, *J. Hazard Mater.* 179 (2010) 552–558.
- [106] H. Milh, D. Cabooter, R. Dewil, Role of process parameters in the degradation of sulfamethoxazole by heat-activated peroxymonosulfate oxidation: radical identification and elucidation of the degradation mechanism, *Chem. Eng. J.* 422 (2021), 130457.
- [107] N.S. Shah, J.A. Khan, H. Ala'a, M. Sayed, B. Murtaza, H.M. Khan, Synergistic effects of HSO₅⁻ in the gamma radiation driven process for the removal of chlorogenic acid: a new alternative for water treatment, *Chem. Eng. J.* 306 (2016) 512–521.
- [108] Z. Zhang, D. Hu, H. Chen, C. Chen, Y. Zhang, S. He, J. Wang, Enhanced degradation of triclosan by gamma radiation with addition of persulfate, *Radiat. Phys. Chem.* 180 (2021), 109273.
- [109] Z. Zhang, Q. Yang, J. Wang, Degradation of trimethoprim by gamma irradiation in the presence of persulfate, *Radiat. Phys. Chem.* 127 (2016) 85–91.
- [110] Z. Zhang, H. Chen, J. Wang, Y. Zhang, Degradation of carbamazepine by combined radiation and persulfate oxidation process, *Radiat. Phys. Chem.* 170 (2020), 108639.
- [111] S. Wang, J. Wang, Degradation of carbamazepine by radiation-induced activation of peroxymonosulfate, *Chem. Eng. J.* 336 (2018) 595–601.
- [112] E. Saputra, Catalytic Oxidation of Toxic Organics in Aqueous Solution for Wastewater Treatment, Curtin University, 2013.
- [113] C. Liang, H.-W. Su, Identification of sulfate and hydroxyl radicals in thermally activated persulfate, *Ind. Eng. Chem. Res.* 48 (2009) 5558–5562.
- [114] J. Sun, M. Song, J. Feng, Y. Pi, Highly efficient degradation of ofloxacin by UV/Oxone/Co²⁺ oxidation process, *Environ. Sci. Pollut. Res. Int.* 19 (2012) 1536–1543.
- [115] J. Wang, S. Wang, Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants, *Chem. Eng. J.* 334 (2018) 1502–1517.
- [116] A. Romero, A. Santos, F. Vicente, G. C. Diuron abatement using activated persulphate: effect of pH, Fe (II) and oxidant dosage, *Chem. Eng. J.* 162 (2010) 257–265.
- [117] S. Rodriguez, L. Vasquez, D. Costa, A. Romero, A. Santos, Oxidation of Orange G by persulfate activated by Fe(II), Fe(III) and zero valent iron (ZVI), *Chemosphere* 101 (2014) 86–92.
- [118] M. Mahdiahmed, S. Chiron, Ciprofloxacin oxidation by UV-C activated PMS in wastewater, *J. Hazard Mater.* 265 (2014) 41–46.
- [119] Y. Yang, X. Lu, J. Jiang, J. Ma, G. Liu, Y. Cao, W. Liu, J. Li, S. Pang, X. Kong, Degradation of sulfamethoxazole by UV, UV/H₂O₂ and UV/PS (PDS): formation of oxidation products and effect of bicarbonate, *Water Res.* 118 (2017) 196–207.
- [120] R. Khazaei, A. Rahmani, A. Seidmohammadi, J. Faradmal, M. Leili, Evaluation of the Efficiency of photocatalytic UV/peroxymonosulfate process in the removal of cefexime antibiotic from aqueous solutions, *Sci. J. Kurdistan Univ. Med. Sci.* 24 (2019) 22–40.
- [121] S. Norzaee, M. Taghavi, B. Djahed, F.K. Mostafapour, Degradation of Penicillin G by heat activated persulfate in aqueous solution, *J. Environ. Manag.* 215 (2018) 316–323.
- [122] Y. Ren, L. Lin, J. Ma, J. Yang, J. Feng, Z. Fan, Sulfate radicals induced from PMS by magnetic ferrosin MFe₂O₄ (M=Co, Cu, Mn, and Zn) as heterogeneous catalysts in the water, *Appl. Catal., B* 165 (2015) 572–578.
- [123] Y. Zhu, S. Chen, X. Quan, Y. Zhang, Cobalt implanted TiO₂ nanocatalyst for heterogeneous activation of PMS, *RSC Adv.* 3 (2013) 520–525.
- [124] Yf Rao, L. Qu, H. Yang, C. W. Degradation of carbamazepine by Fe(II)-activated persulfate process, *J. Hazard Mater.* 268 (2014) 23–32.
- [125] L. Zhou, W. Zheng, Y. Ji, J. Zhang, C. Zeng, Y. Zhang, Ferrous-activated persulfate oxidation of arsenic(III) and diuron in aquatic system, *J. Hazard Mater.* 263 (2013) 422–430.
- [126] M.H. Rasoulifard, H. Majidzadeh, F.T. Demneh, E. Babaei, M.H. Rasoulifard, Photocatalytic degradation of tylosin via ultraviolet-activated persulfate in aqueous solution, *Int. J. Integrated Care* 3 (2012) 16.
- [127] E. Bazzafshan, S. Noorzai, F. Kordmostafapour, Photocatalytic degradation of aniline in aqueous solutions using magnesium oxide nanoparticles, *J-Mazand-Univ-Med-Sci* 26 (2016) 126–136.
- [128] C. Tan, N. Gao, Y. Deng, N. An, J. Deng, Heat-activated persulfate oxidation of diuron in water, *Chem. Eng. J.* 203 (2012) 294–300.

- [129] Y.-Q. Gao, N.-Y. Gao, Y. Deng, Y.-Q. Yang, Y. Ma, Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water, *Chem. Eng. J.* 195–196 (2012) 248–253.
- [130] C.-W. Wang, C. Liang, Oxidative degradation of TMAH solution with UV persulfate activation, *Chem. Eng. J.* 254 (2014) 472–478.
- [131] J. Liu, S. Zhong, Y. Song, B. Wang, F. Zhang, Degradation of tetracycline hydrochloride by electro-activated persulfate oxidation, *J. Electroanal. Chem.* 809 (2018) 74–79.
- [132] F. Edition, Guidelines for Drinking-Water Quality, vol. 38, WHO chronicle, 2011, pp. 104–108.
- [133] L.R. Bennedsen, J. Muff, E.G. Søgaard, Influence of chloride and carbonates on the reactivity of activated persulfate, *Chemosphere* 86 (2012) 1092–1097.
- [134] Y. Ji, L. Wang, M. Jiang, J. Lu, C. Ferronato, J.M. Chovelon, The role of nitrite in sulfate radical-based degradation of phenolic compounds: an unexpected nitration process relevant to groundwater remediation by in-situ chemical oxidation (ISCO), *Water Res.* 123 (2017) 249–257.
- [135] R. Rezaei, M. Mohseni, Impact of natural organic matter on the degradation of 2,4-dichlorophenoxy acetic acid in a fluidized bed photocatalytic reactor, *Chem. Eng. J.* 310 (2017) 457–463.
- [136] Y. Yang, J. Jiang, X. Lu, J. Ma, Y. Liu, Production of Sulfate Radical and Hydroxyl Radical by Reaction of Ozone with Peroxymonosulfate: A Novel Advanced Oxidation Process, vol. 49, Environmental science & technology, 2015.
- [137] C. Fang, D. Xiao, W. Liu, X. Lou, J. Zhou, Z. Wang, J. Liu, Enhanced AOX accumulation and aquatic toxicity during 2,4,6-trichlorophenol degradation in a Co (II)/peroxymonosulfate/Cl⁻ system, *Chemosphere* 144 (2016) 2415–2420.
- [138] M. Karaca, M. Kırancı, S. Karaca, A. Khataee, A. Karimi, Sonocatalytic removal of naproxen by synthesized zinc oxide nanoparticles on montmorillonite, *Ultrason. Sonochem.* 31 (2016) 250–256.
- [139] C. Tan, D. Fu, N. Gao, Q. Qin, Y. Xu, H. Xiang, Kinetic degradation of chloramphenicol in water by UV/persulfate system, *J. Photochem. Photobiol. Chem.* 332 (2017) 406–412.
- [140] B. Li, L. Li, K. Lin, W. Zhang, S. Lu, Q. Luo, Removal of 1,1,1-trichloroethane from aqueous solution by a sono-activated persulfate process, *Ultrason. Sonochem.* 20 (2013) 855–863.
- [141] X. Lei, Y. Lei, J. Guan, P. Westerhoff, X. Yang, Kinetics and transformations of diverse dissolved organic matter fractions with sulfate radicals, *Environ. Sci. Technol.* 56 (2022) 4457–4466.
- [142] W. Song, J. Li, Z. Wang, X. Zhang, A mini review of activated methods to persulfate-based advanced oxidation process, *Water Sci. Technol.* 79 (2019) 573–579.
- [143] S. Liu, S.U. Hassan, H. Ding, S. Li, F. Jin, Z. Miao, X. Wang, H. Li, C. Zhao, Removal of sulfamethoxazole in water by electro-enhanced Co²⁺/peroxydisulfate system with activated carbon fiber-cathode, *Chemosphere* 245 (2020), 125644.
- [144] J. Zhao, Y. Wang, N. Li, S. Wang, J. Yu, X. Li, Efficient degradation of ciprofloxacin by magnetic γ -Fe₂O₃-MnO₂ with oxygen vacancy in visible-light/peroxymonosulfate system, *Chemosphere* 276 (2021), 130257.
- [145] Z. Yang, Y. Li, X. Zhang, X. Cui, S. He, H. Liang, A. Ding, Sludge activated carbon-based CoFe₂O₄-SAC nanocomposites used as heterogeneous catalysts for degrading antibiotic norfloxacin through activating peroxymonosulfate, *Chem. Eng. J.* 384 (2020), 123319.
- [146] Y. Ji, Y. Fan, K. Liu, D. Kong, J. Lu, Thermo activated persulfate oxidation of antibiotic sulfamethoxazole and structurally related compounds, *Water Res.* 87 (2015) 1–9.
- [147] Y. Fan, Y. Ji, D. Kong, J. Lu, Q. Zhou, Kinetic and mechanistic investigations of the degradation of sulfamethazine in heat-activated persulfate oxidation process, *J. Hazard Mater.* 300 (2015) 39–47.
- [148] L. Chu, R. Zhuan, D. Chen, J. Wang, Y. Shen, Degradation of macrolide antibiotic erythromycin and reduction of antimicrobial activity using persulfate activated by gamma radiation in different water matrices, *Chem. Eng. J.* 361 (2019) 156–166.
- [149] J.-F. Yang, L.-M. Yang, S.-B. Zhang, L.-H. Ou, C.-B. Liu, L.-Y. Zheng, Y.-F. Yang, G.-G. Ying, S.-L. Luo, Degradation of azole fungicide fluconazole in aqueous solution by thermally activated persulfate, *Chem. Eng. J.* 321 (2017) 113–122.
- [150] Y. Liu, X. He, Y. Fu, D.D. Dionysiou, Kinetics and mechanism investigation on the destruction of oxytetracycline by UV-254 nm activation of persulfate, *J. Hazard Mater.* 305 (2016) 229–239.
- [151] M. Nie, Y. Yang, Z. Zhang, C. Yan, X. Wang, H. Li, W. Dong, Degradation of chloramphenicol by thermally activated persulfate in aqueous solution, *Chem. Eng. J.* 246 (2014) 373–382.
- [152] A. Ghauch, A. Baalbaki, M. Amasha, R. El Asmar, O. Tantawi, Contribution of persulfate in UV-254 nm activated systems for complete degradation of chloramphenicol antibiotic in water, *Chem. Eng. J.* 317 (2017) 1012–1025.
- [153] R. Khazaei, A. Rahmani, A. Seidmohammadi, J. Faradmal, M. Leili, Evaluation of the Efficiency of photocatalytic UV/peroxymonosulfate process in the removal of cefexime antibiotic from aqueous solutions, *Sci. J. Kurdistan Univ. Med. Sci.* 24 (2019) 22–40.
- [154] S. Wang, L. Xu, J. Wang, Nitrogen-doped graphene as peroxymonosulfate activator and electron transfer mediator for the enhanced degradation of sulfamethoxazole, *Chem. Eng. J.* 375 (2019), 122041.
- [155] M. Mahdi-Ahmed, S. Chiron, Ciprofloxacin oxidation by UV-C activated peroxymonosulfate in wastewater, *J. Hazard Mater.* 265 (2014) 41–46.
- [156] Y. Gao, Q. Wang, G. Ji, A. Li, Degradation of antibiotic pollutants by persulfate activated with various carbon materials, *Chem. Eng. J.* 429 (2022), 132387.
- [157] Y. Zhang, L. Li, Z. Pan, Y. Zhu, Y. Shao, Y. Wang, K. Yu, Degradation of sulfamethoxazole by UV/persulfate in different water samples: influential factors, transformation products and toxicity, *Chem. Eng. J.* 379 (2020), 122354.
- [158] Y. Zhu, M. Wei, Z. Pan, L. Li, J. Liang, K. Yu, Y. Zhang, Ultraviolet/peroxydisulfate degradation of ofloxacin in seawater: kinetics, mechanism and toxicity of products, *Sci. Total Environ.* 705 (2020), 135960.
- [159] Z. Frontistis, D. Mantzavinos, S. Merić, Degradation of antibiotic ampicillin on boron-doped diamond anode using the combined electrochemical oxidation-Sodium persulfate process, *J. Environ. Manag.* 223 (2018) 878–887.
- [160] Z. Zhao, J. Zhao, C. Yang, Efficient removal of ciprofloxacin by peroxymonosulfate/Mn₃O₄-MnO₂ catalytic oxidation system, *Chem. Eng. J.* 327 (2017) 481–489.
- [161] M.P. Rayaroth, C.T. Aravindakumar, N.S. Shah, G. Boczkaj, Advanced oxidation processes (AOPs) based wastewater treatment-unexpected nitration side reactions-a serious environmental issue: a review, *Chem. Eng. J.* 430 (2022), 133002.
- [162] T. Olmez-Hanci, I. Arslan-Alaton, Comparison of sulfate and hydroxyl radical based advanced oxidation of phenol, *Chem. Eng. J.* 224 (2013) 10–16.
- [163] A. Rastogi, S.R. Al-Abed, D.D. Dionysiou, Sulfate radical-based ferrous-peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems, *Appl. Catal. B Environ.* 85 (2009) 171–179.
- [164] A. Rastogi, S.R. Al-Abed, D.D. Dionysiou, Effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols, *Water Res.* 43 (2009) 684–694.
- [165] J. Monteagudo, A. Durán, J. Latorre, A. Expósito, Application of activated persulfate for removal of intermediates from antipyrene wastewater degradation refractory towards hydroxyl radical, *J. Hazard Mater.* 306 (2016) 77–86.
- [166] J. Gao, D. Han, Y. Xu, Y. Liu, J. Shang, Persulfate activation by sulfide-modified nanoscale iron supported by biochar (S-nZVI/BC) for degradation of ciprofloxacin, *Separ. Purif. Technol.* 235 (2020), 116202.
- [167] M. Feng, R. Qu, X. Zhang, P. Sun, Y. Sui, L. Wang, Z. Wang, Degradation of flumequine in aqueous solution by persulfate activated with common methods and polyhydroquinone-coated magnetite/multi-walled carbon nanotubes catalysts, *Water Res.* 85 (2015) 1–10.
- [168] J. Yan, M. Lei, L. Zhu, M.N. Anjum, J. Zou, H. Tang, Degradation of sulfamonomethoxine with Fe₃O₄ magnetic nanoparticles as heterogeneous activator of persulfate, *J. Hazard Mater.* 186 (2011) 1398–1404.
- [169] Y. Ji, Y. Shi, W. Dong, X. Wen, M. Jiang, J. Lu, Thermo-activated persulfate oxidation system for tetracycline antibiotics degradation in aqueous solution, *Chem. Eng. J.* 298 (2016) 225–233.
- [170] M. Sayed, M. Ismail, S. Khan, S. Tabassum, H.M. Khan, Degradation of ciprofloxacin in water by advanced oxidation process: kinetics study, influencing parameters and degradation pathways, *Environ. Technol.* 37 (2016) 590–602.
- [171] Z. Zhou, X. Liu, K. Sun, C. Lin, J. Ma, M. He, W. Ouyang, Persulfate-based advanced oxidation processes (AOPs) for organic-contaminated soil remediation: a review, *Chem. Eng. J.* 372 (2019) 836–851.

- [172] Y. Wang, D. Tian, W. Chu, M. Li, X. Lu, Nanoscaled magnetic CuFe₂O₄ as an activator of peroxymonosulfate for the degradation of antibiotics norfloxacin, *Separ. Purif. Technol.* 212 (2019) 536–544.
- [173] D. Chen, Z. Xie, Y. Zeng, W. Lv, Q. Zhang, F. Wang, G. Liu, H. Liu, Accelerated photocatalytic degradation of quinolone antibiotics over Z-scheme MoO₃/g-C₃N₄ heterostructure by peroxydisulfate under visible light irradiation: mechanism; kinetic; and products, *J. Taiwan Inst. Chem. Eng.* 104 (2019) 250–259.
- [174] H. Wang, Q. Gao, H. Li, B. Han, K. Xia, C. Zhou, One-pot synthesis of a novel hierarchical Co (II)-doped TiO₂ nanostructure: toward highly active and durable catalyst of peroxymonosulfate activation for degradation of antibiotics and other organic pollutants, *Chem. Eng. J.* 368 (2019) 377–389.
- [175] J. Hu, J. Zhang, Q. Wang, Q. Ye, H. Xu, G. Zhou, J. Lu, Efficient degradation of tetracycline by ultraviolet-based activation of peroxymonosulfate and persulfate, *Water Sci. Technol.* 79 (2019) 911–920.
- [176] Y. Luo, R. Su, H. Yao, A. Zhang, S. Xiang, L. Huang, Degradation of trimethoprim by sulfate radical-based advanced oxidation processes: kinetics, mechanisms, and effects of natural water matrices, *Environ. Sci. Pollut. Control Ser.* 28 (2021) 62572–62582.