

Antibiotic removal from synthetic and real aqueous matrices by peroxymonosulfate-based advanced oxidation processes. A review of recent development

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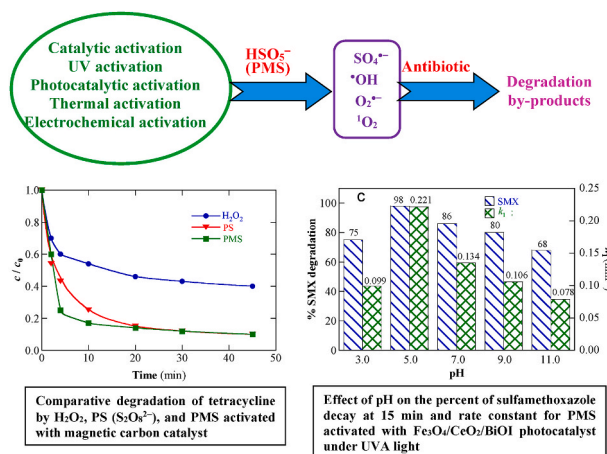
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HIGHLIGHTS

- Recent development of peroxymonosulfate (PMS)-based AOPs for antibiotic removal is summarized.
- PMS activated by catalytic, UV, photocatalytic, thermal, electrochemical, and other processes.
- Radical mechanisms with $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$, and $\text{O}_2^{\cdot-}$ and non-radical ones with $^1\text{O}_2$ are detailed.
- Removal in pure water > in real waters: low Cl^- content activates, H_2PO_4^- , HCO_3^- , CO_3^{2-} , and NOM inhibit.
- Description of the theoretical and experimental detoxification of antibiotic waters.

GRAPHICAL ABSTRACT



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ABSTRACT

The widespread use of antibiotics for the treatment of bacteriological diseases causes their accumulation at low concentrations in natural waters. This gives health risks to animals and humans since it can increase the damage of the beneficial bacteria, the control of infectious diseases, and the resistance to bacterial infection. Potent oxidation methods are required to remove these pollutants from water because of their inefficient abatement in municipal wastewater treatment plants. Over the last three years in the period 2021–September 2023, powerful peroxymonosulfate (PMS)-based advanced oxidation processes (AOPs) have been developed to guaranty the effective removal of antibiotics in synthetic and real waters and wastewater. This review presents a comprehensive analysis of the different procedures proposed to activate PMS-producing strong oxidizing agents like sulfate radical ($\text{SO}_4^{\cdot-}$), hydroxyl radical ($\cdot\text{OH}$), radical superoxide ion ($\text{O}_2^{\cdot-}$), and non-radical singlet oxygen ($^1\text{O}_2$).

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at different proportions depending on the experimental conditions. Iron, non-iron transition metals, biochar, and carbonaceous materials catalytic, UVC, photocatalytic, thermal, electrochemical, and other processes for PMS activation are summarized. The fundamentals and characteristics of these procedures are detailed remarking on their oxidation power to remove antibiotics, the influence of operating variables, the production and detection of radical and non-radical oxidizing agents, the effect of added inorganic anions, natural organic matter, and aqueous matrix, and the identification of by-products formed. Finally, the theoretical and experimental analysis of the change of solution toxicity during the PMS-based AOPs are described.

1. Introduction

The uptake of specific antibiotics by animals and humans allows the healing of many bacteriological diseases, with the consequent increase in their average life expectancy (dos Santos et al., 2021a). Due to their widespread use, low contents (typically $<10 \mu\text{g L}^{-1}$) of antibiotics are accumulated in the aquatic environment like seawater, lake water, river water, and drinking water (Li et al., 2020). The main wastewater sources of these pollutants proceed from pharmaceutical industries, hospitals, and houses also containing the metabolites excreted by the urine of animals and humans (Brillas, 2022b). Other wastewater such as urban runoff and leaching from agricultural flow antibiotic residues into the groundwater streams (Meijide et al., 2021). The damage of beneficial bacteria, the control of infectious diseases, and the resistance to bacterial infection can be raised by the small concentration of these pollutants in water bodies, thus causing serious health risks to animals and humans (Brillas, 2022a). The European Directives 2015/495/EU and 2018/840/EU have recognized the possible harmful effects of antibiotics and recommended the risk assessment of the occurrence, distribution, and frequency of active compounds like ciprofloxacin and amoxicillin.

Antibiotics are classified in families with a similar chemical structure that yields the same action mechanism to kill bacteria. Fig. SM-1 presents the chemical structure and name of the most typical antibiotics analyzed in this review. They belong to the families of amphenicols (chloramphenicol), fluoroquinolones (ciprofloxacin, levofloxacin, ofloxacin), sulfonamides (sulfadiazine, sulfamethazine, sulfamethoxazole), and tetracyclines (oxytetracycline, tetracycline). Another ubiquitous antibiotic such as trimethoprim does not belong to any family.

Typical methods used for the abatement of antibiotics from real wastewater in municipal wastewater treatment plants (WWTPs) are adsorption and biotransformation/biodegradation. However, the stable chemical structure of these pollutants limits their removal in these plants since they are largely persistent in biodegradation, the reason for which, they cannot be efficiently abated. For instance, trimethoprim is only removed in 40–70% during its treatment in WWTPs and thus, it can re-enter the aquatic environment from the released effluents (Monteil et al., 2019). Powerful oxidation processes are then checked to ensure the complete disappearance of antibiotics from water and wastewater. So, biological treatment followed by ultraviolet (UV) irradiation and chlorination has been assessed with WWTP effluents, but both post-treatments are not potent enough to degrade most antibiotics and their metabolites. Coagulation-flocculation and membrane filtration have also been studied to remove these contaminants. Nevertheless, these methods do not solve their degradation because the former transfers the contaminants from one phase to another and the latter produces concentrates that require further treatment (Monteil et al., 2019).

More potent treatments are based on the advanced oxidation processes (AOPs), which are environmentally friendly methods specifically designed for the effective degradation of persistent organic pollutants like antibiotics (Brillas and Garcia-Segura, 2020; Brillas, 2022a). AOPs are chemical, photochemical, electrochemical, and photo-electrochemical methods characterized by the in-situ generation of reactive oxygen species (ROS) such as the strong oxidant hydroxyl radical ($\bullet\text{OH}$). This radical has a high standard reduction potential (E°)

of 2.72 V/SCE at pH = 0 and can attack most organic pollutants usually via hydroxylation and dehydrogenation processes up to their mineralization is attained (Brillas, 2022a, 2022b). Other recently developed powerful methods are based on the emerging sulfate radical ($\text{SO}_4^{\bullet-}$)-based AOPs (dos Santos et al., 2021b; Brillas, 2023). $\text{SO}_4^{\bullet-}$ is a strong oxidant with an $E^\circ = 2.44 \text{ V/SCE}$ at pH = 0, a value comparable to that $\bullet\text{OH}$, although it shows higher selectivity for the attack of organics via electronic transfer and longer half-life ($\approx 40 \mu\text{s}$) than $\bullet\text{OH}$ ($\approx 20 \text{ ns}$) (Hassani et al., 2023). So, many sulfate radical-based AOPs have been checked with a larger efficiency for the removal and mineralization of organic pollutants. Peroxymonosulfate (HSO_5^- , PMS) is a very attractive oxidant that needs to be activated to be transformed into $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$, and hence, the production of both strong oxidants accelerates the pollutant degradation. Other ROS such as the radical superoxide ion ($\text{O}_2^{\bullet-}$) and the non-radical singlet oxygen ($^1\text{O}_2$) can also be generated, depending on the activation method used, operating conditions, and aqueous matrix checked (Honarmandrad et al., 2023). This leads to complex radical and non-radical degradation/mineralization mechanisms of organics. Recent works have demonstrated the high impact of removing antibiotics by PMS activated with different procedures, but a comprehensive review deeply analyzing their characteristics has not been reported yet in the literature.

This paper presents a review of the most relevant recent research on the PMS-based treatments of antibiotics in synthetic and real waters and wastewaters, covering the period 2021–September 2023. PMS processes with iron, non-iron transition metals, biochar, and carbonaceous materials catalysts, UVC, photocatalytic, thermal, and electrochemical activation, and other methods, are summarized. The fundamentals and characteristics of all these procedures are analyzed making special attention to their oxidation power, the effect of operating variables, the generation and identification of radical and non-radical oxidizing agents, the influence of added inorganic anions, natural organic matter (NOM), and reaction matrix, and the detection of by-products formed. Figures-of-merit are used to better understand their performance. Finally, the theoretical and experimental studies on the change of toxicity of antibiotic solutions during the PMS-based AOPs are detailed.

2. Bibliometric analysis

The scientific papers and reviews dealing with the PMS-based AOPs of synthetic and real waters and wastewater polluted with antibiotics were retrieved from the Scopus database. The results were found up to September 2023 by introducing the keyword “Oxidation of antibiotics AND Peroxymonosulfate” in the database. The selected articles were written in English with the exclusion of those related to book chapters and communications in congresses. The acceptance of articles was made by individually analyzing the title and abstract of retrieved publications. Following this procedure, a total of 188 scientific papers and 7 reviews were identified in the latter 3 years, i.e., the period 2021–September 2023, where most articles in this field were published. Only other 56 articles have been previously published in the period 2016–2020. This points to the fast recent interest and development of antibiotic removal with PMS-based AOPs. A deep analysis of the PMS activation methods reported in the scientific papers allowed the conclusion that they were performed with iron, non-iron transition metals, biochar, and carbonaceous materials catalysts, and UVC, photocatalytic, thermal,

electrochemical activation, and other processes. These papers described: (i) the synthesis and/or characterization of catalysts, photocatalysts, and electrocatalysts as activators, (ii) the influence of operating variables like pH, temperature, the concentration of PMS, catalyst, and/or photocatalyst, the electrolytic cell, and the aqueous matrix on antibiotic removal determined from its content abatement monitored by high-performance liquid chromatography (HPLC), (iii) the total organic carbon (TOC) and chemical oxygen demand (COD) related to the antibiotic mineralization, (iv) the evaluation of energetic parameters, (v) the detection of the produced radical and non-radical oxidizing agents by the inhibition from selected specific scavengers, sometimes supported by electron paramagnetic resonance (EPR) analysis, (vi) the effect of added inorganic anions, humic acid as NOM, and water matrix, (vii) the identification of the by-products formed, usually with techniques liquid chromatography-mass spectrometry (LC-MS), allowing proposing a reaction sequence for the degradation/mineralization of the antibiotic, and (viii) in some cases, the assessment of the solution toxicity during the treatment. The present review describes the fundamentals and characteristics of the different methods used for PMS activation, followed by the analysis of the removal of selected antibiotics for each method. The influence of operating variables, the oxidizing species generated giving rise to radical and non-radical mechanisms, and the identification of by-products are especially detailed. The review presents 3 tables and 17 figures, 13 of them exposed in Supplementary Material, which has been designed to remark on the main results shown in the scientific articles.

Seven reviews have been published giving a partial description of the abatement of antibiotics by some PMS-based AOPs. Three reviews have considered the general behavior of radical mechanisms (Peng et al., 2021a), nanomaterials (Li et al., 2022d), and catalytic degradation (Yusuf et al., 2022) of emerging pollutants involved with sulfate radical-based AOPs, with some examples of antibiotics treated with activated PMS. The other two more specific reviews described the antibiotic removal with sulfate radical-based AOPs originated under the partial catalytic action of carbon materials (Gao et al., 2022) and UV light (Song et al., 2022). Thai et al. (2023) presented a general review of the fate of fluoroquinolones with an analysis of selected removal methods including activated PMS. Honarmandrad et al. (2023) detailed the use of several activation methods of persulfate ($S_2O_8^{2-}$, PS) and PMS to remediate some antibiotic waters, preferentially highlighting the role of operating variables. In contrast, our review analyzes the systems used, the action of catalysts, UVC, photocatalysts, and electrocatalysts, the generation of oxidizing agents, the existence of radical and non-radical mechanisms, the by-products formed, and the change in toxicity of treated wastewaters. The present review summarizes all these characteristics of the PMS-based AOPs, remarking on their usage to degrade antibiotics from synthetic and real waters and wastewaters during all the time that such technologies have been more strongly developed, that is, the period 2021–September 2023.

From the bibliometric analysis, 40 scientific papers related to PMS-based processes were identified in 2021, 73 articles in 2022, and 75 articles more up to September 2023, demonstrating the current and increasing interest in such procedures for antibiotic removal. Regarding the activation method applied, catalysts were the most used activators. They were classified according to their structural nature as iron catalysts with 52 articles (27.6%), non-iron transition metals catalysts with 67 articles (35.6%), biochar catalysts with 15 articles (8.1%), and carbonaceous materials catalysts with 9 articles (4.8%). Other papers include UVC activation with 5 articles (2.7%), photocatalytic activation with 23 articles (12.2%), thermal activation with 3 articles (1.6%), electrochemical activation with 9 articles (4.8%), and other methods with 5 articles (2.7%). Most papers described the effectiveness of the PMS-based AOPs in synthetic wastewaters, with a study on the influence of scavengers, inorganics anions, and NOM. The processes with real matrices like tap water, river water, lake water, groundwater, and wastewater (WWTP) effluents have been analyzed in many cases. Comparison with other analogous treatments with PS and H_2O_2 has been

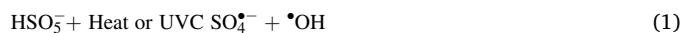
reported as well.

3. Treatment of antibiotic waters and wastewater

This section is devoted to describing and analyzing the PMS-based AOPs developed for antibiotic abatement in synthetic and real water and wastewater. After a brief discussion of the fundamentals and general consideration of such processes, their characteristics and main results reported in the published scientific articles will be detailed considering the type of catalyst such as iron, non-iron transition metals, biochar, and carbonaceous materials, followed by the analysis of UVC, photocatalytic, thermal, and electrochemical activations, and other processes. The iron and non-iron transition metals catalysts are grouped by their chemical nature with similar activation mechanisms.

3.1. Fundamentals and general considerations

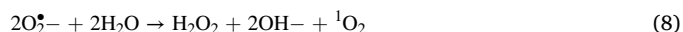
In the PMS/heat and UVC/PMS processes, the energetic activation of the PMS molecule leads to its direct decomposition into $SO_4^{\bullet-}$ and $\bullet OH$ radicals as follows (Milh et al., 2021):



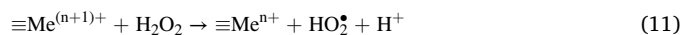
Both strong radicals can attack the organic pollutants. Moreover, $SO_4^{\bullet-}$ is very reactive and can react with H_2O in an acidic medium or OH^- in an alkaline one to produce more $\bullet OH$ by reactions (2) or (3), respectively (He et al., 2022):



Other reactions are involved to form the oxidants $O_2^{\bullet-}$ and $^1O_2$. So, the hydrolysis of HSO_5^- originates $SO_4^{\bullet-}$ and H_2O_2 from reaction (4), whereas the reaction (5) of the latter species with $\bullet OH$ produces $HO_2^{\bullet}$ that it is deprotonated to $O_2^{\bullet-}$ from reaction (6). Further attack of $\bullet OH$, H_2O , or $HO_2^{\bullet}$ over $O_2^{\bullet-}$ yields $^1O_2$ via reactions (7)–(9) (He et al., 2022):



The PMS decomposition depends on the activation method used. In the case of solid catalysts, their surface transition metallic ions, denoted as $\equiv Me^{n+}$, like $\equiv Fe^{2+}$ or $\equiv Co^{3+}$, can produce $SO_4^{\bullet-}$ and OH^- at the catalyst surface by reaction (10). Further reactions (2)–(10) also occur to form $\bullet OH$, $O_2^{\bullet-}$, and $^1O_2$. The resulting surface $\equiv Me^{(n+1)+}$ of reaction (10) can regenerate again $\equiv Me^{n+}$ with H_2O_2 yielding $HO_2^{\bullet}$ by reaction (11) (He et al., 2022):



Other PMS activation processes take place in the photocatalytic and electrochemical treatments, as discussed below. It is noteworthy that the relative oxidation of an antibiotic with the different generated radical and non-radical oxidizing agents is a function of several factors like pH, temperature, and compound and activator contents. Experimentally, the nature of the oxidant is established by two analytical procedures. The most extended method is the use of specific scavengers of each oxidant, which is confirmed through its EPR spectrum.

The most ubiquitous scavengers to verify the generation of $SO_4^{\bullet-}$ and

$\bullet\text{OH}$ are ethanol (or methanol and phenol) and *tert*-butylalcohol (TBA). The primary reactions of ethanol and TBA with both radicals are given in reactions (12)–(15) with the corresponding absolute second-order rate constant k_2 (Ji et al., 2014). One can then establish that ethanol (or methanol and phenol) reacts with both radicals from reactions (12) and (13), whereas TBA only attacks $\bullet\text{OH}$ from reaction (14) due to the very smaller k_2 -value for $\text{SO}_4^{\bullet-}$ from reaction (15). It is thus feasible to determine the oxidative proportion of each reactive oxidant from

comparative trials with both scavengers.

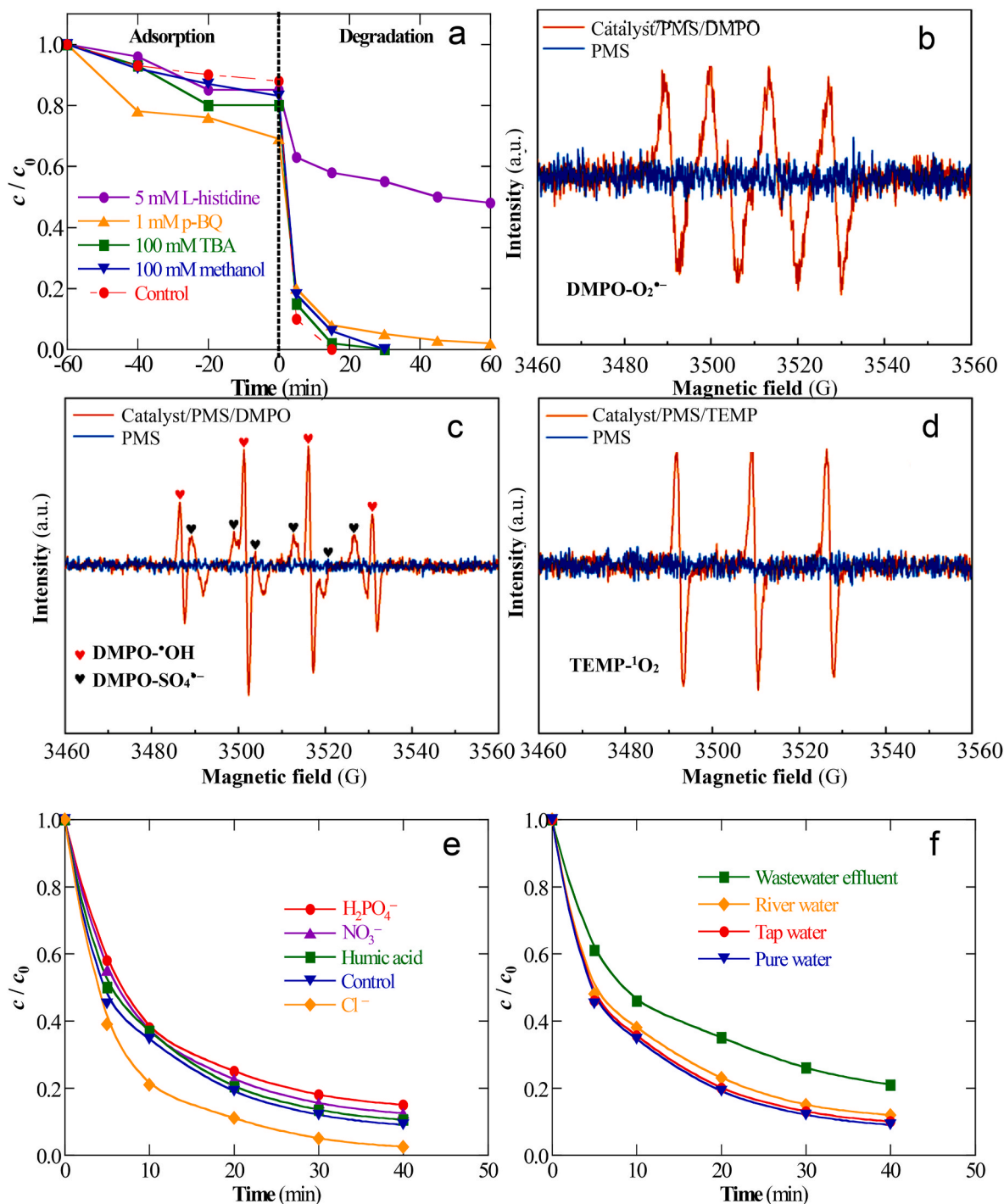
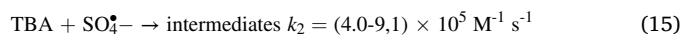
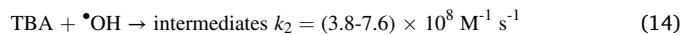
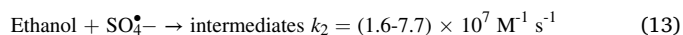
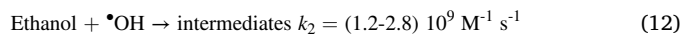
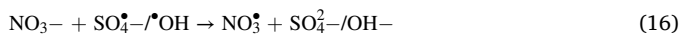


Fig. 1. (a) Quenching effect of different scavengers (TBA = *tert*-butyl alcohol, p-BQ = *p*-benzoquinone) on the treatment of 100 mL of 10 mg L⁻¹ sulfamethoxazole in pure water with 0.5 mM PMS and 150 mg L⁻¹ of Fe/N-carbon catalyst at pH = 7.0. EPR spectra recorded for the adduct of DMPO with generated (b) $\text{O}_2^{\bullet-}$ and (c) $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, and of (d) TEMP with $^1\text{O}_2$ (adapted from He et al. (2022) with permission 5657481151425 from Elsevier). (e) Effect of 20 mM of inorganic anions and 20 mg L⁻¹ of humic acid over the normalized sulfamethoxazole concentration vs. time of 100 mL of 10 mg L⁻¹ antibiotic in pure water with 0.1 M PMS and 50 mg L⁻¹ of Fe atom/N-carbon catalyst at pH = 5.6 (control), and (f) the same degradation process with several real aqueous matrices (adapted from Wang et al. (2023b)).

Common specific scavengers such as *p*-benzoquinone (*p*-BQ) or sodium azide for $O_2^{\bullet-}$, furfuryl alcohol (FFA), L-histidine, or β -carotene for $^1O_2$, and sodium oxalate for $h\nu_B^+$ in photocatalysis, among others, have also been used to identify oxidizing agents. Fig. 1a exemplifies the effect of several scavengers over the normalized sulfamethoxazole content vs. time for 100 mL of 10 mg L⁻¹ antibiotic in pure water with 0.5 mM PMS and 150 mg L⁻¹ of Fe/N-carbon catalyst at pH = 7.0 after 60 min of adsorption in the dark (He et al., 2022). A very strong inhibition can be observed for L-histidine, followed by a smaller scavenging for *p*-BQ > methanol > TBA. This means that $^1O_2$ is the main oxidant in this system, followed by $O_2^{\bullet-}$, $SO_4^{\bullet-}$, and $\bullet OH$ at much lesser extent.

In many cases, the formation of oxidizing agents is confirmed by their EPR spectra by adding high contents of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) or 2,2,6,6-tetramethyl-4-piperidinol (TEMP). While DMPO forms adducts with $SO_4^{\bullet-}$, $\bullet OH$, and $O_2^{\bullet-}$, TEMP complexes $^1O_2$. For the PMS assays of Fig. 1a and b depicts the typical quadruplet (1:1:1:1) recorded for the adduct DMPO- $O_2^{\bullet-}$, Fig. 1c shows the quadruplets (1:2:2:1) for the adducts DMPO- $SO_4^{\bullet-}$ and DMPO- $\bullet OH$, and Fig. 1d presents the triplet (1:1:1) for the adduct TEMP- $^1O_2$. These spectra confirm the generation of all these oxidants, but their relative proportion to attack the antibiotic cannot be known, a feature that can be determined by using specific scavengers. In particular, it is noteworthy that the relative height of the DMPO- $SO_4^{\bullet-}$ quadruplet is always found much smaller than that of DMPO- $\bullet OH$ one (see Fig. 1c) as a result of the destruction of the former by the attack of generated $\bullet OH$.

Inorganic ions like NO_3^- and HCO_3^- act as scavengers of $SO_4^{\bullet-}$ and $\bullet OH$ formed from PMS activation, removing part of these radicals as antibiotic oxidants by the following reactions (Noroozi et al., 2022):



Similar reactions take place with CO_3^{2-} and $H_2PO_4^-$. In contrast, the presence of SO_4^{2-} can also inhibit the removal of antibiotics because it can be transformed into $SO_4^{\bullet-}$ from the stronger oxidant $\bullet OH$ as follows (Noroozi et al., 2022):



A different behavior has been found for the Cl^- anion, which can accelerate the antibiotic oxidation at low concentrations due to the formation of reactive chlorine species like $Cl^{\bullet}$, $ClOH^{\bullet-}$, $Cl_2^{\bullet-}$, and $HClO$ by reactions (20)–(23) (Noroozi et al., 2022):



An inhibition of antibiotic removal also occurs in the presence of other organics and NOM because they competitively react with the oxidizing agents. For instance, Fig. 1e highlights the negative effect of 20 mM of NO_3^- and $H_2PO_4^-$, and 20 mg L⁻¹ of humic acid as NOM, as well as the positive influence of 20 mM of Cl^- , over the normalized sulfamethoxazole concentration vs. time of the solution of Fig. 1a with 0.1 M PMS and 50 mg L⁻¹ of the same catalyst at pH = 5.6 (control) (Wang et al., 2023b).

Inorganic anions, other organic pollutants, and NOM cause the inhibition of antibiotic abatement in natural water and real wastewater in front of pure water. As an example, under the conditions of Fig. 1e and f makes evident that sulfamethoxazole degradation decays in the order: of pure water $\approx$ tap water $\approx$ river water $\gg$ WWTP effluent. This trend can be related to the content of the above scavengers in each aqueous matrix.

The preparation and characterization of new catalysts, photocatalysts, and electrocatalysts to activate PMS play a role fundamental in all the scientific papers published in this field, which are further centered on analyzing and discussing their effectiveness in the PMS-based AOP. Simple and cheap methods are usually reported for the preparation of such materials followed by an exhaustive analysis of their physical and chemical properties. So, scanning electron microscopy (SEM), high-resolution transmission electronic microscopy (HRTEM), and energy dispersive X-ray spectroscopy (EDS) with elemental mapping are typically used for analyzing their surface and qualitative composition. The magnetism is measured by their hysteresis loop. Fourier-transform infrared (FT-IR) spectra identify their chemical bonds and functional groups, whereas X-ray diffraction (XRD) spectroscopy informs over their crystallinity and structure. For semiconductor photocatalysts, UV-Vis diffuse-reflectance spectroscopy allows to construction of the Kubelka-Munk function curve for determining their band gap energy (E_{bg}) value from the corresponding Tauc plot. The electrochemical characteristics are assessed from the faradaic impedance. Other physicochemical parameters such as the static contact angle, porosity, and active surface area, are sometimes determined.

Fig. SM-2 and SM-3 show some examples of the above analytical methods for selected materials. Fig. SM-2a presents the SEM, TEM, and HRTEM images for $CoFe_2O_4$, biochar, and $CoFe_2O_4$ /biochar prepared for the catalytic degradation of tetracycline with PMS, along with the images of the elemental mapping of the latter composite (Huang et al., 2023b). Fig. SM-2b confirms that $CoFe_2O_4$ is a magnetic material from its hysteresis loop. On the other hand, Fig. SM-3a and 3b depict the FT-IR spectra and XRD patterns, respectively, of several photocatalysts prepared as PMS activators to remove sulfamethoxazole (Kohantorabi et al., 2021). The absorbance vs. λ plots measured by UV-Vis diffuse-reflectance spectroscopy for the photocatalysts labeled as CN, CF, and CF/CN used to degrade sulfamethazine with PMS are presented in Fig. SM-3c. From these data, their E_{bg} -values calculated from the Tauc plots are shown in Fig. SM-3d (Sun et al., 2023).

3.2. Iron catalysts

Many catalysts have been prepared containing Fe as a single or combined metal component. From their chemical structure, they can be categorized as single iron, iron oxides, mixed iron-metal oxides, magnetic iron-transition metal, metal-organic frameworks (MOFs) derived with iron, and other catalysts, whose characteristics will be analyzed in this subsection. Table 1 summarizes the main results reported for the removal of antibiotics with PMS activated by these iron materials from selected papers chosen for each category.

3.2.1. Single iron catalysts

A reduced number of authors have considered the catalytic properties of composites of single Fe atoms with *N*-carbon materials to degrade sulfamethoxazole (He et al., 2022; Wang et al., 2023b) and sulfasalazine (Xu et al., 2022b). For the two former works, 100 mL of 10 mg L⁻¹ sulfamethoxazole in pure water was treated and overall degradation was achieved in 15 min with the greater contents of 0.5 M PMS and 150 mg L⁻¹ catalyst at pH = 7.0 due to the generation of more $SO_4^{\bullet-}$ from reaction (10) with surface $\equiv Fe^{2+}$ followed by the production of $\bullet OH$ from reactions (2) or (3) (see Table 1). However, reactions (4)–(9) generating $O_2^{\bullet-}$ and $^1O_2$ were faster, and these oxidants predominated over $SO_4^{\bullet-}$ and $\bullet OH$, as shown in Fig. 1a. The inhibitory and positive effect of the content of added anions and the inhibition with NOM justified the loss of degradation power of the system in different aqueous matrices in the order: pure water $\approx$ tap water $\approx$ river water $\gg$ WWTP effluent (see Fig. 1e and f). An interesting result is that the catalyst gave rise to good reproducibility after 5 consecutive cycles in pure water. This excellent finding is indicative of the good applicability of single iron composites with *N*-carbon for the removal of antibiotics, which should be more deeply studied with real waters and wastewater.

Table 1

Selected results reported for the removal of antibiotics from different aqueous matrices by the activation with iron catalysts of peroxymonosulfate.

Antibiotic	System	Experimental remarks	Best results	Ref.
<i>Single iron catalysts</i>				
Sulfamethoxazole	Stirred tank reactor with Fe/N-carbon catalyst	100 mL of 10 mg L ⁻¹ antibiotic in pure water, 0.5 mM PMS, 150 mg L ⁻¹ catalyst, effect of scavengers (methanol, TBA ^a , <i>p</i> -BQ ^b , and l-histidine) and anions (Cl ⁻ , SO ₄ ²⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), pH = 3.0–11.0, room temperature, 60 min	Total degradation in 15 min at pH = 7.0 with $k_1 = 0.39 \text{ min}^{-1}$ after 60 min of adsorption in the dark. Strong deceleration at pH = 11.0. Much greater inhibition with 5 mM l-histidine than the other scavengers. Larger inhibition with HCO ₃ ⁻ and humic acid. ¹ O ₂ as dominant oxidant in front of SO ₄ ²⁻ , [•] OH, and O ₂ ^{•-} . LC-MS analysis revealed the formation of 6 heteroaromatic, 5 aromatic, and 1 aliphatic derivatives	He et al. (2022)
Sulfamethoxazole	Stirred Erlenmeyer flask with single Fe atom/N-carbon catalyst	100 mL of 10 mg L ⁻¹ antibiotic in pure water and real waters, 0.1 M PMS, 50 mg L ⁻¹ catalyst, effect of scavengers (methanol, TBA, and sodium azide), anions (Cl ⁻ , SO ₄ ²⁻ , and H ₂ PO ₄ ⁻), and humic acid, pH = 5.6, 25 °C, 40 min	100% of loss of antibiotic. Greater inhibition with sodium azide. Scarce deceleration with all anions and humic acid. Predominance of O ₂ ^{•-} over SO ₄ ²⁻ and [•] OH as oxidant. Degradation: pure water ≈ tap water ≈ river water ≫ WWTP effluent. Good reproducibility after 5 consecutive cycles	Wang et al. (2023b)
<i>Iron oxides catalysts</i>				
Ciprofloxacin	Stirred glass test tube with α-FeOOH/kaolinite catalyst	50 mL of 60 mg L ⁻¹ antibiotic in pure water, 0.6 mM PMS, 1.0 g L ⁻¹ catalyst, effect of scavengers (ethanol, TBA, FFA ^c , and phenol) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), pH = 7.0, room temperature, 60 min	86% degradation with 40% α-FeOOH/kaolinite after 30 min of adsorption in the dark. Much greater inhibition with FFA. Acceleration with Cl ⁻ , and inhibition with the other anions. Oxidant ¹ O ₂ predominated over SO ₄ ²⁻ , [•] OH, and O ₂ ^{•-} . 10 heteroaromatic and 1 aromatic intermediates identified by LC-MS	Sun et al. (2022)
Doxycycline	Stirred tank reactor with Fe ₃ O ₄ /N-carbon catalyst	10–40 mg L ⁻¹ antibiotic in pure water and natural water, 0.1–1.0 g L ⁻¹ PMS, 0–0.8 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, and l-histidine) and anions (Cl ⁻ , NO ₃ ⁻ , and SO ₄ ²⁻), pH = 2.7–9.2, room temperature, 20 min	80% degradation for all antibiotic contents with ≥0.5 g L ⁻¹ of PMS and catalyst. Stronger inhibition with TBA and l-histidine. Little effect of pH and anions. Coexistence of SO ₄ ²⁻ , [•] OH O ₂ ^{•-} , and ¹ O ₂ as oxidants. Degradation: pure water ≈ tap water > river water No reproducibility with loss of 50% degradation after 4 successive steps.	Xu et al. (2023b)
Tetracycline	Stirred beaker with ferroferric oxide/charcoal catalyst	150 mL of 150 mg L ⁻¹ antibiotic in pure water and natural water, 2.5–7.5 mM PMS, 0.25–0.75 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>n</i> -butanol, FFA, and phenol), pH = 3.0–6.0, 25 °C, 90 min	14 aromatic by-products detected by LC-MS 82% degradation with 0.75 g L ⁻¹ catalyst at pH = 3.0, regardless of the PMS concentration. Deceleration at lower catalyst dosage and higher pH. Larger inhibition with FFA and phenol. Predominance of oxidants SO ₄ ²⁻ and ¹ O ₂ . No reusability with loss of 30% degradation after 5 consecutive runs. Detection of 24 aromatic by-products and maleic acid by LC-MS	Zhou et al. (2022a)
Tetracycline	Stirred conical flask with Fe ₃ O ₄ /polyaniline catalyst	50 mL of 20 mg L ⁻¹ antibiotic in pure water, 0.5–50 mM PMS, 0.4 g L ⁻¹ catalyst, effect of scavengers (ethanol, TBA, <i>p</i> -BQ, and FFA) and anions (Cl ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), pH = 3.0–9.0, 30 °C, 90 min	Higher antibiotic decay at greater PMS dosage. 90% degradation with 50 mM PMS at any pH value. Larger deceleration with FFA. Scarce effect of anions. ¹ O ₂ dominated over SO ₄ ²⁻ , [•] OH, and O ₂ ^{•-} as oxidant. Low reproducibility losing 15% degradation after 3 successive cycles	Wang et al. (2023b)
<i>Mixed iron-metal oxides catalysts</i>				
Ciprofloxacin	Stirred tank reactor with CuFe ₂ O ₄ /GO ^d catalyst	250 mL of 10–50 mg L ⁻¹ antibiotic in pure water, 0.05–5.0 mM PMS, 0.05–0.6 g L ⁻¹ catalyst, effect of scavengers (ethanol and TBA) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and SO ₄ ²⁻), pH = 3.0–11.0, 25 °C, 60 min	Total degradation for the best conditions with 30 mg L ⁻¹ antibiotic, 2.0 mM PMS, 0.2 g L ⁻¹ catalyst, and pH = 7.0 after 60 min of adsorption in the dark. Ethanol more largely inhibited than TBA. Larger deceleration with NO ₃ ⁻ and HCO ₃ ⁻ . Oxidation with SO ₄ ²⁻ and [•] OH, Good reproducibility after 5 successive steps. Detection of 8 aromatic by-products by GC-MS	Noroozi et al. (2022)
Gatifloxacin	Stirred tank reactor with Bi ₂ Ca ₂ (1-x)Fe ₄ O ₉ catalyst	100 mL of 5 mg L ⁻¹ antibiotic in pure water and real waters, 0.1–0.8 g L ⁻¹ PMS, 0.05–0.4 g L ⁻¹ catalyst, effect of scavengers (ethanol, TBA, and sodium azide), anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and PO ₄ ³⁻), and humic acid, pH = 3.0–9.0, room temperature, 45 min	Higher antibiotic abatement with raising PMS and catalyst dosage, regardless pH, 90% degradations for 0.66 g L ⁻¹ PMS, 0.1 g L ⁻¹ catalyst, and pH = 9.0 with $k_1 = 0.165 \text{ min}^{-1}$. Stronger inhibition with ethanol followed by sodium azide. Greater deceleration with PO ₄ ³⁻ and humic acid. Degradation: pure water ≈ tap water ≈ river water ≫ WWTP effluent. Oxidants: SO ₄ ²⁻ > ¹ O ₂ > [•] OH. Low reproducibility with loss of 15% degradation in 4 successive cycles.	Koo et al. (2022)
Tetracycline	Stirred tank reactor with Fe-CoTiO ₃ catalyst	100 mL of 20 mg L ⁻¹ antibiotic in pure water, 0.3–1.5 mM PMS, 0.05–0.2 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, and l-histidine) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), pH = 3.0–9.0, 25 °C, 40 min	11 heteroaromatic by-products detected by LC-MS Overall removal for ≥1.0 mM PMS and ≥0.1 g L ⁻¹ catalyst at pH ≥ 7.0. Slower abatement in the presence of methanol. Stronger inhibition by adding NO ₃ ⁻ and HCO ₃ ⁻ . Predominance of SO ₄ ²⁻ as oxidant. Moderate reusability losing 10% degradation after 5 successive runs.	Wei et al. (2021)

(continued on next page)

Table 1 (continued)

Antibiotic	System	Experimental remarks	Best results	Ref.
Tetracycline	Stirred tank reactor with ZnFe ₂ O ₄ catalyst	100 mL of 20 mg L ⁻¹ antibiotic in pure water, 0.02–0.5 g L ⁻¹ PMS, 0.2 g L ⁻¹ catalyst, effect of anions (Cl ⁻ , CO ₃ ²⁻ , and H ₂ PO ₄ ⁻), pH = 3.0–11.0, 25 °C, 30 min	88% degradation for 0.5 g L ⁻¹ PMS at pH 7.0 after 30 min in the dark. Faster removal at lower pH. Strong degradation with all the anions at 1.0 mM. Detection of SO ₄ ^{•-} , •OH, O ₂ ^{•-} , and ¹ O ₂ by EPR. Moderate reusability with loss of 12% degradation after 4 consecutive steps. Identification of 13 primary aromatic intermediates by LC-MS	Zhao et al. (2023b)
Trimethoprim	Stirred tank reactor with Co-Fe ₃ O ₄ /α FeOOH catalyst	150 mL of 10 mg L ⁻¹ antibiotic in pure water, 0.05–0.30 mM PMS, 0.05–0.30 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, p-BQ, FFA, and l-histidine), pH = 3.0–11.0, 25 °C, 20 min	Greater antibiotic abatement at higher PMS and catalysts contents, and pH. Overall degradation for 0.30 mM PMS, 0.30 g L ⁻¹ catalyst, and pH = 11.0. Strong inhibition with methanol, FFA, and l-histidine. Predominance of SO ₄ ^{•-} and ¹ O ₂ as oxidants. Scarce reproducibility losing 25% degradation after 6 consecutive cycles. Identification of 12 aromatic intermediates by LC-MS	Xu et al. (2023c)
<i>Magnetic iron-transition metal catalysts</i>				
Ampicillin	Stirred Erlenmeyer flask with CoFe ₂ O ₄ catalyst	100 mL of 1.0–20 mg L ⁻¹ antibiotic in pure water, 0.05–0.025 mM PMS, 0.01–0.3 g L ⁻¹ catalyst, pH = 3.0–11.0, 27 °C, 30 min	Decrease of antibiotic decay at higher content. 100% removal and 61% TOC removal for 1.0 mg L ⁻¹ antibiotic, any PMS content, ≥0.1 g L ⁻¹ catalyst, and pH = 7.0. Moderate reusability losing 12% degradation after 4 successive runs. LC-MS analysis allowed detecting 5 aromatic by-products	Balakrishnan et al. (2021)
Oxytetracycline	Stirred tank reactor with BN/CoFe ₂ O ₄ catalyst	250 mL of 10–30 mg L ⁻¹ antibiotic in pure water, 0.1–0.5 g L ⁻¹ PMS, 0.1–0.5 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, p-BQ, and FFA), anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and HPO ₄ ²⁻), and humic acid, pH = 3.0–11.0, 25 °C, 30 min	Overall abatement achieved under the best conditions of 10–20 mg L ⁻¹ antibiotic, and 0.4 g L ⁻¹ PMS and catalyst at pH = 6.68. FFA and methanol as the stronger scavengers. Stronger inhibition with HCO ₃ ⁻ , HPO ₄ ²⁻ , and humic acid. Major role of SO ₄ ^{•-} and ¹ O ₂ as oxidants. Low reusability with >20% COD decay after 5 consecutive cycles. 10 aromatic and 1 cyclic by-products detected by LC-MS	Jing et al. (2022)
Sulfanilamide	Stirred tank reactor with Fe ₃ O ₄ /Co/hydroxyapatite catalyst	50 mL of 50–600 mg L ⁻¹ antibiotic in pure water, 0.1–0.6 g L ⁻¹ PMS, 0.2 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, and sodium azide) and anions (Cl ⁻ , NO ₃ ⁻ , PO ₄ ³⁻), pH = 3.0–10.0, room temperature, 60 min	Higher removal with increasing PMS content and pH. 93% degradation in 300 s and 73% TOC decay for 50 mg L ⁻¹ antibiotic and 0.6 g L ⁻¹ PMS at pH = 6.7. Stronger scavenging with methanol. Low effect of all the anions added. SO ₄ ^{•-} and •OH dominated as oxidants. Excellent reproducibility after 4 successive cycles	Amedlous et al. (2022)
Tetracycline	Stirred tank reactor with CoFe ₂ O ₄ /biochar catalyst	100 mL of 10–30 mg L ⁻¹ antibiotic in pure water, 0.326–1.629 mM PMS, 0.1–0.9 g L ⁻¹ catalyst, effect of scavengers (TBA and ascorbic acid) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and SO ₄ ²⁻), pH = 3.0–9.0, room temperature, 30 min	Total abatement for 10–20 mg L ⁻¹ antibiotic, 0.977 mM PMS, 0.5 g L ⁻¹ catalyst, and pH = 5.0 and 7.0. Large effect of ascorbic acid as scavenger. Stronger inhibition by adding Cl ⁻ and HCO ₃ ⁻ . SO ₄ ^{•-} predominated over •OH as oxidant. Excellent reusability after 5 successive runs	Huang et al. (2023b)
<i>MOFs derived with iron catalyst</i>				
Tetracycline	Stirred tank reactor with 0.8 Fe ₂ O ₃ from MIL-101(Fe)/Mn ₃ O ₄ catalyst	100 mL of 10 mg L ⁻¹ antibiotic in pure water, 0.5–2.0 mM PMS, 0.05–0.25 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, p-BQ, and l-tryptophan), anions (Cl ⁻ , NO ₃ ⁻ , and SO ₄ ²⁻), and humic acid, pH = 3.2–9.1, room temperature, 40 min	85% degradation with 0.5 mM PMS, 0.20 g L ⁻¹ catalyst, and any pH. Stronger scavenging with p-BQ, and l-tryptophan. Little effect of the anions added and larger inhibition with humic acid. Main oxidant role of O ₂ ^{•-} and ¹ O ₂ . Good reproducibility with loss of 5% degradation after 5 successive steps. 14 aromatic and 2 aliphatic derivatives identified by LC-MS	Tang et al. (2023a)
Tetracycline	Stirred tank reactor with rich carbonyl- carbon-coated Fe ⁰ from MIL-100(Fe) catalyst	50 mL of 50 mg L ⁻¹ antibiotic in pure water, 0.04–1.0 mM PMS, 0.06–0.3 g L ⁻¹ catalyst, effect of scavengers (ethanol, TBA p-BQ, and l-histidine), anions (Cl ⁻ , NO ₃ ⁻ , CO ₃ ²⁻ , and HPO ₄ ²⁻), and humic acid, pH = 2.2–10.7, room temperature, 60 min	98% removal for 0.40 mM PMS and 0.1 g L ⁻¹ catalyst in the pH range of 2.2–5.5. Quicker scavenging with l-histidine and ethanol. Strong inhibition with 20 mM of all the anions added and humic acid. ¹ O ₂ as predominant oxidant. Moderate reusability after catalyst regeneration. 15 aromatic, 3 cyclic, and 2 aliphatic by-products identified by LC-MS	Yang et al. (2022f)
<i>Other catalysts with iron</i>				
Ciprofloxacin	Stirred Erlenmeyer flask with FeOCl/Hydroxylamine catalyst	250 mL of 5 mg L ⁻¹ antibiotic in pure water, 0–2.0 mM PMS, 0–0.4 g L ⁻¹ FeOCl/0–1.0 mM hydroxylamine, effect of scavengers (methanol, TBA, and p-BQ) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and SO ₄ ²⁻), pH = 2.0–11.0, 25 °C, 15 min	Overall abatement with 1.0 mM PMS, 0.2 g L ⁻¹ FeOCl, 1.0 mM hydroxylamine, and pH = 6.5. Lower removal at pH = 2.0. Methanol caused the faster scavenging. Little influence of all the anions added. SO ₄ ^{•-} and •OH dominated as oxidants. Good reproducibility losing >5% degradation after 5 successive runs. Identification of 14 aromatic by-products by LC-MS	Luo et al. (2021a)

(continued on next page)

Table 1 (continued)

Antibiotic	System	Experimental remarks	Best results	Ref.
Levofloxacin	Stirred tank reactor with Fe ₂ P/biocarbon catalyst	100 mL of 5–15 mg L ⁻¹ antibiotic in pure water, 0.1 g L ⁻¹ PMS, 0.15–0.35 g L ⁻¹ catalyst, effect of scavengers (TBA, sodium azide, catalase, and DABCO), anions (Cl ⁻ , NO ₃ ⁻ , and PO ₄ ³⁻), and humic acid, pH = 3.0–9.0, room temperature, 30 min	Total removal for 5 mg L ⁻¹ antibiotic, 0.35 g L ⁻¹ catalyst, and pH = 3.0. Strong inhibition with all the scavengers, except TBA. Moderate inhibition with all the anions, enhanced with humic acid. Oxidation with SO ₄ ^{•-} , [•] OH, O ₂ ^{•-} , and ¹ O ₂ . No reproducibility with loss of 50% degradation after 5 successive steps. LC-MS allowed detecting 19 aromatic and 3 aliphatic intermediates	He et al. (2021c)
Ofloxacin	Stirred tank reactor with Fe single atom NPS/C catalyst	50 mL of 20 μM antibiotic in pure water, 0.2 mM PMS, 20 mg L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, and FFA), anions (Cl ⁻ , NO ₃ ⁻ , and HCO ₃ ⁻), and humic acid, pH = 3.5–9.0, room temperature, 20 min	Complete abatement at pH = 3.5, decreasing at higher pH. Larger scavenging with FFA. Strong inhibition with humic acid, but no deceleration with all the anions added. Oxidation with SO ₄ ^{•-} and [•] OH. Good reusability after 4 consecutive runs. 10 aromatic intermediates identified by LC-MS	Li et al. (2023e)
Sulfamethazine	Stirred tank reactor with Fe ₃ S ₄ catalyst	100 mL of 5 mg L ⁻¹ antibiotic in pure water, 0–0.2 mM PMS, 0–100 mg L ⁻¹ catalyst, effect of scavengers (ethanol, TBA, <i>p</i> -BQ, and L-histidine), pH = 3.0–9.0, 25 °C, 60 min	Total degradation with 0.1 mM PMS, 100 mg L ⁻¹ catalyst, and pH = 5.8. High deceleration at pH = 9.0. Large influence of all scavengers. Main oxidant role of SO ₄ ^{•-} , followed by [•] OH, O ₂ ^{•-} , and ¹ O ₂ . 7 heteroaromatic, 4 aromatic, and 1 aliphatic by-products detected by LC-MS	Xiang et al. (2022)
Sulfisoxazole	Stirred tank reactor with natural CuFeS ₂ catalyst	100 mL of 5 mg L ⁻¹ antibiotic in pure water, 0.05–0.5 mM PMS, 0.25–2.0 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, and FFA), anions (Cl ⁻ and HCO ₃ ⁻), and humic acid, pH = 3.0–7.0, 23 °C, 30 min	Overall abatement with 0.5 mM PMS, 1.0 g L ⁻¹ catalyst, and pH = 3.0. Raising degradation with increasing pH. Stronger influence of methanol and TBA. Large inhibition with the anions added, but little effect of humic acid. Predominance of SO ₄ ^{•-} and [•] OH as oxidants.	Zhou et al. (2022b)

^a TBA: *tert*-Butyl alcohol.

^b *p*-BQ: *p*-Benzoquinone.

^c FFA: Furfuryl alcohol.

^d DABCO: 1,4-diazabicyclo [2.2.2]octane.

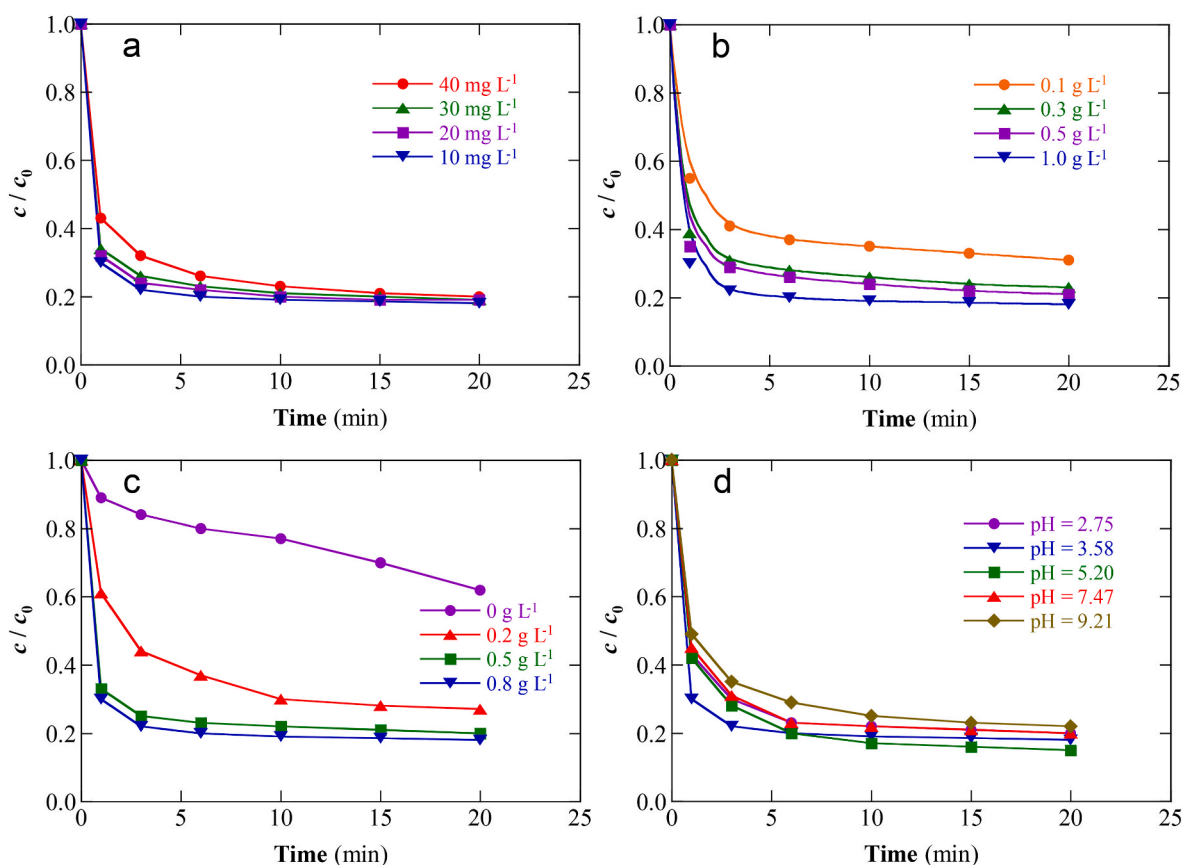


Fig. 2. Normalized doxycycline concentration vs. time for the antibiotic degradation with PMS and Fe₃O₄/N-carbon catalyst. Effect of: (a) antibiotic content for 1.0 g L⁻¹ PMS, 0.8 g L⁻¹ of catalyst, and pH = 3.58, (b) PMS dosage for 10 mg L⁻¹ antibiotic, 0.8 g L⁻¹ catalyst, and pH = 3.58, (c) catalyst dosage for 10 mg L⁻¹ antibiotic, 1.0 g L⁻¹ PMS, and pH = 3.58, and (d) pH for 10 mg L⁻¹ antibiotic, 1.0 g L⁻¹ PMS, and 0.8 g L⁻¹ of catalyst. Adapted from Xu et al. (2023b).

3.2.2. Iron oxide catalysts

Several antibiotics have been abated with iron oxide catalysts as PMS activators. This is the case of ciprofloxacin (Sun et al., 2022) and ciprofloxacin and tetracycline (Yang et al., 2023) with α -FeOOH/kaolinite, doxycycline with Fe_3O_4 /N-carbon (Xu et al., 2023b), ofloxacin with Fe_3O_4 /N-carbon (Xiao et al., 2022a), and tetracycline with ferroferric oxide/charcoal (Zhou et al., 2022a), Fe_3O_4 /polyaniline (Wang et al., 2023b), and $\text{Fe}/\text{Fe}_2\text{O}_3$ (Li et al., 2023a). Solís et al. (2021) treated wastewater containing a mixture of many antibiotics with Fe_3O_4 /graphene.

Fe_3O_4 is magnetic and then, easily extracted from the treated solution with an iman. As can be seen in Table 1, about 80–90% of antibiotics are removed with composites of this oxide or other iron oxides. The surface $\equiv\text{Fe}^{3+}/\equiv\text{Fe}^{2+}$ pair is the main activator to produce $\text{SO}_4^{\bullet-}$ from reaction (10) and the other oxidizing agents can be formed from reactions (2)–(9), being $\text{O}_2^{\bullet-}$ and/or $^1\text{O}_2$ the main reactive species in many cases. Direct electron transfer between the antibiotic and PMS at the support surface has also been confirmed, indicating the existence of non-radical mechanisms including that of $^1\text{O}_2$ in competence with radical mechanisms with the other oxidants.

Fig. 2 shows several effects of operating conditions on the normalized doxycycline concentration vs. time upon PMS activation with Fe_3O_4 /N-carbon catalyst (Xu et al., 2023b). Similar effects are found for any antibiotic degradation by the different PMS activators discussed in this review. Fig. 2a depicts a gradual decay of the degradation rate of doxycycline by raising its content from 10 to 40 mg L^{-1} for 1.0 g L^{-1} PMS, 0.8 g L^{-1} of catalyst, and $\text{pH} = 3.58$. This behavior can be ascribed to the lesser ability of the system to destroy higher amounts of organics by the production of a similar quantity of oxidizing agents. However, about 80% of the antibiotic was removed in 20 min, regardless of its initial concentration. This is indicative of a faster reaction of the antibiotic with higher amounts of oxidants produced from the deceleration of their parasitic non-oxidizing reactions due to their preferred reaction with organics. Fig. 2b and c make evident the enhancement of the antibiotic removal when progressively increased PMS and catalyst concentrations as a result of the formation of more oxidants. In many cases, the antibiotic acceleration occurs up to a limit of PMS and catalyst concentrations when the increasing rate of parasitic reactions inhibits the generation of more reactive oxidants. Fig. 2d highlights the little effect of pH on the process indicating that this parameter did not affect significantly the rate of all the oxidation processes. A similar behavior can be seen in Fig. SM-4a and 4b for tetracycline abatement with ferroferric oxide/charcoal (Zhou et al., 2022a) and Fe_3O_4 /polyaniline (Wang et al., 2023b) as activators.

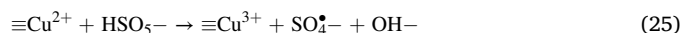
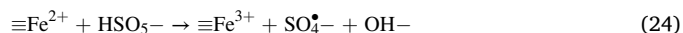
The identification of intermediates by LC-MS is also performed in many papers. Fig. SM-5 exemplifies the general reaction sequence proposed for tetracycline (1a) and anhydrotetracycline (1b) with the activator ferroferric oxide/charcoal involving 25 by-products (Zhou et al., 2022a). Three consecutive steps before mineralization to CO_2 and H_2O can be observed by losing functional groups and ring-opening reactions including hydroxylation, dehydroxylation, demethylation, and amide bond cleavage. Primary intermediates 2–5 are first formed, followed by the production of compounds 6–20 as secondary intermediates. In the third and last step, the benzenic derivatives 21–25 are generated along with the short linear aliphatic maleic acid (26). The knowledge of these by-products is interesting because it allows predicting the evolution of the toxicity of the treated solutions (see section 4).

The main drawback of the iron oxides supported on carbonaceous materials is their low reproducibility with a large loss of degradation power after a few consecutive runs (see Table 1). The phenomenon is related to the adsorption of intermediates over the carbonaceous support reducing the sites for PMS activation. It is suggested the need to prepare composites of iron oxides with other supports with scarce or null ability to adsorb organics continue in this research line.

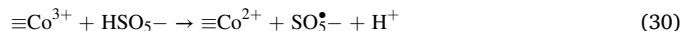
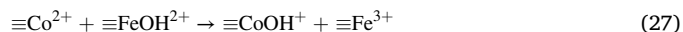
3.2.3. Mixed iron-metal oxides catalysts

The treatments with mixed iron-metal oxides catalysts have been centered in the study of ciprofloxacin with CuFe_2O_4 /graphene oxide (GO) (Noroozi et al., 2022), gatifloxacin with $\text{Bi}_{2x}\text{Ca}_{2(1-x)}\text{Fe}_4\text{O}_9$ (Koo et al., 2022), ofloxacin with CuFe_2O_4 /montmorillonite (Cao et al., 2021), sulfapyridine with Sr_2FeO_4 /SBA-15 (Zhao et al., 2022e), tetracycline with MnFe_2O_4 /zeolite (Wang et al., 2023d), Fe-CoTiO_3 (Wei et al., 2021), and ZnFe_2O_4 (Zhao et al., 2023b), and trimethoprim with $\text{Co-Fe}_3\text{O}_4/\alpha\text{-FeOOH}$ (Xu et al., 2023c).

An inspection of Table 1 reveals that mixed iron-metal oxide catalysts allow faster removal of antibiotics than iron oxide catalysts, especially for CuFe_2O_4 /GO, Fe-CoTiO_3 , and $\text{Co-Fe}_3\text{O}_4/\alpha\text{-FeOOH}$ that yield overall antibiotic abatement. This can be due to the pre-eminent generation of $\text{SO}_4^{\bullet-}$ radical as oxidant by the simultaneous action of the surface transition metallic ions and the iron ions from the reaction (10). So, for CuFe_2O_4 /GO, the main PMS activation corresponds to its parallel attack onto the surface $\equiv\text{Fe}^{2+}$ and $\equiv\text{Cu}^{2+}$ as follows (Cao et al., 2021; Noroozi et al., 2022):



In the case of Co as a co-metal, Wei et al. (2021) proposed the generation of $\equiv\text{FeOH}^{2+}$ from hydrolysis of $\equiv\text{Fe}^{3+}$ by reaction (26), which reacts with $\equiv\text{Co}^{2+}$ to form $\equiv\text{CoOH}^+$ and $\equiv\text{Fe}^{3+}$ by reaction (27) that activates PMS to $\text{SO}_4^{\bullet-}$ by reaction (28). $\equiv\text{Co}^{2+}$ is regenerated from reactions (29) and (30) with production of the weaker $\text{SO}_5^{\bullet-}$ radical.



These authors found overall abatement of 20 mg L^{-1} tetracycline in 100 mL of suspensions in pure water for ≥ 1.0 mM PMS and ≥ 0.1 g L^{-1} Fe-CoTiO_3 at $\text{pH} \geq 7.0$ in 40 min (see Table 1). They determined a strong inhibition by adding NO_3^- and HCO_3^- and the predominance of $\text{SO}_4^{\bullet-}$ as oxidant. An interesting finding was obtained in the effect of pH since the degradation rate progressively increased with increasing pH from 3.0 to 9.0, as can be seen in Fig. SM-4c. This was explained by the inhibition of $\equiv\text{CoOH}^+$ formation from reaction (27) in the acidic medium due to the deceleration of reaction (26), producing less $\text{SO}_4^{\bullet-}$ and decreasing the loss of the antibiotic. In contrast, in an alkaline medium, reaction (26) was strongly enhanced and so, a fast and total removal was achieved in about 20 min at $\text{pH} = 9.0$.

Fig. SM-4d reveals an opposite trend in the pH evolution when 100 mL of 20 mg L^{-1} tetracycline were treated in pure water with 0.1 g L^{-1} PMS and 0.2 g L^{-1} ZnFe_2O_4 catalyst at 25 °C after 30 min of adsorption in the dark, where 83% abatement was attained as maximal at $\text{pH} = 3.0$ in 30 min (Zhao et al., 2023b). This removal gradually decreased with raising pH to reach 60% at $\text{pH} = 11.0$. This decay of oxidation power at higher pH was attributed to the conversion of $\text{SO}_4^{\bullet-}$ into $^{\bullet}\text{OH}$ from reaction (3) because the latter radical possessed lower oxidation power than the former one with increasing pH. These authors did not use specific scavengers to detect the oxidizing agents, although identified the generation of $\text{SO}_4^{\bullet-}$, $^{\bullet}\text{OH}$, $\text{O}_2^{\bullet-}$, and $^1\text{O}_2$ by EPR (see Table 1). They also detected 13 primary aromatics by LC-MS.

The main drawback of applying mixed iron-metal oxides as PMS activators is their low reusability in successive steps, except for CuFe_2O_4 which presented a good reproducibility (Noroozi et al., 2022). Processes with CuFe_2O_4 should then be developed at a pilot scale with real waters with techno-economic studies to show their feasible use at an industrial scale.

3.2.4. Magnetic iron-transition metal catalysts

Several magnetic iron-transition metal catalysts have also been checked as PMS activators. They have been tested for CoFe₂O₄ and composites with ampicillin (Balakrishnan et al., 2021), chloramphenicol (Yang et al., 2021b), ciprofloxacin (Zhu et al., 2022), flurbiprofen (Ding et al., 2023), ofloxacin (Zheng et al., 2023), oxytetracycline (Jing et al., 2022), and tetracycline (Huang et al., 2023a), CoFe₂O₄-Co₃O₄ with chloramphenicol (Yang et al., 2022c), Co(OH)₂/ZnFe₂O₄ with norfloxacin (Wang et al., 2023c), CoFe-CoFe₂O₄/N-C with ofloxacin (Zhang et al., 2023d), and Fe₃O₄/Co/hydroxyapatite with sulfanilamide (Amedlous et al., 2022). The degradation of different fluoroquinolones with CoFe₂O₄ has been reported by Xu et al. (2023d).

Most magnetic oxides contain Co and Fe, being CoFe₂O₄ the most common catalyst. For instance, Huang et al. (2023b) used a stirred tank reactor with a composite CoFe₂O₄/biochar catalyst to treat 100 mL of 10–30 mg L⁻¹ tetracycline in pure water with 0.326–1.629 mM PMS and 0.1–0.9 g L⁻¹ catalyst at room temperature during 30 min. Fig. SM-4e reveals that total degradation was achieved for 10–20 mg L⁻¹ antibiotic, 0.977 mM PMS, 0.5 g L⁻¹ catalyst, and pH = 5.0 and 7.0 (see also Table 1). This behavior differs from that reported in Fig. SM-4c and 4d for the non-magnetic Fe-CoTiO₃ and ZnFe₂O₄ catalysts, respectively. The addition of scavengers such as TBA and ascorbic acid allowed the establishment of the predominance of SO₄^{•-} over •OH as oxidant. The formation of SO₄^{•-} was ascribed to the decomposition of PMS by surface $\equiv \text{Co}^{2+}$ to $\equiv \text{Co}^{3+}$ and $\equiv \text{Fe}^{2+}$ to $\equiv \text{Fe}^{3+}$ following reaction (10) each, whereas the opposite reaction occurs with PMS yielding the weaker SO₅^{•-}. Further reaction (2) or (3) leads to •OH from the hydrolysis of SO₄^{•-}. The slower degradation at pH = 3.0 shown in Fig. SM-4e was associated with the protonation of SO₄^{•-} and •OH lowering their oxidation ability, whereas the deceleration at pH = 9.0 < pH = 11.0 was related to the quicker conversion of SO₄^{•-} into •OH from reaction (3) losing oxidation power in an alkaline medium. Excellent reusability of the catalyst was determined after 5 consecutive runs. In contrast, scarce or low reusability has been found using directly CoFe₂O₄ or BN/CoFe₂O₄ as catalysts, respectively (see Table 1), indicating that the preparation of their composites stabilizes the catalytic performance.

A study by Amedlous et al. (2022) with a magnetic composite Fe₃O₄/Co/hydroxyapatite catalyst confirmed the excellent reusability of this composite during 4 successive runs of 50 mL of 50 mg L⁻¹ sulfadiazine in pure water with 0.6 g L⁻¹ PMS and 0.2 g L⁻¹ catalyst at pH = 6.7, involving 93% degradation in 300 s and 73% TOC decay in 60 min. SO₄^{•-} and •OH was determined as the predominant oxidants from the analysis with the scavengers methanol and TBA, whereas O₂^{•-} exercised a little oxidant influence as found in scavenger assays with sodium azide.

The above findings indicate that composites of magnetic Fe-Co compounds are potent and stable activators of PMS for antibiotic remediation. The fast degradation and high mineralization achieved at the bench scale should be confirmed with pilot plants to show their applicability at the industrial level.

3.2.5. MOFs derived with iron catalysts

The application of MOFs type ZIF and MIL derived with iron catalysts was carried out for ciprofloxacin with ZIF-67/Fe₃O₄ (Alamgholiloo et al., 2021), and tetracycline with 0.8 Fe₂O₃ from MIL-101(Fe)/Mn₃O₄ (Tang et al., 2023a), rich carbonyl-carbon-coated Fe⁰ from MIL-100(Fe) (Yang et al., 2022f), and Fe/C from MIL-88 A (Fe) (Qian et al., 2023b).

Tang et al. (2023a) reported only 85% degradation for 10 mg L⁻¹ of tetracycline in 100 mL of suspension with 0.5 mM PMS and 0.20 g L⁻¹ 0.8 Fe₂O₃/Mn₃O₄ catalyst after 40 min of treatment at any pH between 3.2 and 9.1, as can be seen in Fig. SM-4f and Table 1. By using specific scavengers, they found a main oxidant role of O₂^{•-} and ¹O₂ instead of SO₄^{•-} and •OH. To explain this, they proposed that $\equiv \text{Fe}^{2+}$ and $\equiv \text{Mn}^{2+}$ reacted pre-eminently with PMS to form O₂^{•-} from reactions (31) and (32), respectively, as compared to the corresponding reaction (10) to SO₄^{•-}. Further reaction of the resulting $\equiv \text{Fe}^{3+}$ and $\equiv \text{Mn}^{3+}$ with O₂^{•-} regenerated the initial surface ions with ¹O₂ production from reactions

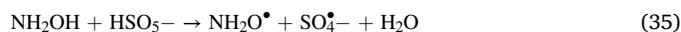
(33) and (34). A positive result to encourage the study of this catalyst for other antibiotics was its good reproducibility achieved after 5 successive steps. The predominance of ¹O₂ has also been described by Yang et al. (2022f) when degrading 50 mL of 50 mg L⁻¹ tetracycline in pure water with a rich carbonyl-carbon-coated Fe⁰. In this case, a higher abatement of 98% was found for 0.40 mM PMS and 0.1 g L⁻¹ catalyst in the pH range of 2.2–5.5 (see Table 1) lasting 60 min. They suggested that ¹O₂ was generated from O₂^{•-} by reaction (8) but this radical was presupposed to be formed by reactions (4)–(6) without the participation of surface iron ions. However, the reusability of the catalysts was only moderate after its regeneration. In the two above works, from 16 to 20 by-products were identified by LC-MS.



3.2.6. Other catalysts with iron

Other catalysts with iron have been tested for amoxicillin, cephalixin, ciprofloxacin, and sulfamethoxazole with CuMgFe-B(OH)₄ (de Melo Costa-Serge et al., 2023), ciprofloxacin with FeOCl/hydroxylamine (Luo et al., 2021a), chloramphenicol with γ-FeOOH/hydroxylamine (He et al., 2023a), levofloxacin with Fe₂P/biocarbon (He et al., 2021c), norfloxacin with α-MnO₂/MnFe₂O₄ (Xu et al., 2021) and FeNi/carbon nanotubes (CNTs) (Liu et al., 2023c), ofloxacin with Fe single atom NPS/C (Li et al., 2023e), sulfadiazine with C-MoS₂/C-Fe³⁺ (Xiao et al., 2023a), sulfamethazine with Fe₃S₄ (Xiang et al., 2022), sulfamethoxazole with Fe-Mn-Cu (Wu et al., 2022a) and Fe-nanoenzymes (Zhang et al., 2023c), sulfathiazole with FeP/carbon (Wang et al., 2023g), sulfoxazole with natural CuFeS₂ (Zhou et al., 2022b), and tetracycline with goethite-MoS₂ (Li et al., 2022f), (NH₄)₂Mo₃S₁₃/MnFe₂O₄ (Li et al., 2023d), FeOOH/MoS₂ (Yi et al., 2021a), and CuFe₂O₄-MoS₂/BC (Wang and Xiao, 2023). Table 1 gives the most interesting results of these papers.

Among these works, it is remarkable the study of Li et al. (2023e) for the degradation of 20 μM ofloxacin in pure water with 0.2 mM PMS and 20 mg L⁻¹ Fe/NPS/carbon catalyst. The complete abatement was reached in 20 min at pH = 3.5, although the degradation rate decreased with raising pH to 9.0, with good reusability after 4 consecutive cycles (see Table 1). The use of specific scavengers revealed the preferent oxidation with SO₄^{•-} and •OH and 10 aromatic by-products were detected by LC-MS. Other interesting work has been reported by Luo et al. (2021a) for ciprofloxacin with a heterogeneous/homogeneous FeOCl/hydroxylamine catalyst. The treatment of 250 mL of 5 mg L⁻¹ antibiotic in pure water with 1.0 mM PMS, 0.2 g L⁻¹ FeOCl, 1.0 mM hydroxylamine, and pH = 5.2 yielded a rapid and total removal in only 15 min (see Table 1). This behavior was associated with the fast formation of SO₄^{•-} and •OH by the homogeneous reactions of PMS with $\equiv \text{Fe}^{2+}$ by reaction (24) and NH₂OH by reaction (35). Good reusability was determined after 5 successive runs with the solid FeClO catalysts and the LC-MS analysis of the degraded solutions disclosed the identification of 14 aromatic intermediates.



While the two above catalytic systems seem useful for further study at large volumes to show their feasible effectiveness at the industrial level, other tested catalysts could be discarded because of their low stability. This is the case of Fe₂P/biocarbon tested by He et al. (2021c) who detailed the total abatement of 20 μM antibiotic in pure water with 0.2 mM PMS, 20 mg L⁻¹ catalyst, and pH = 3.5 for 30 min (see Table 1). However, the catalyst showed so large instability that the degradation

decayed by 50% after 5 consecutive steps, an unacceptable result that discards its applicability.

3.3. Non-iron transition metals catalysts

The design of catalysts with non-iron transition metals has experienced greater development as activators of PMS. According to their chemical nature, they can be classified as single transition metal, single transition metal oxides, mixed transition metal oxides, transition metal compounds, redox pairs of transition metals, and MOFs derived with transition metals catalysts, as well as other catalysts with transition metals. This subsection is devoted to analyzing their application as PMS activators to abate antibiotics. Table 2 summarizes the most relevant results described from selected papers of each catalyst category.

3.3.1. Single transition metal catalysts

Several works have been devoted to the treatment of enrofloxacin with Cu/biochar (Zhao et al., 2022a), sulfadoxin with Co-oxo (Xiao et al., 2023b), sulfamerazine with Co/carbon nanotubes (CN) (Xie et al., 2023b), sulfamethazine with Co/TiO₂ (Zhang et al., 2022b), sulfamethoxazole with Co/mesoporous (Zhang et al., 2023b), and tetracycline with Co/N-CN (Hu et al., 2022), Co/CN (Liu et al., 2023d), Co/mesoporous carbon/N-carbon (Shao et al., 2022) and Co/N-carbon (Zhang et al., 2022a).

Composites with Co atoms have been chosen to activate PMS following the scheme of Fig. 3a (Zhang et al., 2022a). PMS reacts with the surface $\equiv \text{Co}^0$ to yield $\text{SO}_4^{\bullet -}$ and surface $\equiv \text{Co}^{2+}$ by reaction (36), which produces surface $\equiv \text{Co}^{3+}$ and more $\text{SO}_4^{\bullet -}$ by reacting with PMS by reaction (37). The $\equiv \text{Co}^{3+}/\equiv \text{Co}^{2+}$ pair was then activated by the further regeneration of $\equiv \text{Co}^{2+}$ via reaction (30) with $\text{SO}_5^{\bullet -}$ formation. Subsequent reactions (2)–(9) with $\text{SO}_4^{\bullet -}$ originate $\bullet\text{OH}$, $\text{SO}_4^{\bullet -}$, and $^1\text{O}_2$. The latter oxidant can also be formed from hydrolysis of $\text{SO}_5^{\bullet -}$ by reaction (38). These radical and non-radical species were detected under all conditions tested (see Table 2).

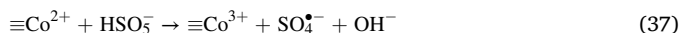
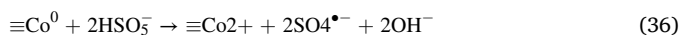


Table 2 makes evident that composites such as Co/TiO₂, Co/mesoporous carbon, and Co/mesoporous carbon/N-carbon showed fast and overall abatement of antibiotics in 15–30 min but with an unacceptable loss of catalytic power after a few consecutive cycles. This behavior can be observed in Fig. SM-6a for 50 mL of 10 mg L⁻¹ sulfamethoxazole in pure water treated with 0.4 g L⁻¹ PMS and 0.1 g L⁻¹ Co/mesoporous carbon catalyst at pH = 5.8 and 25 °C after 15 min of adsorption (Zhang et al., 2023b)). In contrast, Zhang et al. (2022a) highlighted that 100 mL of 10 mg L⁻¹ tetracycline in pure water with 0.15 mM PMS, 0.4 g L⁻¹ Co/N-carbon catalyst, and pH = 4.3 using a stirred tank reactor yielded total degradation in only 15 min with an excellent reusability after 30 consecutive runs. Based on these wonderful results, they prepared a columnar flow fixed bed reactor with 300 mg of catalyst and determined near 100% degradation with 60–70% TOC reduction during 200 h of continuous operation. These excellent results support the possible use of this catalyst in a pilot plant for its application to an industrial level.

3.3.2. Single transition metal oxide catalysts

Several works have considered single transition metal oxides as PMS activators. They include the treatment of azithromycin, ciprofloxacin, sulfachloropyridazine, sulfamethazine, and sulfamethoxazole (Khan et al., 2021), and chlortetracycline and oxytetracycline, and tetracycline (Bi et al., 2021) with MnO₂, ciprofloxacin with Co/CoO/Co₃O₄/K₂N, O-doped carbon (Liang et al., 2022) and CoO/carbon (Zhou et al., 2023a), ofloxacin with Co₃O₄ (Li et al., 2023b) and CuO₂/CuO (Wang et al., 2023f), ornidazole with Co₃O₄/MXene (Hao et al., 2023),

oxytetracycline with CuO/O-graphitic carbon nitrogen (Wei et al., 2023), sulfadiazine with NiOOH (Lyu et al., 2022), sulfamethoxazole with Ag₂O/Ag (Gao et al., 2021) and CoO-3D/mesoporous CN (Nguyen et al., 2021), tetracycline with K₂xMn₈O₁₆ (Chen et al., 2021a), Co₃O₄/carbonized polyaniline (Qian et al., 2023a), Co₃O₄/g-C₃N₄ (Ni et al., 2022), Cu_xO (Tang et al., 2023c), CuO (Zhu et al., 2023), Co/CuO (Zhao et al., 2023a), and Co₃O₄/N-carbon (Zhang et al., 2021b).

Oxides with Mn, Cu, Ni, and mainly Co, alone or as composites, have been used as catalysts to generate $\text{SO}_4^{\bullet -}$ from the PMS activation with surface $\equiv \text{Mn}^{3+}$, $\equiv \text{Cu}^+$, $\equiv \text{Cu}^{2+}$, $\equiv \text{Ni}^{2+}$, and $\equiv \text{Co}^{2+}$ via the corresponding reaction (10). $\bullet\text{OH}$, $\text{SO}_4^{\bullet -}$, and $^1\text{O}_2$ are then expected to be produced from reactions (2)–(10). Direct electron transfer at the catalyst surface was established as well. As an example, Fig. 3b shows the mechanism proposed with a CoO/carbon catalyst by Zhou et al. (2023a). Two pathways can be observed, a radical mechanism for ciprofloxacin removal involving $\bullet\text{OH}$ and $\text{SO}_4^{\bullet -}$ as main oxidant radicals (pathway 1) and the direct electron transfer between the adsorbed antibiotic and PMS at the catalyst surface (non-radical pathway 2).

The data listed in Table 2 for some Co and Cu oxides confirm their high catalytic power for completely degrading antibiotics with good reusability in most cases, upgrading the stability of single Co atoms detailed above. Fig. SM-6b depicts the time course of the normalized sulfamethoxazole concentration of 50 mL of 0.05 mM antibiotic in pure water with 10 mM PMS and 0.1 g L⁻¹ CoO-3D/mesoporous CN catalyst at pH = 7.0 and 25 °C (Nguyen et al., 2021)). Total removal was rapidly achieved in 15 min with $k_1 = 0.314 \text{ min}^{-1}$, attaining a high TOC reduction of 80% under the action of $\text{SO}_4^{\bullet -}$ as a pre-eminent oxidant (see Table 2). Nevertheless, the catalyst showed moderate reproducibility with a loss of 15% degradation after 5 consecutive runs. In contrast, good reproducibility and slower abatement with $k_1 = 0.2538 \text{ min}^{-1}$ has been reported by Zhou et al. (2023a) for the treatment of 100 mL of 10 mg L⁻¹ ciprofloxacin in pure water with 0.5 mM PMS and 50 mg L⁻¹ CoO/carbon catalyst at pH = 7.0 in 30 min, as can be seen in Fig. SM-6c. Similar degradation was determined with pure water, tap water, and lake water, which was enhanced with seawater due to the parallel oxidation with HClO formed from the reaction (23). Moreover, these authors detected 10 primary heteroaromatic intermediates by LC-MS. Similar results have also been described for CuO by Zhu et al. (2023) who found a slower degradation of up to 95% for 20 mg L⁻¹ tetracycline in pure water with 0.1 g L⁻¹ PMS and 0.4 g L⁻¹ catalyst at any pH from 3.0 to 11.0 lasting a longer time of 60 min. The use of specific scavengers confirmed the oxidative action of $\text{SO}_4^{\bullet -}$, $\bullet\text{OH}$, $\text{O}_2^{\bullet -}$, and $^1\text{O}_2$, and 7 aromatic and 6 aliphatic by-products were detected by LC-MS (see Table 2).

From these findings, one can conclude that the PMS activation with single non-ferric transition metal oxides is a good way to remove antibiotics, which should be better explored in the future.

3.3.3. Mixed transition metal oxide catalysts

The treatments with mixed transition metal oxide catalysts have been performed with doxycycline with CoO/MnO/VO₃ (Luo et al., 2022), ofloxacin with CoMn₂O₄/kaolinite or CoMn₂O₄/halloysite (Yang et al., 2022d, 2022e), ornidazole with CoMn₂O₄/halloysite (Zhang et al., 2023f), pefloxacin with CuCo₂O₄ (Xu et al., 2022a), sulfamethoxazole with Mn.SrCo₂O_{2.52} (Yu et al., 2023a), sulfapyridine with Cu_{0.76}Co_{2.24}O₄/SBA-15 (He et al., 2021a), and tetracycline with NiCo₂O₄ (Cong et al., 2022), CoMn₂O₄ flower (Nguyen et al., 2022), NiCo₂O₄/ZIF 67 (Pan et al., 2023b), and CuCo₂O₄/g-C₃N₄ (Zhao et al., 2023c).

The same transition metals, i.e., Mn, Cu, Ni, and Co, have been used to prepare mixed transition metal oxide catalysts for activating PMS, then following similar mechanisms to those of single transition metal oxides. Fig. 3c exemplifies the mechanism proposed by Xu et al. (2022a) for CuCo₂O₄ catalyst to produce $\text{SO}_4^{\bullet -}$ from both, the surface $\equiv \text{Cu}^{2+}/\equiv \text{Cu}^+$ and $\equiv \text{Co}^{3+}/\equiv \text{Co}^{2+}$ pairs to degrade pefloxacin. Additionally, it is suggested the generation of $\text{O}_2^{\bullet -}$ from direct electron transfer to O₂. For the assays performed with 50 mL of 10 mg L⁻¹ antibiotic in pure

Table 2

Selected results obtained for the destruction of antibiotics from different aqueous matrices by the activation of peroxymonosulfate with non-iron transition metals catalysts.

Antibiotic	System	Experimental remarks	Best results	Ref.
<i>Single transition metal catalysts</i>				
Sulfamethazine	Stirred Erlenmeyer flask with Co/TiO ₂ catalyst	50 mL of 10 mg L ⁻¹ antibiotic in pure water, 0.650–0.975 mM PMS, 0.2–0.5 g L ⁻¹ catalyst, effect of scavengers (isopropyl alcohol, TBA, <i>p</i> -BQ, and l-histidine), anions (Cl ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), and humic acid, pH = 3.0–11.0, 25 °C, 30 min	95% removal with composites containing ≥20% Co for 0.975 mM PMS, 0.5 g L ⁻¹ catalyst, and pH = 5.7. Larger scavenging with l-histidine. Strong inhibition with all the anions, except H ₂ PO ₄ ⁻ , and humic acid. Oxidation with ¹ O ₂ > [•] OH > SO ₄ ^{•-} . No reproducibility with loss of 30% degradation after 3 successive runs	Zhang et al. (2022b)
Sulfamethoxazole	Stirred conical flask with Co/mesoporous carbon catalyst	50 mL of 10 mg L ⁻¹ antibiotic in pure water, 0.1–0.6 g L ⁻¹ PMS, 0.05–0.2 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, FFA, and l-histidine), anions (Cl ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), and humic acid, pH = 3.0–11.0, 25 °C, 30 min	Overall degradation for ≥0.4 g L ⁻¹ PMS, 0.1 g L ⁻¹ catalyst, and pH = 5.8. Little effect of pH. Larger scavenging with l-histidine followed by FFA. Strong inhibition with all the anions, except H ₂ PO ₄ ⁻ , and humic acid. Oxidation with SO ₄ ^{•-} , [•] OH, O ₂ ^{•-} , and ¹ O ₂ . Scarce reproducibility with loss of 25% degradation after 4 successive cycles, largely improved after catalyst regeneration. Identification of 6 heterocyclic, 7 aromatic, and 1 aliphatic by-products by LC-MS	Zhang et al. (2023b)
Tetracycline	Stirred tank reactor with Co/mesoporous carbon/N-carbon catalyst	100 mL of 25 mg L ⁻¹ antibiotic in pure water, 0.1–1.0 mM PMS, 0.05–0.5 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, and <i>p</i> -BQ) and anions (Cl ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), pH = 3.0–10.0, 25 °C, 12 min	Total abatement with k ₁ = 0.321 min ⁻¹ for 0.5 mM PMS, 0.25 g L ⁻¹ catalyst, and pH = 4.5. Faster degradation at higher pH. Methanol caused the faster scavenging. Low impact of anions Oxidation with SO ₄ ^{•-} > [•] OH and ¹ O ₂ . No reproducibility with loss of 50% degradation after 4 consecutive cycles	Shao et al. (2022)
Tetracycline	Stirred tank reactor for batch and columnar flow fixed bed reactor for continuous with Co/N-carbon catalyst	100 mL of 10 mg L ⁻¹ antibiotic in pure water, 0.15 mM PMS, 0.4 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, and l-histidine), pH = 4.3, room temperature, 15 min in batch	Total degradation in batch. Larger inhibition with l-histidine. Oxidation: ¹ O ₂ > SO ₄ ^{•-} > [•] OH > O ₂ ^{•-} . Excellent reusability after 30 consecutive runs. For the continuous reactor, near 100% degradation with 60–70% TOC reduction using 300 mg catalyst during 200 h	Zhang et al. (2022a)
<i>Single transition metal oxides catalysts</i>				
Ciprofloxacin	Stirred beaker with CoO/carbon catalyst	100 mL of 10 mg L ⁻¹ antibiotic in pure water and natural waters, 0.125–1.0 mM PMS, 25–100 mg L ⁻¹ catalyst, effect of scavengers (ethanol and TBA), and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), pH = 3.0–11.0, room temperature, 60 min	Total degradation for ≥0.5 mM PMS and ≥50 mg L ⁻¹ catalyst, regardless of pH, with k ₁ = 0.2538 min ⁻¹ at pH = 7.0. Stronger scavenging with ethanol. Little effect of anions, except a strong inhibition with HCO ₃ ⁻ . Similar degradation with pure water, tap water, and lake water, but enhanced with seawater. SO ₄ ^{•-} as main oxidant. After 4 successive cycles, good reproducibility with decreasing Co leaching. LC-MS allowed detecting 10 primary heterocyclic by-products	Zhou et al. (2023a)
Ofloxacin	Stirred tank reactor with Co ₃ O ₄ catalyst	50 mL of 30 mg L ⁻¹ antibiotic in pure water, 0.5 mM PMS, 0.2 g L ⁻¹ catalyst, pH = 7.0, 20 °C, 30 min	Total abatement of the antibiotic. 11 heteroaromatic intermediates identified by LC-MS	Li et al. (2023b)
Sulfamethoxazole	Centrifuge tube upon rotation with CoO-3D/mesoporous CN catalyst	50 mL of 0.05 mM antibiotic in pure water, 10 mM PMS, 0.1 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, and <i>p</i> -BQ), pH = 3.0–11.0, 25 °C, 15 min	Overall removal within the pH range 5.0–9.0 with k ₁ = 0.314 min ⁻¹ . Higher TOC reduction of 80% at pH = 7.0. Stronger scavenging with methanol. SO ₄ ^{•-} as pre-eminent oxidant. Moderate reproducibility losing 15% degradation after 5 consecutive cycles	Nguyen et al. (2021)
Tetracycline	Stirred tank reactor with Co ₃ O ₄ /g-C ₃ N ₄ catalyst	50 mL of 10–40 mg L ⁻¹ antibiotic in pure water and real waters, 0–2.0 mM PMS, 0.1–0.4 g L ⁻¹ catalyst, effect of scavengers (ethanol, isopropyl alcohol, TBA, and sodium azide) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , and H ₂ PO ₄ ⁻), pH = 5.8–11.0, room temperature, 18 min	Total removal for ≤20 mg L ⁻¹ antibiotic in pure water, ≥1.5 mM PMS, ≥0.2 g L ⁻¹ catalyst, and at any pH after 20 min pf adsorption in the dark. Little effect of anions added. Quicker inhibition with isopropyl alcohol and sodium azide. Oxidation with SO ₄ ^{•-} , [•] OH, O ₂ ^{•-} , and ¹ O ₂ . Similar degradation with pure water, tap water, river water, lake water, and WWTP effluent. Moderate reproducibility with loss of 20% degradation after 4 successive runs. Identification of 7 aromatic, 2 cyclic, and 1 aliphatic by-products by LC-MS	Ni et al. (2022)
Tetracycline	Stirred tank reactor for batch with CuO catalyst	100 mL of 5–60 mg L ⁻¹ antibiotic in pure water and natural waters, 0.1–1.0 g L ⁻¹ PMS, 0.05–0.4 g L ⁻¹ catalyst, effect of scavengers (methanol, ethanol, TBA, and FFA), anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and CO ₃ ²⁻), and humic acid, pH = 3.0–11.0, 15 °C, 60 min	95% degradation for 20 mg L ⁻¹ antibiotic in pure water, 0.1 g L ⁻¹ PMS and 0.4 g L ⁻¹ catalyst at any pH. Stronger scavenging with FFA. Little influence of anions added and strong inhibition with humic acid. Similar degradation with pure water, tap water, river water, groundwater, and lake water. SO ₄ ^{•-} , [•] OH, O ₂ ^{•-} , and ¹ O ₂ as oxidants. Good reusability after 8 successive steps.	Zhu et al. (2023)

(continued on next page)

Table 2 (continued)

Antibiotic	System	Experimental remarks	Best results	Ref.
			7 aromatic and 6 aliphatic by-products identified by LC-MS	
<i>Mixed transition metal oxides catalysts</i>				
Doxycycline	Stirred tank reactor with CoO/MnO/WO ₃ catalyst	20 mg L ⁻¹ antibiotic in pure water, 0.05–0.15 g L ⁻¹ PMS, 0.3–0.7 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, and l-histidine) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , and HPO ₄ ²⁻), pH = 3.0–10.0, room temperature, 120 min	80% abatement for all PMS and catalyst dosages at pH ≤ 8.0. Greater inhibition with l-histidine followed by <i>p</i> -BQ. Strong loss of degradation with HCO ₃ ⁻ . Oxidation with ¹ O ₂ > O ₂ ⁻ > •OH > SO ₄ ^{•-} . Good reproducibility after 5 consecutive cycles. Detection of 17 aromatic and 2 aliphatic intermediates by LC-MS	Luo et al. (2022)
Ofloxacin	Stirred tank reactor with CoMn ₂ O ₄ /kaolinite or CoMn ₂ O ₄ /halloysite catalyst	100 mL of 20 μM antibiotic in pure water, 0.10 mM PMS, 0.4 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, and sodium azide), pH = 6.5, 25 °C, 40 min	75% degradation with <i>k</i> ₁ = 0.039 min ⁻¹ for kaolinite and 90% degradation with <i>k</i> ₁ = 0.058 min ⁻¹ for hallosyte. Higher inhibition with sodium azide followed by methanol. Oxidation with ¹ O ₂ > SO ₄ ^{•-} > •OH. Moderate reproducibility losing 12% degradation after 5 successive runs	Yang et al. (2022d)
Pefloxacin	Stirred tank reactor with CuCo ₂ O ₄ catalyst	50 mL of 10 mg L ⁻¹ antibiotic in pure water, 0.1–0.4 g L ⁻¹ PMS, 12.5–75 mg L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, and sodium azide) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , and H ₂ PO ₄ ⁻), pH = 3.0–10.0, 25 °C, 20 min	Total abatement for 0.2 g L ⁻¹ PMS and 25 mg L ⁻¹ catalyst at pH = 5.0. Methanol as the stronger scavenger. Strong inhibition with Cl ⁻ and HCO ₃ ⁻ , much lesser for the other anions. Oxidation with SO ₄ ^{•-} , •OH, O ₂ ⁻ , and ¹ O ₂ . LC-MS revealed the formation of 15 heterocyclic, 1 aromatic and 1 aliphatic intermediates	Xu et al. (2022a)
Sulfapyridine	Stirred tank reactor with Cu _{0.76} Co _{2.24} O ₄ /SBA-15 catalyst	50 mL of 50 μM antibiotic in pure water, 1.0 mM PMS, 1.0 g L ⁻¹ catalyst, effect of scavengers (ethanol, TBA, l-histidine, and superoxide dismutase), pH = 7.0, room temperature, 90 min	98% degradation maintained during 5 consecutive cycles. Stronger inhibition with superoxide dismutase. Greater oxidation with •OH followed by ¹ O ₂ . 4 heterocyclic and 2 aromatic primary by-products detected by LC-MS	He et al. (2021a)
Tetracycline	Stirred tank reactor with NiCo ₂ O ₄ catalyst	50 mL of 100–300 mg L ⁻¹ antibiotic in pure water and natural waters, 0.6–1.4 g L ⁻¹ PMS, 20–300 mg L ⁻¹ catalyst, effect of scavengers (methanol, ethanol, TBA, <i>p</i> -BQ, and l-histidine) and anions (Cl ⁻ , CO ₃ ²⁻ , HCO ₃ ⁻ , and PO ₄ ³⁻), pH = 3.0–10.0, room temperature, 40 min	Greater oxidation rate at lower antibiotic content and higher PMS and catalyst dosages and pH. 98% removal as maximal with <i>k</i> ₁ = 0.0458 min ⁻¹ . Little effect, even positive, with all the anions. Larger inhibition with l-histidine and ethanol. Similar degradation with pure water, tap water, and river water. ¹ O ₂ as dominant oxidant. Good reproducibility after 5 successive runs. LC-MS allowed detecting 10 aromatic intermediates	Cong et al. (2022)
Tetracycline	Tube under a rotator at 70 rpm with CoMn ₂ O ₄ flower catalyst	80 mL of 0.05 mM antibiotic in pure water and natural waters, 0.2 mM PMS, 0.2 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, and sodium azide), pH = 3.0–11.0, 25 °C, 30 min	96% degradation with <i>k</i> ₁ = 0.21 min ⁻¹ and 79% TOC removal at optimum pH = 7.0. Greater scavenging with sodium azide. Degradation: pure water > tap water ≈ lake water. ¹ O ₂ as dominant oxidant. Scarce reproducibility with loss of 25% TOC removal after 10 consecutive cycles	Nguyen et al. (2022)
<i>Transition metal compounds catalysts</i>				
Ciprofloxacin	Stirred tank reactor with (NH ₄) _{1.5} Co _x Cu _{2-x} Cr ₂ O ₈ (OH) _{1.5} H ₂ O catalyst	50 mL of 30.6 μM antibiotic in pure water and real water, 0.5 mM PMS, 0.2 g L ⁻¹ catalyst, effect of scavengers (methanol, and TBA) and anions (Cl ⁻ , SO ₄ ²⁻ , and H ₂ PO ₄ ⁻), pH = 5.6, room temperature, 15 min	Overall abatement in 10 min. Methanol caused higher scavenging. Little effect of all the anions added. Degradation: pure water > wastewater effluent. Good reproducibility after 3 successive steps	Serna-Galvis et al. (2023)
Oxytetracycline	Stirred tank reactor with MoS ₂ catalyst	100 mL of 10 mg L ⁻¹ antibiotic in pure water, 2.0 mM PMS, 80 mg L ⁻¹ catalyst, effect of scavengers (ethanol, TBA, and l-histidine), pH = 7.0, 25 °C, 60 min	98% removal with <i>k</i> ₁ = 0.064 min ⁻¹ . Similar inhibition with all the scavengers. Pre-eminent oxidation with •OH	Wang et al. (2023e)
<i>Redox pairs of transition metals as catalyst</i>				
Ciprofloxacin	Stirred beaker with Mn(II)/Mn(III) and Mn(III)/Mn(IV) pairs on Mn/N-biochar catalyst	100 mL of 15 mg L ⁻¹ antibiotic in pure water, 0.2–2.0 mM PMS, 0–200 mg L ⁻¹ catalyst, effect of scavengers (methanol, ethanol, TBA, DMSO, and l-histidine), anions (Cl ⁻ , NO ₃ ⁻ , CO ₃ ²⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), and humic acid, pH = 3.0–11.0, 25 °C, 120 min	95% of antibiotic decay with <i>k</i> ₁ = 0.01609 min ⁻¹ for 2.0 mM PMS and 100 mg L ⁻¹ catalyst at pH = 3.0 after 30 min of adsorption in the dark. Inhibition with all the anions and humic acid, much stronger with CO ₃ ²⁻ . SO ₄ ^{•-} , •OH, and ¹ O ₂ as oxidants. Scarce reproducibility with loss of 25% degradation after 4 successive steps	Liu et al. (2023e)
<i>MOFs derived with transition metals catalyst</i>				
Ciprofloxacin	Stirred tank in a thermostatic oscillator at 180 rpm with Zn-MOF as ZIP-65/polyaniline catalyst	10 mg L ⁻¹ antibiotic in pure water, 0.1 mM PMS, 0.4 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, FFA, and l-histidine) and anions (Cl ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), pH = 3.05–11.02, 30 °C, 60 min	83% abatement of the antibiotic at pH = 7.0. Increasing degradation at higher pH. Greater scavenging with FFA and l-histidine. Positive effect of HCO ₃ ⁻ and stronger inhibition with H ₂ PO ₄ ⁻ . ¹ O ₂ as main oxidant, followed by SO ₄ ^{•-} and •OH. No reproducibility losing 35% degradation after 5 consecutive runs.	Pu et al. (2022)

(continued on next page)

Table 2 (continued)

Antibiotic	System	Experimental remarks	Best results	Ref.
Sulfamethoxazole	Stirred tank reactor with Co ₃ O ₄ /N-carbon from MOF (ZIF-67) catalyst	100 mL of 20 mg L ⁻¹ antibiotic in pure water, 0.125–0.5 mM PMS, 50–200 mg L ⁻¹ catalyst, effect of scavengers (ethanol, TBA, <i>p</i> -BQ, and l-histidine) and anions (Cl ⁻ , and HCO ₃ ⁻), pH = 2.0–10.0, 25 °C, 15 min	11 primary heterocyclic by-products identified by LC-MS Total removal with $k_1 = 0.79 \text{ min}^{-1}$ and 37% TOC reduction for 0.25 mM PMS and 200 mg L ⁻¹ catalyst at pH = 3.9. Faster degradation at greater pH. Higher scavenging with ethanol followed by TBA. Stronger inhibition by adding 5 mM HCO ₃ ⁻ . Oxidation with generated SO ₄ ^{•-} and [•] OH. Moderate reproducibility with loss of 15% degradation after 5 consecutive cycles	Mohtasham et al. (2023)
Sulfamethoxazole	Stirred flask with Co/MOF catalyst	100 mL of 40 μM antibiotic in pure water and natural waters, 10 mM PMS, 200 mg L ⁻¹ catalyst, 25 mM HCO ₃ ⁻ , effect of scavengers (methanol, TBA, <i>N,N</i> -dimethylaniline, and l-histidine), pH = 8.3, room temperature, 60 min	Total degradation in pure water. Stronger scavenging with methanol and <i>N,N</i> -dimethylaniline. Degradation: pure water > river water ≈ reclaimed water ≈ groundwater. Oxidation with [•] OH, ¹ O ₂ , and CO ₃ ^{•-} . Good reproducibility with loss of 8% degradation after 5 successive steps.	Zhang et al. (2023a)
Tetracycline	Stirred tank reactor with Co/N-carbon from Co-MOF catalyst	100 mL of 20 mg L ⁻¹ antibiotic in pure water, 0–1.0 mM PMS, 20–150 mg L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, FFA, and l-histidine), pH = 2.0–11.0, 25 °C, 80 min	20 degradation by-products detected by LC-MS Complete degradation with $k_1 = 0.042 \text{ min}^{-1}$ for 0.75 mM PMS and 100 mg L ⁻¹ catalyst at pH = 7.0. Faster removal at higher pH. FFA yielded the stronger scavenging. SO ₄ ^{•-} and ¹ O ₂ as predominant oxidants. Moderate reusability losing 20% degradation after 4 consecutive runs.	Li et al. (2022b)
<i>Other catalysts with transition metals</i>				
Sulfamethoxazole	Continuous flow membrane cell with Co ₃ O ₄ /attapulgite based ceramic membrane	10 mg L ⁻¹ antibiotic in pure water, 0.01–0.1 g L ⁻¹ PMS, 0.4 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, and FFA) and anions (Cl ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , and H ₂ PO ₄ ⁻), pH = 4.74–10.74, room temperature, 180 min	70–72% degradation with 0.1 g L ⁻¹ PMS at pH 4.74–9.76. Greater scavenging with FFA followed by methanol. Larger inhibition with HCO ₃ ⁻ followed by H ₂ PO ₄ ⁻ . Oxidation contribution by SO ₄ ^{•-} , [•] OH, and ¹ O ₂ . Moderate reusability with loss of 20% degradation after 5 successive cycles of 180 min.	Zhou et al. (2023b)
Tetracycline	Stirred conical flask with Co/MoS ₂ catalyst	100 mL of 8 mg L ⁻¹ antibiotic in pure water and natural waters, 0.5–3.0 mM PMS, 0.05–0.4 g L ⁻¹ catalyst, effect of scavengers (ethanol, TBA, <i>p</i> -BQ, FFA, l-histidine, and AgNO ₃), anions (Cl ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), and humic acid, pH = 3.0–9.0, 20 °C, 60 min	7 heteroaromatic, 5 aromatic, and 6 aliphatic by-products detected by LC-MS Overall abatement for 2.0 mM PMS and 0.3 g L ⁻¹ catalyst at pH = 7.0. Large inhibition of all the scavengers, pre-eminently l-histidine. Positive effect of adding Cl ⁻ , but inhibition with the other anions and humic acid. Degradation: pure water ≈ tap water > river water. Oxidation with SO ₄ ^{•-} , [•] OH, O ₂ ^{•-} , ¹ O ₂ , and electron transfer. Good reusability losing 8% degradation after 5 consecutive steps.	Li et al. (2022g)
			12 aromatic and 3 cyclic by-products identified by LC-MS	

water with 0.2 g L⁻¹ PMS and 25 mg L⁻¹ catalyst at pH = 7.0, perfloracin rapidly disappeared in 20 min, with detection of 15 heterocyclic, 1 aromatic and 1 aliphatic intermediates by LC-MS (see Table 2). A similar mechanism for generating the oxidizing agents is shown in Fig. 3d for NiCo₂O₄ to destroy tetracycline (Cong et al., 2022). The radical pathway involves the attack of SO₄^{•-}, [•]OH, and O₂^{•-} formed from the PMS decomposition by the surface $\equiv \text{Ni}^{3+}/\equiv \text{Ni}^{2+}$ and $\equiv \text{Co}^{3+}/\equiv \text{Co}^{2+}$ couples, whereas the non-radical pathway corresponded to the attack of ¹O₂ and direct electron transfer between the antibiotic and PMS at the catalyst surface. This system presented a good reproducibility after 5 consecutive cycles of 40 min of treatment of 50 mL of 100–300 mg L⁻¹ tetracycline in pure water with 0.6–1.4 g L⁻¹ PMS, 20–300 mg L⁻¹ catalyst, and pH = 3.0. Faster oxidation was found at lower antibiotic content and higher PMS and catalyst dosages and pH, with 98% abatement as maximal with $k_1 = 0.0458 \text{ min}^{-1}$ (see Table 2). The good performance of the system was confirmed by the similar degradation found with pure water, tap water, and river water. The authors also detected 10 aromatic by-products by LC-MS. A good reproducibility was also found with CoO/MnO/WO₃ (Luo et al., 2022), but much smaller catalytic stability was obtained with CoMn₂O₄/kaolinite or CoMn₂O₄/halloysite Yang et al. (2022d) and CoMn₂O₄ flower (Nguyen et al., 2022) (see Table 2).

The mixed transition metal oxide did not significantly improve the

catalytic power to remove antibiotics from PMS as compared to single transition metal oxides, which seem more appropriate for this purpose because of their easier preparation and lower cost.

3.3.4. Transition metal compounds catalysts

The catalytic power over PMS decomposition has been studied for ciprofloxacin with MoS₂ (Ekande et al., 2023) and (NH₄)_{1.5}Co_xCu_{2-x}Cr₂O₈(OH)_{1.5}H₂O (Serna-Galvis et al., 2023), norfloxacin with CoP₂/N-carbon (Fan et al., 2021), ofloxacin with CoS₂/montmorillonite (Hong et al., 2023), oxytetracycline with MoS₂ (Wang et al., 2023e), sulfamethoxazole with CoP/N-carbon (Fu et al., 2022), Co₉S₈/S, N-graphene (Wang et al., 2022d), and Co₉S₈/S, N, O-carbon (Wang and Wang, 2022), and tetracycline with MoS₂ (Li et al., 2022e), and CoP/-Co₂P (Xu et al., 2023a).

Serna-Galvis et al. (2023) reported the good performance of treating 50 mL of 30.6 μM ciprofloxacin in pure water with 0.5 mM PMS and 0.2 g L⁻¹ (NH₄)_{1.5}Co_xCu_{2-x}Cr₂O₈(OH)_{1.5}H₂O catalyst at pH = 5.6. Under these conditions, Fig. SM-6c highlights the overall antibiotic abatement reached in only 10 min, much faster than using CoO/carbon. The authors ascribed the high oxidation power of this catalyst to the attack of PMS over the surface $\equiv \text{Cu}^{2+}/\equiv \text{Cu}^{+}$ and $\equiv \text{Co}^{3+}/\equiv \text{Co}^{2+}$ pairs, whereas Cr₂O₇²⁻ acted as the carrier/support for the active metallic ions for PMS decomposition. The catalyst also offered good reproducibility after 3

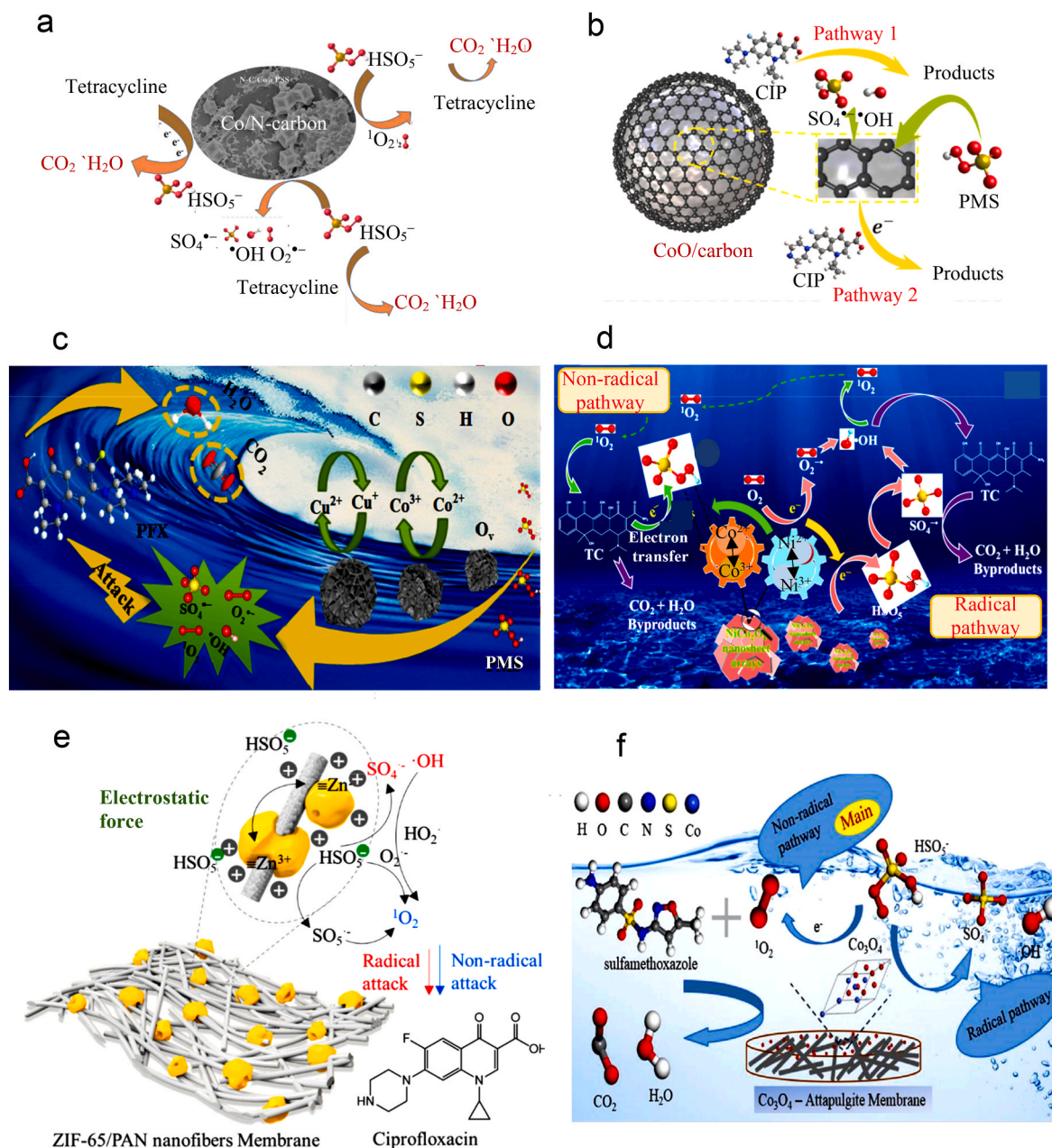
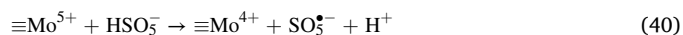
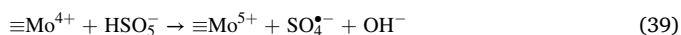


Fig. 3. Schematic illustration of various mechanisms proposed for the degradation/mineralization of antibiotics by PMS activated with catalysts containing non-iron transition metals: (a) Tetracycline with Co/N-carbon catalyst (adapted from Zhang et al. (2022a) with permission 5657490185119 from Elsevier), (b) Ciprofloxacin with CoO/carbon catalyst (adapted from Zhou et al. (2023a) with permission 5657490515840 from Elsevier), (c) perfloroxacin with CuCo₂O₄ catalyst (adapted from Xu et al. (2022a) with permission 5657490871638 from Elsevier), (d) tetracycline with NiCo₂O₄ catalyst (adapted from Cong et al. (2022) with permission 5657491124475 from Elsevier), (e) ciprofloxacin with Zn-MOF as ZIP-65/polyaniline catalyst (adapted from Pu et al. (2022) with permission 5657491474701 from Elsevier), and (f) sulfamethoxazole with Co₃O₄/attapulgite based ceramic membrane (adapted from Zhou et al. (2023b) with permission 5657500280387 from Elsevier).

successive steps, meaning that its performance should be checked with larger volumes to confirm that it can be useful in practice.

Among these compounds, another transition metal Mo was tested as MoS₂. Wang et al. (2023e) showed that this catalyst had lower oxidation power for degrading oxytetracycline. About 98% removal in a longer time of 60 min with $k_1 = 0.064 \text{ min}^{-1}$ was determined for 100 mL of 10 mg L⁻¹ antibiotic in pure water by adding 2.0 mM PMS and 80 mg L⁻¹ catalyst at pH = 7.0. Specific scavengers revealed the pre-eminent oxidation with $\cdot\text{OH}$ produced via reactions (2) or (3), once $\text{SO}_4^{\bullet-}$ was formed from the surface $\equiv\text{Mo}^{4+}/\equiv\text{Mo}^{5+}$ couple as follows:



3.3.5. Redox pairs of transition metals as catalysts

Few papers have used transition metals catalysts to promote the action of surface redox pairs for PMS activation. They treated chloramphenicol and ciprofloxacin with Cu(II)/Cu(I) pair on CuAl_xO_y/g-C₃N₄ (Chen et al., 2021b) and Co(III)/Co(II) pairs on Co₃O₄-MgO/carbon (Liu et al., 2023b), and ciprofloxacin with Mn(II)/Mn(III) and Mn(III)/Mn(IV) pairs on Mn/N-biochar (Liu et al., 2023e). Porous materials with

large active surfaces were prepared for the enhancement of their catalytic properties, although worse results were obtained than previously described catalysts with the same transition metals. So, Liu et al. (2023e) prepared a porous Mn/N-biochar that certainly improved the performance of ciprofloxacin concerning Mn/biochar with smaller porosity. The authors ascribed this feature to the formation of more active sites with the surface $\equiv \text{Mn}^{3+}/\equiv \text{Mn}^{2+}$ and $\equiv \text{Mn}^{4+}/\equiv \text{Mn}^{3+}$ pairs producing more quantity of $\text{SO}_4^{\bullet -}$ from reaction (10). However, the assays carried out with 100 mL of 15 mg L⁻¹ antibiotic in pure water with 2.0 mM PMS and 100 mg L⁻¹ catalyst at pH = 3.0 after 30 min of adsorption in the dark showed a slow degradation achieving 95% of ciprofloxacin decay in 120 min with $k_1 = 0.01609 \text{ min}^{-1}$, as can be seen in Fig. SM-6d, with scarce reproducibility. These results were worse than those reported for other catalysts like CoO/carbon and $(\text{NH}_4)_{1.5}\text{Co}_x\text{Cu}_{2-x}\text{Cr}_2\text{O}_8(\text{OH})_{1.5}\text{H}_2\text{O}$ shown in Fig. SM-6c. This means that the application of porous Mn/biochar is not interesting to be applied in practice.

3.3.6. MOFs derived with transition metals catalysts

PMS activation with MOFs derived with transition metals catalysts have been applied to ciprofloxacin with Zn-MOF/polyaniline (Pu et al., 2022), levofloxacin with ZIF-67/VTM (Wan et al., 2022), oxytetracycline and tetracycline with Co/MOFs (Yu et al., 2023b), pefloxacin with MOFs-derived oxygen vacancy-rich $\text{Co}_3\text{O}_4/\text{ZnO}$ (Liu et al., 2023a), sulfamethoxazole with ZIF-67/Ti membrane (Ma et al., 2022), $\text{Co}_3\text{O}_4/\text{N}$ -carbon from MOF (ZIF-67) (Mohtasham et al., 2023), MgAl/LDH-coated MOFs-derived $\text{Co}_{2.25}\text{Mn}_{0.75}\text{O}_4$ (Su et al., 2023), and Co/MOF (Zhang et al., 2023a), and tetracycline with Co/N-carbon from Co-MOF (Li et al., 2022b).

Pu et al. (2022) synthesized a membrane of Zn-MOF/polyaniline to treat 10 mg L⁻¹ ciprofloxacin in pure water with 0.1 mM PMS and 0.4 g L⁻¹ catalyst at pH = 7.0 using a stirred tank reactor thermostated at 30 °C. Fig. SM-6c reveals that the antibiotic was rapidly removed during the first 15 min of the process, whereupon it decayed much more slowly up to 83% degradation at 60 min. This can be related to a gradual decay in the crystallinity of Zn with a loss of its active sites to decompose the adsorbed PMS. This was confirmed by the loss of 35% degradation after 5 consecutive runs (see Table 2), which was partially improved after Zn recrystallization. Fig. 3e illustrates the sketch of the mechanism proposed for the production of $^1\text{O}_2$ as the main oxidant, followed by $\text{SO}_4^{\bullet -}$ and $^{\bullet}\text{OH}$, on Zn-MOF/polyaniline based on the electrostatic bonding formed between this catalyst and PMS to activate the surface $\equiv \text{Zn}^{3+}/\equiv \text{Zn}^{2+}$ pair from reaction (10). From the 11 primary heterocyclic by-products identified by LC-MS, the reaction sequence of ciprofloxacin (1) degradation shown in Fig. SM-7 was proposed. Two radical and one non-radical parallel pathways can be observed. The radical pathway 1 involves the hydroxylation of 1 from $^{\bullet}\text{OH}$ to form 2, which then evolves to 4 and 5. The non-radical pathway 2 is initiated by the attack of $^1\text{O}_2$ to break the piperazine ring of 1 to give 3, followed by the formation of 6, 7, and 9. In the radical pathway 3, the compound 8 was formed from the attack of $\text{SO}_4^{\bullet -}$ to oxidize the piperazine ring of 1 producing a carbonyl group. Further evolution of 8 yields 6 and 9. Finally, 7 and 9 are oxidized to originate 10–12.

Other transition metal like Co was used as a catalyst from MOFs, showing much better reusability than Zn and then, being preferable for practical application. Fig. SM-6b depicts a slow and overall degradation when 100 mL of 40 μM sulfamethoxazole in pure water were treated with 10 mM PMS, 200 mg L⁻¹ Co/MOF catalyst, and 25 mM HCO_3^- at pH = 8.3/Zhang et al. (2023a). The authors detected with specific scavengers the formation of oxidizing agents like $^{\bullet}\text{OH}$, $^1\text{O}_2$, and $\text{CO}_3^{\bullet -}$ formed from the PMS decomposition with the surface $\equiv \text{Co}^{3+}/\equiv \text{Co}^{2+}$ couple. It was found a large influence of the aqueous matrix with a degradation deceleration in the order: of pure water > river water $\approx$ reclaimed water $\approx$ groundwater. A good reproducibility with determined after 5 successive steps and 20 degradation by-products were detected by LC-MS. It is also remarkable the work of Mohtasham et al. (2023) who treated 100 mL of 20 mg L⁻¹ sulfamethoxazole in pure

water with 0.25 mM PMS and 200 mg L⁻¹ $\text{Co}_3\text{O}_4/\text{N}$ -carbon from MOF (ZIF-67) catalyst at pH = 3.9 and 25 °C. Fig. SM-6b highlights that under these conditions, the antibiotic disappeared in only 6 min with a very high $k_1 = 0.79 \text{ min}^{-1}$ (see Table 2), much more rapidly than the assays made with CoO-3D/mesoporous CN and Co/MOF and shown in the same figure. Unfortunately, a moderate reproducibility was found due to the decay of 15% degradation after 5 consecutive cycles, $\text{SO}_4^{\bullet -}$ and $^{\bullet}\text{OH}$ were the main oxidizing agents.

3.3.7. Other catalysts with transition metals

Other catalysts with transition metals have been used to remove ciprofloxacin with wastes of anodes of lithium-ion batteries (Zhao et al., 2022d), metronidazole with Co_3Mn -layered double hydroxide (He et al., 2021b), sulfamethoxazole with Co_3O_4 /attapulgite based ceramic membrane (Zhou et al., 2023b), and tetracycline with Mn-N (Hu et al., 2023), Co/MoS₂ catalyst (Li et al., 2022g), and Cu/Mo₂C (Yang et al., 2021a).

Zhou et al. (2023b) developed a Co_3O_4 /attapulgite-based ceramic membrane for the continuous removal of sulfamethazole in pure water with a flow cell. It was shown that this membrane enhanced the degradation via $^1\text{O}_2$ oxidant. Fig. 3f schematizes the radical and non-radical pathways proposed for this system by the participation of the surface $\equiv \text{Co}^{3+}/\equiv \text{Co}^{2+}$ pair to decompose PMS by reactions (37), (30), and (38). For 10 mg L⁻¹ sulfamethoxazole 0.1 g L⁻¹ PMS and 0.4 g L⁻¹ catalyst, a continuous abatement of only 70–72% antibiotic was obtained at pH 4.74–9.76 during 180 min (see Table 2). Moreover, moderate reusability with a loss of 20% degradation was determined after 5 successive cycles, making this membrane inefficient for a long-duration treatment of the polluted water. The work of Li et al. (2022g) was centered on the study of 100 mL of 8 mg L⁻¹ tetracycline in pure water and natural waters by adding 0.5–3.0 mM PMS and 0.05–0.4 g L⁻¹ Co/MoS₂ catalyst at pH = 3.0 and 20 °C for 60 min. $\text{SO}_4^{\bullet -}$, $^{\bullet}\text{OH}$, $\text{O}_2^{\bullet -}$, and $^1\text{O}_2$ were identified as oxidizing species formed from the action of the surface $\equiv \text{Co}^{2+}$ and $\equiv \text{Mo}^{4+}$, as pointed out above. Non-radical pathway with electron transfer between the antibiotic and PMS was also detected from specific scavengers. In pure water, overall abatement was obtained for 2.0 mM PMS and 0.3 g L⁻¹ catalyst at pH = 7.0, at a similar rate with tap water and faster than with river water (see Table 2). The possible use of this catalyst in practice was confirmed by its good reusability losing 8% degradation after 5 consecutive steps with a very low Co leaching of 45 μg L⁻¹ avoiding its toxicity in the remaining solution. Finally, the authors identified 12 aromatic and 3 cyclic by-products of tetracycline by LC-MS.

3.4. Biochar activation

Biochar obtained by pyrolysis of natural organic matter has been used as a PMS activator. The studies considered the removal of ciprofloxacin with N-biochar from pinewood (Qu et al., 2022), chloramphenicol with biochar with Fe from petroleum sludge (Qian et al., 2023c), chlortetracycline with biochar from houttuynia cordata (OuYang et al., 2022), levofloxacin with biochar from chicken manure (Ji et al., 2022), ofloxacin with biochar from alkaline lignin (Miao et al., 2023), oxytetracycline with B-biochar from tea seed shells (Pan et al., 2023a), sulfamethoxazole with biochar from pig manure (Wang et al., 2022b) and N-biochar from pomelo peel (Wang and Chen, 2022), sulfathiazole with B,N,O-biochar (Hung et al., 2022), and tetracycline with P,N-biochar from fish scale (He et al., 2023b). Magnetic biochar from dewatered piggery sludge (Luo et al., 2021b), biochar from sludge (Li et al., 2022c), biochar from oil-based drill-cutting ash (Yang et al., 2022a), and rice husk biochar (Song et al., 2023). Table 3 lists the main results obtained in selected papers of this treatment.

The composition and structure of synthesized biochars favor the generation of oxidants in different ways. Fig. SM-8a shows the presence of N atoms in pyridinic, graphitic, and pyrrolic groups within the biochar pyrolyzed from chicken manure (Ji et al., 2022). This composition allowed: (i) the direct electron transfer to PMS to generate $\text{SO}_4^{\bullet -}$ from

Table 3

Relevant results were obtained for the destruction of antibiotics from different aqueous matrices by other activation methods of peroxymonosulfate.

Antibiotic	System	Experimental remarks	Best results	Ref.
Biochar activation				
Chloramphenicol	Stirred conical flask with Fe-biochar catalyst from petroleum sludge	50 mL of 100 mg L ⁻¹ antibiotic in pure water, 1.6–9.3 mM PMS, 0.1–2.0 g L ⁻¹ catalyst, effect of scavengers (ethanol, TBA, and KI), pH = 2.0–9.0, 25 °C, 210 min	Overall abatement in 150 min and 55% TOC removal in 210 min for 6.2 mM PMS and 2.0 g L ⁻¹ catalyst at pH = 2.0. Slower removal at greater pH. Stronger scavenging with ethanol. Key oxidation role of [•] OH. No reproducibility losing 55% degradation after 4 successive cycles. 7 aromatic and 2 aliphatic by-products detected by LC-MS	Qian et al. (2023c)
Levofloxacin	Stirred tank reactor with biochar catalyst from chicken manure	100 mL of 25–100 µM antibiotic in pure water, 0.25–1.0 mM PMS, 0.2–0.5 g L ⁻¹ catalyst, effect of scavengers (methanol, TBA, sodium azide, sodium oxalate, DMSO, AgNO ₃ , and KI), anions (Cl ⁻ , NO ₃ ⁻ , and HCO ₃ ⁻), and humic acid, pH = 3.0–11.0, 25 °C, 40 min	83% degradation for 50 µM antibiotic in pure water, 0.5 mM PMS, 0.3 g L ⁻¹ catalyst, and pH = 5.26 after 25 min of adsorption in the dark. Stronger inhibition with sodium azide, sodium oxalate, DMSO, and KI. Little effect of adding Cl ⁻ , NO ₃ ⁻ , whereas HCO ₃ ⁻ . And humic acid yielded a large inhibition. ¹ O ₂ and holes as main oxidants	Ji et al. (2022)
Oxytetracycline	Stirred beaker with B-biochar catalyst from tea seed shells	100 mL of 20 mg L ⁻¹ antibiotic in pure water, 0.1–1.0 mM PMS, 0.1–1.0 g L ⁻¹ catalyst, the effect of scavengers (ethanol, TBA, <i>p</i> -BQ, and l-histidine), pH = 2.0–10.0, 25 °C, 20 min	92% degradation for 0.5 mM PMS, 0.5 g L ⁻¹ catalyst, and pH = 7.8. Methanol and l-histidine acted as stronger scavengers. Oxidation with [•] OH, O ₂ ^{•-} , ¹ O ₂ , and electron transfer. 14 aromatic and 4 cyclic by-products identified by LC-MS	Pan et al. (2023a)
Sulfamethoxazole	Stirred beaker with N-biochar catalyst from pomelo peel	100 mL of 5–30 mg L ⁻¹ antibiotic in pure water, 0.1–0.9 mM PMS, 0.03–0.2 g L ⁻¹ catalyst, the effect of scavengers (methanol, l-histidine, sodium azide, and KI), and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and H ₂ PO ₄ ⁻), pH = 3.0–9.0, room temperature, 30 min	96% removal for 10 mg L ⁻¹ antibiotic, 0.5 mM PMS, and 0.1 g L ⁻¹ catalyst after 30 min of adsorption in the dark. Large scavenging with l-histidine, sodium azide, and KI. Stronger inhibition with HCO ₃ ⁻ > H ₂ PO ₄ ⁻ . ¹ O ₂ and electron transfer acted as dominant oxidants vs. SO ₄ ^{•-} and [•] OH. Moderate reproducibility losing 15% degradation after 4 successive runs	Wang and Chen (2022)
Sulfathiazole	Stirred tube over a rotator with B, N,O-biochar catalyst from coconut shell	40 mL of 0.05–0.25 mM antibiotic in pure water and natural water, 0.1–0.6 mM PMS, 50–250 mg L ⁻¹ catalyst, the effect of scavengers (methanol, TBA, and sodium azide), pH = 3.0–11.0, 30 °C, 30 min	94% abatement with <i>k</i> ₁ = 0.064 min ⁻¹ for 0.05 mM antibiotic in pure water, 0.5 mM PMS and 15 mg L ⁻¹ catalyst at optimum pH = 7.0. Larger scavenging with sodium azide. Degradation: aquaculture water > pure water. Oxidation with SO ₄ ^{•-} , [•] OH, and ¹ O ₂ . Moderate reproducibility with loss of 18% degradation after 5 consecutive steps	Hung et al. (2022)
Tetracycline	Stirred tank reactor with P,N-biochar catalyst from fish scale	100 mL of 5 mg L ⁻¹ antibiotic in pure water and real water, 0.4 g L ⁻¹ PMS, 0.2 g L ⁻¹ catalyst, the effect of scavengers (methanol, TBA, and sodium azide) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and HPO ₄ ⁻), pH = 3.0–9.0, room temperature, 180 min	In pure water, about 100% degradation in the pH interval 3.0–7.0, decaying up to 74% for pH = 9.0 after 30 min of adsorption in the dark. Stronger scavenging with sodium azide. Little inhibition of all the anions. Degradation: pure water > medical wastewater. SO ₄ ^{•-} , [•] OH, and ¹ O ₂ as oxidants. Good reproducibility after 3 consecutive runs	He et al. (2023b)
Tetracycline	Stirred tank reactor with biochar and magnetic biochar catalyst from dewatered piggy sludge	200 mL of 10 mg L ⁻¹ antibiotic in pure water, 0–40 mg L ⁻¹ PMS, 0–0.75 g L ⁻¹ catalyst, the effect of scavengers (methanol, TBA, and sodium azide), pH = 4.0–10.0, room temperature, 120 min	73% degradation with 40 mg L ⁻¹ PMS and 0.75 g L ⁻¹ catalyst at pH = 9.0 with biochar, whereas 88% was degraded with magnetic biochar. In the latter case, faster scavenging with methanol followed by sodium azide. Oxidation: O ₂ ^{•-} > SO ₄ ^{•-} > [•] OH > ¹ O ₂ . Scarce reusability losing 25% degradation after 4 successive cycles	Luo et al. (2021b)
Carbonaceous materials activation				
Sulfamethoxazole	Stirred tank reactor with N-carbon catalyst	10 mg L ⁻¹ antibiotic in pure water and real water, 0.5–1.5 mM PMS, 50 mg L ⁻¹ catalyst, pH = 3.0–9.0, room temperature, 20 min	Complete removal in 5 min with <i>k</i> ₁ = 1.691 min ⁻¹ for optimum 1.0 mM PMS at pH = 3.0. Slower degradation at greater pH. 8 degradation by-products detected by LC-MS/MS	Cai et al. (2022)
Tetracycline	Stirred conical flask with magnetic carbon catalyst	100 mL of 40 µM antibiotics in pure water and natural waters, 0.2 mM PMS, 0.1 g L ⁻¹ catalyst, the effect of scavengers (methanol, TBA, and β-carotene), anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and SO ₄ ²⁻), and humic acid, pH = 3.0–10.1, 30 °C, 180 min	90% degradation for pH = 3.0–9.0, decreasing to 76% at pH = 10.1. Much greater scavenging with β-carotene. Quick inhibition with HCO ₃ ⁻ , but no effect of the other anions and humic acid. Similar degradation with pure water, tap water, river water, and lake water. ¹ O ₂ as the main oxidant. 8 heterocyclic and 1 cyclic by-products identified by LC-MS	Wu et al. (2022b)
Tetracycline	Stirred tank reactor with F,N-carbon catalyst	100 mL of 10–100 mg L ⁻¹ antibiotic in pure water and natural waters, 20 mg L ⁻¹ PMS, 10 mg L ⁻¹ catalyst, the effect of scavengers (methanol, TBA, <i>p</i> -BQ, and FFA), anions (Cl ⁻ ,	Complete degradation in pure water at pH = 3.0. Slower loss of antibiotic with raising pH. Larger scavenging with FFA. Similar inhibition with all the anions added and humic acid. Degradation: pure water > tap water > river water > lake	Huang et al. (2023a)

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Table 3 (continued)

Antibiotic	System	Experimental remarks	Best results	Ref.
		NO ₃ ⁻ , HCO ₃ ⁻ , and HPO ₄ ⁻), and humic acid, pH = 1.5–11.0, 25 °C, 60 min	water. ¹ O ₂ as the predominant oxidant. No reusability with loss of 30% degradation after 5 consecutive cycles, being recovered after calcination. 14 aromatic and 1 cyclic intermediates detected by LC-MS	
<i>UVC activation</i> Oxytetracycline	Stirred cylindrical quartz photoreactor under 4 external 8 W UVC lights	100 mL of 10 mg L ⁻¹ antibiotic in pure water, 4.0 mM PMS or H ₂ O ₂ , the effect of scavengers (methanol and isopropanol) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and SO ₄ ²⁻), pH = 3.0–11.0, room temperature, 45 min	At pH 7.0, 67% abatement with $k_1 = 0.0175 \text{ min}^{-1}$ using PMS, much higher than 28% with $k_1 = 0.0052 \text{ min}^{-1}$ using H ₂ O ₂ . Quicker degradation under alkaline conditions. Inhibition with both scavengers. Larger enhancement by adding Cl ⁻ and HCO ₃ ⁻ . $E_{EO}^a = 403 \text{ and } 774 \text{ kWh m}^{-3} \text{ order}^{-1}$ for PMS and H ₂ O ₂ , respectively	Varank et al. (2022)
Sulfamethoxazole Trimethoprim	80 L pilot flow plant with 6.21 L under 230 W UVC irradiation	100 µg L ⁻¹ of each antibiotic in wastewater effluent, 0–1.0 mM PMS, liquid flow rate = 36 L h ⁻¹ , pH = 8.17, 28 °C, 180 min	Complete degradation of both antibiotics with 1.0 mM PMS in 90 min. Estimated annual energy cost in a continuous flow reactor: 0.63 € m ⁻³ (0.02 € m ⁻³ with only the UVC lamp)	Berruti et al. (2021)
<i>Photocatalytic activation</i> Ciprofloxacin	Stirred beaker with BiVO ₄ photocatalyst upon a visible light from 300 W Xe light ($\lambda > 420 \text{ nm}$)	100 mL of 10 mg L ⁻¹ antibiotic in pure water, 0.1–1.0 g L ⁻¹ PMS, 0.1–0.8 g L ⁻¹ photocatalyst, effect of scavengers (methanol, TBA, FFA, sodium azide, and sodium oxalate), anions (Cl ⁻ , HCO ₃ ⁻ , CO ₃ ²⁻ , and SO ₄ ²⁻), and humic acid, pH = 3.02–10.94, room temperature, 18 min	Overall removal with $k_1 = 0.41 \text{ min}^{-1}$ in 50 min and 44% TOC decay in 19 min With 0.2 g L ⁻¹ PMS, 0.3 g L ⁻¹ photocatalyst, and pH = 6.34 after 30 min of adsorption in the dark. Faster scavenging with FFA and sodium azide. Little effect of anions, except a stronger inhibition with CO ₃ ²⁻ and humic acid. Oxidation with SO ₄ ²⁻ , [•] OH, ¹ O ₂ , and holes	Chen et al. (2022)
Ciprofloxacin	Stirred cylindrical photoreactor with BiFe _{1-x} Cu _x O ₃ photocatalyst upon a 500 W Xe light	50 mL of 10 mg L ⁻¹ antibiotic in pure water and real waters, 0.5–2.0 mM PMS, 0.05–0.6 g L ⁻¹ photocatalyst, effect of scavengers (ethanol, TBA, FFA, EDTA-2Na, sodium azide, and ascorbic acid) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and SO ₄ ²⁻), pH = 3.0–11.0, room temperature, 180 min	80% abatement with $k_1 = 0.084 \text{ min}^{-1}$ for 1.0 mM PMS, 0.6 g L ⁻¹ photocatalyst, and pH = 6.02. Faster degradation at lower pH. FFA and ascorbic acid gave the stronger scavenging. Positive action of Cl ⁻ and increasing inhibition with SO ₄ ²⁻ $\approx$ NO ₃ ⁻ < HCO ₃ ⁻ . Oxidation with SO ₄ ²⁻ , [•] OH, O ₂ ^{•-} , and ¹ O ₂ . Good reproducibility after 3 successive runs	Wang et al. (2022a)
Levofloxacin	Stirred flask reactor with ZnFe ₂ O ₄ upon a 5 W LED light ($\lambda = 320\text{--}780 \text{ nm}$)	50 mL of 10 mg L ⁻¹ antibiotic in pure water, 1.0 mM PMS, 1.0 g L ⁻¹ photocatalyst, the effect of scavengers (ethanol, isopropyl alcohol, l-histidine, l-carnosine, and sodium oxalate) and anions (Cl ⁻ , CO ₃ ²⁻ , H ₂ PO ₄ ⁻ , and acetate), pH = 3.0–11.0, room temperature, 180 min	92% degradation with $k_1 = 0.024 \text{ min}^{-1}$ at pH = 7.0. Greater scavenging with l-carnosine and l-histidine. The addition of CO ₃ ²⁻ and H ₂ PO ₄ ⁻ Caused a larger inhibition. SO ₄ ²⁻ , [•] OH, O ₂ ^{•-} , and ¹ O ₂ as oxidants. Moderate reproducibility with loss of 17% degradation after 4 successive steps. 15 aromatic intermediates identified by LC-MS	Zhong et al. (2021)
Sulfamethazine	Stirred cylindrical quartz tube with CuFeO ₄ /g-C ₃ N ₄ photocatalyst upon a 500 W Xe light ($\lambda > 420 \text{ nm}$)	25 mL of 10 mg L ⁻¹ antibiotic in pure water and natural waters, 0.025–0.2 g L ⁻¹ PMS, 0.5–3.0 g L ⁻¹ photocatalyst, the effect of scavengers (methanol, TBA, p-BQ, and tryptophan), anions (HCO ₃ ⁻ And H ₂ PO ₄ ⁻), and humic acid, pH = 3.0–11.0, 25 °C, 30 min	Overall removal with $k_1 = 0.024 \text{ min}^{-1}$ and 45% TOC reduction in pure water for 0.1 g L ⁻¹ PMS and 2.0 g L ⁻¹ photocatalyst at optimum pH = 7.0. Tryptophan is the stronger scavenger. Large inhibition with all the anions and humic acid. Degradation: pure water > tap water > surface water. ¹ O ₂ as the dominant oxidant, Moderate reproducibility losing 18% degradation after 5 consecutive runs. 3 heteroaromatic, 4 aromatic, and 1 cyclic by-products detected by LC-MS	Sun et al. (2023)
Sulfamethoxazole	Stirred tube photoreactor with Fe ₃ O ₄ /CeO ₂ /BiOI photocatalyst upon a UVA light from the LED lamp	20 mL of 0.05 mM antibiotic in pure water and natural water, 0.2 mM PMS, 0.1 g L ⁻¹ photocatalyst, the effect of scavengers (ethanol, TBA, p-BQ, sodium oxalate, and sodium azide) and anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , and HPO ₄ ²⁻), pH = 3.0–11.0, room temperature, 15 min	98% of abatement with $k_1 = 0.221 \text{ min}^{-1}$ in 15 min in pure water and 68% TOC reduction in 60 min at pH = 5.0. Greater scavenging with ethanol. Cl ⁻ , NO ₃ ⁻ , and HCO ₃ ⁻ as the main inhibitors. Slower degradation with tap water. Pre-eminent oxidation with SO ₄ ²⁻ and [•] OH, Good reproducibility after 4 consecutive runs.	Kohantorabi et al. (2021)
Sulfamethoxazole	Stirred Pyrex jacketed photoreactor with TiO ₂ /CuCo ₂ O ₄ photocatalyst under a 600 W m ⁻² Xe light ($\lambda > 290 \text{ nm}$)	150 mL of 5 mg L ⁻¹ antibiotic in pure water, 0.05 mM PMS, 250 mg L ⁻¹ photocatalyst, effect of scavengers (ethanol, TBA, phenol, and p-BQ) anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and SO ₄ ²⁻), and humic acid, pH = 3.0–11.0, 25 °C, 360 min	14 degradation by-products identified by LC-MS Complete removal with $k_1 = 0.098 \text{ min}^{-1}$ at pH = 5.9. Phenol followed by p-BQ as the main scavengers. Quicker inhibition with Cl ⁻ , NO ₃ ⁻ , and humic acid. Preferential oxidation with SO ₄ ²⁻ , [•] OH, and O ₂ ^{•-}	Mertah et al. (2022)
Tetracycline	Stirred tank photoreactor with CuBi ₂ O ₄ /BiOBr photocatalyst upon a 300 W Xe light ($\lambda > 420 \text{ nm}$)	100 mL of 10 mg L ⁻¹ antibiotic in pure water, 2.0 mM PMS, 200 mg L ⁻¹ photocatalyst, effect of scavengers (methanol, TBA, p-BQ, EDTA-2Na, and l-histidine), pH = 2.5–10.5, 25 °C, 35 min	90% removal with $k_1 = 0.0961 \text{ min}^{-1}$ at pH = 6.5. Higher scavenging with methanol followed by TBA. SO ₄ ²⁻ , [•] OH, O ₂ ^{•-} , and holes as oxidants. Good reproducibility after 4 consecutive runs. 9 aromatic and 2 aliphatic by-products detected by LC-MS	Dou et al. (2022)

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Table 3 (continued)

Antibiotic	System	Experimental remarks	Best results	Ref.
Tetracycline	Stirred tank photoreactor with Mo ₂ C/MoO ₃ film photocatalyst upon a 300 W Xe light ($\lambda > 420$ nm)	20 mL of 10–100 mg L ⁻¹ antibiotic in pure water, 0.1–0.5 g L ⁻¹ PMS, film of photocatalyst, effect of scavengers (methanol, isopropyl alcohol, and tryptophan) anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , and SO ₄ ²⁻), pH = 3.0–11.0, 25 °C, 60 min	95% abatement with $k_1 = 0.0417$ min ⁻¹ for 50 mg L ⁻¹ antibiotic, 0.5 g L ⁻¹ PMS, and pH = 5.0 after 30 min of adsorption in the dark. Tryptophan is a more powerful scavenger. Stronger inhibition with HCO ₃ ⁻ . Oxidation: ¹ O ₂ > SO ₄ ^{•-} ≈ •OH > O ₂ ^{•-} . Excellent reusability after 10 successive cycles.	Lian et al. (2023)
Tetracycline	Stirred sandwich cup with CoO/rectorite photocatalyst upon a 300 W Xe light	100 mL of 20–40 mg L ⁻¹ antibiotic in pure water, 0.1–0.5 g L ⁻¹ PMS, 0.1–0.3 g L ⁻¹ photocatalyst, the effect of scavengers (methanol, TBA, <i>p</i> -BQ, and sodium oxalate) and anions (Cl ⁻ , NO ₃ ⁻ , and HCO ₃ ⁻), pH = 3.0–9.0, 25 °C, 60 min	23 degradation by-products identified by LC-MS 98% removal with $k_1 = 0.0459$ min ⁻¹ for 20 mg L ⁻¹ antibiotic, 0.5 g L ⁻¹ PMS, 0.3 g L ⁻¹ photocatalyst, and pH = 7.0. Greater scavenging with methanol. Little influence of all the anions. SO ₄ ^{•-} , •OH, O ₂ ^{•-} , and holes as oxidants. Moderate reproducibility losing 17% degradation after 4 successive steps. 7 primary aromatic by-products detected by LC-MS	Yi et al. (2021b)
Thermal activation Sulfamethoxazole	Stirred cylindrical, jacketed reactor	900 mL of 10 mg L ⁻¹ antibiotic in pure water, 0–0.5 mM PMS, the effect of scavengers (ethanol and TBA), pH = 3.0–11.0, 40–80 °C, 60 min	92% removal with $k_1 = 0.045$ min ⁻¹ for 0.4 mM PMS at optimum pH = 9.5 and 70 °C. Degradation is enhanced at higher temperatures. $E_a^b = 36.9$ kJ mol ⁻¹ . High inhibition of both scavengers. Oxidation; SO ₄ ^{•-} (59%) > •OH (41%).	Milh et al. (2021)
Electrochemical activation Oxytetracycline	Stirred undivided cell with a Vo-MnO/C/Pt _x Au _{1-x} anode and a graphite cathode	50 mL of 10–80 mg L ⁻¹ antibiotic in pure water and natural waters, 0.2–2.0 mM PMS, effect of scavengers (methanol, ethanol, <i>p</i> -BQ, and FFA), anions (Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , and H ₂ PO ₄ ⁻), and humic acid, pH = 3.0–11.0, $j^c = 3$ –17 mA cm ⁻² , room temperature, 60 min	93% removal for 10 mg L ⁻¹ antibiotic in pure water with 2.0 mM PMS at optimum pH = 9.0 and $j = 10$ mA cm ⁻² after 30 min of adsorption in the dark. Larger scavenging with <i>p</i> -BQ followed by FFA. Higher inhibition with great contents of NO ₃ ⁻ , H ₂ PO ₄ ⁻ , and humic acid. Similar degradation with pure water, river water, underwater, and seawater. ¹ O ₂ and O ₂ ^{•-} as dominant oxidants. Moderate reproducibility with loss of 12% degradation after 6 consecutive runs. Detection of 10 aromatic and 3 aliphatic by-products by LC-MS	Shen et al. (2023)
Sulfamethoxazole	Stirred undivided flat square cell with a Pt anode and a C/Fe/nickel foam cathode	100 mL of 10 mg L ⁻¹ antibiotic in pure water, 50 mM Na ₂ SO ₄ , 0.65 mM PMS, the effect of scavengers (methanol, TBA, <i>p</i> -BQ, and FFA), pH = 4.0, $j = 12.5$ mA cm ⁻² , 25 °C, 60 min	96% degradation with $k_1 = 0.0972$ min ⁻¹ in pure water. Larger scavenging with FFA followed by <i>p</i> -BQ. Dominant oxidation role of ¹ O ₂ . Excellent reusability after 10 consecutive steps. Detection of 6 heteroaromatic and 7 aromatic by-products by LC-MS	Tang et al. (2022)
Tetracycline	Stirred undivided cell with a carbon plate anode, an S-Co/Ti cathode, and an Ag AgCl reference electrode	50 mL of 25 μ M antibiotic in pure water and real waters, 0.1 M Na ₂ SO ₄ , 0–3.0 mM PMS, effect of scavengers (methanol, DMSO, <i>p</i> -BQ, and FFA), anions (Cl ⁻ , HCO ₃ ⁻ , and SO ₄ ²⁻), and humic acid, pH = 3.0–11.0, $E_{cat}^d = 0$ to -1.2 V/Ag AgCl, room temperature, 20 min	Complete abatement in pure water for ≥ 1.0 mM PMS, pH ≥ 5.0 , and $E_{cat} \geq 0.8$ V. Faster degradation at higher pH. DMSO and FFA as stronger scavengers. Little influence of the anions added and humic acid. Similar degradation with pure water, surface water, and groundwater. Oxidation with SO ₄ ^{•-} , •OH, O ₂ ^{•-} , ¹ O ₂ , and Co ⁴⁺ . Excellent reusability after 5 successive steps	Tang et al. (2023b)
Other methods Norfloxacin	Stirred Erlenmeyer flask with calcite catalyst	300 mL of 1–50 mg L ⁻¹ antibiotic in pure water, 0.05–1.0 mM PMS, 0–1.0 g L ⁻¹ catalyst, the effect of scavengers (methanol, TBA, <i>p</i> -BQ, FFA, and l-histidine), anions (Cl ⁻ , NO ₃ ⁻ , and HPO ₄ ²⁻), and humic acid, pH = 7.0, room temperature, 60 min	95% abatement for 5 mg L ⁻¹ antibiotic, 0.2 mM PMS, and 0.5 g L ⁻¹ catalyst. l-histidine is the most effective scavenger. Strong inhibition by adding HPO ₄ ²⁻ . And humic acid, ¹ O ₂ as major oxidant. Moderate reusability with loss of 17% degradation after 4 successive steps. 5 heteroaromatic and 3 aromatic intermediates detected by LC-MS	Chu et al. (2021)
Ornidazole	Stirred tank reactor with BaTiO ₃ /MoS ₂ under piezocatalysis (100 W power energy, 40 kHz frequency) catalyst	20 mL of 10 mg L ⁻¹ antibiotic in pure water, 0.25 g L ⁻¹ PMS, 0.1 g L ⁻¹ piezocatalyst, effect of scavengers (methanol, TBA, <i>p</i> -BQ, FFA, EDTA-2a, ascorbic acid, and l-histidine), pH = 5.0, 25 °C, 40 min	92% degradation with $k_1 = 0.0559$ min ⁻¹ . Stronger scavenging with methanol, TBA, FFA, and l-histidine. SO ₄ ^{•-} , •OH, O ₂ ^{•-} , and ¹ O ₂ as oxidants. Identification of 5 primary heteroaromatic by-products by LC-MS	Chen et al. (2021c)

^a E_{EO}: Electrical energy per order.^b E_a: Activation energy.^c j: current density.^d E_{cat}: Cathodic potential.

reaction (41) and $\bullet\text{OH}$ from reaction (42), (ii) the electron migration within the catalyst to produce $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$, and (iii) the formation of holes (h^+) that oxidizes $\text{O}_2^{\bullet-}$ to $^1\text{O}_2$ by reaction (43). However, Fig. SM-8b depicts that the treatment of 100 mL of 50 μM levofloxacin in pure water only yielded 83% degradation in 40 min under optimum conditions of 0.5 mM PMS and 0.3 g L^{-1} biochar at pH = 5.26 after 25 min of adsorption in the dark (see also Table 3). This performance strongly decayed to 52% in 3 consecutive cycles, probably due to the damage of its carbon structure or the loss of reactive sites by its agglomeration, making it useless in practice. $^1\text{O}_2$ and h^+ were the main oxidants as identified by specific scavengers, as can be seen in Fig. SM-8c.



An analogous mechanism has been proposed for the biochar synthesized from pomelo peel with a high N content (Wang and Chen, 2022), in which the direct electron transfer between sulfamethoxazole and PMS was also remarked. This catalyst showed a better performance for the removal of this antibiotic operating at optimum conditions of 100 mL of 10 mg L^{-1} sulfamethoxazole in pure water by adding 0.5 mM PMS and 0.1 g L^{-1} catalyst after 30 min of adsorption in the dark, giving rise to 96% degradation in 30 min, with moderate reproducibility after 4 successive runs (see Table 3). When the biochar pyrolyzed from tea seed shells was doped with B (Pan et al., 2023a), the decay of the energy required to excite the electrons in the B-biochar favored its transfer to PMS from reactions (41) and (42). In this case, a rapid decay of 92% was found for 20 mg L^{-1} oxytetracycline with 0.5 mM PMS and 0.5 g L^{-1} catalyst at pH = 7.8. Due to the oxidation with $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, $^1\text{O}_2$, and electron transfer (see Table 3). The use of biochars rich in iron (Luo et al., 2021b; Luo et al., 2021b) and B,N,O-biochar (Hung et al., 2022) did not improve their stability. (see Table 3). A good reusability, as required for practical application, was only found for the biochar prepared with fish scales rich in P and N (He et al., 2023b). These authors proposed the transfer of the electrons of the graphitic N, alongside the P-C groups, to PMS-producing $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ from reactions (41) and (42). A content of 0.2 g L^{-1} catalyst allowed 100% degradation for 100 mL of 5 mg L^{-1} tetracycline in pure water with 0.4 g L^{-1} PMS, in the pH interval 3.0–7.0 in 120 min after 30 min of adsorption in the dark, well reproduced after 3 consecutive steps (see Table 3). Moreover, a 95% degradation was determined using medical wastewater as a matrix, showing the potential practical use of this catalyst.

3.5. Carbonaceous materials activation

The works of carbonaceous materials for PMS activation were centered in ciprofloxacin with N,S-carbon (Gasim et al., 2023), levofloxacin with N,O-carbon (Zhang et al., 2023e), sulfamethoxazole with S,O-graphitic carbon nitride (Hasija et al., 2023) and N-carbon (Cai et al., 2022), sulfathiazole with spirulina residue-derived GO (Wang et al., 2022c), sulfonamide with magnetic carbon (Li et al., 2022a), and tetracycline with magnetic N-carbon (Wu et al., 2022b), B,N-carbon (Xie et al., 2022) and F,N-carbon (Huang et al., 2023a).

The carbonaceous materials are synthetic products such as g-C₃N₄ GO, or a mixture of organics that are pyrolyzed and usually doped with organics containing N, S, O, N, and/or F. The carbon structure of these materials favors the adsorption of PMS to be activated to $^1\text{O}_2$ to oxidize the adsorbed antibiotic, as schematized in Fig. SM-9a for magnetic N-carbon (Wu et al., 2022b). With 0.1 g L^{-1} of this catalyst, Fig. SM-9b depicts the normalized tetracycline concentration vs. time for 100 mL of 40 μM antibiotic in pure water treated with 0.2 mM of several oxidants such as H₂O₂, persulfate (PS), and PMS at pH = 7.0 and 30 °C. H₂O₂ generated $\bullet\text{OH}$ and PS ($\text{S}_2\text{O}_8^{2-}$) originated the same oxidizing agents as

PMS. As can be seen, a 60% abatement was only achieved with H₂O₂, whereas PS and PMS gave 90% removal, more rapidly with the latter. This confirms the higher oxidation power of PMS as an oxidant. The effect of several scavengers with activated PMS is shown in Fig. SM-9c. The scarce influence of methanol and TBA revealed a very poor oxidation with $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$, whereas the large inhibition with β -carotene confirmed the large production of $^1\text{O}_2$ as the main oxidant. The authors remarked on the similar degradation found with pure water, tap water, river water, and lake water (see Table 3), indicating the good oxidation power over the antibiotic in the presence of inorganic anions and other organic matter.

Table 3 shows that complete degradation was achieved for sulfamethoxazole with N-carbon and tetracycline with F,N-carbon. In the latter case, $^1\text{O}_2$ was the predominant oxidant and the best results were obtained for 100 mL of 10–100 mg L^{-1} tetracycline in pure water after 50 min of treatment with 20 mg L^{-1} PMS and 10 mg L^{-1} catalyst at pH = 3.0, which decayed with increasing pH up to 11.0. A clear effect of the aqueous matrix was found with the loss of degradation in the order: of pure water > tap water > river water > lake water (see Table 3), dependent on the nature and composition of their inorganic and organic components. The applicability of the catalyst was limited by the rapid decay in 30% of degradation after 5 consecutive cycles because of the adsorption of by-products formed, although it was recovered after regeneration by calcination. Moreover, 14 aromatic and 1 cyclic intermediates were detected by LC-MS.

Powerful and reusable carbonaceous materials should be searched for the treatment of large water volumes to potentiate their viability at an industrial scale.

3.6. UVC activation

UVC light with $\lambda = 200$ –285 nm has been applied to activate PMS for oxytetracycline (Varank et al., 2022), sulfamethoxazole (Wang and Wang, 2021), sulfamethoxazole and trimethoprim (Berruti et al., 2021), and tetracycline (Arslan-Alaton et al., 2021). The latter work also considered the activation with UVA light with $\lambda = 315$ –400 nm, which has been checked to degrade a mixture of antibiotics in a WWTP effluent by Guerra-Rodríguez et al. (2021).

The UVC light provides energy enough to photodecompose PMS into $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ following reaction (1). Fig. SM-10a shows the setup of a stirred cylindrical quartz photoreactor under 4 external 8 W UVC lights designed for the degradation of oxytetracycline to comparatively activate H₂O₂ or PMS (Varank et al., 2022). Fig. SM-10b and 10c make evident the superiority of UVC/PMS over UVC/H₂O₂ to remove the antibiotic. So, for 100 mL of 10 mg L^{-1} oxytetracycline in pure water with 4.0 mM PMS or H₂O₂ at pH = 7.0 lasting 45 min, the antibiotic decayed by 67% with $k_1 = 0.0175 \text{ min}^{-1}$ using PMS, much higher than 28% with $k_1 = 0.0052 \text{ min}^{-1}$ using H₂O₂ (see Table 3). Similarly, under optimum conditions, the electrical energy per order (E_{EO}) was 403 kWh $\text{m}^{-3} \text{ order}^{-1}$ for PMS, much lower than 774 kWh $\text{m}^{-3} \text{ order}^{-1}$ for H₂O₂. All these findings suggest that the treatments with PMS-based AOPs are preferable concerning conventional H₂O₂-based AOPs.

Interesting assays have been reported by Berruti et al. (2021) with an 80 L pilot flow plant with 6.21 L of volume irradiation under 230 W UVC irradiation operating in batch mode upon a liquid flow rate of 3.6 L h^{-1} . Complete degradation of 100 $\mu\text{g} \text{L}^{-1}$ of sulfamethoxazole and trimethoprim in wastewater effluent was achieved with 1.0 mM PMS in 90 min. This excellent result was supported with a low estimated annual energy cost in a continuous flow reactor of 0.63 € m^{-3} , corresponding 0.02 € m^{-3} only to the spent of the UVC lamp. This work demonstrates the good performance of the UVC/PMS process at the industrial level, which should be confirmed in further study.

Other works with light irradiation have been focused on taking advantage of visible light for the application of free and renewable sunlight, making the process more cost-effective. This requires the use of photocatalysts to promote the PMS decomposition, as will be discussed in the next subsection.

3.7. Photocatalytic activation

The photocatalytic activation of PMS has been mainly devoted to the irradiation with visible light at $\lambda > 400$ nm of suspensions containing a solid photocatalyst. The works described the behavior of amoxicillin,

ofloxacin, metronidazole, sulfamethoxazole, and tetracycline with Bi_2WO_6 /hematite (Li et al., 2022h), ciprofloxacin with $\text{CoFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ (Shi et al., 2021), $\gamma\text{-Fe}_2\text{O}_3\text{-MnO}_2$ (Zhao et al., 2021), BiVO_4 (Chen et al., 2022), CoAl-LDH/BiOBr (Liu et al., 2021) and Co doping ZnAl-LDH (Ma et al., 2023b), doxycycline with $\text{MFeO}_3/\text{SBA-15}$ (Zhao et al., 2022b),

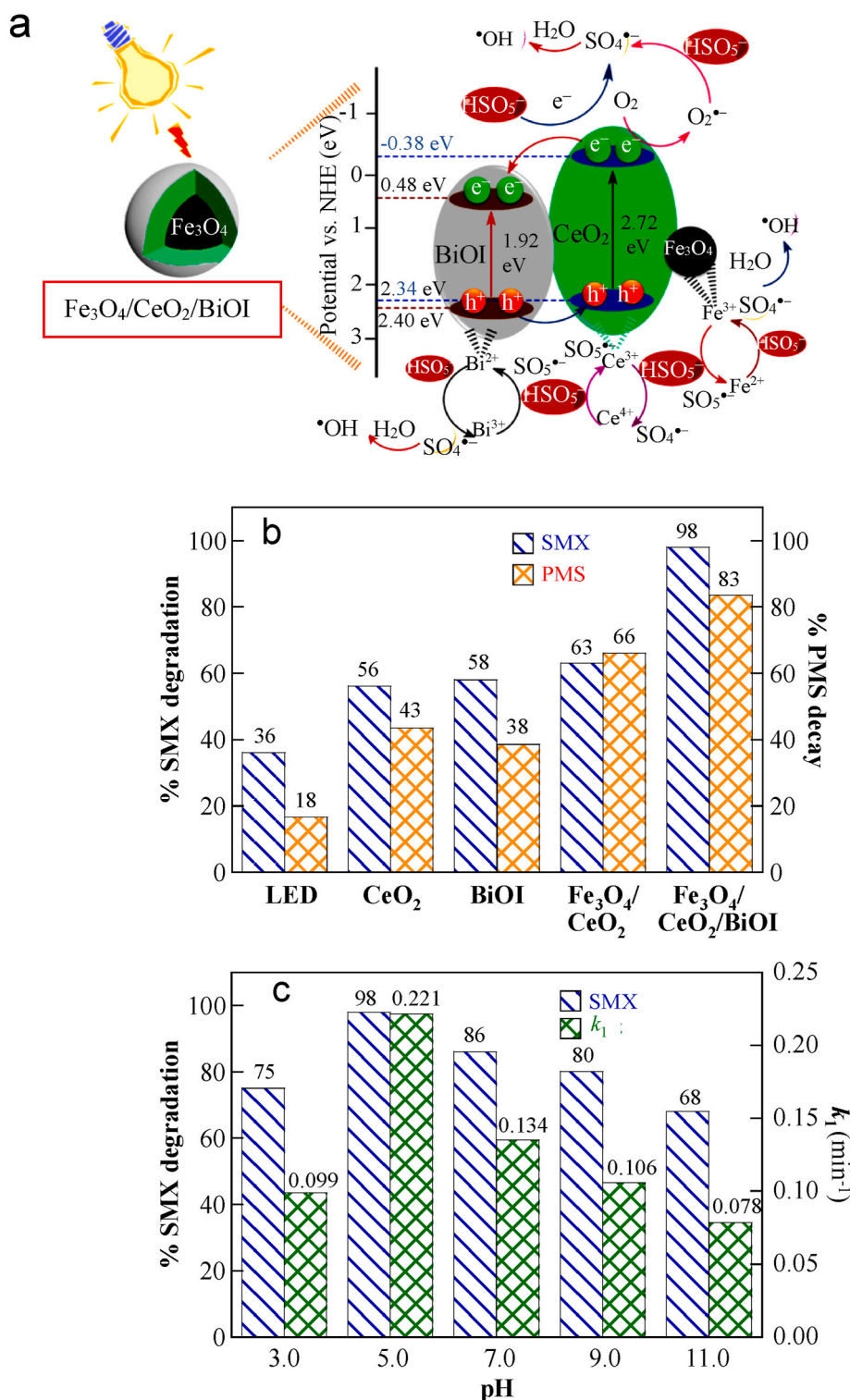
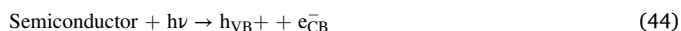


Fig. 4. (a) Schematic diagram of the integrated heterojunction mechanism proposed for the generation of oxidizing agents during the sulfamethoxazole degradation by PMS activated by $\text{Fe}_3\text{O}_4/\text{CeO}_2/\text{BiOI}$ photocatalyst upon UVA light. (b) Percentage of sulfamethoxazole (SMX) degradation and of PMS decay for the photocatalytic treatments of 20 mL of 0.05 mM antibiotic in pure water with 0.2 mM PMS and 0.1 g L⁻¹ of each photocatalyst at pH = 5.0 and room temperature for 15 min. (c) Effect of pH on the percentage of sulfamethoxazole content and the corresponding pseudo-first order rate constant upon the above conditions using the $\text{Fe}_3\text{O}_4/\text{CeO}_2/\text{BiOI}$ photocatalyst. Adapted from Kohantorabi et al. (2021) with permission 5657501329609 from Elsevier.

sulfamethazine with CuFeO₄/g-C₃N₄ (Sun et al., 2023), sulfamethoxazole with FeVO₄ (Zhang et al., 2021a) and K-carbon nitride (Tian et al., 2022b), and tetracycline with Cu/hematite (Guo et al., 2021), CuBi₂O₄/BiOBr (Dou et al., 2022), Bi₃O₄Br/CuBi₂O₄ (Tian et al., 2022a), Mo₂C/MoO_x (Lian et al., 2023), and Mo₂C/MoO₃ (Lian et al., 2023). Other studies have considered sunlight simulated with a Xe or LED lamp or direct sunlight ($\lambda = 300\text{--}800\text{ nm}$) to degrade ceftiofur with Ag/ZnO (Pugazhenthiran et al., 2023), ciprofloxacin with BiFe_{1-x}Cu_xO₃ (Wang et al., 2022a), levofloxacin with ZnFe₂O₄ (Zhong et al., 2021), norfloxacin with UV/hydrated Fe(III) oxide (Pan et al., 2022), sulfamethoxazole with TiO₂/CuCo₂O₄ (Mertah et al., 2022), and tetracycline with CoO/rectorite (Yi et al., 2021b) and MoO₃/Bi₂O₃/g-C₃N₄ (Alnagar et al., 2021). UVA light has been used for the treatment of sulfamethoxazole with Fe₃O₄/CeO₂/BiOI (Kohantorabi et al., 2021). Some papers have used a UVC light for the degradation of cefixime with ZnOCoFe₂O₄/CN (Tian et al., 2023).

A photocatalyst is a semiconductor material suspended in a polluted solution that upon light irradiation, suffers the promotion of an electron e_{CB}^- of its valence band (VB) up to its conduction band (CB). A hole h_{VB}^+ in the VB was then produced by reaction (44) (Brillas and Garcia Segura, 2023). The energy of the incident photons has to be higher or equal to the band gap energy (E_{bg}) of the semiconductor to make feasible the separation of charges with the formation of the e_{CB}^-/h_{VB}^+ pair. Typical photocatalysts such as TiO₂ and ZnO are effective under UVA light, the reason for which, new materials that can absorb the visible light have been checked to profit the overall wavelength of sunlight. The photo-generated h_{VB}^+ can directly oxidize the organics or react with water by reaction (45) or OH⁻ by reaction (46) to form the oxidant $\bullet\text{OH}$. For his part, the e_{CB}^- reduces O₂ to O₂⁻, and H₂O₂ to $\bullet\text{OH}$ from reactions (47) and (48), respectively. Furthermore, e_{CB}^- can attack PMS to form SO₄⁻ by reaction (41) and $\bullet\text{OH}$ by reaction (42). The efficiency of photocatalysis is limited by the fast recombination of the photoproduced h_{VB}^+ and e_{CB}^- by reaction (49).



Different mechanisms have been suggested to justify the kind and proportion of the oxidizing agents in the photocatalysts tested, as can be seen in Table 3. Fig. 4a schematizes the integrated heterojunction mechanism proposed to activate PMS with Fe₃O₄/CeO₂/BiOI photocatalyst (Kohantorabi et al., 2021). Apart from the separation of e_{CB}^- and h_{VB}^+ charges with their transfer between the CeO₂ and BiOI semiconductors and the reduction of O₂ to O₂⁻ from reaction (47), it is noticeable the decomposition of PMS to SO₄⁻ and $\bullet\text{OH}$ upon the action of the surface $\equiv\text{Fe}^{3+}/\equiv\text{Fe}^{2+}$, $\equiv\text{Ce}^{3+}/\equiv\text{Ce}^{2+}$, and $\equiv\text{Bi}^{3+}/\equiv\text{Bi}^{2+}$ pairs from the corresponding reaction (10) that enhances the antibiotic oxidation. Fig. SM-11a illustrates the complex mechanism proposed for the PMS activation in the CB of a BiVO₄ photocatalyst to finally produce ¹O₂ as the main oxidant, alongside the holes formed in its VB (Chen et al., 2022). Fig. SM-11 b shows the separation of charges of TiO₂ and CuCo₂O₄ photocatalysts before contact, and the heterojunction formed when contacted where the main oxidants were formed from reaction (47) and PMS decomposition with the participation of the surface $\equiv\text{Cu}^{3+}/\equiv\text{Cu}^{2+}$ and $\equiv\text{Co}^{3+}/\equiv\text{Co}^{2+}$ pairs (Mertah et al., 2022). In the case of CuBi₂O₄/BiOBr photocatalyst, Fig. SM-11c proposes the oxidation of OH⁻ to $\bullet\text{OH}$ with h_{VB}^+ in its VB from reaction (46) and the reduction of surface $\equiv\text{Cu}^{2+}$ to $\equiv\text{Cu}^+$ by the e_{CB}^- followed by the attack of PMS over $\equiv\text{Cu}^+$ to form SO₄⁻ with $\equiv\text{Cu}^{2+}$ regeneration (Dou et al., 2022)).

The treatment of 20 mL of 0.05 mM antibiotic in pure water has been tested with 0.2 mM PMS and 0.1 g L⁻¹ of single and combined Fe₃O₄, CeO₂, and BiOI photocatalysts at pH = 5.0 for 15 min upon UVA light (Kohantorabi et al., 2021). Fig. 4b depicts a maximum percentage of sulfamethoxazole degradation of 98% with a maximum PMS consumption of 83% when the combined Fe₃O₄/CeO₂/BiOI photocatalyst was applied because of the larger generation of the dominant oxidants SO₄⁻ and $\bullet\text{OH}$, as is shown in Fig. 4a. The effect of pH on the percentage of sulfamethoxazole content and the corresponding k_1 -value upon the above conditions with the Fe₃O₄/CeO₂/BiOI photocatalyst is presented in Fig. 4c. The maximum values (98% and 0.221 min⁻¹) were achieved at pH = 5.0, gradually decreasing up to pH = 11.0 due to the gradual loss of adsorption and reactivity of the negative form of sulfamethoxazole onto the negative surface of the nanostructured photocatalyst having a zero-charge potential = 6.5. The feasible viability of this catalyst for industrial application was confirmed by the good reproducibility found after 4 consecutive runs (see Table 3). The authors identified 14 degradation by-products by LC-MS as well.

The irradiation with Xe light mimicking sunlight yielded total sulfamethoxazole removal with TiO₂/CuCo₂O₄ photocatalyst (Mertah et al., 2022) due to the preferential oxidation with SO₄⁻, $\bullet\text{OH}$, and O₂⁻, as shown in Fig. SM-11 b. The experiments performed with 150 mL of 5 mg L⁻¹ antibiotic in pure water gave the best performance for 0.05 mM PMS and 250 mg L⁻¹ photocatalyst at pH = 5.9 for a long time of 360 min with a small $k_1 = 0.098\text{ min}^{-1}$ (see Table 3). An almost complete degradation has been described for tetracycline with CoO/rectorite photocatalyst (Yi et al., 2021b). The decay of 20 mg L⁻¹ antibiotic with 0.5 g L⁻¹ PMS and 0.3 g L⁻¹ photocatalyst at pH = 7.0 was slower than the above work, with $k_1 = 0.0459\text{ min}^{-1}$ (see Table 3). SO₄⁻, $\bullet\text{OH}$, O₂⁻, and holes were identified as oxidants, with moderate reproducibility losing 17% degradation after 4 successive steps. The LC-MS analysis of the degraded solutions allowed the detection of 7 primary aromatic by-products.

Further research should be focused on the implementation of direct sunlight irradiation to pilot plants with the development of stable photocatalysts to show their viability at a large scale. Techno-economic studies should also be made to benchmark their applicability with respect to comparative conventional methods, e.g., with H₂O₂.

3.8. Thermal activation

The simple heating of the antibiotic solution with PMS following the reaction (1) has been tested for sulfamethoxazole (Ulucan-Altuntas et al., 2022) and sulfamethoxazole (Milh et al., 2021). The thermal activation of tetracyclines has been studied with Fe,N-carbon (Xiao et al., 2022b). Milh et al. (2021) described 92% of sulfamethoxazole removal in 60 min with $k_1 = 0.045\text{ min}^{-1}$ for treating 900 mL of 10 mg L⁻¹ antibiotic in pure water with 0.4 mM PMS at optimum pH = 9.5 and 70 °C. Degradation was enhanced at higher temperatures and it was determined a small activation energy (E_a) of 36.9 kJ mol⁻¹. From specific scavengers, these authors calculated that the oxidation involved 59% with SO₄⁻ > 41% with $\bullet\text{OH}$ originated from reactions (2) or (3).

Although the PMS/heat processes presented a good performance for antibiotic abatement, their general use with large water volumes does not seem economically viable due to the excessive cost of the heating process. However, it could be directly utilized with hot waters and wastewater contaminated with antibiotics, thus obtaining a more cost-effective treatment, although this requires a deep study of the performance of each remediation process.

3.9. Electrochemical activation

Undivided electrochemical systems were used to activate PMS for cefadroxil, tetracycline and levofloxacin with a Ti/La₂O₃-PbO₂ anode and a stainless-steel cathode (Yu et al., 2022), chloramphenicol by electro-Fenton-like process (Li et al., 2023c), norfloxacin with graphite

or iron anode and a graphite cathode (Liu et al., 2022a), oxytetracycline with a Vo-MnO/C/Pt_xAu_{1-x} anode and a graphite cathode (Shen et al., 2023), sulfamethoxazole with a Pt anode and a C/Fe/nickel foam cathode (Tang et al., 2022), and tetracycline with a Cu-polyaniline-SBA-15/nickel foam anode, a carbon cathode, and a saturated calomel electrode (SCE) reference electrode (Ramírez-Hernández et al., 2021), a carbon plate anode, a S-Co/Ti cathode, and an Ag|AgCl reference (Tang et al., 2023b), and a Co@ZIF-8/CN-carbon felt anode and a Pt cathode (Xie et al., 2023a).

Fig. SM-12 shows examples of the two approaches developed for the electrochemical activation of PMS. A first arrangement corresponds to the use of a complex Vo-MnO/C/Pt_xAu_{1-x} anode (Shen et al., 2023). In this case, it is assumed that the cathode can reduce O₂ to O₂^{•−} via a similar reaction to (47), whereas at the anode, the surface ≡Pt⁴⁺/≡Pt²⁺, ≡Mn⁴⁺/≡Mn³⁺, and ≡Au³⁺/≡Au⁺ decompose the PMS to the main oxidants O₂^{•−} and ¹O₂ (see Fig. SM-12a). A 93% removal was reached for 10 mg L^{−1} oxytetracycline in pure water with 2.0 mM PMS at optimum pH = 9.0 and *j* = 10 mA cm^{−2} during 60 min after 30 min of adsorption in the dark (see Table 3). Similar degradation was determined with pure water, river water, underwater, and seawater, demonstrating the good oxidation ability of the system in different media. However, the reproducibility after 6 consecutive runs was rather low with a loss of 12% degradation. The authors detected 10 aromatic and 3 aliphatic by-products by LC-MS.

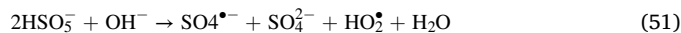
A second arrangement with a C/Fe/nickel foam cathode (see Fig. SM-12 b) considered the direct reduction of PMS at the cathode of the electrolytic cell to produce SO₄^{•−} and [•]OH by reactions (41) and (42), respectively, then generating O₂^{•−} and ¹O₂ from reactions (4)–(9) (Tang et al., 2022). The electrolysis of 100 mL of 10 mg L^{−1} tetracycline in pure water with 50 mM Na₂SO₄ and 0.65 mM PMS at pH = 4.0 yielded 96% degradation in 60 min with *k*₁ = 0.0972 min^{−1}. An excellent reusability was obtained after 10 consecutive steps and 6 heteroaromatic and 7 aromatic by-products were detected by LC-MS (see Table 3). Fig. SM-12c schematizes an electrolytic system with a more complex S-Co/Ti cathode that led to the electronic reduction of ≡Co³⁺ to ≡Co²⁺, PMS to SO₄^{•−}, [•]OH, and ¹O₂, and O₂ to O₂^{•−}, as well as the dissolution of Co⁴⁺ that acts as oxidant (Tang et al., 2023b). A complete abatement of 25 μM tetracycline in pure water was found for ≥1.0 mM PMS, pH ≥ 5.0, and by applying a cathodic potential (*E*_{cat}) ≥ 0.8 V in only 20 min (see Table 3). The oxidation power of the system was maintained by comparing the assays with pure water, surface water, and groundwater. An excellent reusability was determined after 5 successive steps.

Powerful electrochemical systems should be tested in flow pilot plants with appropriate anodes and cathodes for a good generation of oxidants from PMS to achieve fast and overall decontamination of water and wastewater polluted with antibiotics. These systems could be competitive with others composed of catalysts and photocatalysts, although their viability should be elucidated from comparative technoeconomic studies.

3.10. Other methods

Finally, PMS was activated to remove norfloxacin with calcite (Chu et al., 2021), and ordiazole with BaTiO₃/MoS₂ under piezocatalysis (Chen et al., 2021c). Hybrid methods were studied for levofloxacin with photo-Fenton-like process (Liu et al., 2022b), sulfadiazine with pulsed electro-oxidation and electrolysis (Ma et al., 2023a), and tetracycline with electrocatalytic Cu/carbon membrane filtration (Zheng et al., 2021) and photoelectroactive nanohybrid filter (Zhao et al., 2022c).

Calcite (CaCO₃) is a natural mineral that can decompose PMS to originate SO₄^{•−} from reactions (50) and (51), followed by the generation of O₂^{•−} from reaction (52). This species can then form ¹O₂ as the predominant oxidant from reaction (7) (Chu et al., 2021):



The treatment of 300 mL of 5 mg L^{−1} norfloxacin in pure water with 0.2 mM PMS, and 0.5 g L^{−1} catalyst at pH = 7.0 yielded 95% abatement in 50 min, with moderate reusability of calcite with loss of 17% degradation after 4 successive steps (see Table 3). This is an unexpected behavior since CO₃^{2−} has been reported as a scavenger of PMS-based AOPs. The low cost and abundance of this mineral suggest that it could be continuously added to large water volumes in continuous PMS treatment of antibiotic removal, a procedure that could be investigated in the future.

Chen et al. (2021c) proposed to activate the PMS decomposition via reaction (1) by supplying piezocatalysis of high energy to BaTiO₃/MoS₂. This method caused the production of e_{CB}/h_{VB} pairs that can react with PMS in a similar way to that described above in photocatalysis. Its effectiveness was demonstrated by the 92% degradation with *k*₁ = 0.0559 min^{−1} achieved in 40 min for 20 mL of 10 mg L^{−1} ordiazole in pure water with 0.25 g L^{−1} PMS and 0.1 g L^{−1} piezocatalyst at pH = 7.0. Note that this study has only an academic interest because its energy source does not seem viable in practice.

4. Change of toxicity of antibiotic waters during the PMS-based AOPs

The reuse of antibiotic waters is linked to the loss of their toxicity after PMS treatment. A high number of papers have reported the theoretically calculated relative toxicity of the by-products formed from several antibiotics, previously identified by LC-MS during the PMS treatment. So, the evolution of the solution toxicity can be predicted giving added value to the research. Several authors have described the use of a Toxicity Estimation Software Tool (T.E.S.T.) to determine the toxicity of the by-products of ciprofloxacin with ZnAl-LHD photocatalyst (Ma et al., 2023b), oxytetracycline with MoS₂ (Wang et al., 2023e) and B-biochar (Pan et al., 2023a) catalysts, and in a stirred undivided cell with a Vo-MnO/C/Pt_xAu_{1-x} anode and a graphite cathode (Shen et al., 2023), and tetracycline with Cu_xO catalyst (Tang et al., 2023c). Other authors have considered the Quantitative Structure-Activity Relationship (QSAR) software of T.E.S.T. to calculate the actual toxicity of the intermediates formed from ofloxacin with Co₃O₄ catalyst (Li et al., 2023b) and biochar from alkaline lignine (Miao et al., 2023), sulfamethoxazole with Fe/N-carbon catalyst (He et al., 2022) and CuFeO₄/g-C₃N₄ photocatalyst (Sun et al., 2023), and tetracycline with Bi₃O₄Br/CuBi₂O₄ photocatalyst (Tian et al., 2022a). Finally, the Ecological Structure Activity Relationships (ECOSAR) software has been applied to analyze the transformation products of chloramphenicol by combining PMS + H₂O₂ with hydroxylamine and γ-FeOOH (He et al., 2023a), doxycycline with CoO/MnO/WO₃ catalyst (Luo et al., 2022), sulfamethoxazole with CoMn-MOF/MgAl/LDH (Su et al., 2023) and Co₂P/biochar (Peng et al., 2021b) catalysts, and a stirred undivided flat square cell with a Pt anode and a C/Fe/nickel foam cathode (Tang et al., 2022), sulfathiazole with FeP/carbon catalyst (Wang et al., 2023g), and tetracycline with ferroferric oxide/charcoal (Zhou et al., 2022a) and carbonyl-carbon-coated Fe⁰ from MIL-100(Fe) (Yang et al., 2022f) catalysts.

A reduced number of papers have directly assessed the organism inhibition of the treated solution to show its change in toxicity. In general, the PMS-based AOPs detoxified the waters polluted with antibiotics as standard behavior, but the detoxification extent depends on the method used, experimental conditions, and treatment time. So, Hu et al. (2023) treated tetracycline and sulfamethoxazole solutions with PMS and Mn/N-g-C₃N₄ catalyst and found a low decay of the acute toxicity with *Daphnia magna* as a model freshwater crustacean. In contrast, a low antimicrobial activity for the gram-negative *Escherichia coli* and gram-positive *Staphylococcus aureus* has been shown for the residual components of tetracycline solutions treated with

PMS-activated with NiCo_2O_4 (Cong et al., 2022) and $\text{NiCo}_2\text{O}_4/\text{ZIF-67}$ (Pan et al., 2023b) catalysts, demonstrating the non-toxicity of the by-products formed. Similar results have been described by Wu et al. (2022b) for tetracycline upon degradation with PMS and magnetic carbon catalyst from the loss of microalgae toxicity measured with *Coelastrella* sp. Fig. SM-13a and b highlight the change of optical density (OD) determined at 600 nm for the growth of *Escherichia coli* and *Staphylococcus aureus*, respectively, in 100 mL of 5 mg L^{-1} levofloxacin in pure water at pH = 3.0 (He et al., 2021c). A total inhibition of both bacteria with OD₆₀₀ near zero can be observed by the initial solution (marked as LEV), which is strongly reduced with increasing OD₆₀₀ in the control solution after 30 min of treatment with 0.1 g L^{-1} PMS and 0.35 g L^{-1} Fe_2P /biocarbon catalyst, meaning the scarce toxicity of the by-products formed. The same behavior can be seen in Fig. SM-13c for the OD at 600 nm measured for *Escherichia coli* in 50 mL of $25 \text{ }\mu\text{M}$ tetracycline in pure water with $0.1 \text{ M Na}_2\text{SO}_4$ and 1.0 mM PMS at pH = 7.0 using a stirred undivided cell with a carbon plate anode, a S-CoO/Ti cathode, and an Ag|AgCl reference electrode at $E_{\text{cat}} = -0.80 \text{ V}$ (Tang et al., 2023b). This parameter grew with raising the electrolysis time, indicating the gradual generation of by-products that possessed less toxicity. Fig. SM-13c depicts the change of the relative growth of the Chinese abbage seeds *Brassica rapa* spp in 100 mL of pure water (control) and after 30 min of addition of 10 mg L^{-1} sulfamethoxazole, 0.5 mM PMS, and/or 0.1 g L^{-1} N-biochar catalyst from pomelo peel (Wang and Chen, 2022). While the growth of the bacteria was strongly inhibited after only adding the toxic antibiotic, it was enhanced in the presence of PMS and more slightly when the catalyst was added as an activator to degrade it, pointing to the production of non-toxic/toxic species.

5. Conclusions and prospects

It has been shown the effective removal of antibiotics from synthetic and real waters and wastewaters by PMS-based AOPs from recent work from 2021 to September 2023. Antibiotic degradation can occur via radical and non-radical mechanisms as established with the detected oxidizing agents. The acceleration/inhibition effect of common inorganic ions and the deceleration with specific scavengers and NOM have been widely assessed. The theoretical evolution of their toxicity from the identified by-products and/or the experimental total or partial loss of toxicity of the degraded solutions was sometimes determined. Some comparative assays with other weaker oxidants, preferentially PS and H_2O_2 , have also been reported. PMS seems more effective than PS in removing antibiotics, and both sulfate radical-based AOPs are superior to H_2O_2 . However, the feasible benefit of PMS-based AOPs as compared to these methods for their application to antibiotic decay has to be analyzed from techno-economic studies, which require assessment in the next research.

Most works over PMS-based AOPs have been performed at a bench scale that does not offer useable information for their applicability at a large scale. It is necessary to improve this experimental drawback in the future by analyzing the oxidation power and characteristics of such processes using flow pilot plants for the treatment of large volumes of natural and real wastewater. The degradation performance of the effluent mixed with the PMS solution should be examined at different flow rates, and the influence of the activator and its reusability should be analyzed to determine the best operating conditions. The optimum dosage of the solid iron, non-iron transition metal, biochar, and carbonaceous materials catalysts should be found and an appropriate procedure for their recovery and reuse should be established. This last task is simpler using magnetic materials because of their easy separation with an imant. No release of toxic ions should be confirmed during the process to ensure water reuse in the scaled-up at the industrial scale. Novel photocatalysts activated with free direct sunlight should be developed to improve the oxidation power and cost of PMS photosystems from the most favorable conditions for industrial application. Flow electrochemical pilot plants with potent and stable electrodes for generating

strong oxidants should be tested and compared with catalytic and photocatalytic PMS systems to benchmark their competitive use for antibiotic remediation. In all cases, the activators could also be checked at bench scale to confirm their good reusability, a requirement to do the assays of long duration.

Fe/N-carbon catalysts showed a good performance and reproducibility with dominant oxidation with $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$. About 80–90% of antibiotics were removed with composites of Fe_3O_4 or other iron oxides. Good reusability was only obtained for CuFe_2O_4 , whose viability should be tested at a pilot scale. Magnetic oxides like CoFe_2O_4 /biochar and Fe_3O_4 /Co/hydroxyapatite were also very stable. Among the MOFs derived with iron catalysts, $\text{Fe}_2\text{O}_3/\text{Mn}_3\text{O}_4$ was useful for the treatment of tetracycline, whereas other iron catalysts like Fe/NPS/carbon and FeOCl/hydroxylamine also offered good performance and stability.

High catalytic power has been reported for single transition metal oxides with Mn, Cu, Ni, and Co, alone or as composites. Lower oxidation ability has been shown by mixed transition metal oxide catalysts. A transition metal compound like $(\text{NH}_4)_{1.5}\text{Co}_x\text{Cu}_{2-x}\text{Cr}_2\text{O}_8(\text{OH})_{1.5}\text{H}_2\text{O}$ was useful for ciprofloxacin abatement. Good degradation results were also reported for some MOF-derived transition metal catalysts like Co/MOF with acceptable reusability. The use of a stable Co/MoS₂ catalyst at pH = 3.0 yielded an overall abatement of tetracycline.

Most biochars prepared by pyrolysis of natural organic matter were not useful for antibiotic remediation because of their low reproducibility, except that prepared from fish scales rich in P and N. Carbonaceous materials did not show good reusability as catalysts. A study with a magnetic N-carbon revealed a higher oxidation ability of PMS for removing tetracycline than PS and H_2O_2 . The degradation of oxytetracycline with UVC light as an activator also revealed the superiority of UVC/PMS over UVC/ H_2O_2 . Interesting work with an 80 L pilot plant demonstrates the applicability of UVC/PMS at the industrial level. Photocatalysts under light irradiation enable antibiotic oxidation with PMS, and further research with stable materials should be focused on the implementation of direct sunlight irradiation to pilot plants to show their viability at a large scale. Thermal activation is very effective for PMS decomposition but with a high cost of heating. Effective electrochemical PMS activation can be made at the anode and/or cathode of the electrolytic cell and these procedures should be tested in a flow pilot plant with stable electrodes.

A high number of papers have reported the theoretically calculated relative toxicity of the by-products formed using T.E.S.T., QSAR, and ECOSAR approaches. The experimental loss of toxicity during the PMS-based AOPs has been assessed from its impact on the growth of crustaceans, bacteria, or microalgae. While poor detoxification has been found for tetracycline and sulfamethoxazole using Mn/N-g-C₃N₄ catalyst, tetracycline solutions treated with NiCo_2O_4 and $\text{NiCo}_2\text{O}_4/\text{ZIF-67}$ catalyst or electrochemically with a S-CoO/Ti cathode were detoxified. Complete detoxification of levofloxacin solutions with Fe_2P /biocarbon catalyst was also found. These positive results allow proposing the reuse of detoxified antibiotic waters at least for agricultural purposes.

CRedit authorship contribution statement

Enric Brillas: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Juan M. Peralta-Hernández:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

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

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2024.141153>.

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