

Review

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# Perovskite and Spinel Catalysts for Sulfate Radical-Based Advanced Oxidation of Organic Pollutants in Water and Wastewater Systems

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Abstract: Since environmental pollution by emerging organic contaminants is one of the most important problems, gaining ground year after year, the development of decontamination technologies of water systems is now imperative. Advanced oxidation processes (AOPs) with the formation of highly reactive radicals can provide attractive technologies for the degradation of organic pollutants in water systems. Among several AOPs that can be applied for the formation of active radicals, this review study focus on sulfate radical based-AOPs (SR-AOPs) through the heterogeneous catalytic activation of persulfate (PS) or peroxymonosulfate (PMS) using perovskite and spinel oxides as catalysts. Perovskites and spinels are currently receiving high attention and being used in substantial applications in the above research area. The widespread use of these materials is based mainly in the possibilities offered by their structure as it is possible to introduce into their structures different metal cations or to partially substitute them, without however destroying their structure. In this way a battery of catalysts with variable catalytic activities can be obtained. Due to the fact that Co ions have been reported to be one of the best activators of PMS, special emphasis has been placed on perovskite/spinel catalysts containing cobalt in their structure for the degradation of organic pollutants through heterogeneous catalysis. Among spinel materials, spinel ferrites (MFe<sub>2</sub>O<sub>4</sub>) are the most used catalysts for heterogeneous activation of PMS. Specifically, catalysts with cobalt ion in the A position were reported to be more efficient as PMS activators for the degradation of most organic pollutants compared with other transition metal catalysts. Substituted or immobilized catalysts show high rates of degradation, stability over a wider pH area and also address better the phenomena of secondary contamination by metal leaching, thus an effective method to upgrade catalytic performance.

**Keywords:** perovskite; spinel; persulfate; peroxymonosulfate; sulfate radicals; advanced oxidation processes; water; wastewater

### 1. Introduction

The contamination of aquatic resources by both organic and inorganic compounds, especially by the most resistant or continuously emitted ones, is one of the most important environmental problems in recent years. Therefore, their presence on aquatic systems has led to the need for development of methods and technologies suitable for their degradation or removal and, consequently, the decontamination of aquatic media [1]. In recent years, advanced oxidation processes (AOPs) have emerged and started to be established as efficient technologies to decontaminate aquatic matrices by such pollutants as they can deal with the destruction of complex organic compounds that cannot be degraded or removed efficiently through conventional biological or other physicochemical processes. Essentially, AOPs rely on the activation of reactants or catalysts for the generation of highly effective free radicals (radical driven processes), in concentrations sufficient to oxidize partly or mineralize the great majority of emerging and persistent organic pollutants [2], such as pharmaceuticals, pesticides, flame retardants plasticizers, etc. as well as in the removal of inorganic compounds [3]. Most often AOP are applied to either convert these pollutants into substances exhibiting higher biodegradability and/or lower toxicity potential that can be removed by conventional methods and can be degraded easier in the environmental media. In some cases, a combination of the above outcomes may occur [4].

A great variety of AOPs have been developed in recent years that differ both in the methods employed for the formation of reactive oxidant species (ROS), as well as the type of these species. Photochemical [5], sonochemical [6], electrochemical [7], photocatalytic [8] and catalytic processes are among the most used-ones, leading to the formation of ROS, either directly or indirectly [9]. Lately, sulfate radical ( $SO_4^{\bullet-}$ ) based technologies, activating persulfate (PS,  $S_2O_8^{2-}$ ) or peroxymonosulfate oxidants (PMS,  $HSO_5^{--}$ ) have begun to gain ground in the scientific field of aquatic decontamination due to many attractive advantages in addition to well-known hydroxyl radical ( $^{\bullet}OH$ )-based technologies, such as the photo-Fenton method (Table 1), which has been until recent years the most widespread and widely used photocatalytic AOP for the activation of another oxidant, i.e.,  $H_2O_2$ .

As shown in Table 1, sulfate radicals exhibit better decontamination prospectives than hydroxyl radicals, which is not only attributed to the higher redox potential at circum-neutral pH (2.5–3.1 V for  $SO_4^{\bullet-}$  vs. 2.8 V for  $\bullet$ OH) but also to the higher half-life [9,10] as well as their formation in a broader pH range [11,12]. Finally,  $SO_4^{\bullet-}$  is a more selective reactant which may be used for the oxidation on specific functional groups bearing the toxicity action of the pollutant. It is a feature of  $SO_4^{\bullet-}$  which is not observed in the case of  $\bullet$ OH, as they react non-selectively in the major part of the cases through a series of reactions such as electron transfer, hydrogen atom abstraction etc. [13–15]. Based on all the above, it's clear that SR-AOPs emerge as promising decontamination technologies with increasing interest among the academic and industrial communities.

	SR-AOPs	Photo-Fenton
Radical species	$(SO_4^{\bullet -})$	(•OH)
Oxidation potential (V)	2.5-3.1	2.8
Selectivity	Reacts selectively	Reacts non selectively
Main reaction mechanism	Electron transfer	Electron transfer/Hydrogen atom abstraction
Half-life	30–40 μs	20 ns
pH range	2-8	2–4

**Table 1.** Comparison between sulfate radical based AOPs and hydroxyl radical based AOPs such as photo-Fenton process.

PS and PMS are the most used oxidants to produce  $SO_4^{\bullet-}$  and some basic properties will be presented below. The common commercialized form of PMS, the so-called Oxone<sup>®</sup>, a triple potassium salt of formula (2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>) [15], is easily dissolved in water as its solubility is greater than 250 g L<sup>-1</sup> (20 °C), is very stable in a broad pH range, non-toxic with a comparable cost to other chemical oxidants (e.g., oxone cost \$2.2 per kg vs. H<sub>2</sub>O<sub>2</sub> cost \$1.5 per kg) [16]. Although it is a relatively strong oxidant itself, (PMS oxidation potential 1.82 V), it cannot be used alone for the degradation of organic pollutants due to low reaction rates, thus an activation method is required [9]. Interestingly, for PMS two of the three sulfur-containing salts are practically inactive as they cannot take part in the activation pathways [3], while by PS activation, hydroxyl radicals are formed besides the sulfate radicals [17].

Unlike PMS, which has an asymmetrical structure, PS is an oxidant with a symmetrical structure [18]. The most common and stable form in which we can encounter persulfate ion is in the form of colorless or white crystalline salts, such as potassium-PS ( $K_2S_2O_8$ ), sodium-PS ( $Na_2S_2O_8$ ) and ammonium-PS [( $NH_4$ )<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]. In terms of their use in decontamination technologies, the most commonly used salt is sodium-PS ( $Na_2S_2O_8$ ) having greater solubility (730 g L<sup>-1</sup>, 25 °C)

than potassium-PS while the use of  $(NH_4)_2S_2O_8$  leads to secondary contamination due to ammonia formation [19]. In Table 2, some basic features of PS and PMS is resumed.

Properties	PMS	PS	References
Formula	HSO <sub>5</sub> -	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	
Structure	o <sup>-</sup> /s <sup>-</sup> o <sup>-</sup>		
Molecular weight (g/mol)	113.07 (614.738 as Oxone <sup>®</sup> )	192.12 (238.03 as sodium-PS)	
Solubility in $H_2O$ at 25 $^\circ C$	>250 1	730 <sup>2</sup>	[3]
Oxidation potential (V)	1.8	2.01	
O-O bond dissociation energy (kJ/mol)	377	92	[3]
O-O bond length (Å)	1.460	1.493	[20]
Preferred activation method	Activation via electron transfer (metal-catalysts and nanocarbons)	Activation via energy transfer (thermolysis, photolysis, etc.)	[21]

Table 2. Basic properties of PMS and PS.

<sup>1</sup> Refers to Oxone<sup>®</sup>; <sup>2</sup> Refers to sodium-PS.

#### 1.1. Activation of PMS and PS

PMS and PS activation may be accomplished by several methods such as transition metals, carbon catalysts, ultrasound (US), ultraviolet (UV), heat and electron conduction. Each method is based on a different activation mechanism for the formation of reactive intermediates. Among transition metal catalysts, this review study deals with the activation of PMS and PS with perovskite and spinel catalyst. Besides, carbon materials such as activated carbon, biochar, graphene oxide etc. are used frequently as metal-free materials for PMS activation. Carbonaceous materials have been widely used either/both as adsorbents and catalysts in different water and wastewater treatment applications due to their high specific surface area and pore volume.

Activation of PMS and PS using transition metal containing catalysts is more economical and simpler than the methods that require energy [20]. Catalysts that can be used as activators are either transition metals (Co, Mn, Cu, Ni, Fe, etc.) or their oxides in two different regimes, homogeneous and heterogeneous [9,22] which embodies different advantages and disadvantages, thus their applications is depending on the purpose-efficiency each time.

Figure 1 shows the general activation mechanism of PMS and PS and applies to both heterogeneous and homogeneous catalytic activation mechanisms. In the case of PMS, besides sulfate radicals, hydroxyl radicals are also formed. PMS can also react with the oxidized form of the metal, thus producing an additional oxidizing agent, sulfur pentoxide radical  $(SO_5^{\bullet-})$ , which can react also with organic pollutants although being less active (1.1 V) [17]. This is not observed in the case of PS, as it does not react with the oxidized form of the metal. The activation mechanism can be described with the help of the following reactions [11], in the case of PMS:

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

$$HSO_5^- + M^{n+} \to M^{(n+1)+} + SO_4^{2-} + {}^{\bullet}OH$$
 (2)

$$HSO_5^- + M^{(n+1)+} \to SO_5^{\bullet-} + M^{n+} + H^+$$
 (3)

and in the case of PS:

$$S_2 O_8^{2-} + M^{n+} \to M^{(n+1)+} + SO_4^{\bullet-} + SO_4^{2-}$$
 (4)

$$SO_4^{\bullet-} + M^{n+} \to M^{(n+1)+} + SO_4^{2-}$$
 (5)

$$S_2 O_8^{2-} + 2M^{n+} \rightarrow 2M^{(n+1)+} + 2SO_4^{2-}$$
 (6)

$$S_2 O_8^{2-} + M^{n+1} \rightarrow No \text{ radicals}$$
 (7)

Regarding studies carried out for the activation of PMS and PS in homogeneous systems, the results showed that in the case of PMS prevail cobalt ions  $(Co^{2+})$  [23], while in the case of PS, iron ions  $(Fe^{2+} \text{ and } Fe^{3+})$  have been shown to be more effective [3]. In general, compared to other metals, more emphasis has been placed on iron, which is less toxic, environmentally friendly and has a lower cost [24]. In addition, a comparison between iron ions showed that  $Fe^{3+}$  ions exhibit lower activity in PMS and PS activation than  $Fe^{2+}$  ions [25]. However, in the case of homogeneous systems, the additional stages required to remove metal catalysts can either increase the cost of the method or is difficult to be perform [26] while secondary contamination by metal ions is more probable. In addition, the efficiency of the process is highly affected by both pH and composition of the water with precipitation of metal ions in slightly acidic or basic conditions and their hydration in acidic conditions [22].



Figure 1. Schematic activation of (a) PMS and (b) PS by transition metals.

On the other hand, heterogeneous catalytic systems make use of solid catalysts in combination with different oxidants (e.g.,  $O_3$ ,  $H_2O_2$ , PMS) to achieve the degradation of organics and are able to overcome the above-mentioned drawbacks of homogeneous catalysis. Initially, the problem of secondary contamination of these metals is minimized as it is possible to recover and reuse the catalyst for several catalytic cycles, a fact that significantly reduces also the cost of the method [27,28]. Furthermore, heterogeneous systems can operate on a wide range of pH [20]. Besides, the performance of these systems depends on the properties of the materials used each time and is mainly affected by their surface properties [17]. Figure 2 shows the activation of PMS in both homogeneous and heterogeneous systems.



Figure 2. Schematic representation of PMS activation in (a) homogeneous and (b) heterogeneous system.

There are several review articles that have mentioned the various applications of SR-AOPs for environmental remediation [29,30], and as decontamination technologies for organic pollutants in aqueous systems [9,11,13,22,31] using various activation methods to degrade different organic pollutants such as pharmaceuticals, chlorophenols, plasticizers, chlorinated hydrocarbons, etc. [32–37]. Complementary, this review article focuses on the applications of perovskite and spinel materials as heterogeneous catalysts for the activation of PMS and PS towards the degradation of organic pollutants in water and wastewater systems.

#### 1.2. Perovskites and Spinel Catalysts

In recent years, among metal catalysts used for the activation of PMS and PS in decontamination technology, a particular interest has been placed on perovskites and perovskite-type materials. Perovskites have the simple chemical structure ABX<sub>3</sub>, where A and B are the metal cations and specifically A is the larger sized rare earth or alkaline earth metal and B is 3d transition metal, while X is an anionic group, usually oxygen [32,33]. Figure 3 shows the structure of a simple ABO<sub>3</sub> perovskite with A and B being the larger and smaller size cations and anion X, in this case oxygen, being the connecting link between the two cations. The structure of such perovskite is ideally cubic, with the larger A cations occupying the corners of this cube and the smaller B cations being at the center while the anionic groups are placed at the center of each side of the formed cube [38]. Depending on the metal cations rhombohedral, hexagonal, tetragonal and orthorhombic structures can be also formed [39].



Figure 3. Structure of (a) perovskite crystal and (b) spinel structure.

Perovskites can exist in various forms, from the simplest ones which are ABO<sub>3</sub> or  $A_2BO_4$  perovskites to the most complex structures such as  $A_2BB'O_6$  (double perovskite) or  $A_2A'B_2B'O_9$  (triple perovskite) [39]. The wide use of these materials lies mainly in the possibilities provided by their structure i.e., the insertion of various metal ions in the perovskite structure and the substitution of the

cations in positions A and B without destroying the perovskite structure. This interesting structure makes these materials able to incorporate more than 90% of the metallic elements present in the periodic table. By regulating the synthesis procedures and the ratios between the metal elements, it can be prepared a battery of perovskite materials which show significant differences in physicochemical and electrochemical properties.

As a result, perovskites display a variety of properties, such as optical and dielectric properties, ferroelectricity, superconductivity, catalytic activity, etc. and received wide applications in many different fields, such as sensors [40], electrochemistry [41], solar cells [42], fuel cells [43], adsorbents [44], magnetic and electrode materials [45] and catalysis [40,41].

There are several ways in which these materials can be synthesized, i.e., solid-state reactions, precipitation method, hydrothermal synthesis, sol-gel method, pechini method, low temperature solution combustion method, microwave synthesis, gas phase preparations [39]. Initially, various methods were used based on solid phase reactions that take place at high temperatures [46]. However, these methods have many disadvantages due to grinding and heating operations, either of metal oxides or their respective salts, which were carried out before the calcination step [47]. As a result, the final materials show an inhomogeneity or even incorporate various impurities into their structure. The synthetic method can be chosen depending on the needs of the perovskite application. For example, the sol-gel method is a widely used method for composing thin films at low temperatures, while in the case of hydrothermal synthesis we obtain perovskites in the form of crystalline powder without the need for further calcination step [48].

Spinels are also a category of materials with a great interest as catalysts. Normal spinels have a typical structure  $AB_2X_4$ , where  $A^{2+}$  ions occupy one eighth of the tetrahedral sites, while  $B^{3+}$  ions occupy one-half of the octahedral sites and X is an anion (typically O or F) closely packed within a face-centered cubic configuration. The structure is called after the mineral MgAl<sub>2</sub>O<sub>4</sub>, and oxide spinels have the generic formula  $AB_2O_4$ . Inverse spinels have a closely related structure where the A-site ions and half of the B-site ions switch places. Thus inverse spinels have the formula B(AB)O<sub>4</sub>, where the (AB) ions occupy octahedral sites and the other B ions are on tetrahedral sites. There are also mixed spinels, which are intervening between the normal and inverse spinel structure [49]. The metal sites can be substituted in lattice by different kinds of cations, which have low crystal field stabilization energies for octahedral and tetrahedral sites, so for this reason defects and non-stoichiometry of spinel structures is often observed [50]. Spinels commonly are formed in high temperature processes.

Among spinel materials, spinel ferrites nanoparticles (SFNPs), with the general formula MFe<sub>2</sub>O<sub>4</sub> (M = Fe, Cu, Co, Ni, etc.), are receiving more and more attention due to their excellent catalytic activity, the stable crystalline structure, the extremely low solubility and their easily magnetic separation. However, the catalytic applications of perovskite and spinel catalysts suffered from low specific area of these materials and thus for this reason their immobilization on porous supports is an effective method to upgrade their catalytic performance [51]. For example, ceramic membranes, metal-organic frameworks (MOFs), zeolite imidazolate skeletons (ZIFs) can be used [52]. Moreover, carbonaceous supports like graphene, activated carbon and chars provide a promising technique for the enhancement of many catalytic reactions as well as PMS activation for the degradation organic pollutants.

#### 2. Perovskite Catalysts for the Activation of PMS, PS and Degradation of Organic Pollutants

#### 2.1. Simple Perovskite Catalysts

As mentioned above, simple perovskites refer to those materials with ABO<sub>3</sub> structure and either A or B position in the perovskite structure can be substituted by a single element at time. Therefore, as there are many possible combinations, in this section we will focus firstly on perovskites with a fixed metal in position B and different elements in position A.

				Concentration		Treatment	Efficiency	
Catalyst	Synthesis Method	Pollutant	Catalyst (g L <sup>-1</sup> )	Pollutant (mg L <sup>-1</sup> )	PMS (mM)	% Degradation (Time)	TOC Removal	Reference
SrCoO <sub>3</sub>		phenol	0.2	20	0.1	100% (3 h)	-	
LaCoO <sub>3</sub>	citric acid sol-gol	phenol	0.2	20	0.1	95% (3 h)	-	[52]
BaCoO <sub>3</sub>	entre actu sol-ger	phenol	0.2	20	0.1	84% (3 h)	-	[55]
CeCoO <sub>3</sub>		phenol	0.2	20	0.1	80% (3 h)	-	
LaCoO <sub>3</sub>	precipitation method		0.22	5	5	100% (4.5 min)	-	
LaCoO <sub>3</sub> -CTAB	modified precipitation method	PBSA	0.22	5	5	100% (3.5 min)	-	[54]
LaCoO3-SiO2	aCoO <sub>3</sub> -SiO <sub>2</sub> single-stage hydrothermal		0.5	5	5	100% (30 min)	-	
LaCoO3-500		CBZ	0.05	5	0.5	100% (30 min)	-	
LaCoO3-600	sol-gel	CBZ	0.05	5	0.5	100% (30 min)	-	[55]
LaCoO <sub>3</sub> -700		CBZ	0.05	5	0.5	98% (30 min)	-	
LaCoO <sub>3</sub>	citric acid sol-gel	metazachlor	0.5	1	0.1	100% (<1 min)	-	[56]
LaCoO <sub>3</sub>	citric acid sol-gel	tembotrione	0.5	1	0.1	100% (<1 min)	-	
LaCoO <sub>3</sub>	citric acid sol-gel	tritosulfuron	0.5	1	0.1	90% (>90 min)	-	[56]
LaCoO <sub>3</sub>	citric acid sol-gel	ethofumesate	0.5	1	0.1	100% (<1 min)	-	
LaFeO <sub>3</sub> -500	sol-gel	DCF	0.1	7.5	0.5	100% (30 min)	-	
LaFeO <sub>3</sub> -600	sol-gel	DCF	0.1	7.5	0.5	80% (30 min)	-	[57]
LaFeO3-700	sol-gel	DCF	0.1	7.5	0.5	60% (30 min)	-	[57]
LaFeO3-900	sol-gel	DCF	0.1	7.5	0.5	20% (30 min)	-	
LaFeO <sub>3</sub>	sol-gel	DCF	0.6	7.5	0.3	100% (60 min)	50% (120 min)	[58]
aMnO <sub>3</sub> -3 bar-600	post synthesis	RhB	0.2	20	4.9	100% (45 min)	-	
LaMnO <sub>3</sub> -5 bar-600	post synthesis	RhB	0.2	20	4.9	100% (30 min)	-	
LaMnO <sub>3</sub> -8 bar-600	post synthesis	RhB	0.2	20	4.9	100% (45 min)	-	[59]
LaMnO <sub>3</sub> -5 bar-300	post synthesis	RhB	0.2	20	4.9	100% (45 min)	-	
LaMnO <sub>3</sub> -5 bar-900	post synthesis	RhB	0.2	20	4.9	100% (60 min)	-	
$La_{1.15}MnO_{3+\delta}$	complexing sol-gel	RhB	0.2	20	1.3	100% (40 min)	-	
LaMnO <sub>3+δ</sub>	complexing sol-gel	RhB	0.2	20	1.3	86% (40 min)	-	[60]
LaMnO <sub>3+δ</sub>	novel post synthesis	RhB	0.2	-	-	100% (30 min)		

Table 3. Overview of peroxymonosulfate (PMS) activation by different perovskite catalysts for the degradation of various organic pollutants.

Table	3.	Cont.	
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				Concentration		Treatment Efficiency			
Catalyst	Synthesis Method	Pollutant	Catalyst (g L <sup>-1</sup> )	Pollutant (mg L <sup>-1</sup> )	PMS (mM)	% Degradation (Time)	TOC Removal	Reference	
LaCoO <sub>3</sub> /ZrO <sub>2</sub>	Piccini (LaCoO <sub>3</sub> ) hydrothermal (ZrO <sub>2</sub> )	RhB	0.1	10	0.16	100% (60 min)	-	[61]	
23% wt LaCoO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	citrate sol-gel	ATZ	0.1	20	0.16	100% (30 min)	30.8% (30 min)	[62]	
LaFeO <sub>3</sub> /CeO <sub>2</sub>	citric sol-gel	AO7	0.1	20	0.5	59% (120 min)	28.4%		
LaFeO <sub>3</sub> /SiO <sub>2</sub>	citric sol-gel	AO7	0.1	20	0.5	52,3% (120 min)	26.3%		
LaFeO <sub>3</sub> /TiO <sub>2</sub>	citric sol-gel	AO7	0.1	20	0.5	32.2% (120 min)	8.1%	[63]	
LaFeO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	citric sol-gel	AO7	0.1	20	0.5	86.2% (120 min)	56.5%		
LaFeO <sub>3</sub>	citric sol-gel	AO7	0.1	20	0.5	70.8% (120 min)	40.7%		
LaFeO <sub>3</sub>	glycine combustion	RhB	0.1	10	0.16	70% (60 min)	-	[(4]	
LaCuO <sub>3</sub>	glycine combustion	RhB	0.1	10	0.16	90% (60 min)	-	[64]	
LaNiO <sub>3</sub>	glycine combustion	RhB	0.1	10	0.16	100% (60 min)	-	[(1]	
LaCoO <sub>3</sub>	glycine combustion	RhB	0.1	10	0.16	100% (60 min)	-	[64]	
LaFeO <sub>3</sub>	sol-gel	OFX	0.2	10	0.8	15% (30 min)	-		
LaMnO <sub>3</sub>	sol-gel method	OFX	0.2	10	0.8	90% (30 min)	-	[65]	
LaNiO <sub>3</sub>	sol-gel method	OFX	0.2	10	0.8	93% (30 min)	-		
PrBaCo <sub>2</sub> O <sub>5+δ</sub>	combined EDTA-citric acid	phenol	0.1	20	3.25	100% (15 min)	39.3% at pH 2	[66]	
$SrCo_{1-x}Ti_{x}O_{3-\delta} (SCTx, x = 0.1, 0.2, 0.4, and 0.6)$	combined EDTA-citric acid	phenol	0.1	20	3.25	100% (15 min) (SCT <sub>0.2</sub> )	82% (5h) (SCT <sub>0.2</sub> )	[67]	
SrCo <sub>0.6</sub> Ti <sub>0.4</sub> O <sub>3-δ</sub> @CoOOH	post-synthesis hydrothermal treatment method	phenol	0.06	20	3.25	100% (20 min)	-	[68]	
LaCo <sub>0.6</sub> Cu <sub>0.4</sub> O <sub>3</sub>	citric acid sol-gel method	phenol	0.1	20	0.32	99% (12 min)	30% (60 min)	[69]	
LaCo <sub>1-x</sub> Mn <sub>x</sub> O <sub>3+<math>\delta</math></sub> (LCM, x= 0, 0.3, 0.5, 0.7)	combined EDTA-citric acid	phenol	0.1	20	3.25	100% (20 min)	-	[70]	
$La_{0.4}Sr_{0.6}MnO_{3\text{-}\delta}$	EDTA-citric acid sol-gel method	phenol	0.2	20	6.5	100% (90 min)	70.1% (5 h)	[71]	
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	sol-gel	phenol	0.1	20	6.5	100% (30 min)	-	[72]	

			Concentration			Treatment	Efficiency	
Catalyst	Synthesis Method	Pollutant	Catalyst (g L <sup>-1</sup> )	Pollutant (mg L <sup>-1</sup> )	PMS (mM)	% Degradation (Time)	TOC Removal	Reference
$La_2CoMnO_{6-\delta}$	evaporation-induced self-assembly	ATZ	0.1	2	1	97% (30 min)	-	[73]
$LaFe_{0.8}Cu_{0.2}O_{3-\delta}$	$_{40.2}O_{3-\delta}$ citrate sol-gel ATZ		0.5	5	0.5	100% (60 min)	52% (120 min)	[74]
Ag-La <sub>0.8</sub> Ca <sub>0.2</sub> Fe <sub>0.95</sub> O <sub>3-δ</sub> /Al <sub>2</sub> O <sub>3</sub> sol-gel		MB	0.3	20	0.5	100% (45 min)	-	[75]
Ag-La <sub>0.8</sub> Ca <sub>0.2</sub> Fe <sub>0.94</sub> O <sub>3-δ</sub>	sol-gel (LCF) phase inversion/sintering (Ag-LCF)	MB	-	10	0.6	90% (75 min)	-	[76]
$La_{0.8}Ca_{0.2}Fe_{0.94}O_{3-\delta}$	sol-gel method	MB	1	10	0.4	84% (45 min)	-	[77]
$Ag-La_{0.8}Ca_{0.2}Fe_{0.94}O_{3-\delta}$	silver doping of La <sub>0.8</sub> Ca <sub>0.2</sub> Fe <sub>0.94</sub> O <sub>3-δ</sub>	MB	1	10	0.4	90% (45 min)	-	[, , ]
LaAl <sub>0.8</sub> Cu <sub>0.2</sub> O <sub>3</sub>	sol-gel	TAP	0.25	5	0.8	97.4% (30 min)	71.4% (30 min)	
	solvothermal	DCF	0.25	5	0.8	99.3% (30 min)	52.2% (30 min)	[78]
$LaAl_{0.8}Cu_{0.2}O_3$	solvothermal	IBF	0.25	5	0.8	93.8% (30 min)	59.2% (30 min)	[70]
	solvothermal	PR	0.25	5	0.8	97.7% (30 min)	42.3% (30 min)	
$La_{0.8}Sr_{0.2}CoO_{3-\delta}$	Combustion method	SMX	0.5	0.5	0.4	100% (45 min)	-	[79]

Table 3. Cont.

La<sub>0.8</sub>Sr<sub>0.2</sub>CoO<sub>3-δ</sub>Combustion methodSMX0.50.4100% (45 min)-[79]MB: Methylene Blue, PBSA: 2-pheryl-5-sulfobenzimidazole acid, RhB: Rhodamine B, SMX: Sulfamethoxazole, DCF: Diclofenac, CBZ: Carbamazepine, OFX: Ofloxacin, ATZ: Atrazine, AO7: Acid Orange 7, TAP: Thiarphenicol, IBF: Ibuprofen, PR: Paracetamol, SMX: Sulfamethoxazole.0.50.4100% (45 min)-[79]

#### 2.1.1. Co-Based Perovskites

Various metals such as  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$  and  $Co^{2+}$  have been used in position-B of simple perovskite structure, in order to activate PMS for the degradation of organic pollutants [20]. The most encouraging results in the literature concerned  $Co^{2+}$  [9,13], thus a great emphasis was placed on such perovskites. Originally, Hammouda et al. [53] studied the activity of ACoO<sub>3</sub> perovskites with La, Ba, Sr and Ce elements in position A, for the degradation and mineralization of phenol in wastewater systems. The synthesis of these perovskite catalysts was carried out with the citric acid sol-gel method [80]. The degradation rate of the pollutant followed the trend:  $SrCoO_3 > LaCoO_3 > BaCoO_3$ > CeCoO<sub>3</sub> with their respective degradation percentages being ~100%, 95%, 84% and 80% (Table 3). The authors studied the activation mechanism of PMS and the formation of active radicals, but mainly sulfate radicals, which were verified with the use of quenching agents. The efficiency differences between perovskite catalysts were attributed to differences in surface properties (BET surface area, pore volume and pore size) and cobalt content.

For the more efficient catalysts,  $SrCoO_3$  and  $LaCoO_3$ , the effect of operational factors such as catalyst concentration, PMS concentration and pH have been investigated. An increase in degradation rate was observed with an increase in the concentration of the catalyst, up to a point (0.3 g  $L^{-1}$ ), while further increase did not improve phenol degradation, a fact that was attributed to the suppressive effect of excess cobalt concentration. With regard to the effect of oxidant concentration, an increase in the degradation of phenol was observed, which reached both 100% for SrCoO<sub>3</sub> and 95% for LaCoO<sub>3</sub> within 30 min. Finally, regarding the effect of pH, it was observed that the maximum efficiency occurred at pH = 3 while decreasing continuously at higher pH values. Alkaline conditions may either inhibit the action of sulfate radicals with hydroxyl radicals being the dominant oxidants, or promote self-dissociation. They examined also the scenario of homogeneous catalysis, from the cobalt ions released into solution, and noticed that for this regime the degradation of phenol at pH = 3 was 37% and 48% for SrCoO3 and LaCoO3, in consistence to previous results showing that cobalt catalysts are not particularly stable in acidic conditions [13,81]. SrCoO<sub>3</sub> and LaCoO<sub>3</sub>, under optimal experimental conditions (PMS and catalyst concentration) and without pH adjustment, maintain their stability and performance even for five catalytic cycles, where after each catalytic cycle, the catalyst was filtered, rinsed with deionized water and then dried for 1h at 100 °C. Regarding on phenol degradation mechanism, a general mechanism of PMS activation was proposed on the basis of one-electron transfer process and it was pointed out that degradation can either take place on the surface of the catalyst, where the phenol has been adsorbed, or by sulfate radicals formed in the solution.

Finally, based on the identification of catechol, hydroquinone and benzoquinone as intermediate products, degradation pathways such as hydrolysis, hydroxylation and hydrogen atom abstraction reaction were proposed. Further oxidation led to the formation of short chain acids, such as oxalic, acetic and formic acid, in the final oxidation stages before mineralization of phenol.

Several other studies used LaCoO<sub>3</sub> as a typical perovskite catalyst for the degradation of various organic pollutants. Pang et al. [54] studied the degradation of 2-phenyl-5-sulfobenzimidazole (PBSA), an organic UV absorber, used in materials sensitive to UV radiation, which is classified as toxic; Solís et al. [56] studied the degradation of four types of herbicides, metazachlor, tembotrione, tritosulfuron and ethofumesate and more recently, Guo et al. [55] studied the degradation of carbamazepine pharmaceutical in aqueous solution.

In two out of the three cases, the synthesis of the catalyst LaCoO<sub>3</sub> was carried out with the citric acid sol-gel method while Pang et al. [54] studied the effect that the synthetic path had on the catalyst performance as they used three different methods for synthesizing LaCoO<sub>3</sub>. The first was a precipitation method (named as LCO), the second method is a variant of the precipitation method in which cetyltrimethylammonium bromide (CTAB) was used to produce a catalyst with a smaller particle size and a larger specific surface area (named as LCO-CTAB) and the third method was a single-stage hydrothermal process in which silica (SiO<sub>2</sub>) was introduced (named as LCO-SiO<sub>2</sub>).

On the one hand, Guo et al. [55] studied the effect of calcination temperature on the degradation of CBZ and they observed that an increase in temperature from 500 °C to 600 °C resulted in increased degradation while a further increase in temperature to 700 °C resulted in decreased efficiency of the catalyst. The reduced activity of the catalyst calcined at 500 °C was attributed to the appearance of a non-crystalline structure while in the case of 700 °C it was attributed to the presence of fewer active sites due to the lower BET surface area and pore volume.

Solís et al. [56] have studied the effect of pH on the degradation of herbicides as well as cobalt leaching. Maximum efficiency occurred in low pH ranges, between 3–5, with 100% degradation in just one minute for three of the four herbicides, metazachlor, tembotrione, and ethofumesate, while for tritosulfuron 100 min of reaction were required in order to achieve a degradation rate of 90%. The amount of cobalt released into the solution in this pH range reached a concentration up to 10 mg  $L^{-1}$ , which means that homogeneous catalysis had also a significant role in the degradation process. On the contrary, under neutral or basic conditions, a reduced release of cobalt into the solution and a reduced rate of degradation of these herbicides were observed. Similar results were observed in the degradation of CBZ by Guo et al. [55], i.e., increased degradation in acidic pH areas (higher at pH range 3–5) while further increase in alkaline areas led to reduced performance. In both cases this trend was attributed to the properties of the perovskite catalyst, the surface of which is positively charged in pH regions 3–5 and thus it is possible to adsorb PMS which is negatively charged.

Studying the effect of both oxidant and perovskite catalyst concentration, Solís et al. [56] conducted their study under pH = 7 in order to have a low rate of cobalt release. Regarding the concentration of PMS, they observed the rapid degradation of metazachlor, tembotrione and ethofumesate when the concentration level of PMS was  $5 \times 10^{-4}$  M, while 60 min were required in order to degrade tritosulfuron at a rate of 90%. Further increase in oxidant concentration had no effect on reaction performance. Similar results are observed in the degradation of CBZ by Guo et al. [55], i.e., an increase in degradation yield from 57.5% (30 min) to 100% in just 7.5 min with an increase in PMS concentration (0.1 mM to 1 mM). In addition, a positive effect of perovskite catalyst concentration on the process performance was monitored.

Guo et al. [55] studied also the effect of various inorganic ions as well as the organic matter present in the water matrix. Their results showed that in the case of CBZ degradation, ions such as  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and humic acid had little effect on the catalytic performance, whereas the presence of  $HCO_3^$ ions greatly affected the degradation rate. It was suggested that  $HCO_3^-$  ions can either scavenge the produced radicals [82], or they can be adsorbed on the perovskite surface due to electrostatic attraction, thus occupying the active centers for the generation of radical species [58].

As for the active radicals involved in the degradation of CBZ and herbicides, it appeared that both •OH and  $SO_4^{\bullet-}$  played an important role, with  $SO_4^{\bullet-}$  however having the dominant role. In addition, Guo et al. [55] suggested one electron transfer mechanism for the degradation of CBZ by LaCoO<sub>3</sub>/PMS system pointing out that oxygen vacancies can influence the interaction of LaCoO<sub>3</sub> and PMS, as also noticed elsewhere [66]. In addition, the generated radicals can react with CBZ either on the surface of the perovskite catalyst or in the solution. Finally, on the stability and reuse of the perovskite catalyst, Solís et al. [56] report that perovskite catalyst maintained its performance even after six catalytic cycles, while in the case of Guo et al. [55], the catalyst collected by centrifugation and washed with methanol and ultrapure water 60 °C overnight retained its catalytic activity for three cycles with a slight decrease in the fourth cycle. Finally, regarding the formation of transformation products and toxicity evolution along the degradation process of CBZ, they mentioned the formation of ten intermediate products, with much lower toxicity than the original compound, which proves that although the complete mineralization of CBZ into CO<sub>2</sub> and H<sub>2</sub>O did not take place, its disintegration into intermediate products with less toxicity was achieved.

As mentioned above, in the study of Pang et al. [54] the effect of synthetic method of  $LaCoO_3$  catalysts on the degradation of PBSA was examined. The synthetic method influenced the characteristics of perovskite catalyst with LCO showing higher values in terms of pore volume and pore diameter,

following by LCO-CTAB and LCO-SiO<sub>2</sub>. Both the introduction of cetyltrimethylammonium bromide (LCO-CTAB) and silica (LCO-SiO<sub>2</sub>) affected also the surface chemical properties of these catalysts by decreasing the surface oxygen vacancies, which can lead to reduced activity. However, LCO-CTAB showed the greatest activity (100% PBSA degradation in just 3.5 min), followed by the LCO (100% PBSA degradation in 4.5 min) and finally, the LCO-SiO<sub>2</sub> showing the lowest activity probably due to the contribution of homogeneous catalyzed-activation. The pH of the solution was fixed at about 2.5, thus large percentages of cobalt ion leaching were shown for LCO-CTAB and LCO, while the smallest percentage appeared in LCO-SiO<sub>2</sub>. Regarding the effect that pH had on the performance of these systems, it was observed that in all three cases, the performance of the system initially increases in the acid region and as evolved towards alkaline regions, it decreases.

Regarding the degradation mechanism of PBS in LCO/PMS, LCO-CTAB/PMS and LCO-SiO<sub>2</sub>/PMS systems, appropriate quenchers were used to determine the major oxidant species. In the cases of the LCO and LCO-CTAB catalysts,  $SO_4^{\bullet-}$  were principally formed, followed by the formation of  ${}^{\bullet}OH$  to a lesser extent. Importantly, in both cases, heterogeneous and homogeneous catalysis takes place, because of cobalt and lanthanum ion leaching. However, this is not observed in the case of LCO-SiO<sub>2</sub>, where only SO<sub>4</sub> ${}^{\bullet-}$  are formed though electron transfer mechanism. Moreover, due to the very low ion leaching rate observed in this case, the degradation of PBSA took place only by heterogeneous catalysis. The analysis of intermediate products formed during the degradation of PBSA showed that degradation pathways include benzene ring substitution by HO<sub>3</sub>SO<sup>-</sup>, hydroxylation, and dehydrogenation, i.e., pathways suggesting the synergistic action of SO<sub>4</sub> ${}^{\bullet-}$  and  ${}^{\bullet}OH$ . On the contrary, when LCO-SiO<sub>2</sub> is used as a catalyst, then a single degradation path of the pollutant dominated by SO<sub>4</sub> ${}^{\bullet-}$  is observed and only electron transfer process takes place.

#### 2.1.2. Fe-Based Perovskites

Although cobalt-based perovskites have been shown to be effective catalysts for the degradation of organic pollutants in water systems, it was deemed necessary to use less toxic and more environmentally friendly catalysts based on other metals [83]. This was due to cobalt ion leaching, resulting in secondary contamination as cobalt is classified as potentially carcinogenic [84]. An alternative to which scientists were led was the use of iron-based perovskite catalysts (named as LFO) and the up-to-date results of their applications for the activation of PMS and PS will be discussed below.

At first, Rao et al. [58] synthesized BiFeO<sub>3</sub> perovskite catalysts with a sol-gel method and studied the degradation of diclofenac (DCF), an anti-inflammatory drug that is constantly detected in the environment due to its widespread global use and the lack of effective methods for its removal [85]. Complete degradation of DCF was observed for LFO/PMS system in only 30 min, while in the case of BiFeO<sub>3</sub> 40% of DCF was degraded within the same time period. Investigating the mechanism of DCF degradation by LFO/PMS system, PMS activation by the active metal centers of the catalyst through covalent binding or by forming an inner-sphere complexation was proposed. In addition, using appropriate scavengers (*tert*-butyl alcohol (*t*-BuOH) for  $^{\circ}$ OH, methanol (MeOH) for SO<sub>4</sub> $^{\circ-}$  and  $^{\circ}$ OH), they pointed out that although SO<sub>4</sub> $^{\circ-}$  and  $^{\circ}$ OH radicals were formed, the ones that played the decisive role in the degradation were SO<sub>4</sub> $^{\circ-}$  radicals leading to 100% degradation of DCF along with the formation of 15 intermediate products. The main degradation pathways included decarboxylation, dechlorination, C–N cleavage, hydroxylation, intramolecular ring closure and benzene ring opening (Figure 4).



**Figure 4.** Schematic representation of simple perovskite catalyzed activation of PMS for the degradation of organic pollutants [53,54,58,59].

In another study, Rao et al. [57] studied the influence of various operational factors and the influence of catalyst's calcination temperature on catalytic activity. Both Fe(III) ions and hydroxyl groups located on the catalyst surface play a key role in the catalytic activity of LFO. Based on their experiments, the calcination temperature does not affect the oxidative state of Fe on the catalyst surface, but it does affect the number of hydroxyl groups on the catalyst surface. In particular, an increase in temperature from 500 °C to 900 °C had a negative effect on the amount of oxygen belonging to hydroxyl groups (OH) on the surface of LFO, as there was a decrease from 58.6% to 28.2% respectively, resulting in a decrease of LFO catalytic activity, with LFO-500 (calcination at 500 °C) being the most active catalyst for DCF degradation.

On the effect of various operational parameters, an increase of both PMS and LFO concentration up to a point (0.5 mM PMS and 0.6 g L<sup>-1</sup> LFO, respectively) resulted in increased degradation rates while a further increase in both cases led to an opposite effect. An excessive PMS concentration was found to act repressively as it can react with the formed sulfate radicals. In addition, increasing catalyst concentration did not led to the expected enhancement of DCF degradation. As has been reported by Zhang et al. [86], this may be due to restrictions from side reactions.  $HSO_5^-$  ions may dissipate more quickly towards the active centers of the catalyst than diclofenac, due to both their small size and the hydrophilic character of the catalyst's surface [87]. The formed sulfate radicals react with each other or with PMS, thus leading to an ineffective consumption of PMS, before even DCF reach the surface of the catalyst. As a result, quenching of the formed active radicals and a decrease in the degradation of diclofenac took place.

The effect of pH is related once more both with catalyst surface charge and PMS form. The fastest degradation was observed when pH was 7, as there were strong electrostatic forces between the positively charged surface of the catalyst and the negatively charged HSO<sub>5</sub><sup>-</sup> ions. In acidic conditions, there was a decrease in DCF degradation due to the possible neutralization of the negative charge of HSO<sub>5</sub><sup>-</sup> ions through the formation of a hydrogen bond between the O-O group of HSO<sub>5</sub><sup>-</sup> and hydrogen and thus reducing the interaction with the positively charged surface of the catalyst [86].

In experiments conducted to observe the effect of various inorganic ions, they observed that chloride, sulfate and nitrate ions had little effect on DCF degradation. However, this was not observed in the case of  $H_2PO_4^-$ . A significant decrease in DCF degradation occurred in the presence of these ions as they can be linked to Fe(III) on the catalyst surface and lead to the formation of inner sphere complexes. Finally, a toxicity study was carried out along with the degradation path of DCF. While the formation of toxic intermediate products was observed at the beginning, the following degradation steps led to ring opening and non-toxic organic acids of low molecular weight. As a final outcome,

LFO/PMS system was proposed for the degradation of pharmaceutical products and their simultaneous toxicity elimination.

#### 2.1.3. LaMnO<sub>3</sub> Catalyst

Another alternative to cobalt-based perovskites is manganese-based perovskites. In this category we will present two interesting and relatively recent studies that aimed to show ways to enhance the catalytic action of these materials without doping. The first research was presented by Miao et al. [59], who, after proposing a strategy to enhance the catalytic activity of perovskite catalysts, and in particular LaMnO<sub>3</sub> (LMO), by controlling the non-stoichiometry of oxygen in these materials, compared their catalytic action with that of the precursor material in relation to decomposition of rhodamine B (RhB) dye in aqueous matrix.

A post-synthesis treatment of these materials was carried out. Briefly, pristine LMO was synthesized via a glycine combustion method at different temperatures (first stage) and further treated in a high-pressure tube furnace at various oxygen pressures (second stage) resulting in final materials with different interstitial oxygen contents. In this way, the synthesized materials presented higher surface oxygen content and subsequently an increase in the concentration of  $Mn^{4+}$  ions than the original catalyst. Different temperature conditions (300, 600 and 900 °C) and oxygen atmosphere (3, 5 and 8 bar) were tested during their synthesis (Table 3). Better results were observed in the case of the LMO-5 bar-600 (oxygen atmosphere = 5 bar, calcination temperature = 600 °C), which also had the highest percentage of oxygen while all synthesized materials showed increased catalytic action in terms of RhB decomposition, compared to the pristine LaMnO<sub>3</sub> catalyst. The use of LMO-5 bar-600 catalyst achieved total decomposition of RhB in just 30 min through a non-radical pathway playing the major role in the decomposition mechanism [59] as confirmed by the use of suitable scavengers but also with the help of an electrochemical study. Based on their results, the participation of  $Mn^{3+}$  ions in the formation of sulfate radicals was not the main catalytic pathway but the formation of  $^{1}O_2$  by catalyst interstitial oxygen played the dominant role and the corresponding plausible mechanism was proposed.

Additional studies on the stability of these catalysts showed that the LMO-P-600 catalysts (P = 3 bar, 5 bar) showed the lowest percentage of manganese ion leaching, while the effect of the various ions present in aquatic systems was negligible. This is because the mechanism is based on generation of non-radical ROS, while these ions usually act as scavengers for the radical species. In addition, the catalytic action of the catalysts remained in a wide pH range (3–11). Finally, the degradation of RhB resulted in the formation of some intermediate products, which were identified by means of LC-MS, pointing out de-ethylation, chromophore cleavage (dominant pathway) and ring opening pathways.

In a more recent study conducted by Li et al. [60], the catalytic activity of different manganese-based perovskites by enhancing the oxygen vacancies amount towards RhB degradation was studied in different water systems. The catalysts synthesis was performed by means of a complexing sol-gel method which aimed at the non-stoichiometry of A and B cations, a different mindset from that previously mentioned by Miao et al. [59]. In particular, Li et al. [60] aimed at the synthesis of a manganese-based perovskite which would have a 15% excess of cation A, based on the assumption that the introduction of excess cation into the structure of the perovskite leads to the formation of more oxygen vacancies or to higher oxidative state of cation B, and as a result, the perovskite becomes oxygen deficient with a parallel increase in the ratio Mn<sup>3+</sup>/Mn<sup>4+</sup>. Therefore, the as-prepared La<sub>1.15</sub>MnO<sub>3</sub> catalyst showed a higher percentage of oxygen vacancies and an increased concentration of Mn<sup>3+</sup> ions, characteristics that contributed to the enhancement of its catalytic activity. Indeed, RhB was fully degraded in just 40 min compared to LaMnO<sub>3</sub> which, in the same time, achieved 86% degradation of RhB. Trying to explain the difference in the catalytic activity of the above materials, appropriate scavengers (furfuryl alcohol (FFA) for <sup>1</sup>O<sub>2</sub>, MeOH for SO<sub>4</sub><sup>•-</sup> and <sup>•</sup>OH and *tert*-butyl alcohol (TBA) for •OH) were used to determine which ROS were predominant in this process. Although sulfate, hydroxyl radicals and  ${}^{1}O_{2}$  appeared to be formed in the case of both the pristine perovskite and the La<sub>1.15</sub>MnO<sub>3</sub>, there was a major difference between them. Specifically, in the case of the La<sub>1.15</sub>MnO<sub>3</sub>/PMS, the generation of the ROS occured at a faster rate, while the dominant ROS in this case was  ${}^{1}O_{2}$  with sulfate and hydroxyl radicals having a smaller contribution. Regarding the process mechanism, electron transfer between the active surface centers of the catalyst (Mn<sup>3+</sup>/Mn<sup>4+</sup> and oxygen vacancies) and PMS was suggested. Finally, there was also a reduced rate of manganese ion leaching and a higher rate of degradation of RhB in the case of L<sub>1.15</sub>MnO<sub>3</sub> in relation to LMO.

#### 2.1.4. Various LaMO<sub>3</sub> Perovskite Catalysts

In this category we will present some examples in which different metal cations were introduced in position B of La-based perovskite and then a comparison of their catalytic activity was made regarding the degradation of organic pollutants with the activation of PMS. The first study was conducted by Lin et al. [64] who studied the effect of Co<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup> and Ni<sup>2+</sup> cations insertion on the perovskite's B-position in order to compare their catalytic activity for the activation of PMS and the degradation of RhB dye in aqueous solution.

The synthesis of LaMO<sub>3</sub> perovskites (M = Co, Cu, Fe and Ni) was carried out with the glycine combustion method. Although all catalysts have been able to activate PMS, better results have been obtained in the case of LaCoO<sub>3</sub>, which is consistent with above-mentioned results. Specifically, the catalytic activity followed the trend LaCoO<sub>3</sub> > LaNiO<sub>3</sub> > LaCuO<sub>3</sub> > LaFeO<sub>3</sub>. The catalytic activity of LaMO<sub>3</sub> is directly related to the cation (M = Co, Cu, Fe and Ni) of position B of the perovskite. The higher catalytic activity that occurred in the case of LaCoO<sub>3</sub> is mainly due to the possible formation of C<sub>0</sub>OH<sup>+</sup> intermediate, which has been reported as the most effective species for PMS activation [88] and the favorable cycle Co(III)/Co(II), which contribute to the activation of PMS. Therefore, this was the catalyst selected for further investigation of process operational conditions.

Both PMS and catalyst concentration (from 50 to 200 mgL<sup>-1</sup>) had a positive effect on this system. On the other hand, the effect of changing the pH on the system is more complex. Enhanced degradation was observed in acidic pH areas (3 and 5), with reaction rate being faster at pH = 5, while increasing the pH to alkaline areas had an inhibitory effect and in fact annihilation of the degradation was observed when pH = 11. The effect of Cl<sup>-</sup> ion addition showed a decrease in decolorization kinetics which is probably due to the reaction with sulfate radicals resulting in chlorine radicals which have a lower redox potential.

In order to shed light on the degradation mechanism of RhB, some scavengers (ascorbic acid as a universal radical inhibitor, MeOH for  $SO_4^{\bullet-}$  and  $\bullet$ OH and TBA for  $\bullet$ OH), have been used to examine which types of active radicals played a role. Based on their results, the formation of both sulfate and hydroxyl radicals was confirmed, although the first were those that played the decisive role. Cobalt ions, specifically the Co(III)/Co(II) cycle, and La<sup>3+</sup> ions contributed significantly to the activation of the PMS. Finally, LaCoO<sub>3</sub> catalyst showed increased stability as it was able to be used effectively for 7 catalytic cycles while maintaining high rates of RhB degradation.

The second study was few years later by Gao et al. [65] who used LaBO<sub>3</sub> catalysts (B = Fe, Mn, Ni) for the PMS activation and the degradation of ofloxacin (OFX) antibiotic in wastewater systems. The catalysts were synthesized using the sol-gel method. The catalyst that showed the greatest catalytic activity was LaNiO<sub>3</sub> with the order being LaNiO<sub>3</sub> > LaMnO<sub>3</sub> > LaFeO<sub>3</sub>. There was a direct correlation between the activity of the catalysts and the surface oxygen defects as they observed that the catalyst that showed the lowest activity, i.e., LaFeO<sub>3</sub>, had the lowest amount of oxygen defects, and similarly LaNiO<sub>3</sub>, which had the largest amount of oxygen defects, showed the highest activity (Table 3). Thus, LaNiO<sub>3</sub> was selected for further research. Using various scavengers [FFA for <sup>1</sup>O<sub>2</sub>, MeOH for SO<sub>4</sub><sup>•-</sup> and <sup>•</sup>OH, TBA for <sup>•</sup>OH and sodium azide (NaN<sub>3</sub>) for <sup>1</sup>O<sub>2</sub>], they concluded that the formed ROS that contributed to the degradation of OFX were hydroxyl radicals and <sup>1</sup>O<sub>2</sub> with the latter species playing the dominant role in OFX degradation. As a final outcome, OFX was completely degraded by LaNiO<sub>3</sub>/PMS system and to some extent (50%) mineralized. The catalyst was effectively used for five catalytic cycles maintaining high degradation rates of OFX while interestingly the process was not affected either by pH or by the presence of existing anions and natural organic matter (NOM).

Perovskite-based catalysts supported on porous supports, such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub> oxides, etc. are another interesting category for applications in sulfate radical-based processes. In this case, a larger surface area, as well as high thermal and chemical stability, i.e., reduced metal ion leaching, is usually achieved. The first example comes from Lin et al. [61] with the use of LaCoO<sub>3</sub> catalyst supported on ZrO<sub>2</sub> material for the degradation of organic pollutants by PMS activation. ZrO<sub>2</sub> was used as a support material because, in addition to all the above-mentioned advantages, it displays both acid and base properties and also does not interfere with the catalytic processes [89]. The support material was first synthesized using a hydrothermal method [90] and then added to the catalyst solution, which was synthesized with the Picini method [91] with 12.5% wt as the fraction of  $LaCoO_3$  on  $ZrO_2$  (LCZ). LCZ catalysts exhibited faster decoloration kinetics than LaCoO<sub>3</sub>. The optimized conditions for the decolorization of RhB have been examined. Both the increase of the oxidant's concentration as well as the catalyst's concentration resulted in an increase in RhB discoloration. Regarding temperature effect, increasing the temperature from 30 °C to 60 °C resulted in decolorization within 60 min and 10 min, respectively. In the case of pH, complete decolorization was observed in inherent pH of the solution (pH = 5). Further decrease led to a decrease in decolorization kinetics, due to the fact that the activation of the oxidant is slower in this area as Oxone<sup>®</sup> is more stable in relatively acidic conditions. In addition, increasing pH above 5, also led to a decrease in discoloration, either due to the inhibitory effect of OH<sup>-</sup> ions to Oxone<sup>®</sup> activation [92] or due to their deposition on the surface of the catalyst [93]. Regarding the study on the effect of co-existing compounds, it was observed that the presence of some salts (NaCl, NaF) in concentrations equal to this RhB, had minimal effect on the system performance. Similar results were observed in the case of anionic surfactants such as SDS. With the help of appropriate scavengers (ascorbic acid as a universal radical inhibitor, MeOH for  $SO_4^{\bullet-}$  and •OH and TBA for •OH), not only the significant contribution of sulfate and hydroxyl radicals was confirmed, but also the presence of some other ROS, such as  $HO_2^{\bullet}$ ,  $O_2^{\bullet}$  and  ${}^1O_2$ . These are some of the ROS that have been reported to be formed during the Oxone activation process [94]. Also, the Oxone® activation mechanism for RhB discoloration was attributed to either  $La^{3+}$  or  $Co^{3+}$  ions. Finally, they highlighted the enhanced performance of LCZ against LaCoO<sub>3</sub> and confirmed reuse of catalysts for four catalytic cycles maintaining the high rates of RhB decolorization.

Another example of a La-based perovskite catalyst was presented by Zhang et al. [62] which deposited LaCoO<sub>3</sub> (LCO) on a different support material, i.e., Al<sub>2</sub>O<sub>3</sub> and studied its catalytic activity towards atrazine (ATZ) herbicide degradation [95]. The catalyst synthesis was performed using the citrate sol-gel method [80] and the interest in this research is that different amounts of catalyst deposition were tested on the support material and their catalytic activity was studied. Increasing the amount of catalyst deposition in Al<sub>2</sub>O<sub>3</sub> increases the degradation rate of ATZ. Although the most encouraging results occurred in the case of 55% wt LaCoO3/Al2O3 (55LCA), the 23LCA catalyst was used for further study, which showed satisfactory ATZ degradation rates and very low percentages of cobalt leaching. In addition, high deposition rates of the metal catalyst in the support material could lead to the contribution of the homogeneous catalysis mechanism in the degradation of ATZ. Increasing catalyst and PMS concentration led to an increase in the degradation of ATZ while opposite results were observed with increasing concentration of ATZ. In addition, the change of pH also had a significant effect on the 23LCA/PMS efficiency. As in other scientific publications, the favorable pH reported was 5, while an increase or decrease beyond this value led to a decrease in ATZ degradation. The effect of various co-existing ions on the degradation of ATZ was also studied and it was observed that the presence of  $H_2PO_4^-$ ,  $CO_3^{2-}$  and  $HCO_3^-$  acted as inhibitors. However, the presence of Cl<sup>-</sup> ions had a different effect as they may have acted repressively in small concentrations due to the formation of radicals with lower redox potential ( $HClO^{\bullet}, Cl_2^{\bullet-}$ ) and contrary beneficially in higher concentrations (from 1 to 10 mM) due to the formation of chlorine species (HClO<sup> $\bullet$ </sup> and Cl<sub>2</sub><sup> $\bullet-$ </sup> converted to Cl<sup>•</sup>), with high redox potentials which can also lead to the formation of more sulfate radicals.

Regarding the stability of the catalyst, there was a gradual decrease in the degradation of ATZ during the use of the catalyst in three catalytic cycles. In addition, a degradation mechanism was proposed based on the identification of six intermediate products resulting from dealkylation, dechlorination-hydroxylation and alkyl chain oxidation reactions. During ATZ degradation, the formation of both hydroxyl and sulfate radicals took place, with the latter, as can be seen in Figure 5, being the main active type of radicals that contributed to the degradation mechanism as confirmed by the use of appropriate scavengers (EtOH for  $SO_4^{\bullet-}$  and  $\bullet$ OH and TBA for  $\bullet$ OH).



**Figure 5.** General catalyzed PMS radical activation mechanism by supported perovskites for the degradation of organic pollutants [61–63].

In the last example of this category we will refer to a recent study conducted by Wu et al. [63], which examined the role of various support materials (CeO<sub>2</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) on the catalytic activation of PMS by a classic Fe-based catalyst, LaFeO<sub>3</sub>, synthesized using the citric sol-gel method, towards Acid Orange 7 (AO7) degradation. LaFeO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was the one that showed the highest degradation rate with the rest of the supported catalysts showing percentages smaller than that of unsupported LaFeO<sub>3</sub>. Thus, it appeared the superiority of Al<sub>2</sub>O<sub>3</sub> as the LaFeO<sub>3</sub> support material with respect to the other materials used, mainly attributed to larger surface area, suitable redox property, plentiful chemisorbed surface-active oxygen and faster electron transfer compared to the others. In addition, lower iron ion leaching rates were observed in contrast to the relatively high lanthanum ion leaching rates (5.13 mgL<sup>-1</sup>). However, this amount of lanthanum did not significantly affect the degradation process as it mainly took place on the surface of the LaFeO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst while the Fe(II)/Fe(IIII) cycle was the one that contributed to the formation of the active radicals that led to dye degradation.

After studying the effect of pH on the LaFeO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>/PMS system and observing that the optimal performance occurs at pH = 3, then, using appropriate scavengers, it was confirmed that although sulfate and hydroxyl are formed during the degradation process of AO7, the latter are the ones that have the dominant role in the degradation mechanism. The proposed catalytic steps firstly involve the adsorption of the dye on the surface of the catalyst, then the formation of sulfate radicals on its surface through the Fe(II)/Fe(III) cycle and finally the AO7 degradation. Finally, LaFeO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst can maintain high degradation rates for two catalytic cycles while in the next three catalytic cycles (five in total), a decrease in its efficiency begins, which is probably due to ion leaching and the coverage of active sites from the intermediate products formed. However, the performance in each catalytic cycle is still higher than that of unsupported LaFeO<sub>3</sub>.

#### 2.3. Simple Substituted Perovskites

#### 2.3.1. Substituted in Position B Perovskites

Miao et al. [67] studied the Ti-doping of perovskite  $SrCoO_{3-\delta}$  in order to enhance its catalytic activity for the degradation of phenol through PMS activation in water matrices. The synthesis of  $SrCo_{1-x}TixO_{3-\delta}$  series of catalysts (SCTx, x = 0.1, 0.2, 0.4, and 0.6) was performed by a combined EDTA-citric acid complexing sol-gel method and a comparison was made between these catalysts and  $Co_3O_4$  spinel. Among these catalysts, the greatest catalytic activity was displayed by the SCT0.2/PMS system, allowing complete degradation of phenol in just 15 min with the series being SCT0.2/PMS > SCT0.1/PMS > SCT0.4/PMS > SCT0.6/PMS, while the  $Co_3O_4$ /PMS system showed an even lower catalytic activity than that of substituted perovskites. However, due to the fact that a correlation was found between the Ti fortification in the structure of perovskite and cobalt ion leaching, and specifically a high percentage of Ti led to a decrease in cobalt ion leaching and phenol oxidation rate, SCT0.4 was used for further study of the effect of various experimental conditions.

A positive correlation was found between the increase of catalyst, oxidant concentration, temperature and phenol degradation. However, the opposite effect had the increase in the concentration of phenol while pH variation seemed to affect both the number of active radicals in the system and metal ion leaching. The authors observed that maximum system performance occurred at pH = 7, with complete degradation of phenol reached at just 10 min. Finally, regarding the mechanism of reaction, it was reported that the Co(II)/Co(III) cycle contributed to the activation of PMS leading to the formation of the active species  $SO_4^{\bullet-}$  and  $\bullet OH$ , with the latter being produced and participated to a lesser extent in phenol degradation.

Another interesting example, concerning SCT, was also presented by Zhu et al. [68], who synthesize the perovskite catalyst  $SrCo_{0.6}Ti_{0.4}O_{3-\delta}CoOOH$  (SCT@CoOOH) and examined its activity in terms of phenol degradation and its ability to activate PMS. The synthesis of this SCT@CoOOH took place in two stages. In the first stage, the original SCT catalyst was synthesized through a combined EDTA-citric acid sol gel method and then the post-synthesis hydrothermal treatment followed to receive the final SCT@CoOOH. In this way, the in-situ growth of CoOOH nanoflakes (NFs) on the perovskite surface was achieved. This led to changes in the surface of perovskite, faster electron transfer and an abundance of oxygen defects, elements that helped to enhance the catalytic activity. In the case of SCT 35 min are required for complete phenol degradation while in the presence of new SCT@CoOOH catalyst phenol was completely degraded in just 20 min showing one of the best heterogeneous catalyst yields for phenol degradation. In addition, increased stability of the catalyst was shown with reduced metal ion leaching rates and enhanced activity on both neutral and alkaline pH range. Regarding on the effect of various ions (HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>), NO<sub>3</sub><sup>-</sup> ions did not presented any effect on the system, HCO<sub>3</sub><sup>-</sup> showed an inhibiting role while Cl<sup>-</sup> ions contributed to the enhancement of the catalytic activity. Finally, it was reported that the catalytic mechanism of phenol degradation by the SCT@CoOOH/PMS system was carried out through two different paths. In the first one, formation of SO<sub>4</sub><sup>•-</sup> and •OH radicals took place, with sulfate radicals being characterized as the dominant ROS, while the second-one, the non-radical path, proceeded through the formation of  ${}^{1}O_{2}$  from surface oxygen vacancies.

Lu et al. [69] focused on the synthesis of perovskite with different Cu contents  $LaCo_{1-x}Cu_xO_3$  (x = 0.2, 0.4, 0.6, 0.8) for the degradation of phenol and other organic pollutants through activation of PMS. Synthesis of perovskite was carried out by citric acid sol-gel method and the predominance of  $LaCo_{0.6}Cu_{0.4}O_3$  was observed not only over the rest of the substituted perovskite catalysts, but also over pristine heterogeneous cobalt-based perovskite catalysts, as 99% of phenol degradation was achieved in just 12 min. In addition, the low rate of cobalt ion leaching ( $Co^{2+} = 1.37 \text{ mgL}^{-1}$ , which corresponds to 1.37%) was also mentioned, which was the lowest among cobalt-based perovskite catalysts.

Regarding the effect of various parameters on the degradation of phenol by  $LaCo_{0.6}Cu_{0.4}O_3/PMS$  system, an enhancement was shown in cases where the temperature of the system and the concentration

of catalyst and PMS were increased. In the case of pH, the performance of the system was enhanced in the pH range 4.6–9.0 as once again important role played the form of the oxidant and the form of the catalyst's surface. Finally, various scavengers (EtOH for  $SO_4^{\bullet-}$  and  $\bullet OH$ , TBA for  $\bullet OH$  and L-histidine for  $^1O_2$ ) were used to determine which active species contributed to the degradation of phenol. As a result, the formation of  $SO_4^{\bullet-}$  and  $\bullet OH$  and  $^1O_2$  as ROS was observed, while it was also reported that the combination of redox pairs Co(II)/Co(III) and Cu(I)/Cu(II) played an important role in the activation of PMS. Finally, the catalyst  $LaCo_{0.6}Cu_{0.4}O_3$ , collected by filtrationand washed with deionized water, was able to degrade phenol even after four catalytic cycles, although there was a decrease in its performance of about 20% after the second catalytic cycle.

A series of nanostructured Co-Mn perovskite catalysts,  $LaCo_{1-x}Mn_xO_{3+\delta}$  (LCM, x = 0, 0.3, 0.5, 0.7), have been synthesized by Miao et al. [70] in different calcination temperatures with over-stoichiometric oxygen and used to degrade organic pollutants through PMS activation. The greater catalytic activity was shown by pristine LaCoO<sub>3</sub> catalyst, while the lowest activity was observed by LaMnO<sub>3</sub> catalyst. This was attributed on the activity of the metal in position B and Co was found more active than Mn. For the substituted perovskite catalysts, the order of activity followed the trend: LaCo<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3+\delta</sub>-900 °C (LCM55-900) > LCM73-900 > LCM37-900. The authors suggested a correlation between interstitial oxygen and the catalytic activity of these perovskites as an appropriate amount of these groups promotes electron transfer. Regarding the catalytic mechanism, redox pairs Co(II)/Co(III) and Mn(IV)/Mn(III) were involved in the activation of PMS by LCM55-900, while the formation of SO<sub>4</sub><sup>•-</sup> and •OH was observed as the active species that contributed to its degradation, with sulfate radicals being the predominant species.

A significant effect on the LCM55-900/PMS system was observed to have both pH and the presence of natural organic matter (humic acid, HA) and inorganic ions. At neutral pH, the maximum catalytic activity and low rates of cobalt ion leaching occurred. The presence of increased Cl<sup>-</sup> ion concentration led to enhanced degradation while on the contrary, the presence of HA acted as an inhibitor. Nevertheless, the LCM55-900 catalyst appeared effective for four catalytic cycles, although there was a slight decrease in the third and fourth cycles. Finally, LCM55-900 catalyst is reported to be effective towards the degradation of other organic pollutants such as dyes and pharmaceutical compounds.

Wang et al. [74] studied the synthesis of Cu-doped LaFeO<sub>3</sub> catalyst, LaFe<sub>1-x</sub>Cu<sub>x</sub>O<sub>3- $\delta$ </sub> (LFCx, x = 0.1, 0.2, 0.3, 0.4, 0.5), for the degradation of atrazine by PMS activation. The increase in copper content in the perovskite catalyst led to an increase in the creation of oxygen vacancies and a decrease in crystallite sizes. All LFCx catalysts showed enhanced atrazine degradation activity relative to the pristine LaFeO<sub>3</sub> catalyst but on the other hand increased Cu leaching is also detected. Although that both heterogeneous and homogeneous activation of PMS took place, the latter contributed to a very small extent. Combining both the performance of each catalyst and the percentages of metal ion leaching as well as the contribution of homogeneous activation, they resulted in the use of  $LFC_{0.2}$  for further study. Regarding the effect of the various factors on the LFC<sub>0.2</sub>/PMS system, the increase in the catalyst's concentration acted was beneficial while the increase in the oxidant's concentration had a positive effect up to a certain degree with further increase provoked an opposite effect. Increased catalytic activity was observed in the pH range 2–10, while catalytic efficiency did not fall below 90% even in the fourth catalytic cycle showed the enhanced stability of the catalyst. Regarding the mechanism of PMS activation and degradation of atrazine, the formation of  $SO_4^{\bullet-}$  and  $\bullet OH$  was reported and Fe(III), Cu(II) acted as the active metal centers of the catalyst while the reduction of Fe(III) by Cu(I) promoted the formation of the active radicals. In addition, the presence of oxygen vacancies contributed to the low oxidation state of Fe and Cu, thus favoring the transfer of electrons to PMS for the formation of ROS, as can be seen in Figure 6. Finally, twelve by-products were identified during the degradation of atrazine, denoting a degradation mechanism with four different paths, dechlorination-hydroxylation, alkyl-hydroxylation/oxidation, dealkylation and deamination-hydroxylation.

Oxygen Vacancy

Active Oxygen



Singlet

oxyger

Figure 6. General mechanism of the substituted perovskites for the degradation of organic pollutants via two different (radical and non-radical) pathways.

Non-Radical

pathway

Radical

pathway

In a recent study done by Chen et al. [78], the synthesis of 3D-hollow sphere-like Cu-incorporated LaAlO<sub>3</sub> and application for the activation of PMS and degradation of pharmaceutical substances, namely thiamphenicol (TAP), diclofenac sodium (DCF), ibuprofen (IBF) and paracetamol (PR), was studied in water and wastewater systems.  $LaAl_{1-x}Cu_xO_3$  materials, where x = 0, 0.1, 0.2, 0.3, 0.4, were prepared through a solvothermal (ethylene glycol) process. The catalyst that showed the greatest activity in terms of pharmaceutical degradation was LaAl<sub>0.8</sub>Cu<sub>0.2</sub>O<sub>3</sub> (LAC82O), whose activity appeared greater than that of unsubstituted LAO. The authors choose the synthesis of a perovskite catalyst with hollow architecture because such structure exhibit attractive physico-chemical properties compared to solid particles due to large specific surface, pore structure and low mass transfer resistance. On the other hand, the choice of Cu incorporation in the structure of perovskite was made because it leads to a uniform dispersion of spherical particles, which enhances the interaction of the catalyst with the contaminant compounds. As an outcome LAC82O/PMS system degraded the four pharmaceutical compounds TAP, DCF, IBF and PR at 97.4%, 99.3%, 93.8% and 97.7% respectively, in just 30 min. Other oxidants, such as  $H_2O_2$  and PDS, were also used to degrade TAP, however the catalyst had a lower activity to activate these two oxidants than PMS. In addition, the effect of different parameters in the LAC82O/PMS/TAP catalytic efficiency was studied. As in previous cases, an increase in oxidant and catalyst concentration led to increased TAP degradation due to larger amounts of active centers and generated radicals. An opposite effect had the presence of natural organic matter (NOM), specifically humic acid (HA), and the presence of inorganic ions (HCO<sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>) as they quench the formed radicals leading to the creation of lower redox potential radicals. Regarding the catalytic mechanism, the transfer of electrons and redox cycle Cu(II)/Cu(I) as well as the presence of oxygen defects (ODs) played an important role for the activation of PMS and the entailed formation of active species ( $SO_4^{\bullet-}$ , •OH and  ${}^{1}O_{2}$ ). Finally, on the reuse of the catalyst, encouraging results were observed due to its increased stability and low copper leaching rate, which led to effective use for 5 catalytic cycles.

#### 2.3.2. Substituted in Position A Perovskite Catalysts

Miao et al. [71] focused on substituting the position A of perovskite LaMnO<sub>3</sub> by Sr<sup>2+</sup> ions in order to enhance its catalytic activity.  $La_{0.4}Sr_{0.6}MnO_{3-\delta}$  (LSMO46) was prepared via a complexing EDTA-citric acid sol-gel method and it was evaluated for phenol degradation via PMS activation in wastewater systems. For the maintenance of electrical neutrality after the substitution of position A by  $Sr^{2+}$  ions the creation of oxygen vacancies, and/or an increase in the oxidation state of the cation in position B can be observed. Enhanced performance of LSMO46 was observed as complete degradation of phenol took place at 90 min while in the case of LMO the degradation reached 82.1% within the

same time period. In addition, a relatively reduced percentage of metal ion leaching was also observed, contributing to the stability of the catalyst. This was shown by the successful use of LSMO46 for 5 catalytic cycles, where the catalyst was easily separated and washed off several times with ethanol and deionized water, with the efficiency maintained above 90% in the first two cycles but falling to 55% in the last-one. Regarding the mechanism of this reaction, it was reported that the redox pair Mn(III)/Mn(IV) participated in the activation of PMS, while in addition to the formation of SO<sub>4</sub><sup>•-</sup> and •OH, oxygen vacancies created by doping of Sr<sup>2+</sup> contributed to the creation of another ROS,  $^{1}O_{2}$ , which also played a decisive role. This was also confirmed by the wide pH range in which the catalyst was active, as singlet oxygen are not affected by pH, but also by the fact that the LSMO46/PMS system was not affected by co-existing anions, other than HCO<sub>3</sub><sup>-</sup> as well as HA.

Han et al. [75] focused on the synthesis of a perovskite with calcium doping in position A and cation deficiency in position B. Thus, the synthesis of Ag-La<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.95</sub>O<sub>3- $\delta$ </sub> (LCFA) via a sol-gel method and the immobilization of catalyst on Al<sub>2</sub>O<sub>3</sub> support was carried out in order to address also the problem of potentially secondary contamination by the use of powder catalysts. The LCFA/Al<sub>2</sub>O<sub>3</sub>/PMS system was used for the degradation of methylene blue (MB) and the effect of various factors on the catalyst activity and the performance of this system were studied. A complete degradation of MB from the LCFA/Al<sub>2</sub>O<sub>3</sub>/PMS system was observed in just 45 min, while an increase in the catalyst's concentration, reaction temperature and pH (from 7–9) had a positive effect. In addition, an unsurprisingly decrease in the metal ion leaching was observed via the immobilization of catalyst on Al<sub>2</sub>O<sub>3</sub> support. LCFA catalyst could not be used for several catalytic cycles as there was a significant decrease in its performance during the third catalytic cycle (degradation percentage of 55.7% in the third catalytic cycle) which was attributed to contamination of the active centers by intermediate products. However, the authors reported that the catalyst was effective in the degradation of other organic pollutants as the complete degradation of Rhodamine B (RhB) and the degradation of tetrabromobisphenol A (TBBPA) with 40% of degradation achieved in one hour. This enhanced catalytic activity of LCFA was attributed to redox cycle Fe(II)/Fe(III), to the enhancement of electron transfer between the catalyst and PMS, as doping of nanosized silver particles resulted in improved conductivity of the catalyst, and the presence of oxygen vacancies created by the substitution of Ca. Finally, by using electron paramagnetic resonance (EPR), it was reported the formation of  $SO_4^{\bullet-}$ ,  $\bullet OH$  and  $^1O_2$  ROS.

A similar example of perovskite catalyst was also used by Ma et al. [76], who synthesized perovskite Ag-La<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.94</sub>O<sub>3- $\delta}$ </sub> (Ag-LCF) for the purpose of degrading methylene blue (MB), through heterogeneous activation of PMS. Initially, La<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.94</sub>O<sub>3- $\delta$ </sub> (LCF) was synthesized by sol-gel method and then Ag-LCF was prepared via a phase inversion/sintering technique. Enhanced activity of Ag-LCF hollow fiber membrane was observed with approximately 90% of degradation in 75 min of reaction. The catalyst active metal centers participating in the activation of PMS appeared to be Ag(I) and Fe(III) ions, while SO<sub>4</sub><sup>•-</sup> and •OH were formed as the main ROS. Finally, this study highlighted also the advantages of immobilized systems, such as their ease of use, great stability and reuse, as well as the low rates of required energy.

The same catalyst, namely Ag-La<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.94</sub>O<sub>3- $\delta}$  (Ag-LaCaFeO<sub>3- $\delta$ </sub>), which was synthesized via a classic sol gel method, as well as its precursor perovskite catalyst La<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.94</sub>O<sub>3- $\delta$ </sub>, was studied by Chu et al. [77] both in terms of their action against organic pollutants and the antimicrobial activity. Perovskite La<sub>0.8</sub>Ca<sub>0.2</sub>Fe<sub>0.94</sub>O<sub>3- $\delta$ </sub> was first synthesized via a classic sol-gel method and then silver doping was performed with the addition of appropriate amounts of AgNO<sub>3</sub> in order to achieve the desired ratio of La:Ca:Fe:Ag. Although in the case of LaCaFeO<sub>3- $\delta$ </sub>, the degradation of MB dye was performed at 84% in 45 min, this catalytic activity was slightly enhanced in the case of Ag-LaCaFeO<sub>3- $\delta$ </sub> where MB was degraded at 90% in the same time. In addition, the Ag-LaCaFeO<sub>3- $\delta$ </sub>/PMS system was also studied for its catalytic activity against other organic pollutants, such as rhodamine 6G and phenol, as well as to suppress the growth of *E. coli* and methicillin-resistant *Staphylococcus aureus* (MRSA). The formation of sulfate and hydroxyl radicals was observed upon activation of PMS, while the synergistic effect of free radicals and incorporated Ag was reported to contribute in bacterial cell disinfection and</sub> thus in growth inhibition of *E. coli* and MRSA. Finally, it was reported that the enhanced activity of Ag-LaCaFeO<sub>3- $\delta$ </sub> is mainly due to silver incorporation and Ca<sup>2+</sup> substitution with subsequent increase of oxygen vacancies and p-type conductivity.

Another case of substituted perovskite in A position was  $La_{0.8}Sr_{0.2}CoO_{3-\delta}$  (LSC) which was used to degrade sulfamethoxazole (SMX) pharmaceutical, through activation of persulfate in different water and wastewater systems [79]. The synthesis of the perovskite catalyst was carried out through a combustion method and full SMX degradation was achieved in just 45 min with the use of LSC/SPS system. Unsurprisingly, the increase in catalyst concentration resulted in enhanced degradation of SMX but on the other hand, opposite effect was observed with an increase in the concentration of SMX. In the case of SPS concentration effect, an increase in the catalytic activity of the system with an increase in concentration was observed initially due to the formation of more sulfate radicals, however further increase acts repressively, as has been also mentioned in previous cases, because quenching of the formed radicals with SPS takes place. SMX degradation in bottled water and secondary treated wastewater matrices were slower compared to ultrapure water. This was mainly attributed to the presence of inorganic ions and natural organic matter with humic acid compounds exhibiting the greatest effect even in small concentrations followed by the presence of bicarbonate ions. Finally, the greatest activity of the system occurred at neutral pH, as in previously mentioned cases. Regarding the catalytic mechanism, it was reported the formation of both  $SO_4^{\bullet-}$  and  $\bullet OH$ . In addition, based on the identified intermediate products it was suggested that degradation took place through three different pathways i.e., oxidation of amine group, hydroxylation of isoxazole moiety and destruction of the sulfonamide bond. Finally, the catalyst was able to maintain its performance for five catalytic cycles.

#### 2.3.3. Doubly Substituted in Position A, B Perovskites

Doubly substituted (both A and B positions) perovskite catalyst  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  (BSCF) was synthesized via a classic sol-gel method by Duan et al. [72] and studied for its catalytic activity towards phenol degradation. BSCF effectively activate PMS but not other oxidants such as PDS. An increase in degradation was observed with an increase in pH from 2.5 to 8. The formation of both  $SO_4^{\bullet-}$  and  $\bullet OH$  has been reported, with hydroxyl radicals forming first and participating in reactions for the formation of the dominant sulfate radicals. It was also mentioned, as in previous cases, the important role of oxygen vacancies and the presence of a metal ion with lower electronegativity than that of Co in position A of the perovskite structure. This makes easier the interaction between the PMS and the catalyst via a rapid charge transfer process to form the active radicals. The complete degradation of phenol was achieved in just 30 min for BSCF/PMS system, while 19.9% and 60.7% in 60 min were achieved for CoFeO<sub>4</sub>/PMS and Co<sub>3</sub>O<sub>4</sub>, respectively. Finally, the BSCF catalyst was effectively used for three catalytic cycles, with a slight decrease observed in the third cycle where 60 min was required for the complete degradation of phenol.

#### 2.4. Double Perovskite Catalysts

Luo et al. [73] focused on the targeted synthesis of a mesopore double perovskite catalyst,  $La_2CoMnO_{6-\delta}$  (MLCMO), performed via a facile method of transformation-induced self-assembly (EISA) using PEO-b-PS as the template and its activity was evaluated for the degradation of atrazine and other organic pollutants. The MLCMO's mesoporous structure showed greater catalytic activity than bulk MLCMO, as 97% of atrazine degradation was achieved in just 30 min in the first case, while in the same conditions 73% was achieved by bulk MLCMO. It also showed higher catalytic activity among other catalysts that have been used effectively in the activation of PMS such as a-MnO<sub>2</sub>,  $Co_3O_4$ , and  $CoFe_2O_4$ . In addition, this mesoporous MLCMO was effectively used for the degradation rates being 99, 91, 82, and 98%. This powerful catalytic activity was attributed mainly to the mesoporous structure of the catalyst, oxygen vacancies also worked synergistically in the activation

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of PMS. This resulted, in addition to the formation of  $SO_4^{\bullet-}$  and  $^{\bullet}OH$ , which were designated as the dominant ROS, to the formation of  $^1O_2$ , which however contributed to a small extent to the degradation of atrazine.

In another case, Su et al. [66] used a double perovskite,  $PrBaCo_2O_{5+\delta}$  (PBC), to degrade phenol and methylene blue (MB) through activation of PMS, giving more basis to the mechanistic part of the reaction. The catalyst was synthesized by a combined EDTA-citric acid complex sol-gel method and its catalytic activity was compared to that of  $Co_3O_4$  spinel. Both in the case of phenol and MB degradation, the double perovskite showed a markedly better catalytic activity as their complete degradation was achieved in just 20 and 15 min, respectively. In order to determine what are the types of active radicals that contribute to the degradation of these organic pollutants, scavenging experiments have been used with electron paramagnetic resonance (EPR) and the use of 5,5 dimethyl-1-pyrroline (DMPO) as spin-trapping agent. Thus, it appeared that hydroxyl and sulfate radicals were formed through the activation of PMS by PBC, although it was reported that sulfate radicals were formed in a larger percentage and therefore were the dominant ones in the degradation mechanism. Su et al. [66] tried to focus on the reasons that PBC showed greater catalytic activity against spinel. This difference was attributed mainly to the increased concentration of oxygen vacancies but also to the ability of perovskite to make easier the change in valence state of metal cations of position B, without showing any phase transition as they proposed that the redox processes of Co(II)-Co(III)-Co(II) and Co(III)-Co(IV) took place in the activation of PMS. The perovskite catalyst was successfully used for 3 catalytic cycles, after collection by filtration and washing (deionized water and methanol).

#### 2.5. Metal Leaching and Secondary Pollution

As mentioned above, a major problem that appeared in several cases of perovskite catalyst applications is the metal ion leaching. In addition to the reduction of catalyst's efficiency and life time, secondary contamination take place due to the release of metal ions consisting the perovskites in the water matrix. Most of the studies reviewed herein focus on the loss of catalyst's activity and the contribution of homogeneous catalysis rather than the assessment of environmental impacts. However, in some cases, the concentrations arising from metal ion leaching of the catalyst are mentioned. For example, in the case of Hammouda et al. [58], they report that cobalt leaching into aqueous matrix ranged from 0.1  $\mu$ g L<sup>-1</sup> to 1.047 mg L<sup>-1</sup> for LaCoO<sub>3</sub> and from 0.04 mg L<sup>-1</sup> to 0.792 mg L<sup>-1</sup> for SrCoO<sub>3</sub>, at different pH values. In the case of Solís et al. [56], although high cobalt leaching values (up to 10 mg L<sup>-1</sup> in some cases) were reported, in the optimum pH range where the experiments were performed it did not exceed 0.2 mg L<sup>-1</sup> while in the case of Duan et al. [72] ranged from 3.61 mg L<sup>-1</sup> to 5.9 mg L<sup>-1</sup>. However, based on the studies reviewed, metal leaching phenomenon can be controlled through the optimization of operational parameters, mainly pH of the system, as well as by catalyst deposition. As a result, in many cases the available water quality standards and toxicity threshold can be surpassed.

#### 3. Spinel Catalysts for the Activation of PMS, PS and Degradation of Organic Pollutants

#### 3.1. Cobalt-Ferrite ( $Co_xFe_{3-x}O_4$ ) Spinels

Transition metal spinel oxide nanoparticles are also extensively studied as catalysts in sulfate-based advanced oxidation processes. As already mentioned, among common transition metals (e.g., Co, Cu, Mn, Fe, etc.), Co exhibits also the highest activity for PMS activation [96] and similarly to Co-based perovskites Co-based spinels  $Co_xM_{2-x}O_4$  ( $1 \le x \le 2$ , M = Fe, Mn, Zn, Cu, etc.) present remarkable catalytic activity and reduced metal leaching. Especially cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub>) and derivatives are the most studied spinel materials for the heterogeneous activation of PMS (Table 4). The excellent catalytic activity, stability, reusability, and strong magnetic response of CoFe<sub>2</sub>O<sub>4</sub> enable potential applications for the elimination of organic pollutants in wastewater. Beyond the beneficial magnetic properties for separation and reuse, they also easily harvest sunlight energy due to their low energy band gap so, they can be used also as photocatalysts [97].

				Concentration		Treatment Efficiency		
Catalyst	Synthesis Method	Target Pollutant	Catalyst (g L <sup>-1</sup> )	Pollutant (mg L <sup>-1</sup> )	PMS (mM)	Degradation	TOC Removal	Reference
CoFe <sub>2</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	Combustion	SMX	0.15	10	0.66	90% (90 min)	-	[98]
CoFe <sub>2</sub> O <sub>4</sub> -QS	Combustion	SCP	5	20	0.5	90% (30 min)	6.1% (30 min)	[99]
CoFe <sub>2</sub> O <sub>4</sub> -GO	Hydrothermal treatment—ultrasound	NOR	0.3	4.8	0.5	100% (20 min)	64.1% (60 min)	[100]
CoFe <sub>2</sub> O <sub>4</sub> -rGO	Hydrothermal treatment	OFX CFZ	0.1 0.1	14 18	1 0.1	100% (60 min) 100% (60 min)	-	[101]
CoFe <sub>2</sub> O <sub>4</sub> /Gr	Hydrothermal treatment	AMX	0.5	20	3	99.3% (60 min)	61.1% (60 min)	[102]
010204/01	Hydrothermal treatment	DMP	0.5	9.7	2	100% (30 min)	24% (60 min)	[103]
CoFe <sub>2</sub> O <sub>4</sub> /TNTs	Hydrothermal treatment—combustion	RhB Phenol	0.02 0.02	100 20	26 20	97% (60 min) 97.2% (60 min)	50% (60 min) 81.3% (60 min)	[51]
CoFe <sub>2</sub> O <sub>4</sub> /CN	Hydrothermal treatment with melamine	LVF	0.15	10	0.5	89.4% (60 min)	30% (40 min)	[104]
CoFe <sub>2</sub> O <sub>4</sub> /HPC	Pyrolysis	BPA	0.05	10	3.3	86% (8 min)	-	[105]
CoFe <sub>2</sub> O <sub>4</sub> /OMC	Hydrothermal treatment	RhB	0.05	100	1.5	92.7% (60 min)	-	[106]
CoFe <sub>2</sub> O <sub>4</sub> /OMC	Hydrothermal treatment	RhB	0.05	100	1.5	92.7% (60 min)	-	[106]
CoFe <sub>2</sub> O <sub>4</sub> /CCNF	Hydrothermal treatment	DMP	0.5	9.7	1.5	100% (30 min)	-	[107]
CF@CNF	Electrospinning techniques	Amaranth dye	0.05	10	1.3	100% (120 min)	-	[108]
CoFe <sub>2</sub> O <sub>4</sub>	Hydrothermal treatment	ATZ	0.4	10	0.8	99% (30 min)	27% (30 min)	[109]
CoFe <sub>2</sub> O <sub>4</sub>	Sol-Gel process	AO7 AML	0.5 0.04	20 4	0.8 10	96% (40 min) 92.5% (30 min)	- 70% (120 min)	[110] [111]
CoFe <sub>2</sub> O <sub>4</sub>	Sol-Gel process	TPhP	0.25	3.3	0.2	80% (30 min)	<7% (180 min)	[112]

Table 4. Degradation of pollutants by the combination of peroxymonosulfate (PMS) and spinele
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				Concentration		Treatment	Efficiency	
Catalyst	Synthesis Method	Target Pollutant	Catalyst (g L <sup>-1</sup> )	Pollutant (mg L <sup>-1</sup> )	PMS (mM)	Degradation	TOC Removal	Reference
CoFe <sub>2</sub> O <sub>4</sub> /WTRs	co-precipitation combustion	ATZ	0.03	2	0.25	98.2% (20 min)	-	[113]
CoFe <sub>2</sub> O <sub>4</sub> /HA	co-precipitation	SMX	0.1 0.1 mM HA	20	1	96% SMX (120 min)	-	[114]
Co <sub>3</sub> O <sub>7</sub> -CoFe <sub>2</sub> O <sub>4</sub>	Pyrolysis	2,4-DCP	0.05	50	8.2	93.8% 2,4-DCP (30 min)	55.7% (30 min)	[115]
FeCo <sub>2</sub> O <sub>4</sub>	Sol-Gel	2,4-DCP	0.06	100	4	95.8% (90 min)	44.7% (90 min)	[116]
$\begin{array}{c} Co_x Fe_{3-x}O_4 \\ (x=0.1,0.5,0.7 \text{ and} \\ 1) \end{array}$	Combustion	PBSA	0.17	11	0.1	70% (240 min)	32% (240 min)	[117]
CoMn <sub>2</sub> O <sub>4</sub>	Sol-Gel	PBSA	0.05	5	1.6	93.7% (60 min)	30% (30 min)	[118]
CoMn <sub>2</sub> O <sub>4</sub> /MD	Solvothermal	SA	0.05	10	0.66	100% (30 min)	-	[119]
Co <sub>x</sub> Mn <sub>2-x</sub> O <sub>4</sub> (8:1, 4:1, 2:1, 1:2, 1:4 and 1:8)	Precipitation	TCS	0.02	10	0.33	96.4% (30 min)	-	[50]
CuCo <sub>2</sub> O <sub>4</sub>	Combustion	SMZ	0.1	50	6.5	98% (30 min)	-	[120]
NiFe <sub>2</sub> O <sub>4</sub>	Combustion	BA	0.1	1.2	1	82.5% (60 min)	-	[121]
CuCo <sub>2</sub> O <sub>4</sub>	Solvothermal	SMZ	0.01	5	0.13	87.5% (20 min)	-	[122]
ZnCo <sub>2</sub> O <sub>4</sub>	Microwave-assisted	BPA	0.2	20	0.26	99.2% (5 min)	70% (30 min)	[123]
ZnFeCoO <sub>4</sub>	Sol-gel and combustion	BPA	0.2	10	1	100% (4 min)	-	[124]

Table 4. Cont.

MB: Methylene Blue, PBSA: 2-phenyl-5-sulfobenzimidazole acid, RhB: Rhodamine B, NOR: Norfloxacin, SMX: Sulfamethoxazole, LVF: Levofloxacin, OFX: Ofloxacin, CFZ: Cefazolin, DMP: Dimethyl phthalate, SCP: Sulphachloropyridazine sodium, AMX: Amoxicillin, ATZ: Atrazine, AO7: Acid Orange 7, AML: Amlodipine, TPhP: Triphenyl phosphate, BPA: Bisphenol A, 2,4-DC:P 2,4-diclorophenol, SA: Sulfanilamide, TCS: Triclosan.

Spinel CoFe<sub>2</sub>O<sub>4</sub>, as can be seen in Table 4, was synthesized via hydrothermal, sol-gel and combustion methods and has been studied by many researchers for the degradation of various pollutants, such as atrazine (ATZ), amlodipine (AML), triphenyl phosphate (TPhP), dyes and 2-phenylbenzimidiazole-5-sulfonic acid (PBSA) from wastewater systems. Firstly, Li et.al, 2018 investigated the removal efficiency of atrazine in the CoFe<sub>2</sub>O<sub>4</sub>/PMS system [109]. The  $SO_4^{\bullet-}$  was determined to be the main reactive radical succeeding nearly complete (>99%) ATZ removal and about 22.1% mineralization efficiency within 30 min under the following operating conditions: 0.4g L<sup>-1</sup> CoFe<sub>2</sub>O<sub>4</sub>, 0.8 mM PMS and initial pH 6.3. Moreover, Song et al. [112] composed CoFe<sub>2</sub>O<sub>4</sub> by sol-gel process and Niu et al. [110] used the sol-gel method with natural cellulose fibers as template for the heterogeneous activation of PMS and subsequent degradation of triphenyl phosphate (TPhP) and Acid Orange 7 (AO7) azo dye, respectively. Natural cellulose fibers have been widely used as hard template to prepare various materials because of their low cost and easy removal. The template use can efficiently prevent aggregation of catalyst during the post-heating treatment, which often decreases the specific surface areas and limits PMS activation. The results indicated that TPhP could be efficiently degraded, reaching 99.5% removal, by  $CoFe_2O_4$  at pH 7, 0.5 mM PMS and 0.25 g  $L^{-1}$   $CoFe_2O_4$ in 6 min with  $SO_4^{\bullet-}$  being the predominant radicals. It is also found that  $CoFe_2O_4$  showed high catalytic activity for AO7 degradation, suggesting that the increase of pH and catalyst concentration could be favorable to remove AO7 completely in 40 min. In another study, Shao et al. [111] explored different parameters that affect the removal of AML (concentration level 10  $\mu$ M) in CoFe<sub>2</sub>O<sub>4</sub>/PMS system using Milli-Q-water with the focused attention on the effect of PMS concentration. They found that AML could be completely removed with 0.025 mM PMS concentration within 30 min and a further increasing of PMS concentration led to a better removal of TOC. The degradation followed pseudo-first-order kinetics and the best performance occurred at pH 7.0. They also conducted experiments in real wastewater, where the removal of AML was >80% when the highest PMS concentration (250  $\mu$ M) was used.

Finally, Al-Anazi et al. [117] fabricated cobalt ferrite nanoparticles with different stoichiometry  $(Co_{0.1}Fe_{2.9}O_4, Co_{0.5}Fe_{2.5}O_4, Co_{0.7}Fe_{2.3}O_4 \text{ and } Co_{1.0}Fe_{2.0}O_4)$  for the degradation of PBSA (concentration level 4µM) via a combustion method in the presence of a PMS and Milli-Q-water matrix. They revealed that  $Co_{1.0}Fe_{2.0}O_4$  had the highest activation for PMS among all prepared catalysts by removing ~75% PBSA (240 min of reaction time, 0.1 mM PMS), indicating the advantage of higher cobalt to iron ratio in the composition of catalyst in PMS activation. Although  $Co_{1.0}Fe_{2.0}O_4$  performed the optimum catalytic activity under the current experimental conditions,  $Co_{0.7}Fe_{2.3}O_4$  was selected among the other prepared catalysts to examine the roles of catalyst loading and oxidant initial concentration.

All these magnetic nanoparticles showed a promising reusability behavior and a remarkable stability, which could be reused several times for decomposition of organic pollutants with high catalytic performance. Specifically,  $CoFe_2O_4$  nanoparticles can be reused five times with a high removal rate from the first to third run but a slower rate in the fourth and fifth cycle [96]. The leaching concentrations of  $Co^{2+}$  and  $Fe^{3+}$  were tested using ICP-MS. The results indicated that both the concentration of  $Co^{2+}$  and  $Fe^{3+}$  were lower than the environmental quality standards from European Union for surface water (1 mgL<sup>-1</sup> for Co and 2 mgL<sup>-1</sup> for Fe) [110].

Zhou et al. [116] synthesized through sol-gel process the  $FeCo_2O_4$  spinel and investigated the effects of various important parameters in the degradation of 2,4-dichlorophenol (2,4-DCP) in aqueous solution. When  $FeCo_2O_4$  or PMS was used alone, no degradation and 22% degradation of 2,4-DCP within 90 min was observed. On the contrary, the degradation efficiency of 2,4-DCP reached 95.8% in the presence of  $FeCo_2O_4$ /PMS at nearly neutral pH conditions. Moreover, the maximum concentrations of leached Co and Fe ions were lower than the corresponding standard limits for surface water and groundwater in China, suggesting that the catalyst could be used for environmental applications.

A possible reaction mechanism of  $CoFe_2O_4/PMS$  process or  $FeCo_2O_4/PMS$  is depicted in Figure 7a,b, where the redox pairs of  $Co^{3+}/Co^{2+}$  and  $Fe^{3+}/Fe^{2+}$  are responsible for the activation of PMS to generate radicals in the degradation processes.

The metal ions would act as Lewis acid sites and  $H_2O$  molecules were absorbed onto the surface of  $CoFe_2O_4$ . The formation of  $Co^{2+}$ -OH<sup>-</sup> was a primary step and affect the whole reaction [109]. In addition, when PMS was added in the solution,  $HSO_5^-$  is bonded in the form of  $CoFe_2O_4$ -O-H-HSO<sub>5</sub><sup>-</sup> through hydrogen bonds and would react with  $Co^{2+}$ -OH<sup>-</sup> to generate  $SO_4^{\bullet-}$  and  $CoO^+$  which was then oxidized into  $Co^{3+}$  with the existence of H<sup>+</sup> according to Equations (8)–(13). To make the cycle reaction continue,  $HSO_5^-$  reacted with  $Co^{3+}$  to form  $SO_4^{\bullet-}$  and  $Co^{2+}$ . Furthermore,  $Fe^{3+}$  followed the similar process as  $Co^{3+}$ .  $Fe^{3+}$  obtained electron from  $HSO_5^-$  to generate  $Fe^{2+}$  as well as  $SO_5^{\bullet-}$  and then  $Fe^{2+}$  reacted with  $HSO_5^-$  to produce  $SO_4^{\bullet-}$ . Finally,  $\bulletOH$  might be produced through the reactions between  $SO_4^{\bullet-}$  and water/hydroxide ions. Subsequently, the generated radicals participate in the degradation of organic pollutants [112,125].



**Figure 7.** (a) The reactive species and reaction pathways for BPA degradation by CoFe<sub>2</sub>O<sub>4</sub> spinel and (b) The series of reactions for the formation of sulfate radicals by PMS/CoFe<sub>2</sub>O<sub>4</sub> spinel system [9,126].

$$Co^{2+} + H_2O \rightarrow Co^{2+} - OH^- + H^+$$
 (8)

$$Co^{2+} - OH^- + HSO_5^- \to CoO^+ + SO_4^{\bullet-} + H_2O$$
 (9)

$$CoO^{+} + 2H^{+} \rightarrow Co^{3+} + H_2O$$
 (10)

$$\text{Co}^{3+} + \text{HSO}_5^- \to \text{Co}^{2+} + \text{H}^+ + \text{SO}_5^{\bullet-}$$
 (11)

$$Fe^{3+} + HSO_5^- \rightarrow Fe^{2+} + H^+ + SO_5^{\bullet-}$$
 (12)

$$Fe^{2+} + HSO_5^- \to Fe^{3+} + SO_4^{\bullet-} + OH^-$$
 (13)

Hydroxylamine (HA), acting as a reductant, could be used complementary to accelerate peroxymonosulfate activation and promote the redox cycle Co(II)/Fe(III) on the surface of CoFe<sub>2</sub>O<sub>4</sub>. Based on previous findings the interaction between Co-Fe in the spinel cobalt ferrite is very strong, contributing to low cobalt dissolution. The Fe<sup>3+</sup> in CoFe<sub>2</sub>O<sub>4</sub> can activate PMS, but electron transfer from  $Fe^{3+}$  to PMS is thermodynamically less favorable than from  $Co^{2+}$ , so the contribution of  $Fe^{3+}$  to PMS activation seems to be insignificant [127]. To overcome this drawback Oh et al. [114] composed  $CoFe_2O_4$  and introduced HA as a reductant into the Fe<sup>2+</sup>/PMS system to activate the Fe<sup>3+</sup>/Fe<sup>2+</sup> cycle, promoting simultaneously the generation of reactive •OH and SO4 •- radicals and the degradation of organic compounds in distilled water. By CoFe<sub>2</sub>O<sub>4</sub>/PMS the degradation rate of SMX was 40% within 120 min due to the low PMS activation efficiency of the Fe<sup>3+</sup> in the CoFe<sub>2</sub>O<sub>4</sub> structure. On the other hand, the addition of HA to the  $CoFe_2O_4/PMS$  system increased the SMX removal at 96% in 120 min and promoted the PMS activation. For real wastewater sample, the efficiency of SMX degradation was slightly dropped to 87.5%. Especially,  $Co^{2+}$  and  $Fe^{3+}$  on the surface of catalyst reacted with PMS to generate •OH and SO<sub>4</sub>•- radicals according to Figure 8. The regeneration of Co<sup>2+</sup> and Fe<sup>2+</sup> on the surface is thermodynamically favorable comparing the reduction potential of Co<sup>3+</sup>/Co<sup>2+</sup> and Fe<sup>3+</sup>/Fe<sup>2+</sup> redox pair and the reduction reaction of HA. Moreover, the regenerated Co<sup>2+</sup> decreases the excessive amount of •OH that contribute to the self-decomposition of PMS. So, this system could maximize the efficiency of sulfate radical and minimize the disadvantage of sole cobalt-based PMS activation.



Figure 8. Proposed reaction mechanism for the SMX degradation by a CoFe<sub>2</sub>O<sub>4</sub>/PMS/HA system [114].

As reported in the case of perovskite catalysts, a serious problem in PMS activation is the decreased catalytic efficiency after some catalytic cycles due to metal leaching. In order to fix the mentioned problem the catalysts can be immobilized on various materials. It has been proved that spinel ferrite nanoparticles immobilized on stable supports, which might be inorganic or organic materials, exhibited much better catalytic activity than the catalyst in powder form. Firstly, Bao et al. [98] prepared via a urea-assisted combustion method the spinel CoFe<sub>2</sub>O<sub>4</sub> deposited into an Al<sub>2</sub>O<sub>3</sub> ceramic membrane and investigated the SMX degradation pathway through sulfate radicals in a CoFe<sub>2</sub>O<sub>4</sub>/membrane/PMS system. As mentioned above, the redox cycles of Co(II)/Co (III) and Fe (II)/Fe (III) participated in the generation of sulfate radicals. However, it is proved that there is no significant difference in SMX

degradation with increasing CoFe<sub>2</sub>O<sub>4</sub> load on the membrane, thus the determining step was the mass-transfer. SMX was completely removed with a middle flow rate ( $0.2 \text{ mL min}^{-1}$ ) in acidic conditions (pH = 3–7). It is observed that with no Oxone<sup>®</sup> addition the removal of SMX is negligible, while the increase of PMS dosage resulted in a higher SMX degradation rate. The calcination temperature had also a significant role in the degradation efficiency, i.e., when the calcination temperature was increased from 300 to 800 °C, the SMX removal, in 60 min time period, decreased from 92.4% to 24.5%, respectively. This could be due by the lower crystallinity of the catalyst prepared at 300 °C, indicating that there are more defects which is in favor of electron transfer while the surface area difference caused by the catalyst loading was not considered. Finally, best catalyst loading was 0.035 g g<sup>-1</sup> Al<sub>2</sub>O<sub>3</sub>.

Since the discovery of multilayered titanate nanotubes (TNTs), they rapidly become popular nanomaterials with exciting applications in the fields of catalysis. In view of this fact, Du et al. [51] prepared via hydrothermal process a highly effective heterogeneous catalyst  $CoFe_2O_4/TNTs$  for PMS activation by innovatively coupling spinel ferrite nanoparticles with TNTs to remove phenol and Rhodamine B (RhB). The results showed that the removal of RhB was negligible (<10%) using only  $CoFe_2O_4/TNTs$  and  $CoFe_2O_4$ , but it can be significantly enhanced with the presence of both PMS and catalysts in the reaction system. The  $CoFe_2O_4$  and  $CoFe_2O_4/TNTs$  system can raise the degradation efficiency to 97% and 97.9% respectively while TOC removal can reach 50.9%. Similar data were collected for phenol degradation, in which the removal efficiency was 97.2% and the TOC removal 81.3%. In  $CoFe_2O_4/PMS$  system without the TNTs support, the degradation efficiency reached 83.9% and the TOC removal 65.2%. Particularly, TNTs with large specific area provide an appropriate support to disperse spinel ferrite nanoparticles and enhance the catalytic efficiency and they can also, bind free metal cations released from the reaction process and promise less ion leaching as compared to sole spinel ferrites. These experiments endowed  $CoFe_2O_4/TNTs$  with better catalytic performance and promising applications for wastewater treatment as compared to pure  $CoFe_2O_4$  particles.

The substrates mentioned above such as  $Al_2O_3$ , TNTs etc. are relatively high-priced and the introduction of these supporting materials makes the synthesis process more complicated. As a result, low-cost supports are frequently studied as alternatives. As a first example, Gao et al. [99] introduced quartz sand (QS) as catalyst support in order to reduce the cost and improve also the treatment rate. The CoFe<sub>2</sub>O<sub>4</sub> (1%wt)-QS was synthesized by combustion method in a wide calcination temperature range with a urea-assisted solution to degrade sulfachloropyridazine (SCP) (20 mg L<sup>-1</sup>) in ultrapure water. When CoFe<sub>2</sub>O<sub>4</sub> was prepared at higher calcination temperatures of 600 and 700 °C, the structural property of the loaded CoFe<sub>2</sub>O<sub>4</sub> changed from amorphous to crystalline which eliminated the electron transfer and showed a weaker catalytic activity. Hence, the amorphous phase was the reason for the better catalytic effect of CoFe<sub>2</sub>O<sub>4</sub>-QS catalyst, which prepared at 300 °C, for the SCP removal. The CoFe<sub>2</sub>O<sub>4</sub>-QS-300 removed 90.4% of the SCP in 30 min in the pH range 4.2–9, however the mineralization of SCP was very low with an average removal efficiency of TOC being 6.1%, (Table 4), due to the low PMS dosage used in this reaction system.

In another case, drinking water treatment residuals (WTRs) are adopted as a low-cost support. The use of ferric and aluminum salts as coagulants in water treatment plants leads to the generation of iron-rich WTRs that might be used as support of  $CoFe_2O_4$ , targeting the uniform distribution of catalyst, prevention of aggregation, and preservation of catalytic activity. So, Li et al. [113] prepared  $CoFe_2O_4$ /WTRs catalyst and studied the catalytic efficiency to activate PMS for the degradation of atrazine. WTRs can act both as iron source to provide iron ions required for the synthesis of  $CoFe_2O_4$  and the substrate to disperse  $CoFe_2O_4$ . The results indicated 98% of ATZ removal at pH 4.01 while only 8% and <1% of ATZ was removed within 20 min in the presence of sole PMS and  $CoFe_2O_4$ /WTRs systems, respectively. Both homogeneous and heterogeneous reactions took place in this reaction system for PMS activation. For PMS heterogeneous activation,  $CoFe_2O_4$  was the active component of  $CoFe_2O_4$ /WTRs and  $Co^{2+}$  was the main catalytic center. On the other hand, in the homogeneous activation processes, the dissolved metal ions could activate PMS to form free radical and degrade ATZ. In order to identify the reactive radical species involved in the  $CoFe_2O_4$ /WTRs/PMS

system, electron spin resonance (ESR) experiments using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin-trapping agent were performed. The results showed that sulfate and hydroxyl radicals produced simultaneously through the activation process. Moreover, radical quenching experiments were carried out using EtOH and tert-butyl-alcohol (TBA) as scavengers. EtOH strongly inhibited the ATZ degradation from 98.2% to 9%, while TBA concentration didn't affect so much the removal rate, from 98.2% to 75%.

Moreover, Zhou et al. [115] coupled CoFe<sub>2</sub>O<sub>4</sub> with Co<sub>3</sub>Fe<sub>7</sub> alloy in order to make durable and high-performance catalysts for the removal of 2,4-DCP. The results indicated that Co<sub>3</sub>Fe<sub>7</sub>-CoFe<sub>2</sub>O<sub>4</sub> nanoparticles had a smaller particle size and they can efficiently remove 2,4-DCP within 30 min at a wide pH range from 3 to 11. The synergistic effects between Co<sub>3</sub>Fe<sub>7</sub> alloy and CoFe<sub>2</sub>O<sub>4</sub> not only improved the catalytic activity but also provided a long-term durability of the catalyst. The main findings for the activation mechanism were: (i) both SO<sub>4</sub><sup>•-</sup> and •OH radicals participated simultaneously in the Co<sub>3</sub>Fe<sub>7</sub>-CoFe<sub>2</sub>O<sub>4</sub>/PMS system, (ii) Co<sup>2+</sup> and Fe<sup>2+</sup> for the spinel and Co<sup>0</sup> and Fe<sup>0</sup> for the alloy acted as active sites to generate radicals by activating PMS and (iii) the alloy accelerated the redox cycle of Co<sup>3+</sup>/Co<sup>2+</sup> and Fe<sup>3+</sup>/Fe<sup>2+</sup>. Following magnetic separation, the catalyst can be reused effectively for the degradation of 2,4-DCP removal for at least five cycles.

The immobilization of magnetic catalysts onto carbon materials has been demonstrated to be an effective way to reinforce PMS activation for degrading organic pollutants in wastewater system applications. The carbonaceous supports opposed to metallic supports are much more favorable due to their earth abundance and non-toxicity [103]. Chen et al. [100] prepared  $CoFe_2O_4$  nanoparticles supported in graphene oxide (GO) through a simple hydrothermal method and investigated the degradation of Norfloxacin (NOR) by CoFe<sub>2</sub>O<sub>4</sub>/PMS and CoFe<sub>2</sub>O<sub>4</sub>-GO/PMS systems. It was observed that CoFe<sub>2</sub>O<sub>4</sub>-GO/PMS system exhibited a much higher catalytic activity and the degradation of NOR was almost completed within 20 min indicating that GO has a significant role in the degradation process. It is also proved that extremely alkaline or acidic conditions were not preferred, but an average pH at 9 showed good catalytic activity. Finally, the CoFe<sub>2</sub>O<sub>4</sub>-GO/PMS system accomplished better mineralization than CoFe<sub>2</sub>O<sub>4</sub>/PMS with TOC being 64.1% and 35.3%, respectively, after 60 min (see Table 4). It was clearly indicated that NOR degradation in CoFe<sub>2</sub>O<sub>4</sub>-GO/Oxone<sup>®</sup> system followed both radical and non-radical processes, whilst non-radical mechanism dominated the degradation process. On one hand, in the radical mechanism the active Co<sup>2+</sup> species react with hydroxyl group dissociated from water to form Co-OH complexes. Then, the Co-OH complexes react with  $HSO_5^-$  directly to generate  $SO_4^{\bullet-}$ . Simultaneously, the  $Co^{2+}$  was oxidized into  $Co^{3+}$ . On the other hand, GO with excellent adsorption ability toward organic compounds via  $\pi$ - $\pi$  interactions and oxygen-containing groups, such as ketonic groups, which are rich in electrons could promote a redox process. Consequently, in the non-radical process the oxidant would be first activated by the defective oxygen-groups and then oxidize the adsorbed pollutant directly via electron transfer and H abstraction.

Similar results are reported by Fan et al. [101], Xu et al. [103] and Lashkaryani et al. [102], who used also spinel CoFe<sub>2</sub>O<sub>4</sub> nanoparticles supported on reduced graphene oxide (r-GO) and graphene for the degradation of different antibiotics such as ofloxacin (OFX), cefazolin (CFZ), amoxicillin (AMX) and a plasticizer dimethyl phthalate (DMP). CoFe<sub>2</sub>O<sub>4</sub>-rGO catalyst as well as CoFe<sub>2</sub>O<sub>4</sub>-Gr was synthesized by hydrothermal treatment and the results showed that they had a high PMS activation efficiency and organic pollutants removal. Specifically, nearly 100% of OFX and CFZ was eliminated within 30 min under slightly acidic conditions (pH 6) and CoFe<sub>2</sub>O<sub>4</sub>-rGO dosage 0.1 g L<sup>-1</sup>, while in optimum conditions, 100% degradation of DMP was achieved. Around 99.3 and 61.1% of AMX (20 mg L<sup>-1</sup>) and TOC were removed respectively, during 60 min reaction over CoFe<sub>2</sub>O<sub>4</sub>@Gr/PMS system. The degradation mechanism for these pollutants, except cefazolin, evolved through the radical process, where the transition metal plays a crucial role to generate sulfate radicals, as shown in the Equations (8)–(13) above. For CFZ degradation the non-radical process had a dominant role, where HSO<sub>5</sub><sup>-</sup> itself could act as a two-electron oxidant in redox reactions, and it could directly oxidize reagents via two-electron transfer (i.e., oxygen transfer) process Equations (14)–(18). In conclusion,

catalysts with graphene sheets (GO, r-GO) exhibited an enlarged specific surface area and good dispersion of CoFe<sub>2</sub>O<sub>4</sub> particles, resulting in more efficient catalytic activity than CoFe<sub>2</sub>O<sub>4</sub>/PMS system. Both the prepared catalysts indicated good stability and reusability for multiple runs (four cycles [101] and seven cycles [100]), an easy separation, high catalytic activity and good mineralization of organic pollutants. Only 79.5  $\mu$ g L<sup>-1</sup> cobalt ion and 15.5  $\mu$ g L<sup>-1</sup> iron ion were detected from CoFe<sub>2</sub>O<sub>4</sub>-GO after the reaction. This proved that there are strong interactions between CoFe<sub>2</sub>O<sub>4</sub> and GO nanosheet [100]. Finally, only 279  $\mu$ g L<sup>-1</sup> cobalt ions and 21  $\mu$ g L<sup>-1</sup> iron ions were detected from CoFe<sub>2</sub>O<sub>4</sub>-Gr after reaction, since the oxygen-containing functional groups on rGO could chelate the metal ions released from CoFe<sub>2</sub>O<sub>4</sub>, preventing their release into solution [101].

$$HSO_5^- + Gr \rightarrow SO_4^{\bullet-} + OH^- + Gr^+$$
(14)

$$HSO_5^- + Gr \to SO_4^{\bullet-} + {}^{\bullet}OH + Gr^+$$
(15)

$$HSO_5^- + SO_4^{\bullet-} \to HSO_4^- + SO_5^{\bullet-}$$
(16)

$$HSO_5^- + {}^{\bullet}OH \to H_2O + SO_5^{\bullet-}$$
(17)

$$HSO_5^- + Gr \to SO_4^{\bullet-} + {}^{\bullet}OH + Gr^+$$
(18)

In another case, ordered mesoporous carbon (OMC), a carbon material with good chemical and high thermal stability, open-pore structure, large specific surface area, and large pore size was used by Deng et al. [106] to synthesize CoFe<sub>2</sub>O<sub>4</sub>/OMC catalyst and investigated the removal of Rhodamine B by PMS activation. About 97% degradation of RhB was accomplished within 60 min by CoFe<sub>2</sub>O<sub>4</sub>/OMC/PMS system and the degradation mechanism can be seen in Figure 9. The observed enhanced degradation was explained by the key features of OMC. First of all, OMC has high surface area and pore volume that can adsorb effectively RhB through  $\pi$ - $\pi$  electro-donor-acceptor interactions and thus favor the probability of reaction with the generated SO<sub>4</sub><sup>•-</sup>. OMC contains also oxygen functional groups on its surface that reduce the surface energy of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles, which is beneficial for the catalyst in order to have a good dispersion on its surface. Thus, the mass transfer of RhB and PMS toward the active sites during the reaction is enhanced. Lastly, there is a strong interaction between CoFe<sub>2</sub>O<sub>4</sub> nanoparticles and OMC that favor the electron transfer towards them and accelerate the production of sulfate radicals.



Figure 9. Mechanism for RhB degradation in CoFe<sub>2</sub>O<sub>4</sub>/OMC activated PMS system [106].

Furthermore, another carbonaceous support is biochar, which is the solid pyrolysis product from various biomass substrates. Li et al. [105] supported  $CoFe_2O_4$  on biochar activated using KHCO<sub>3</sub> (HPC) and studied the removal of BPA. Biochars perform like OMC and enhance the generation of  $SO_4^{\bullet-}$ . Firstly, they prepared the biochar by pyrolysis at 400 °C (C400) and then synthesized a mixture of C400 and KHCO<sub>3</sub> pyrolyzed at 800 °C (C800). These prepared materials were used as catalysts for PMS activation towards BPA degradation. Specifically, the best catalytic performance was showed for C800 and achieved 98% removal of BPA within 10 min. For all the biochar and PMS systems, both radical and non-radical pathways were involved with the radical way being the dominant one. The synergistic effect between graphitized structures and  $CoFe_2O_4$  nanoparticles played the crucial role on the excellent performance of the catalysts.

Additionally, in recent years, carbon nitride (CN,  $g-C_3N_4$ ) has been studied and used as catalyst or co-catalyst due to its non-toxicity, its strong photochemical corrosion resistance and its visible absorption potential (2.73 eV). Pi et al. [104] conducted experiments with CoFe<sub>2</sub>O<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> composites and investigated the degradation of organic contaminants in wastewater matrix. Catalysts with different ratios of CoFeO<sub>2</sub>, namely 9%, 13% 17% and 23%, were prepared. The results indicated that CoFeO<sub>2</sub> content had a significant effect in the catalytic process and the material with 13% CoFeO<sub>2</sub> showed the best performance. The removal of Levofloxacin (LVF) reached 89.4% at 50 min. Finally, recyclability tests were conducted and revealed that composite catalyst was stable and reusable. The catalytic activity of CoFeO<sub>2</sub>/CN did not decrease significantly after five cycles and the removal of LVF remained at >70%. The sheet structure of g-C<sub>3</sub>N<sub>4</sub> possess characteristic functional groups such as primary and secondary amino groups, oxygen species, hydroxyl groups and contains partially delocalized  $\pi$  electrons providing better access to the reactants (PS), which further enhance the catalytic activity. Fe(III) and Co(II) are adsorbed to the surface of  $g-C_3N_4$  and react with HSO<sub>5</sub><sup>-</sup> to produce  $SO_4^{\bullet-}$ . In these experiments, the pH value decreased rapidly to ~3.0 when the reaction began and then only a small quantity of  ${}^{\bullet}OH$  is being produced. Therefore, SO<sub>4</sub> ${}^{\bullet-}$  played the critical role in the degradation of LVF, while the role of •OH was limited.

The last group of carbon materials that is used as spinel catalyst support is carbon nanofibers (CNF). These materials have high pore volumes, a large specific surface area and abundant active sites with oxygen functional groups, which can also be used for catalysts immobilization. The most common preparation method for spinel/CNF composites is by carbonizing an electrospun cobalt-ferrite-embedded polyacrylonitrile (PAN) fiber [128]. Lin et al. [108] prepared such a composite (CoFe<sub>2</sub>O<sub>4</sub>/CNF) and investigated the catalytic activity for PMS activation and dye degradation. Specifically, the combination of PMS and CoFe<sub>2</sub>O<sub>4</sub>/CNF rapidly eliminated amaranth anionic dye in 80 min under slight acidic conditions (pH = 5). However, the development of CNF by pyrolysis of electrospun nanofibers from alternative, cheap and renewable carbon matrices such as cellulose (CCNF), is more attractive. Gan et al. [107] used for the first time such carbon nanofibers from cellulose to enhance the performance of  $CoFe_2O_4$  for PMS activation and subsequent degradation of dimethyl phthalate (DMP). It was reported that DMP was completely degraded in about 30 min indicating a promising catalyst support. As stated previously for graphitic structure carbon materials properties like high specific area, porosity and oxygen functional groups provide diverse beneficial effects such as the prevention of catalyst's particle agglomeration and Co(II) leaching as well as the stabilization of the active electrons and radicals, resulting in higher efficiency.

#### 3.2. Cobalt-Manganese ( $Co_x Mn_{2-x}O_4$ ) Spinels

It has been demonstrated that Mn-based spinel possess some special characteristics compared with other transition metals due to its unique  $Mn^{2+}/Mn^{3+}/Mn^{4+}$  redox pairs including more electron transfer pathways. Additionally, Mn(III) is not a stable oxidation state and rapidly is transformed to Mn(II) and Mn(IV), which would greatly improve oxygen mobility [129]. Chen et al. [50] synthesized  $Co_xM_{2-x}O_4$  through precipitation with different molar ratios (Co/Mn = 8:1, 4:1, 2:1, 1:2, 1:4, 1:8) to activate PMS in the degradation of triclosan (TCS) and investigated also the critical role of singlet oxygen formation.

TCS degradation followed pseudo-first order kinetic model and the removal reached up to 96.4% within 30 min at neutral conditions, when 0.05 g L<sup>-1</sup> PMS and 0.02 g L<sup>-1</sup> Co<sub>2</sub>Mn<sub>1</sub>O<sub>4</sub> were added. The proposed activation mechanism was based to SO<sub>4</sub><sup>•-</sup> radical process and non-radical <sup>1</sup>O<sub>2</sub> process. For the radical way, manganese cations in octahedral site are thermodynamically favorable to reduce Co(III) to Co(II) due to the higher oxidation states (E(Co<sup>II</sup>/Co<sup>III</sup>) = -1.82 V, E(Mn<sup>III</sup>/Mn<sup>IV</sup>) = -0.95 V, E(Mn<sup>II</sup>/Mn<sup>III</sup>) = -1.51 V). So, manganese and cobalt ions promote the production of sulfate radicals. According to XPS spectra, Co(II) and Mn(II) ions donated electrons to PMS to produce sulfate radicals and the catalyst after reaction was enriched with metal ions of higher oxidation state. It is confirmed that more oxygen vacancies were generated during catalytic reaction and lattice oxygen was involved in the generation of <sup>1</sup>O<sub>2</sub>. Moreover, excess electrons were induced by oxygen vacancies to promote the reduction of metal ions with high valence. Non-radical oxidation process by <sup>1</sup>O<sub>2</sub> also promoted the rate of reaction. Manganese ions with larger ionic radius substituted the cobalt ions in the tetrahedral sites and thus generate vacancies on the O sites. Moreover, some active oxygen \*O might further transform to <sup>1</sup>O<sub>2</sub> and help the redox couple in the lattice crystal according to Equations (19)–(21).

$$HSO_5^- + *O \to HSO_4^- + {}^1O_2 \tag{19}$$

$$2M^{(n+1)+} + O_2^- \to 2M^{(n+1)+} + O^* \to 2Mn^+ + O^*$$
(20)

$$HSO_5^- + SO_5^{2-} \to HSO_4^- + SO_4^{2-} + {}^1O_2$$
 (21)

In conclusion, heterogeneous metal redox cycle and non-radical reaction coexisted in the  $Co_2Mn_1O_4/PMS$  system and the generation of singlet oxygen promoted further TCS oxidation. Additionally, Lin et al. [118] synthesized  $CoMn_2O_4$  via a sol-gel method and observed similar results. The degradation of the PBSA was clearly affected by the catalyst dosage, PMS concentration, and reaction temperature. Finally, the TOC removal rate of PBSA in the  $CoMn_2O_4/PMS$  system was 29.59% after 60 min, indicating also the capability in mineralization process. Finally, the catalyst was separated, dried after the catalytic reaction and used effectively three more times in wastewater treatment.

#### 3.3. Copper Cobaltite (CuCo<sub>2</sub>O<sub>4</sub>) Spinels

CuCo<sub>2</sub>O<sub>4</sub> spinels have gained more and more attention due to their excellent electrical and catalytic properties. However, the synergistic effect of Cu-Co in the catalytic activation of PMS is still unclear and demands more research. Several researchers such as Chen et al. [120] and Feng et al. [122] synthesized  $CuCo_2O_4$  and examined the degradation pathway of sulfamethazine (SMZ) as a model pollutant. They studied a lot of parameters that affect the degradation rate such as the PMS dose, catalyst dose, reaction temperature and pH. The catalytic performance of Co species was enhanced with the addition of Cu species, showing a high catalytic activity and stability in a wide pH range from 7 to 11. The best catalytic activity was observed at 0.04 g  $L^{-1}$  catalyst and 20 mg  $L^{-1}$  PMS concentration, achieving 97% removal of SMZ. The interaction of redox pairs Cu(II)/Cu(I) and Co(III)/Co(II) are responsible in PMS activation to form the reactive species. CuCo<sub>2</sub>O<sub>4</sub> exhibited a higher current density and electric conductivity according to the EIS Nyquist plots, providing faster electron transfer that improves the activation of PMS. Cu<sup>2+</sup> in spinel surface is least likely reduced to Cu<sup>+</sup> in the first step when being used as the catalyst. So, first the  $Cu^{2+}_{OH}OSO_{3}^{-}$  complex is formed and through one electron transfer inside the complex,  $SO_4^{\bullet-}$  can be generated, which is accompanied by the production of Cu<sup>3+</sup>\_OH<sup>-</sup>. Then Cu<sup>3+</sup>\_OH<sup>-</sup> reduced to Cu<sup>2+</sup>\_OH<sup>-</sup> by HSO<sub>5</sub><sup>-</sup> producing additional sulfate radicals. Thus, sulfate radicals are the dominant radical oxidation species while  ${}^{1}O_{2}$  is the dominant non-radical oxidant that contributes to the rapid removal of SMZ from wastewater.

#### 3.4. Zinc Ferrite and Cobaltite (ZnFe<sub>2</sub>O<sub>4</sub>, ZnCo<sub>2</sub>O<sub>4</sub>) Spinels

Another catalyst studied for PMS activation and pollutant degradation is ZnFe<sub>0.8</sub>Co<sub>0.4</sub>O<sub>2.4</sub> nanoparticles rich in surface oxygen vacancies which promote the electron transfer and tended to

absorb oxygen because of the defect structure, forming active oxygen species on the surface of catalysts. Zhang et al. [124] synthesized lattice-doping Co into  $ZnFe_2O_4$  spinel using the sol-gel combustion method and studied its catalytic activity for the decomposition of Bisphenol A (BPA). The degradation of BPA by  $ZnFe_{0.8}Co_{0.4}O_{2.4}/PMS$  system was 70 % in just 1 min and the TOC removal reached 70% within only 15 min, which was better than the removal of BPA in  $ZnFe_2O_4/PMS$  suspension. Two pathways have been proposed for the pollutant degradation: (i) the direct oxidation at electron deficient Co sites, and (ii) the production of  ${}^{\bullet}OH$ ,  $SO_4{}^{\bullet-}$  from PMS activation near the surface oxygen vacancy.

Finally, Hu et al. [123] investigated the removal of BPA using  $ZnCo_2O_4$  prepared by a microwave-assisted method with response surface methodology (RSM) using the common Box-Behnken design (BBD), for PMS activation. Parameters such as microwave temperature, microwave time, calcination temperature, and calcination time were optimized. The degradation efficiency of BPA reached 99.28% within 5 min in the presence of  $[ZnCo_2O_4] = 0.2 \text{ g L}^{-1}$  and [PMS]/[BPA] = 2.0 molar ratio. Firstly,  $Co^{2+}$  bounded on the catalyst's surface activate HSO<sub>5</sub><sup>-</sup> to generate  $Co^{3+}$  and  $SO_4^{\bullet-}$ . Then, the obtained  $Co^{3+}$  could turn back to  $Co^{2+}$  through the reaction with HSO<sub>5</sub><sup>-</sup> with concurrent generation of  $SO_5^{\bullet-}$  and subsequent generation of  $SO_4^{\bullet-}$ . The stability and reusability of the catalyst were also tested including centrifugation, drying (70 °C with 2 h) and re-dispersion into fresh BPA-containing solution with BPA removal remained 83.45% after 5 catalytic cycles.

#### 3.5. Nickel Ferrite (NiFe<sub>2</sub>O<sub>4</sub>) Spinel

A typical member of spinel ferrites is the nickel ferrite which performs an excellent catalytic activity in PMS activation for the degradation of organic pollutants. Wang et al. [121] synthesized this catalyst by thermal decomposition of transition metal oxalate and studied the degradation rate of benzoic acid (BA). According to the results, over 82.5% of BA was eliminated in 60 min showing that nickel species were very eligible for PMS activation. This degradation efficiency was affected by operational parameters such as pH, PMS dose, catalyst dose. The best catalytic conditions were 1 mM PMS dose, 0.1 g L<sup>-1</sup> of catalyst and pH 10.0. Lower degradation rates were obtained when decreasing PMS concentration and increasing pH above 10. Finally, this catalytic system was used under different water matrices such as surface water, ground water and E-WWTP (water from wastewater treatment plants) with BA degradation efficiencies reaching 60.7%, 23.6% and 19.8%, respectively. Chloride, bicarbonate and organic compounds have been taken as the main factors that lowered too much the BA degradation efficiency in the case environmental waters and wastewaters.

#### 4. Current Trends and Future Research Needs

Regarding perovskite catalysts, mostly simple perovskites were studied so far for sulphate-radical-based treatment methods with various combinations of metals in either position A or position B of the ABO<sub>3</sub> perovskite structure. In the first case, the most encouraging results appeared in the cases of Sr- and La-perovskites, with La employed mostly as an A-site metal because its crystal structure is conducive to the exposure of active sites. In the second case, for La-based perovskites, which have been studied using various metals in the position B (Fe, Mn, Ni, Co, Cu), the greatest yields were observed mainly for Co and Ni. The selection of B-site cations can exert a significant impact on catalytic efficiency because their valence states impact the electron-transfer capability. In the case of simple supported perovskites, although not enough studies have been made, not only the superiority of  $Al_2O_3$  over other support materials has been observed, but also the achievement of smaller metal ion leaching rates and greater stability, compared to the cases of other perovskites. The immobilization on carbon materials such as graphene oxide, activated carbon, etc. could be also studied for further developments. Several studies were presented which examined the effect of partial substitution in position B of perovskite, where the best catalytic activity was presented in the case of partial substitution of Co by Cu, while its superiority was evident not only over the other substituted perovskites but also over simple perovskites. Partially substitution of Co cations with other transition metals (TM) could ameliorate the catalytic activity through Co-O-TM bond formation that

favor the electron transfer between  $Co^{2+}/Co^{3+}$  and  $M^{n+}/M^{(n+1)+}$  redox couples as well as by inducing oxygen vacancies which are catalytically active sites for PMS activation. Although there were several studies conducted in this category, it would also be interesting to study substituted perovskites of the type  $ACo_xNi_zO_3$  (x + z = 1), something that has not yet been presented, as  $LaCoO_3$  and  $LaNiO_3$ were the simple perovskites that showed the greatest activity, and to compare with the pristine simple perovskites but also other efficient substituted perovskites such as Co-Cu perovskites. In the same direction, various other combinations of metal substitutes could be examined in further studies for illuminating the interplay between the metals in the structure of perovskite. In addition, the cases of double perovskites are of great interest lately, showing encouraging results and activity at competitive levels, however, there are only few studies that have been done so far. Regarding the stability and reuse of the catalyst, the plethora of perovskites mentioned above maintained its catalytic action for at least 3–5 catalytic cycles. The appropriate metal cation substitution and the introduction of oxygen vacancies result also in reduced metal leaching and a better stability-recyclability of the catalysts. Therefore, the rationale for high-performance perovskite catalysts in PMS or PS activation should follow the appropriate substitution of both A and B generating favorable redox couples and the modification of the number and mobility of oxygen vacancies.

As far as the operational parameters, the pH range with the maximum activity displayed was between 5–7, with some occasional exceptions. In the case of substituted perovskites, the perforation of increased catalytic activity was observed in a wider pH range, mainly 5–10, but there were also cases where the activity was maintained at high levels even in pH 2–10 regions. The dominant ROS formed during the activation of PMS by simple perovskites, were mainly sulfate and hydroxyl radicals, while the degradation of organic pollutants in these cases was carried out through radical pathways. However, in the case of substituted perovskites and double perovskites, the degradation of organic pollutants took place not only through radical but also via non-radical pathways.

Regarding spinels, the most studied catalyst is the cobalt ferrite CoFe<sub>2</sub>O<sub>4</sub> which showed enhanced catalytic activity towards various organic pollutants. The best catalytic conditions were at nearly neutral pH (6–7) where dominate the CoOH+ species that help the PMS activation to generate sulfate radicals. PMS concentration at 1.0 mM and catalyst dose ranges from 0.1 to 0.4 gL<sup>-1</sup> showed the best results in most cases. The degradation process occurs by radical and non-radical pathways. As in the case of perovskites, the introduction of oxygen vacancies in spinel structure is a promising strategy to boost the catalytic performance. Besides cobalt ferrite, in general, ferrite or cobaltite spinels with Cu, Zn and Ni metals were mostly examined but not in a systematic way. They are also promising catalysts for PMS activation and can remove efficiently organic pollutants but more research is needed for further developments in the field of environmental treatment. Furthermore, it has been reported that spinel nanostructures combined with a support could enhance the catalytic behavior. Specifically, the most efficient supports are the carbon materials such as graphene oxide, r-GO, graphene, biochar etc., which have excellent adsorption ability toward organic compounds via the  $\pi$ - $\pi$  interactions. All these materials have high pore volumes, a large specific surface area and abundant active sites with functional groups ( $O_2$ ,  $OH^-$ ), that help the catalyst dispersion on its surface. Sulfate radicals appear to act as a major player in the contaminant degradation, and non-radical oxidation by PMS itself via direct two-electron transfer comes to a second place. All catalysts performed an acceptable stability and recyclability since they can be used after 4–6 catalytic cycles. In the last years, spinels such as CoFe<sub>2</sub>O<sub>4</sub> and Co<sub>x</sub>M<sub>2-x</sub>O<sub>4</sub>, have been also applied as catalysts in Fenton/photo-Fenton processes and in catalytic/photo-catalytic ozonation due to their flexible composition and high stability. Future studies on the comparison of different advanced oxidation approaches based on the same catalyst would be of great interest. Overall, spinels are promising catalysts with various applications in the field of water and wastewater treatment, able to activate PMS and remove organic pollutants. However, further studies are warranted to evaluate the optimal molar ratio of metal species, the toxicity of the transformation products, and the effect of actual water matrix on degradation. We believe that

the current sum-up of available results may open up a new avenue for the design and preparation of various novel heterogeneous catalysts for PMS activation in advanced oxidation processes.

By last, comparisons made using the same matrices and pollutants between sulphate radical-AOPs using best perovskite and spinel catalysts and other activation methods [9] as well as versus other catalytic or non-catalytic AOPs in terms of removal efficiency, limitations and overall cost would provide crucial information for future technology establishment.

#### 5. Conclusions

In this review study we have summarized the applications of both perovskites and spinels as catalysts in heterogeneous sulfate-radical based advanced oxidation processes for the degradation of priority and emerging organic pollutants present in water and wastewater systems. Regarding the heterogeneous activation of PMS with perovskite catalysts, simple perovskites, with the general type ABO<sub>3</sub>, have been used in numerous cases for the degradation of organic pollutants and, the one that showed the greatest activity over the others was  $LaCoO_3$ , in the case of  $LaBO_3$  perovskites, while in the case of ACoO<sub>3</sub> the greatest activity was presented by the LaCoO<sub>3</sub> and SrCoO<sub>3</sub> perovskites. Therefore, cobalt-based perovskites were the most efficient catalysts so far for the degradation of organic pollutants. The most important disadvantages of this category being the low pH range in which the optimal yields appear and the metal ion leaching phenomenon. These disadvantages can be abrogated by the deposition of perovskite catalysts in support materials but also by the synthesis of substituted perovskites. In the first case, the predominance of Al<sub>2</sub>O<sub>3</sub> over other inorganic supports was observed while for substituted perovskites, Co-Cu combination showed the best results. Furthermore, in few cases of double perovskites encouraging results were obtained. The appropriate substitution of both A and B ions generating favorable redox couples and the modification of the number and mobility of oxygen vacancies are key issues for designing of effective catalysts. The degradation of organic pollutants could take place via radical pathway (formation of sulfate and hydroxyl radicals) and non-radical pathway (formation of  ${}^{1}O_{2}$ ). On the other hand, in the case of spinel catalysts, cobalt ferrite  $CoFe_2O_4$  is by far the most studied catalyst showing remarked activity. Other cobaltite or ferrite spinels were also studied with promising results but not in systematic way. The study of carbon based material-supports is more evolved as compared to perovkite catalysts. Further studies are needed to explain the interplay between metals constituents of the spinel structures. Overall, perovskites and spinels are efficient, attractive and promising catalysts for sulphate-based AOPs applications in the field of water and wastewater treatment and future research on appropriate substitution and/or supporting could provide significant developments towards the tracking of best catalysts and comparison with already established oxidation technologies.

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