REVIEW PAPER

Heterogeneous metals and metal-free carbon materials for oxidative degradation through persulfate activation: A review of heterogeneous catalytic activation of persulfate related to oxidation mechanism

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Abstract−Activated persulfate has gained substantial interest owing to its potential removal efficiency toward recalcitrant organic pollutants, including pharmaceuticals, pesticide products, and industrial dyes. Various investigations into the activation of persulfate have been conducted to achieve a higher oxidation efficiency. Specifically, heterogeneous catalysts have been extensively applied to the activation of persulfate, enabling a more simplistic and practical method compared to other approaches. Therefore, the present review concentrates closely on various types of heterogeneous activators for the activation of persulfate and its proposed oxidation mechanisms.

Keywords: Heterogeneous Catalysts, Activation of Persulfate, Carbonaceous Catalysts, Heterogeneous Transition Metals

INTRODUCTION

As an increasingly widespread environmental problem, water pollution has become the most dangerous threat jeopardizing the future of humanity. In fact, urbanization and industrialization have resulted in the discharge of massive amounts of contaminants into the environment. For a remediation of contaminated water, physicochemical water treatment, such as separation and oxidation (including biotechnology), has been introduced to remove such waste materials [1]. Oxidation technology, in particular, has become a promising water treatment method, chemically transforming organic pollutants into minerals such as water and carbon dioxide.

Various oxidants have been used for the oxidation of water pollutants. Persulfate (collectively indicated as peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $S_2O_8^{2-}$)) has been intensively investigated for the purification of contaminated water for several reasons (including easy control, non-dependence on the pH, and a strong redox potential ($E^0(HSO_5^-/SO_4^{2-})=1.75\,V_{NHE}$ [2] and $E^0(S_2O_8^{2-}/SO_4^{2-})=1.96\,V_{NHE}$ [3])). Furthermore, the sulfate radical ($SO_4^{\bullet-}$, E^0 $(SO_4^{\bullet-}/SO_4^{2-})=2.43\,V_{NHE}$ [4]), a strong and effective oxidant, can be generated from the activation of persulfate. In fact, PDS has effectively remediated soil and groundwater through *in situ* chemical oxidation [5-8]. In addition, PMS has shown a high oxidation efficiency toward organic substances such as pesticides [9], pharmaceuticals [10], and dyes [11]. Based on many different studies, $SO_4^{\bullet-}$ is believed to be responsible for the oxidation mechanism because the hemolytic or heterolytic cleavage of persulfate bonds through an energy or electron transfer causes the production of $SO_4^{\bullet-}$.

The breaking of a peroxide bond has been carried out using various activation processes. Thermolysis [12,13], sonolysis [14], and photolysis [15] are representative methods for an energy transfer activation. The catalysis through an electron transfer activation method has attracted the interest of researchers owing to the lack of an external energy requirement, a fast reaction rate, and its effectiveness. Specifically, a heterogeneous catalyst has been intensively studied because it can be separated from a water environment after use. In addition, a heterogeneous catalyst can be modified in various ways to improve the catalytic activity. Metal species and carbon materials have mainly been utilized in the development of a heterogeneous catalyst for persulfate activation. Oh et al. systematically summarized the synthesis and preparation methods of different heterogeneous catalysts [16].

An $SO_4^{\bullet-}$ based advanced oxidation process (SR-AOP) was recently studied as an alternative technology to a conventional hydroxyl radical (·OH) based oxidation process (HR-AOP) owing to the unique properties of $SO_4^{\bullet-}$. Many metal- and carbon-based heterogeneous catalysts have been developed and tested to activate a persulfate for SR-AOP. However, oxidation, which does not rely on the reactivity of $SO_4^{\bullet-}$, has been reported in different research articles, contrasted with the scheme of SR-AOP. Such aspects are based on the following observations: (i) no radical scavenging effect and (ii) no specific electron paramagnetic resonance (EPR) spectrum detection using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO). Although the correct role of a heterogeneous catalyst (such as the electron donor behavior of metal species in a Fenton-like reaction) has yet to be fully understood, two possible explanations regarding the non-radical aspect have been proposed according to the experimental evidence. First, electron transfer mediation was suggested because oxidation occurs only if the three components (electron acceptor (persulfate), electron transfer mediator (heterogeneous catalyst), and electron donor (pollutant)) coexist. Second, a singlet oxygen generation was suggested owing to the observations of the quenching effect using L-histidine and azide ions and the identifiable specific EPR signal of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO). Such sug-

gestions are controversial, and more information is needed to unveil the non-radical oxidation mechanism.

In this review, we focus on heterogeneous catalyst-based persulfate activation and its oxidation mechanism. A heterogeneous catalyst can be a single metal element or a carbon frame, or they can be mixed together to enhance the activation efficiency. The oxidation mechanism of the activated persulfate was varied based on the type of catalyst. Furthermore, some studies have indicated that different oxidation mechanisms can contribute together for an organic pollutant degradation. We therefore classified the oxidation mechanism into radical and non-radical cases, and then surveyed the relationship between the materials and mechanisms. In this respect, the role of a heterogeneous catalyst is also elucidated herein.

PHYSICOCHEMICAL PROPERTIES OF PERSULFATE

As mentioned, a persulfate can be described as one of two chemical compounds, PMS or PDS (Table 1). PMS (H_2SO_5) originates from Caro's acid [17] but is difficult to handle owing to its reactive and explosive characteristics. It has two dissociation constants (pK_a) of 0.4 and 9.3. Therefore, under neutral and weak acidic conditions, HSO_5^- is the dominant species. To generate a more stable form, Oxone (containing the three salts $2KHSO_5$, $KHSO_4$, K_2SO_4) with a powerful oxidation potential was invented. An unsymmetrical reactive O-O bond can produce more reactive radicals when activated through the numerous methods mentioned above, effectively remove recalcitrant organic compounds, and further mineralize into CO_2 and H_2O, such as a highly reactive species of hydroxyl radical. Oxone is commercially available and has numerous merits including non-toxicity, affordability, and high solubility in water, and has been widely used as an oxidizing agent in swimming pools and spas to maintain the water quality.

PDS was first discovered by a French chemist, Marcelin Berthelot, in 1878 [18]. PDS is an inorganic compound composed of a symmetrical O-O bond with the chemical formula $Na_2S_2O_8$ that remains highly stable in an aqueous solution. Along with its many advantages, including high solubility in water and lower cost compared with other oxidants, PDS is a promising method for the effective removal of organic pollutants in groundwater and soil treatment [19]. The stable form of PDS has demonstrated its strength in many different industrial processes and commercial products for various applications including polymerization, organic and inorganic synthesis, gas and oil production for enhanced oil recovery, and soil remediation and wastewater cleanup.
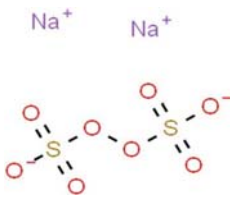
UNDERSTANDING OF PERSULFATE OXIDATION MECHANISM USING CARBON NANOMATERIALS

Unlike heterogeneous transition metal catalysts, carbonaceous catalysts have been considered promising alternatives for persulfate activation owing to the lack of toxic metals leaching into water, catalytic stability and abundance in nature [20]. In addition, carbon catalysts not only demonstrate an excellent catalytic activity with their large surface area, they also enhance the catalytic efficiency with their long-term reusability. To achieve persulfate activation, chemical modification on the surface of the carbon materials is also strongly recommended to substantially increase the catalytic reactivity (Fig. 1).

For these reasons, carbonaceous nanomaterials have been extensively studied for their water remediation, and various carbon-based nanomaterials (including activated carbon (AC) [21-29], carbon nanotubes (CNTs) [30-39], mesoporous carbon (MC) [40-42], surface modified graphene oxide (GO) [43-50], biochar (BC) [51-53], metal cored composites surrounded by graphitic carbon layers (M@C) [54-58], and nanodiamonds (NDs) [59-63]) have further exhibited an activated persulfate that promotes the generation of a reactive oxygen species (ROS) in an aqueous solution.

Interestingly, the oxidation process for persulfate activation using carbon catalysts remains unsolved, although numerous studies have demonstrated that most of the oxidation process is responsible for $SO_4^{\cdot-}$ formation. By contrast, some authors have suggested that carbon nano materials act as an electron mediator, obtaining an efficient removal of the organic components through an electron transfer between phenols, which is an electron donor, to PS, an electron acceptor (involving no radical attack). Numerous other aspects, such as quenching effects, selectivity in the degradation of the phenolic compounds, and EPR spectroscopy, have shown different results

Table 1. Basic chemical properties of persulfate (PMS and PDS)

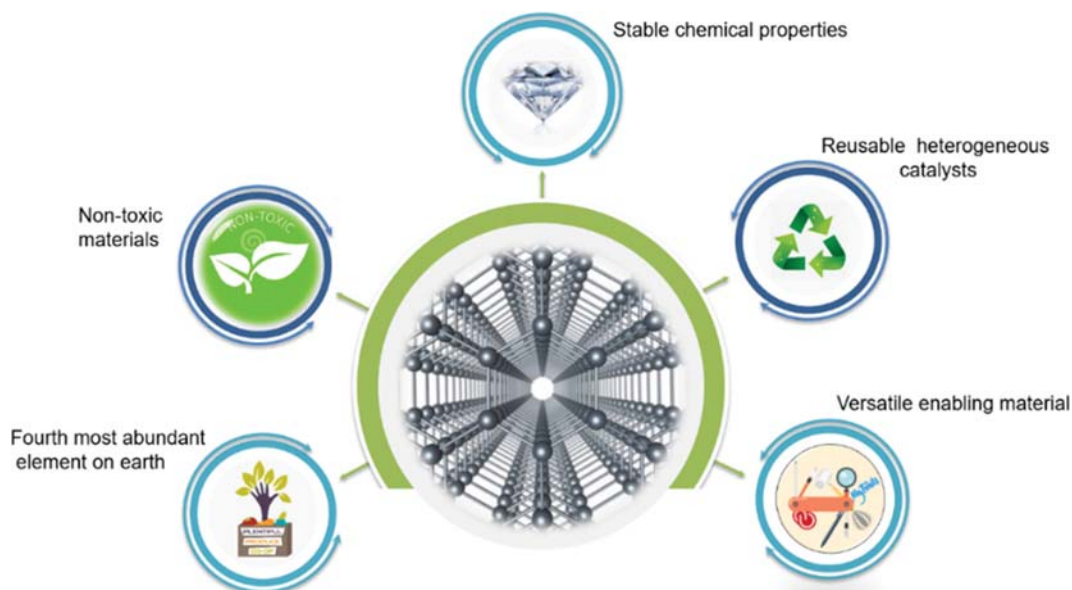| Type	PDS (sodium peroxydisulfate)	Oxone, PMS (potassium peroxymonosulfate)
Physical form	Crystalline	Crystalline
Molecular formula	$Na_2S_2O_8$	$2KHSO_5$, $KHSO_4$, K_2SO_4
Molecular weight (g/mol)	238.1	307.38
Color	White	White
Redox potential (V)	1.96	1.75
Odor	None	None
Solubility (g/L in H_2O at 20 °C)	556	298
Chemical structure		

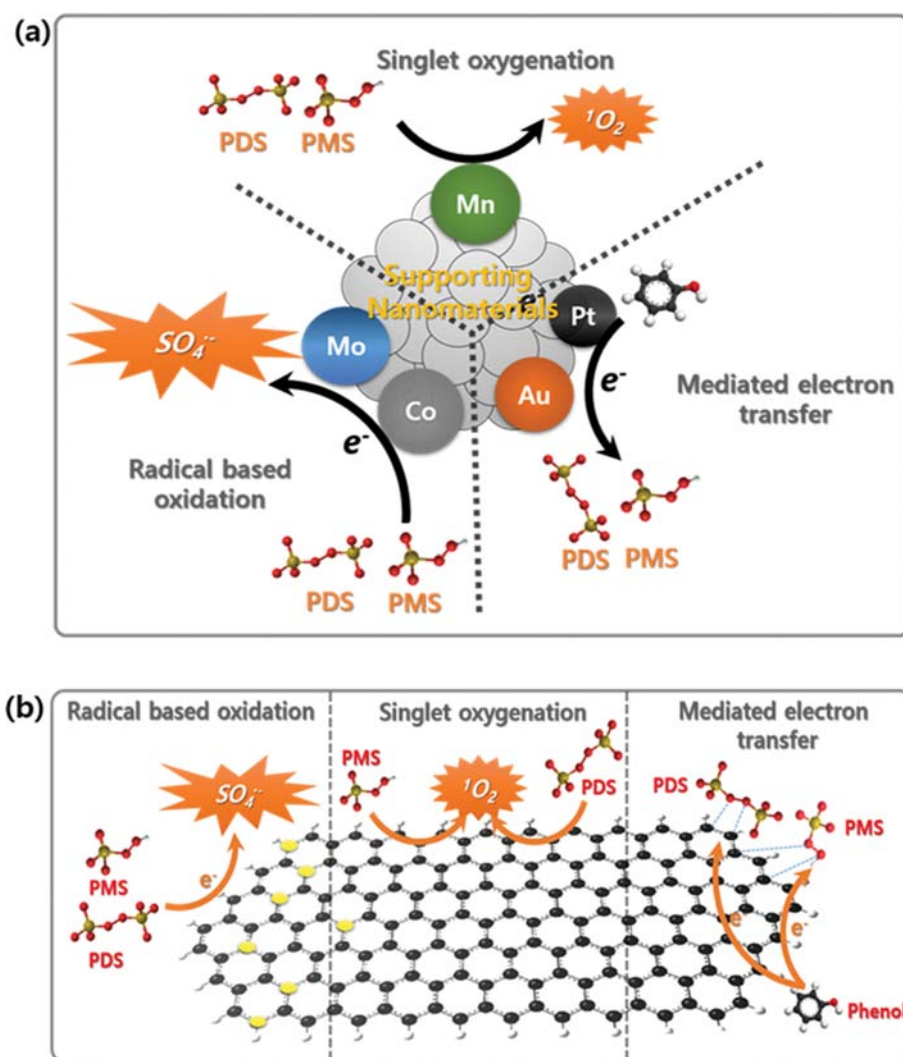**Fig. 1. Advantages of carbon nanomaterial for environmental remediation.**

Fig. 2. Suggested oxidation pathways for activating persulfate via (a) heterogeneous metallic catalysts and (b) carbonaceous catalysts.

based on a sulfate radical process. Alternatively, persulfate activation by nano carbon materials has triggered another debate in that singlet oxygen can be primarily responsible for the decomposition of organic pollutants. Cheng et al. observed a clear triplet spectrum from EPR spectroscopy corresponding to singlet oxygen in an aqueous CNT/PDS system.

Therefore, the following section provides a comprehensive review on elucidating and better understanding the oxidation mechanisms for the activation of persulfate through various carbon-based nanomaterials (Fig. 2).

1. Carbon Nanotubes (CNTs)

The unique nature of carbon nanotubes has received significant attention owing to its high electrical and thermal conductivity, structural flexibility and elasticity, mechanical strength, and chemical stability, among other merits. CNTs consist of cylindrical structures with one (SWNTs) or multiple (MWNTs) rolled up graphene sheets. These special physiochemical properties with sp^2 hybridized carbon atoms demonstrate superior electronic characteristics and mechanical strength, and have been proposed for use in the removal of organic compounds in wastewater treatment.

In general, the purified or modified surfaces of CNTs have shown remarkably higher adsorption capabilities toward halogen ions and trace organic compounds and heavy metals compared to other materials [36]. At present, persulfate activation by CNTs has shown excellent activity towards organic chemical destruction. As a metal-free catalyst, organic compounds such as ethylbenzene remarkably turn into acetophenone in a liquid phase through π-π interactions between the radical species and active sites of the CNTs [64]. Chemical modification of the surfaces of the CNTs results in a significant enhancement for the removal of phenolic compounds as compared to pristine carbon nanotubes, whereas nitrogen dopants do not demonstrate a decisive effect on the persulfate activation [33]. Most of the oxidation process is primarily induced by the generation of sulfate radicals, of which the unique sp^2 structure of CNTs and oxygen containing groups contribute to a superior activity with persulfate. To identify the radical species during catalytic oxidation, EPR spectra are applied and result in the detection of the $SO_4^{\cdot-}$ signal in the presence of DMPO [30-33]. In addition, the oxidation rate is inhibited after the addition of excessive amounts of radical scavengers. In contrast, Lee and coworkers proposed that CNTs activate the persulfate through a non-radical mechanism, and are not involved in the formation of radical species [34]. To identify the non-radical oxidation mechanism of persulfate activation using CNTs, two different activation systems were compared (CNTs used for a mediated electron transfer and nFe^0 used as a reducing agent for initiating the radical-induced reaction pathway), the results of which further confirmed that the primary oxidation mechanisms are fundamentally different in terms of their scavenging effects, no radical detection in the EPR spectra, a different substrate specificity and product distribution, and current generation [37]. Meanwhile, Cheng et al. suggested that a singlet oxygen is formed through a recombination during the PS/C non-photochemical production of a singlet oxygen in the activation of persulfate using a carbon nanotube system as proved based on the ESR and quenching effect [39].

2. Activated Carbon (AC)

AC, also known as activated charcoal, is mainly composed of car-

bon atoms with properties of highly porous adsorptive networks. It is manufactured from various carbonaceous sources including wood, coconut shells, lignite, and coal. Activated carbon can be categorized into three different types: granular activated carbon (GAC), powdered activated carbon (PAC), and extruded carbon. With an excellent ability toward organic compounds, ACs have begun to be applied to persulfate activation for phenol removal. The catalytic activity for PMS results in a better removal efficiency among three different oxidants (H_2O_2, PDS, and PMS) with the generation of a radical species. In addition, the special chemical structure of AC can help effectively remove the organic dyes by activating with persulfate through the generation of $SO_4^{\cdot-}$ [23]. The size of the AC is closely related to the catalytic efficiency in that powder AC is more effective in activating persulfate as compared with the use of granular AC. Graphitic carbon nitride and AC composites were evaluated to activate persulfate for the destruction of the phenolic compounds. The semiconducting properties of modified carbon nitride have shown synergetic effects toward the removal of dye compounds under visible light, although the results are not sufficient for phenol degradation. However, it seems that it has not been clearly identified whether the oxidation mechanism is responsible for singlet oxygenation or the production of a radical species [21,22].

3. Graphene Oxide (GO)

Graphene oxide is a unique carbon material obtained by chemically modifying a single layer of graphene through a powerful oxidation process. As one of the thinnest layer materials (approximately 1.1 ± 0.2 nm thick) available, graphene oxide has many advantages, including sustainable resilience, chemically stable structure, high mechanical strength, and relatively high conductivity, making it potentially useful for the exploration of various environmental applications. Sun et al. first conducted a catalytic oxidation of persulfate activation using reduced graphene oxide. Phenol and 2,4-dichlorophenol are effectively degraded in the activating persulfate, producing $SO_4^{\cdot-}$ [44]. The activity of graphene oxide is dependent on the defect sites on the surface of the GO, whereas localized zigzag edges make the π electrons more available for activating the persulfate.

Moreover, the addition of nitrogen (N) and sulfur (S) atoms through chemically modified graphene has emerged to enhance the catalytic activity for persulfate activation [43,47]. It was reported that N-doped reduced graphene oxide shows an excellent catalytic performance regarding PMS activation through which the radical species play a critical role in the phenol oxidation [48]. Interestingly, Liang et al. suggested that, through a different oxidation mechanism, singlet oxygen is the main species contributing to a degradation of the phenolic compounds instead of sulfate or hydroxyl radicals [49]. To further verify the singlet oxygenation, the efficiency of phenol degradation was remarkably inhibited by the addition of NaN_3, whereas ethanol and *tert*-butanol as a sulfate radical scavenger shows no significant influence on the phenol oxidation. Additionally, the oxidation pathways were investigated by EPR spectra using spin trapping agent (TEMP) and obtained a clear $^1O_2$ peaks that would oxidize TEMP into TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy, free radical, 2,2,6,6-Tetramethylpiperidine 1-oxyl). The special properties of graphene oxide with various functional groups provide an outstanding performance in the activation of persulfate.

4. Mesoporous Carbon (MC)

MC nanoparticles are a flexible material with a high surface area, and are composed of ordered nano-sized pores (diameters of between 2 and 50 nm). Along with its effective electrical conductivity, it is also considered a promising application for electrochemical materials used in supercapacitors and energy storage devices. MC has recently been applied to persulfate activation. Duan et al. suggested that three-dimensional cubic mesoporous carbon (CMK) materials provide an excellent phenol removal efficiency, demonstrating a similar performance as classical persulfate activation through zero valent iron [40,42]. Rapid phenol removal is mainly responsible through the presence of sulfate radicals generated on the MS surface, although a non-radical activation pathway also has a partial contribution. In addition, chemically modified MD through the nitrogen functionalization process demonstrates an enhanced adsorption capacity of Pb, and further provides an excellent efficiency in the degrading of p-nitrophenol.

5. Nanodiamond (ND)

ND has been studied deeply owing its numerous merits, including its low cost with a large-scale synthetic process, non-toxicity, large accessible area at a nanoparticle size (less than 5 nm), and potential application to a surface modification. With their unique sp^2/sp^3 hybridized properties, a distinctive ND surface can be easily modified and functionalized to promote an enhanced catalytic activity. Specifically, nitrogen doped with the simultaneous surface graphitization on ND shows a highly efficient catalytic activity for PMS activation. The enhanced performance is mainly due to the production of sulfate and hydroxyl radicals based on the results of the radical scavenging effects, EPR analysis, and cyclic voltammetry. In addition, the thermal treatment of ND has a pivotal role in the dramatic improvement of the persulfate activation, suggesting that the graphitized shell of ND becomes enlarged with surface defects sites, which can effectively interact with persulfate. In contrast, Lee et al. demonstrated a different oxidation process for phenol removal as compared to a conventional activation process, which generates sulfate radical species. Persulfate activation using graphitized ND has shown contradictory results including no inhibitory effects by the radical scavengers, partial inhibition by the addition of NOMs, and selective reactivity on phenolic compounds [63]. In general, bromate is generated as a final product from bromide oxidation through the sulfate radical process. However, according to Yun et al., there has been no detection of a bromate formation in a PMS/graphitized ND system [61].

6. Metal-cored Encapsulated Carbon (M@C)

A recent study proposed that metal-cored encapsulated carbon shows high efficiency in the catalytic oxidation of phenol through the activation of persulfate. Magnetic metals can contribute to the synergetic effects on the carbon layers, increasing the outstanding catalytic performance and stability for persulfate activation [54]. Some studies have shown that nitrogen on the surface of encapsulated carbon can remarkably enhance the catalytic activity and stability for recycling purposes [55]. In the case of a catalytic oxidation, a surface modified with nitrogen sources shows a significant enhancement in the catalytic activity available to the activation of persulfate for the generation of a radical species for a phenol degradation [57].

7. Biochar (BC)

BC is an enriched carbon material usually obtained from biomass residue after a thermochemical conversion under anoxic conditions [53]. Interest in the use of BC has increased owing to its benefits for soil health and agricultural productivity. Magnetized nano-composite biochar was recently applied to persulfate activation for the removal of organic pollutants. The effects of metal cations (Fe^{3+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}) effectively enhance the ability to activate persulfate for the removal of organic pollutants, resulting in the generation of sulfate radicals [52]. According to Yan et al., zero valent iron (nZVI) with BC composites for persulfate activation shows a synergistic effect in enhancing the redox reaction and the electron transfer for the formation of $SO_4^{\cdot-}$, effectively removing trichloroethylene [51].

RESEARCH INTO PERSULFATE ACTIVATION USING METAL SPECIES

Metals with high electron-donating potentials can reductively transform PMS and PDS into $SO_4^{\cdot-}$ through a one-electron reduction in the same manner as Fe^{2+} activates H_2O_2 to yield $\cdot OH$ in a Fenton reaction. In fact, Thompson et al. anticipated the free radical reaction by a 1-equiv reduction of PMS and reported the generation of $SO_4^{\cdot-}$ using a 1-equiv reducing agent VO^{2+} with HSO_5^- in an acidic medium [65]. In contrast, some recent studies have increased the possibility of persulfate activation degrading organic
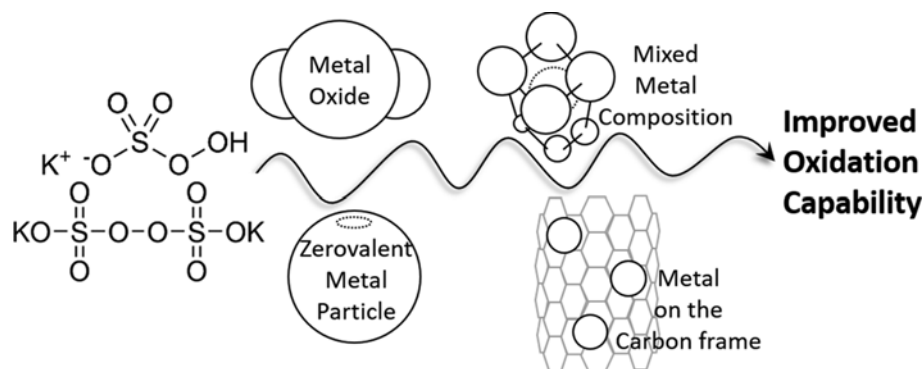

Fig. 3. Type of heterogeneous metal catalysts for persulfate activation.

pollutants without a radical formation (i.e., non-radical mechanism). The occurrence of persulfate activation, based not on the oxidizing power of $SO_4^{•-}$, has been evidenced primarily through (i) no quenching effects of chloride and alcohol (e.g., methanol and ethanol) and (ii) no detection of an $SO_4^{•-}$ adduct with the exception of a single electron-transfer oxidized nitroxide radical (i.e., 5,5-dimethylpyrrolidone-2-(oxy)-(1) (DMPOX)) in the EPR spectrum. For this reason, to address the concerns regarding a non-radical mechanism, the following section summarizes the development of heterogeneous persulfate activators, such as Co-based, Fe- or Cu-derived, and metal-carbon mixed materials, and describes the suggested oxidation mechanism (Fig. 3 and Table 2-5).

1. Cobalt

Cobalt is highly reactive to PMS. Anipsitakis et al. reported that the activation mechanism of PMS by cobalt ions is similar to the activation of hydrogen peroxide, i.e., it is a Fenton-like reaction. The authors believe that Co^{2+} loses an electron for a 1-equiv reduction of PMS, generating $SO_4^{•-}$ [66]. Later, they surveyed nine types of metal ion species in three types of common peroxides (H_2O_2, PDS, and PMS), and found that Co^{2+} is the most effective regarding PMS activation for 2,4-dichlorophenol degradation [67]. Based on its high efficiency, the cobalt species has been widely utilized in the development of a heterogeneous catalyst for PMS activation. Cobalt oxides such as Co_3O_4 are a simple heterogeneous activator and are

Table 2. Sulfate radical based oxidation process for persulfate activation

Oxidation mechanism	Catalysts	Type of persulfate	Supportive results	Reference
Radical based oxidation process via carbonaceous catalysts	Nitrogen doped MWNTs	PMS and PDS	• Speculated to generate sulfate radical	Sun et al. [32]
	Nitrogen doped SWNTs	PMS	• EPR spectrometry with DMPO adducts • Radical scavenging effects (ethanol)	Duan et al. [33]
	Nitrogen and sulfur co-doped CNT-COOH	PMS	• Speculated to generate sulfate radical	Liu et al. [31]
	Reduced graphene oxide	PMS	• Comparison to Transition Metal-Based Catalyst in catalytic activity	Sun et al. [44]
	Nitrogen doped graphene oxide	PMS	• Theoretical calculations for the role of nitrogen • EPR spectrometry with DMPO adducts	Duan et al. [43]
	Nitrogen doped reduced graphene oxide	PDS	• EPR spectrometry with DMPO adducts	Kang et al. [48]
	Nitrogen, boron, and phosphorus doped or co-doped graphene	PMS	• EPR spectrometry with DMPO adducts	Duan et al. [47]
	Nitrogen doped graphene oxide	PMS	• EPR spectrometry with DMPO adducts	Wang et al. [46]
	Sulfur and nitrogen co-doped reduced graphene oxide	PMS	• EPR spectrometry with DMPO adducts	Duan et al. [50]
	Mesoporous carbons	PDS	• EPR spectrometry with DMPO adducts	Duan et al. [42]
	3D hexagonally-ordered mesoporous carbon (CMK-3)	PMS	• EPR spectrometry with DMPO adducts • Radical scavenging effects (ethanol, T-butyl alcohol)	Indrawirwan et al. [41]
	Powder activated carbon (PAC)	PMS	• Speculated to generate sulfate radical	Saputra et al. [27]
	Activated carbon (AC)	PDS	• Speculated to generate sulfate radical	Liang et al. [26]
	Granular activated carbon (GAC)	PMS	• Speculated to generate sulfate radical	Zhang et al. [23]
	Activated carbon fiber	PMS	• Radical scavenging effects (T-butyl alcohol)	Yang et al. [29]

Table 2. Continued

Oxidation mechanism	Catalysts	Type of persulfate	Supportive results	Reference
Radical based oxidation process via carbonaceous catalysts	Activated carbon fiber	PDS	• Radical scavenging effects (ethanol)	Chen et al. [24]
	Surface modified activated carbon fiber	PMS	• Speculated to generate sulfate radical	Yang et al. [22]
	Granular-activated carbon and activated carbon fiber	PMS	• Radical scavenging effects (methanol)	Yang et al. [25]
	Nitrogen modified nanodiamond (N-AND)	PMS	• EPR spectrometry with DMPO adducts • Radical scavenging effects (ethanol, tert-butyl alcohol)	Duan et al. [62]
	N_2-annealed nanodiamonds	PDS	• EPR spectrometry with DMPO adducts • Radical scavenging effects (ethanol, humic acid)	Duan et al. [60]
	Nitrogen doped Fe^0/Fe_3C @C micro-cubes	PDS	• EPR spectrometry with DMPO adducts • Radical scavenging effects (ethanol, tert-butyl alcohol)	Jin et al. [56]
	Magnetic metal (Fe, Co, Ni) encapsulated in N doped carbon nanotubes	PMS	• Radical scavenging effects (methanol, *tert*-butyl alcohol, benzoquinone, and KI)	Yao et al. [58]
	Cobalt nanoparticles embedded in N-doped carbon nanotubes (Co@NC)	Sulfite	• EPR spectrometry with DMPO adducts • Radical scavenging effects (methanol, T-butyl alcohol, benzoquinone)	Wu et al. [57]
	Nano zero-valent iron encapsulated in carbon spheres (Fe^0/Fe_3C@CS)	PMS	• EPR spectrometry with DMPO adducts • Radical scavenging effects (Ethanol, humic acid)	Wang et al. [54]
	Metals (Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) loaded biochar	PDS	• EPR spectrometry with DMPO adducts	Fang et al. [108]
	Nano magnetite biochar composite (nFe_3O_4/biochar)	PDS	• EPR spectrometry with DMPO adducts • Radical scavenging effects (Ethanol, T-butyl alcohol)	Quyang et al. [52]
	Biochar (BC) supported nanoscale zerovalent iron (nZVI) composite	PDS	• Speculated to generate sulfate radical	Yan et al. [51]

used for the degradation of pollutants such as phenol, chlorophenol, Acid Orange 2, and Acid Orange 7 [68-71]. However, the stability of the oxide becomes a problem owing to the dissolution of the cobalt species, depending on the pH of the solution. In addition, an agglomeration possibly occurs during a catalytic reaction that might reduce the catalytic performance. For the development of a stable activator that is insensitive to the pH of the system, immobilization of the cobalt species onto another metal oxide frame, such as iron oxide or a carbon-based support, was also synthesized and tested [72-74]. Iron species have been widely used as metal cata-

lysts, and their utilization has been intensively studied for the application of PMS activation. Hence, an iron oxide (e.g., spinel ferrite) supported cobalt material has attracted interest owing to its high-level performance, utility, stability, and expectation regarding the synergistic effect of the bimetallic form, including the magnetic property. Hu et al. mentioned that the presence of the hydroxyl group on the Fe surface introduces a $CoOH^+$ formation, and therefore affects the abundant Co^{2+} content in a combined form as compared with a single Co_2O_3 [75]. In addition, metal ions on the surface capture H_2O, forming hydroxyls and increasing the attraction

Table 2. Continued

Oxidation mechanism	Catalysts	Type of persulfate	Supportive results	Reference
Radical based oxidation process via heterogeneous metallic catalysts	Cobalt oxide	PMS	• Speculated to generate sulfate radical	Zhiyong et al. [68]
	Cobalt oxide with spinel iron oxide	PMS	• XPS spectra • Radical scavenging effects (phosphate)	Wu et al. [72]
	Zero-valent iron	PMS, PDS	• Speculated to generate sulfate radical	Ghanbari et al. [76]
	Ferrite	PMS	• XPS spectra • Regeneration of Fe^{2+} by NH_2OH • EPR spectrometry with DMPO adducts	Zhang et al. [79]
	Magnetite	PMS	• XPS spectra • EPR spectrometry with DMPO adducts	Tan et al. [80]
	Copper oxide	PDS	• Radical scavenging effects (methanol, T-butyl alcohol)	Liang et al. [90]
	Co/Activated carbon	PMS	• Speculated to generate sulfate radical	Shukla et al. [104]
	Ru/Activated carbon	PMS	• Speculated to generate sulfate radical	Muhammad et al. [106]
	Pd/graphitic N-carbon	PMS	• Radical scavenging effects (methanol, T-butyl alcohol, benzoquinone, L-histidine) • EPR spectrometry with DMPO and TEMP adduct	Wang et al. [107]
	Palladium/Aluminum oxide	PMS	• Radical scavenging effects (methanol) • XPS spectra • PMS stability • Generation of formaldehyde	Feng et al. [109]

to HSO_5^-, thus bringing about an improved PMS activation [73].

2. Iron

As mentioned, an iron species has been widely utilized as a support material. By contrast, the single elemental use of iron has also been investigated owing to its persulfate activation. One example is ZVI. The 2-equiv oxidation of ZVI by persulfate proceeds to a Fe^{2+} dissolution from the ZVI surface [76-78]. Accordingly, the one-electron transfer oxidation of Fe^{2+} by persulfate proceeds toward an SO_4^{-} generation. Ghanbari et al. reported better textile wastewater decolorization performance of ZVI/PMS system than ZVI/H_2O_2, despite Fe^{2+} being an effective Fenton reagent activating H_2O_2 [76]. Hussain et al. claimed that the reaction between Fe^{3+} and ZVI produces Fe^{2+} and brings about an effective PDS activation through the reproduction of Fe^{2+} [77]. Li et al. compared Fe^{2+}, nano-Fe_3O_4, and nano-ZVI at the same iron dose regarding PDS activation, and demonstrated the superior activation efficiency of nano-ZVI over the other species [78]. However, the dosing ratio between ZVI and persulfate must be considered to achieve an effective performance because ZVI competitively reacts with the radical species. Furthermore, the high aggregation property and high deposition rate of ZVI are also limitations, as is the requirement of a continuous ZVI supply [16].

When using iron oxide as a persulfate activator, a reduction of Fe^{3+} to Fe^{2+} is essential for a repetitive operation. Zhang et al. employed hydroxylamine as a reducing agent for a Fe^{3+} reduction to improve the PMS activation performance of Fe_2O_3 [79]. Tan et al. demonstrated the effective catalytic performance of Fe_3O_4 magnetic nanoparticles for PMS activation and presented XPS results in which the oxidation of Fe^{2+} is accompanied by the generation of SO_4^{-} [80]. Lin et al. assessed the electrochemical process to reduce Fe^{3+} to Fe^{2+} in Fe_3O_4 particles for PDS activation. Under a recycling experiment, the stability of Fe_3O_4 was confirmed and the regeneration of Fe^{2+} on the surfaces of the Fe_3O_4 particles was also observed according to the XPS spectrum [81].

3. Manganese

Manganese can exist in diverse oxidation states ranging from Mn^0 to Mn^{7+} but naturally exists in Mn^{2+} and Mn^{4+} oxide forms (i.e., Mn_2O_3 and MnO_2) [82]. In fact, a variety of factors can affect the catalytic activity of Mn oxide, including the diverse oxidation states mentioned above. Oh et al. summarized such factors as (i)

Table 3. Mediated electron transfer oxidation process for persulfate activation

Oxidation mechanism	Catalysts	Type of persulfate	Supportive results	Reference
Mediated electron transfer oxidation process via carbonaceous catalysts	CNTs	PDS	• EPR spectrometry (DMPOX) • Substrate–specific reactivity • Negligible radical scavenging effects (methanol, DMSO, and humic acid)	Lee et al. [34]
	Graphitized nanodiamonds	PDS	• Electrochemical analysis (LSV) • Negligible radical scavenging effects (methanol, DMSO, L-histidine, Azide, NOM)	Lee et al. [63]
	Graphitized nanodiamonds	PMS	• EPR spectrometry (DMPOX) • No bromate formation from bromide • Substrate–specific reactivity • Negligible radical scavenging effect (DMSO)	Yun et al. [61]
Mediated electron transfer oxidation process via heterogeneous metallic catalysts	Copper oxide	PDS	• Radical scavenging effects (ethanol, chloride) • Comparison with sulfate radical oxidation	Zhang et al. [93]
	Palladium/Aluminum oxide	PMS	• Radical scavenging effects (methanol) • Substrate specificity	Ahn et al. [102]
	Platinum/Aluminum oxide	PMS	• Radical scavenging effects (methanol) • Substrate specificity • PMS stability	Ahn et al. [102]
	Gold/Aluminum oxide	PMS	• Radical scavenging effects (methanol) • Substrate specificity • PMS stability	Ahn et al. [102]
	Rhodium/Aluminum oxide	PMS, PDS	• Radical scavenging effects (methanol) • EPR spectrometry with BMPO adducts • No bromate formation from bromide • PDS activation capacity • PMS stability	Ahn et al. [110]
	Iridium/Aluminum oxide	PMS, PDS	• Radical scavenging effects (methanol) • EPR spectrometry with BMPO adducts • No bromate formation from bromide • PDS activation capacity • PMS stability	Ahn et al. [110]
	Amorphous manganese dioxide	PMS	• Radical scavenging effects (ethanol, *tert*-butyl alcohol) • EPR spectrometry with DMPO adducts • Intermediate analysis	Wang et al. [88]

the presence of the oxygen liability, (ii) the density of the exposed reactive facets, (iii) the presence of a mixed valence Mn, (iv) the different redox potentials along with the Mn oxidation state, (v) the specific surface area, and (vi) crystallinity [16]. Specifically, MnO_2 was intensively studied to determine the property dependency of a Mn catalytic activity. For example, Saputra et al. reported that α-MnO_2 can be utilized toward phenol degradation through a catalytic PMS activation, and investigated the influence of the Mn oxidation state on the PMS activation [83,84]. Wang et al. investigated the shape-dependence of the MnO_2 catalytic efficiency for PMS activation using nanorods, nanotubes, and nanowires [85]. Huang et al. synthesized differently structured MnO_2, namely, tunnel structures (α-, β-, γ-MnO_2) and a layered structure (δ-MnO_2), and tested

the PMS activation efficiency for bisphenol A degradation [86]. These studies suggest that the radical species is responsible for the oxidation of organic compounds, and is generated from the catalytic decomposition of PMS through the Mn. By contrast, the oxidation mediated non-radical mechanism, instead of a radical attack, on a Mn catalyzed persulfate activation has also been recently reported. It is noteworthy that the MnO_2 itself can behave as an oxidant owing to its multivalent nature. However, it was revealed that a non-radical oxidation does not account for direct oxidation through MnO_2. Here, $^1O_2$ was considered a reactive oxidation species based on a radical quenching experiment and EPR measurement. Tian et al. observed the increase of dissolved oxygen during BioMnOx derived PMS activation. Based on the oxygen evolution

Table 4. Combined oxidation processes between mediated electron transfer and radical based oxidation for persulfate activation

Oxidation mechanism	Catalysts	Type of persulfate	Supportive results	Reference
Combined oxidation systems between mediated electron transfer and radical based oxidation sulfate radical based oxidation process via carbonaceous materials	Nitrogen doped SWNTs	PMS, PDS	• N-doping can induce nonradical oxidation in PMS activation • EPR spectrometry with DMPO adducts • Radical scavenging effects (ethanol, *tert*-butyl alcohol)	Duan et al. [30]
	Cubic mesoporous carbon	PDS	• Radical scavenging effects (methanol)	Duan et al. [42]
	Nitrogen-doped bamboo-like carbon nanotubes encapsulated with nickel nanoparticles	PDS	• N-doping can induce nonradical oxidation in PMS activation • EPR spectrometry with DMPO adducts • Radical scavenging effects (ethanol)	Kang et al. [55]
Combined oxidation systems between mediated electron transfer and radical based oxidation sulfate radical based oxidation process via heterogeneous metallic catalysts	Fe-N-codoped carbonaceous catalyst	PMS	• EPR spectrometry with DMPO and TEMP adduct • Comparing effects of singlet oxygen lifetimes in D_2O solution • XPS spectra	Long et al. [105]
	Fe/S modified carbon nanotubes	PDS	• Radical scavenging effects (methanol, *tert*-butyl alcohol) • PDS stability	Cheng et al. [111]

Table 5. Singlet oxygenation process for persulfate activation

Oxidation mechanism	Catalysts	Type of persulfate	Supportive results	Reference
Singlet oxygenation process via carbonaceous catalysts	CNTs	PDS	• EPR spectrometry with TEMP adducts • Radical scavenging effects (L-histidine, azide)	Cheng et al. [39]
	Nitrogen doped graphene	PMS	• EPR spectrometry with TEMP adducts • Radical scavenging effects (ethanol, L-histidine, azide)	Liang et al. [49]
	Nanodiamonds	PMS	• EPR spectrometry with TEMP adducts	Shao et al. [59]
Singlet oxygenation process via heterogeneous metallic catalysts	δ-Manganese oxide	PMS	• Radical scavenging effects (ethanol, tert-butyl alcohol) • XPS spectra • ATR-FTIR analysis	Huang et al. [86]
	Biogenic manganese oxide	PMS	• EPR spectrometry with TEMP adducts • Radical scavenging effects (ethanol, *tert*-butyl alcohol, azide) • XPS spectra • Intermediate analysis	Tian et al. [87]

with the result of ESR and quenching experiment, they concluded that the singlet oxygen is the main oxidant. They pointed out that the $^1O_2$ can be generated from PMS self-decomposition process and they proposed that this feature is responsible for $^1O_2$ generation [87]. In addition, the PMS-MnO$_2$ complex was also considered to be responsible for the oxidation [88].

4. Copper

Copper has been conventionally employed for H_2O_2 activation. In this respect, a copper-derived persulfate activation system was also investigated to degrade the organic contaminants. Ji et al. attempted to achieve phenol degradation using CuO/PMS as an alternative to the highly efficient Co/PMS because they anticipated good catalytic effect of CuO based on its striking ability to induce H_2O_2 activation [89]. Liang et al. found that CuO/PDS results in p-chloroaniline degradation, and they mentioned that dissolved Cu^+ ions from the CuO surface are a key factor under both an acidic and a neutral pH [90]. Zhang et al. prepared CuFe$_2$O$_4$ for PMS activation to obtain Cu stability, reusability, and a magnetic separation. During iopromide degradation, they demonstrated the high stability of CuFe$_2$O$_4$ while CuO dissolved into the solution at pH 6 [91]. Ding et al. concluded that the sulfate radical is dominant in a CuFe$_2$O$_4$/PMS system because Cu^{2+} and Fe^{3+} were detected from the XPS

result [92]. Afterward, a new oxidation mechanism using Cu was introduced instead of a free radical mechanism. Zhang et al. proposed that the 2,4-dichlorophenol oxidation pathway derived from CuO/PDS is not involved in the radical oxidation because they observed an ineffective radical scavenger effect. They delved into the detailed mechanism by measuring the ATR-FTIR and confocal Raman spectrum, and proved the outer-sphere interaction between PDS and CuO [93].

5. Noble Metal Species

Noble metals are usually stable during a chemical reaction. However, they are commonly used as catalysts because they exhibit a high catalytic activity [94,95]. Specifically, electrochemical processes utilize noble metal electrodes owing to a high electrical conductivity and catalytic performance [96]. In addition, the noble metal incorporated TiO_2 showed improved photochemical reactivity [97]. During the water treatment process, in particular, the reductive characteristic of palladium (Pd) was used for a reduction of oxyanion-type pollutants such as nitrate (NO_3^-), nitrite (NO_2^-), bromate (BrO_3^-), chlorate (ClO_3^-), and perchlorate (ClO_4^-) [98]. In addition, a reductive elimination of organic contaminants was also accomplished using Pd mediated catalysis [99-101]. To apply a noble metal species for persulfate activation, their reductive activity can be applied to a reduction of persulfate. Anipsitakis et al. showed that 2,4-dichlorophenol is more effectively eliminated by Ru^{3+}/PMS than by another metal ion/PMS system [67]. However, noble metal mediated persulfate activation has been reported less frequently than other transition metal species because species such as Co and Fe are less expensive than noble metal and show a high persulfate activation efficiency. However, if a small amount of noble metal can be used to achieve persulfate activation as effectively as a large amount of transition metal, an activation system applying such a metal can be considered. Furthermore, unlike a transition metal species that generates $SO_4^{\cdot-}$ as a primary oxidant, a noble-metal activated PMS system is likely to follow a different oxidation mechanism [102]. For example, the oxidation of an organic compound is negligible if the three components, Pt, PMS, and the target organic compound, do not coexist. This feature is significantly different from the circumstance in which $SO_4^{\cdot-}$ can be generated through the interaction of PMS and Co^{2+}. A detailed description of the characteristics of such a non-radical oxidation mechanism has not been well established, and to obtain various design options of the PMS activation, more systematic studies are needed to reveal its mechanism.

6. Metal-carbon Mixture

As a support material, carbonaceous materials such as activated carbon, graphite, carbon nanotubes, and graphene oxide are promising because they have a high specific area, good absorption property, and conductivity [40,103]. Activated carbon has been widely used for wastewater treatment and has therefore been utilized as a metal support in many cases. In such cases, the catalytic property of the metal species was likely to be affected by the carbon support. For example, Shukla et al. reported that a fast $SO_4^{\cdot-}$ generation and phenol degradation were achieved through activated carbon supported Co. They speculated that the reduction of the Co species by the activated carbon was responsible for the improvement because Co_2O_3 was found to have a dominant Co formation [104]. The carbon material, which is utilized as a support for Fe^{3+} immo-

bilization, also affects the recovery of Fe^{2+} owing to the surface hydrophilic group, and demonstrates good decontamination through PMS activation [105].

Carbon-based materials have also been combined with a noble metal species to improve the catalytic characteristics for PMS activation. Muhammad et al. used an activated carbon supported ruthenium catalyst for phenol degradation through PMS activation [106]. In addition, Pd nanoparticles anchored on a graphitic nitride carbon hybrid catalyst were utilized for PMS activation by Wang et al. [107].

Further, owing to the development of manufacturing technology, a highly ordered carbon frame was appropriated in the fabrication of a highly efficient carbocatalyst. Graphene oxide, which is one such category, is an extremely popular material owing to its versatility regarding the chemical modifiability used to improve its functionalities. A number of results have demonstrated an improved catalytic activity for PMS activation and a degradation of organic pollutants using graphene oxide and a metal combined catalyst over the sole application of a metal species. According to Hu et al. the improvement of a graphene supported cobalt species is due to the following properties of graphene oxide: (a) its unique electronic structure, (b) strong covalent bond interactions with Co, (c) a reductive catalytic property, and (d) an extraordinary adsorption capacity [75].

CHALLENGES AND PROSPECTS

Activating persulfate offers many advantages, including excellent chemical stability, low cost, and high oxidation power that is widely studied for remediation in contaminated soils and underground water. Among many activating methods, heterogeneous catalysis is one of the facile ways to activate persulfate, particularly focused on the kinetics and degradation pathways for wastewater remediation. Therefore, this critical review summarizes recent studies using a heterogeneous catalyst for persulfate activation, including various carbon materials and single metals. The aspects of kinetic efficiency by the catalysts mostly are dependent on the type of functional groups on carbon surfaces or different characteristics from metallic compounds. On the other hand, understanding the activation mechanism has not yet been clearly elucidated. Until now, various approaches were applied to improve our understanding for oxidation mechanisms involved in persulfate activation. One proposed mechanism is radical based mechanism, $SO_4^{\cdot-}$, which is generated from the reduction of persulfate and non-selectively oxidizes the target pollutant. Another suggestion is to produce singlet oxygen, $^1O_2$, following after process of persulfate activation. Finally, heterogeneous catalysts play a pivotal role as electron mediator. In other words, catalysts, facilitating the electron transfer from organic pollutants to persulfate, should be responsible for the non-radical mechanism. To sharpen our understanding of the persulfate activation mechanism, fundamental probes require more attention.

Despite the inherent advantages of persulfate activation, scale-up in the actual process of wastewater treatment has significant challenges due to a lack of practical experiences of persulfate application. For example, one critical issue is how to deal with real environmental circumstances where contain natural organic matter (NOM) and inorganic matrix that practically hindered in degrada-

tion efficiency on target compounds. The other problem is the presence of sulfate ions in contaminated solution after the treatment process. High concentration of sulfate ions are considered as toxic pollutants that cause long-term ill effects for human beings. Furthermore, complete removal of sulfate ions in aqueous solutions needs complicated procedure that requires considerably high maintenance cost. Therefore, it is important to put more effort to solve the fundamental obstacles that overcome the limited practical application in current wastewater treatment.

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