Review

Review of Advanced Oxidation Processes Based on Peracetic Acid for Organic Pollutants

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Abstract: In recent years, the removal of organic pollutants from water and wastewater has attracted more attention to different advanced oxidation processes (AOPs). There has been increasing interest in using peroxyacetic acid (PAA), an emerging oxidant with low or no toxic by-products, yet the promotion and application are limited by unclear activation mechanisms and complex preparation processes. This paper synthesized the related research results reported on the removal of organic pollutants by PAA-based AOPs. Based on the research of others, this paper not only introduced the preparation method and characteristics of PAA but also summarized the mechanism and reactivity of PAA activated by the free radical pathway and discussed the main influencing factors. Furthermore, the principle and application of the newly discovered methods of non-radical activation of PAA in recent years were also reviewed for the first time. Finally, the shortcomings and development of PAA-based AOPs were discussed and prospected. This review provides a reference for the development of activated PAA technology that can be practically applied to the treatment of organic pollutants in water.

Keywords: advanced oxidation processes; peracetic acid-based; activation; degradation; influence factors

1. Introduction

In recent decades, water shortage and pollution have drawn worldwide attention with the development of science and technology, the sharp increase in population and the acceleration of urbanization [1]. It was reported that some refractory organics in found water, such as dyes, leather, pharmaceuticals, rubber and pesticides, come from chemical industries. These materials are synthetic organic products with stable chemical properties, which can migrate and transform in the environment and exist for a long time [2–4]. In addition [2,4], some pollutants, such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, organophosphorus and organochlorine pesticides, are carcinogenic, teratogenic and mutagenic, accumulating in the human body through the food chain and posing a huge threat to human health [5–7]. Therefore, water pollution treatment is becoming more complex and challenging. At present, the commonly used organic pollutant treatment methods include the biological treatment method [8], adsorption method [9,10] and oxidation method [11,12], etc. However, these technologies have diverse limitations of pollutants transfer, incomplete degradation and high energy requirements [13]. For example, the efficiency of biological treatment methods is limited by pollution and easy-to-breed resistant strains [14,15]. Adsorption techniques also have problems recovering and disposing of irreversible adsorbents [13].

Chemical oxidation technology includes direct oxidation and catalytic oxidation. At present, the limitations of direct oxidation cannot be avoided. For example, although ferrate (VI) has a strong oxidizing ability [16], it has poor stability and high pH requirements [17,18]. Hydrogen peroxide (H2O2) is a mild oxidant with limited oxidizing ability,
and there are residual and subsequent disposal problems [19–21]. Chlorine dioxide needs to be provisionally prepared when used and has high toxicity [12,22–24]. Ozone has a remarkable treatment effect but produces bromate, a potential carcinogen, which threatens human health [25,26]. Catalytic oxidation generates active species with strong oxidation, such as hydroxyl radicals (·OH) and sulfate radicals (SO$_4^{\bullet-}$) under external conditions (heating, light, catalysts, etc.) to oxidize organic pollutants. For example [12,19–22,25,27,28], advanced oxidation processes (AOPs) based on Fenton, ozone and persulfate can remove pollutants more effectively by generating ·OH and SO$_4^{\bullet-}$ [27], but they are limited by acidic conditions and high selectivity. In addition, Kosar found that photo-Fenton combined with ozonation showed faster and better efficiency than that of separate oxidation, but the reaction was under pH = 3 [28]. In recent years, non-thermal plasma has also attracted much attention, but high cost and immature technology limit its application and development [29]. Researchers have also studied peracetic acid (PAA) as an emerging oxidant in recent years, which can generate a special alkoxy radical (R-O·) [30,31] with excellent resistance to reaction conditions and has been widely used in foreign countries [32,33].

PAA has been used in sterilization and disinfection and is extensively studied in the field of organic wastewater degradation [33–37]. Compared with traditional chlorine-containing disinfectants, PAA has a stronger oxidizing ability, higher disinfection efficiency and lower toxicity [38–42]. Therefore, PAA is considered an alternative to chlorinated disinfectants. PAA can not only directly oxidize organic compounds such as 17 β-estradiol, 17 α-vinyl estradiol and ibuprofen using its high redox potential [41] but can also be activated by ultraviolet (UV), transition metal ions (such as iron and cobalt ions), transition metal oxides, carbonaceous materials and some composite materials to generate HO·, methyl (CH$_3$·), acetoxy (CH$_3$COO·), acetyl peroxy (CH$_3$C(O)OO·) and some metal complexes to degrade organic pollutants in water and wastewater via its low peroxy bond energy (38 kcal·mol$^{-1}$) [42–45]. PAA-based AOPs have been applied to remove phenols, dyes and antibiotics with excellent effect [34,46–49], but problems such as the unclear activation mechanism, complex preparation process and secondary pollution cannot be ignored. At present, there are few reviews on the degradation of organic pollutants by PAA. AO et al. [32] introduced the mechanism and application of PAA technology for water purification and disinfection in detail but ignored the non-radical degradation pathways. Based on the research of others, this paper introduces the preparation method and characteristics of PAA, summarizes the mechanism and reactivity of the free radical pathway and non-radical pathway for the first time and discusses the main influencing factors. Finally, the shortcomings of the current PAA-based treatment systems are analyzed, and its development is prospected. This review aims to provide a reference for the development of PAA-based technologies that can be practically applied to the treatment of organic pollutants in water.

2. Preparation and Characteristics of PAA

2.1. Characteristics of PAA

PAA is colorless with a pungent acidic smell similar to that of acetic acid. Due to the intramolecular hydrogen bonding between carbonyl oxygen and hydroxyl hydrogen [50,51], as shown in Table 1 and Figure 1a, PAA has a low boiling point (110 °C), a low melting point (0.2 °C), a high pK$_a$ (8.2) [52,53] and a five-membered ring [49,52], which makes the neutral form (PAA$^0$) more stable than the anionic form (PAA$^-$), existing mainly as a neutral substance even in weakly basic water [53]. Moreover, PAA$^0$ has a higher oxidation capacity than PAA$^-$ [54]. PAA is unstable and volatile; when the concentration is higher than 15 %, it has the risk of combustion and explosion [32]. In addition, the redox potential of PAA is between 1.06 and 1.96 V, as shown in Table 1, stronger than H$_2$O$_2$ (1.78 V), Cl$_2$ (1.48 V), ClO$_2$ (1.28 V) and Fe$^{VI}$ (0.9–1.9 V). Therefore, PAA is widely used in the food processing, textile and healthcare industries as a disinfectant, considered one of the most promising alternatives to chlorine-based disinfectants [55]. Apart from direct disinfection and oxidation, PAA can also produce CH$_3$C(O)O·, CH$_3$C(O)OO· (R-O·) and HO· to improve
the disinfection and degradation efficiency by activating [56]. As shown in Figure 1b,c, the stronger polarity of the O-O bond indicated that it is more prone to break. Furthermore, the peroxide bond energy of PAA (159 kJ/mol) is weaker than that of H\textsubscript{2}O\textsubscript{2} (213 kJ/mol), so PAA may exhibit more efficiency [49]. Long-term exposure to high levels of PAA can cause severe irritation to the eyes, skin, mucous membranes and upper respiratory tract [49,54], while low levels may cause occupational asthma [57].

Table 1. Properties of PAA and other oxides.

<table>
<thead>
<tr>
<th>Items</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKa</td>
<td>8.2</td>
</tr>
<tr>
<td>Eh\textsuperscript{0} (V)</td>
<td></td>
</tr>
<tr>
<td>PAA</td>
<td>1.0–1.96</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>1.78</td>
</tr>
<tr>
<td>Cl</td>
<td>1.48</td>
</tr>
<tr>
<td>ClO\textsubscript{2}</td>
<td>1.28</td>
</tr>
<tr>
<td>Fe\textsuperscript{VI}</td>
<td>0.9–1.9</td>
</tr>
<tr>
<td>O\textsubscript{3}</td>
<td>2.08</td>
</tr>
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</tr>
<tr>
<td>Density (g/mol)</td>
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</tr>
<tr>
<td>Boiling point (°C)</td>
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<td>Melting point (°C)</td>
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<tr>
<td>Henry’s law constant (M/atm)</td>
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</tr>
<tr>
<td>log K\textsubscript{ow} (at pH 7)</td>
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</tr>
<tr>
<td>O-OH bond (kJ/mol)</td>
<td></td>
</tr>
<tr>
<td>PAA</td>
<td>159</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>213</td>
</tr>
</tbody>
</table>

Figure 1. (a) PAA molecular formula; Molecular electrostatic potential diagram of (b) PAA and (c) H\textsubscript{2}O\textsubscript{2}.

PAA in solution is prone to decomposition and hydrolysis, as shown in Equations (1)–(3), where the hydrolyzed PAA is reduced to acetic acid and H\textsubscript{2}O\textsubscript{2}. Da Silva et al. [49] showed that PAA undergoes five stages of hydrolysis in acidic media, and the main factor maintaining the equilibrium between PAA and H\textsubscript{2}O\textsubscript{2} is the small energy difference in each stage. In addition, there are two mechanisms for the spontaneous decomposition of PAA: the acid spontaneously decomposes in response to protonation and PAA\textsuperscript{−} attacks on the PAA.
molecule, forming an active intermediate [49]. Moreover, in the presence of metals, the PAA molecule is catalytically decomposed, as shown in Equation (6). Studies have shown that solutions containing 40% PAA lose 1–2% of the active ingredient per month, with lower concentrations losing more [58,59]. Therefore, we believe that it is essential to determine PAA concentration regularly.

\[
\begin{align*}
\text{CH}_3\text{C(O)OOH} + \text{H}_2\text{O} &\rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}_2. \\
2\text{CH}_3\text{C(O)OOH} &\rightarrow \text{CH}_3\text{COOH} + \text{O}_2 \\
\text{CH}_3\text{C(O)OOH} &\rightarrow \text{CH}_3\text{COOH} + \text{O}_2 + \text{other product.}
\end{align*}
\]

2.2. Synthesis and Detection of PAA

The synthesis of PAA was first investigated by Food Machinery Chemical Co. in the early 20th century [60]. There are two general methods to synthesize PAA: \( \text{H}_2\text{O}_2 \) oxidation and acetaldehyde oxidation. However, the latter is not commonly applied in practice. \( \text{H}_2\text{O}_2 \) oxidation involves the reaction of acetic acid (Equation (4)) or acetic anhydride (Equation (5)) with \( \text{H}_2\text{O}_2 \). However, the reaction of acetic anhydride with \( \text{H}_2\text{O}_2 \) is difficult to control and may produce diacetyl peroxide as a by-product. In addition, the reaction is exothermic and may cause an explosion. Therefore, acetic acid is the most commonly utilized substance in the preparation of PAA. The reaction of acetic acid with \( \text{H}_2\text{O}_2 \) is reversible, so researchers add a strongly acidic catalyst to promote the reaction [61]. For example, Saha et al. used a gas diffusion electrode to generate \( \text{H}_2\text{O}_2 \) in situ for the synthesis of PAA [62].

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 \xrightleftharpoons{\text{catalyst}} \text{CH}_3\text{C(O)OOH} + \text{H}_2\text{O}. \\
(\text{CH}_3\text{CO})_2\text{O} + 2\text{H}_2\text{O}_2 &\rightarrow 2\text{CH}_3\text{C(O)OOH} + \text{H}_2\text{O}.
\end{align*}
\]

A commercial PAA solution is a mixture of acetic acid, \( \text{H}_2\text{O}_2 \), PAA and water [57,61]. Therefore, the amount of \( \text{H}_2\text{O}_2 \) in PAA solutions should be considered during the study [54,56].

A direct method for the determination of PAA is not yet available. We need to determine the sum of PAA and \( \text{H}_2\text{O}_2 \) concentrations by iodine titration and the \( \text{H}_2\text{O}_2 \) concentration in the PAA solution by potassium permanganate titration. The final concentration difference is the concentration of PAA [63,64]. For the remaining PAA concentration in the reaction solution, the N,N-diethyl-p-phenylenediamine colorimetric method is generally used [65]. In addition, Tashkhourian et al. [66] introduced a novel sensor for the simultaneous determination of PAA and \( \text{H}_2\text{O}_2 \) using silver nanoparticles as a chromogenic reagent.

3. Methods and Mechanisms of Activating PAA

There are two categories according to the main reactants in the PAA activation system: free radical and non-free radical pathways. There are different activation methods for PAA. The free radical pathway can be divided into energy radiation, transition metal catalysis and activated carbon catalysis according to the activation methods. They can generate radicals such as HO·, R-O· and so on, accelerating the degradation of organic pollutants. The non-radical pathway mainly occurs in the transition metal catalysis process, where PAA forms complexes with transition metals. However, there are different mechanisms of different methods.

3.1. Free Radical Pathway

3.1.1. Energy Radiation

As shown in Equation (6), driven by the applied energy radiation, the O-O bond of PAA is cleaved to generate HO· and CH₃C(O)O·. This process is the key step of energy radiation, which directly determines the degradation rate of pollutants. In addition, the PAA solution also contains a small amount of \( \text{H}_2\text{O}_2 \), which can also be activated by energy radiation to generate HO· to participate in the subsequent reaction (Equation (7)).
CH$_3$C(O)OOH $\xrightarrow{\text{energy}}$ CH$_3$C(O)O· + HO·. \hspace{1cm} (6)

H$_2$O$_2$ $\xrightarrow{\text{energy}}$ 2HO·. \hspace{1cm} (7)

Subsequently, HO· extracts hydrogen atoms to attack PAA to generate radicals, of which CH$_3$C(O)OO· is the main one, as shown in Equations (8)–(10).

\[
\begin{align*}
\text{CH}_3\text{C(O)OOH} + \text{HO·} &\rightarrow \text{CH}_3\text{C(O)OO·} + \text{H}_2\text{O}. \hspace{1cm} (8) \\
\text{CH}_3\text{C(O)OOH} + \text{HO·} &\rightarrow \text{CH}_3\text{CO·} + \text{O}_2 + \text{H}_2\text{O}. \hspace{1cm} (9) \\
\text{CH}_3\text{C(O)OOH} + \text{HO·} &\rightarrow \text{CH}_3\text{COOH} + \cdot\text{OOH}. \hspace{1cm} (10)
\end{align*}
\]

CH$_3$C(O)O can be turned into a methyl radical (CH$_3$·) and carbon dioxide (CO$_2$) by a decarboxylation reaction (Equation (11)). Additionally, CH$_3$· can rapidly react with oxygen to form peroxo radical (CH$_3$OO·) (Equation (12)), followed by CH$_3$OO· attacking PAA to form CH$_3$C(O)OO· (Equation (13)). Meanwhile, CH$_3$OO· can also undergo bimolecular decay by itself (Equations (14)–(16)), while CH$_3$C(O)OO· and CH$_3$C(O)O· may undergo radical–radical coupling (Equations (17) and (18)).

\[
\begin{align*}
\text{CH}_3\text{C(O)O} &\rightarrow \text{CH}_3\cdot + \text{CO}_2. \hspace{1cm} (11) \\
\text{CH}_3\cdot + \text{O}_2 &\rightarrow \text{CH}_3\text{OO·}. \hspace{1cm} (12) \\
\text{CH}_3\text{C(O)OOH} + \text{CH}_3\text{C(O)O·} &\rightarrow \text{CH}_3\text{C(O)OO·} + \text{CH}_3\text{COOH}. \hspace{1cm} (13) \\
\text{CH}_3\text{OO·} + \text{CH}_3\text{OO·} &\rightarrow \text{HCHO} + \text{CH}_3\text{OH} + \text{O}_2. \hspace{1cm} (14) \\
\text{CH}_3\text{OO·} + \text{CH}_3\text{OO·} &\rightarrow 2\text{HCHO} + \text{H}_2\text{O}_2. \hspace{1cm} (15) \\
\text{CH}_3\text{OO·} + \text{CH}_3\text{OO·} &\rightarrow 2\text{CH}_3\text{CO·} + \text{O}_2. \hspace{1cm} (16) \\
\text{CH}_3\text{C(O)OO·} + \text{CH}_3\text{C(O)OO·} &\rightarrow 2\text{CH}_3\text{C(O)O·} + \text{O}_2. \hspace{1cm} (17) \\
\text{CH}_3\text{C(O)O·} + \text{CH}_3\text{C(O)O·} &\rightarrow (\text{CH}_3\text{C(O)O})_2. \hspace{1cm} (18)
\end{align*}
\]

The above reaction also involves HO· reacting with CH$_3$C(O)O· to form PAA (Equation (19)), forming a cyclic reaction system.

\[
\text{CH}_3\text{C(O)O·} + \text{HO·} \rightarrow \text{CH}_3\text{COOOH}. \hspace{1cm} (19)
\]

H$_2$O$_2$ in PAA solution can produce other radicals besides HO·, making the energy activation system of PAA more complex. Zhang et al. proposed a reaction mechanism of UV/PAA in the presence of H$_2$O$_2$ and acetate ions [67] (Figure 2), where a high steady-state concentration of superoxide radicals, superoxide radical anions and -OOCCH$_2$C(O)O$^-$ was observed.
3.1.2. Transition Metal Catalysis

There are two types of transition metal catalysis: homogeneous and heterogeneous catalysis, both of which have similar activation principles. As shown in Figure 3, unlike the energy activation mechanism, transition metals can both gain and lose electrons, resulting in a cyclic activation mechanism (Equations (20) and (21)).

\[
X^{n+} + \text{CH}_3\text{C}(\text{O})\text{OOH} \rightarrow X^{(n+1)+} + \text{CH}_3\text{C}(\text{O})\text{O}^- + \text{OH}^-.
\]

(20)

\[
X^{(n+1)+} + \text{CH}_3\text{C}(\text{O})\text{OOH} \rightarrow X^{n+} + \text{CH}_3\text{C}(\text{O})\text{OO}^- + \text{H}^+.
\]

(21)

The current transition metal catalysts for PAA are mainly based on Co, Fe and Mn. Taking Fe as an example, we introduced the PAA activation mechanism in detail. In Equations (22)–(25), R-O· radicals and CH₃C(O)O⁻, Fe⁴⁺O²⁺, HO⁻ and CH₃COOH are generated. Subsequently, Fe⁴⁺O²⁺ continues to react with PAA or H₂O to form Fe³⁺, which participates in the reaction of Equations (26) and (27). Reactions of Equations (8)–(19) are still present in the process, so lots of free radicals and other products are formed.

\[
\text{Fe}^{2+} + \text{CH}_3\text{C}(\text{O})\text{OOH} \rightarrow \text{Fe}^{3+} + \text{CH}_3\text{C}(\text{O})\text{O}^- + \text{OH}^-.
\]

(22)

\[
\text{Fe}^{3+} + \text{CH}_3\text{C}(\text{O})\text{OOH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OO}^- + \text{Fe}^{2+} + \text{H}^+.
\]

(23)

\[
\text{Fe}^{2+} + \text{CH}_3\text{C}(\text{O})\text{OOH} \rightarrow \text{Fe}^{3+} + \text{CH}_3\text{C}(\text{O})\text{O}^- + \text{HO}^-.
\]

(24)

\[
\text{Fe}^{2+} + \text{CH}_3\text{C}(\text{O})\text{OOH} \rightarrow \text{Fe}^{4+}\text{O}^{2+} + \text{CH}_3\text{COOH}.
\]

(25)

\[
2\text{Fe}^{4+}\text{O}^{2+} + \text{CH}_3\text{C}(\text{O})\text{OOH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}^- + 2\text{Fe}^{3+} + \text{OH}^- + \text{O}_2.
\]

(26)

\[
\text{Fe}^{4+}\text{O}^{2+} + \text{H}_2\text{O} \rightarrow \text{HO}^- + \text{Fe}^{3+} + \text{OH}^-.
\]

(27)

Under acidic conditions, H₂O₂ in PAA solution also experiences the reaction of Equations (28)–(31) [54], which is known as the Fenton reaction. The Fenton reaction is widely used for wastewater treatment.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{HO}^- + \text{Fe}^{3+} + \text{OH}^-.
\]

(28)

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{4+}\text{O}^{2+} + \text{H}_2\text{O}.
\]

(29)

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{Fe}^{2+} + \text{H}^+.
\]

(30)

\[
\text{Fe}^{4+}\text{O}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{Fe}^{3+} + \text{OH}^-.
\]

(31)
which is controversial as it depends on the dominant reaction of the free radical. However, Co(III) and R-O· play a major role rather than free radicals [31]. Zhao et al. [68] also found that the oxygen atom coordinates with Co(II) to form Co(II)-OO(O)CCH₃, which plays a key role in the degradation of organic pollutants, and Co(III) and R-O· are the secondary reaction species. In addition, as shown in Figure 5b, Liu et al. [44] pointed out that Co(IV) may be transferred to PAA, promoting the formation of free radicals. Similar to energy radiation, as shown in Figure 4, Zhou et al. used density functional theory to simulate the reaction process and found that the addition of ACF grew the length of the O-O bond of PAA, resulting in the O-O bond breaking more easily and generating CH₃C(O)OO· and HO· radicals [48].

3.1.3. Activated Carbon Catalysis

Activated carbon fiber (ACF) has a high specific surface area, a large number of active sites, functional groups and nonbonding free electrons. Unpaired free electrons in ACF may be transferred to PAA, promoting the formation of free radicals. Similar to energy radiation, as shown in Figure 4, Zhou et al. used density functional theory to simulate the reaction process and found that the addition of ACF grew the length of the O-O bond of PAA, resulting in the O-O bond breaking more easily and generating CH₃C(O)OO· and HO· radicals [48].

3.2. Non-Free Radical Pathway

In the system of activating PAA by transition metal, it is widely believed that R-O· is the main reactive substance. There are many researchers who have largely used radical quenching experiments combined with electron paramagnetic resonance radical detection pathways to determine the major reactive substance in transition metal/PAA systems, which is controversial as it depends on the dominant reaction of the free radical. However, research has shown that when transition metal activates persulfate, high-valent metals play a major role rather than free radicals [31]. Zhao et al. [68] also found that the oxygen atom transfer pathway plays a primary role in the activation of PAA by Co. As shown in Figure 5a, the oxygen atom coordinates with Co(II) to form Co(II)-OO(O)CCH₃, which plays a key role in the degradation of organic pollutants, and Co(III) and R-O· are the
secondary reaction species. In addition, as shown in Figure 5b, Liu et al. [44] pointed out that Co(IV) acts as an oxidant rather than active free radicals in the Co(II)-doped g-C3N4-PAA system. They proposed two catalytic hypotheses: the atom Co is coordinated to an atom O near the atom H, and the atom O is coordinated to a peroxide bond near the atom C. The positively charged Co in the first hypothesis acts as an electron donor, decreases the activity of PAA and lengthens the O-O band, triggering the spontaneous dissociation of PAA. The second hypothesis of PAA acting as an electron donor allows electrons to be transferred from PAA to the electron-deficient region, forming surface-bound CH3C(O)OO−. Furthermore, Manoli et al. used the Fe(VI)-PAA process to degrade carbamazepine and found that the most dominant active species in the system was Fe(VI) with CH3C(O)OO− reacting to produce Fe(V)/Fe(IV) as shown in Equations (32) and (33) [69].

\[
\begin{align*}
\text{Fe}^{VI}O_4^{2-} + \text{CH}_3\text{C}(O)\text{OO}^- & \rightarrow \text{Fe}^{V}O_4^{3-} + \text{CH}_3\text{C}(O)\text{OO}^-. & (32) \\
\text{Fe}^{VI}O_4^{2-} + \text{CH}_3\text{C}(O)\text{OO}^- & \rightarrow \text{Fe}^{IV}O_4^{2-} + \text{CH}_3\text{C}(O)O^- + O_2. & (33)
\end{align*}
\]

Figure 5. Non-radical pathway of Co (II)-PAA. Reprinted with permission from Ref. [68]. 2021, Zihao Zhao, Xinhong Li, Hongchao Li, Jieshu Qian, Bingcai Pan. (a), Co (II)-doped g-C3N4-PAA. Reprinted with permission from Ref. [44]. 2021, Banghai Liu, Wanqian Guo, Wenrui Jia, Huazhe Wang, Qishi Si, Qi Zhao, Haichao Luo, Jin Jiang, and Nanqi Ren. (b) process.

4. Reactivity of PAA-Based AOPs

4.1. Oxidation of PAA Alone

PAA has been used as a broad-spectrum, highly effective disinfectant in the food industry, medical devices/pharmaceuticals, textiles and water treatment processes. PAA is selective when used alone. As shown in Table 2, the degradation rates of different pollutants with PAA under the same conditions were found to be different. For example, metenamic acid (∼90%) and ibuprofen (∼30%), owing to the acetyloxy radical, showed high reactivity to electron-rich functional groups. Several studies have shown that water quality also plays a major role in the degradation of pollutants by PAA [70–72]. Wang et al. found that there were differences in the degradation effects of the same pollutant under different water quality conditions by PAA, which were attributed to PAA generally reacting more uniformly with the pharmaceutical ingredients from wastewater containing low COD [72]. In addition, the dosage of PAA also influences the oxidation effect of PAA. Concentrations of 50 µg·L−1 17 β-estradiol and 17 α-ethyl estradiol were able to be completely removed by 15 mg·L−1 PAA, whereas 50 µg·L−1 Brilliant Red X-3B was removed by less than 5% with 380 mg·L−1 mM PAA [41,48]. Furthermore, as shown in Table 2, many studies have shown that the removal efficiencies of PAA for other organic pollutants are also less than 20%. Therefore, PAA alone was not effective in degrading pollutants.
Table 2. An overview of research on the direct oxidation of aqueous pollutants by PAA.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>(C_0) (µg L(^{-1}))</th>
<th>(C_{\text{PAA}}) (mg L(^{-1}))</th>
<th>pH</th>
<th>Time (min)</th>
<th>Max. Removal Efficiency (%)</th>
<th>Matrixes</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>17 β-Estradiol</td>
<td>50</td>
<td>15</td>
<td>7.9</td>
<td>10–20</td>
<td>100</td>
<td>WW(^1)</td>
<td>[41]</td>
</tr>
<tr>
<td>17 α-ethinyl estradiol</td>
<td>50</td>
<td>15</td>
<td>7.9</td>
<td>10–20</td>
<td>100</td>
<td>WW</td>
<td>[71]</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>20 mg (\cdot) L(^{-1})</td>
<td>4 mM</td>
<td>5</td>
<td>30</td>
<td>−5</td>
<td>DI water</td>
<td>[46]</td>
</tr>
<tr>
<td>Reactive Brilliant Red X-3B</td>
<td>50 μM</td>
<td>5 mM</td>
<td>7</td>
<td>40</td>
<td>&lt;5</td>
<td>DI water</td>
<td>[48]</td>
</tr>
<tr>
<td>sulfamethazine</td>
<td>8 mg L(^{-1})</td>
<td>0.4 mM</td>
<td>6.3</td>
<td>60</td>
<td>−20</td>
<td>DI water</td>
<td>[74]</td>
</tr>
<tr>
<td>2,4-dichlorophenol</td>
<td>20 μM</td>
<td>0.26 mM</td>
<td>7</td>
<td>20</td>
<td>&lt;5</td>
<td>DI water</td>
<td>[55]</td>
</tr>
<tr>
<td>sulfamethazine</td>
<td>10 μM</td>
<td>100 μM</td>
<td>7 ± 0.2</td>
<td>15</td>
<td>&lt;5</td>
<td>DI water</td>
<td>[56]</td>
</tr>
<tr>
<td>Clofibric acid</td>
<td>0.05 mM</td>
<td>0.5 mM</td>
<td>7</td>
<td>90</td>
<td>&lt;5</td>
<td>DI water</td>
<td>[75]</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>40</td>
<td>50</td>
<td>6.7 (WW 1(^3)), 7.0 (WW 2(^4) and WW 3(^5))</td>
<td>n.r.(^6)</td>
<td>−45 (WW 1), −20 (WW 2), &lt;5 (WW 3)</td>
<td>WW 1, WW 2, WW 3</td>
<td>[76]</td>
</tr>
<tr>
<td>Naproxen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diclofenac</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mefenamic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Clofibric acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blue 29 dye</td>
<td>30 mg (\cdot) L(^{-1})</td>
<td>CH(_3)C(O)OH/dye = 344/1</td>
<td>3–8</td>
<td>60–180</td>
<td>20.2–56.4</td>
<td>DI water</td>
<td>[37]</td>
</tr>
</tbody>
</table>

Note(s): \(^1\) Wastewater. \(^2\) Deionized water. \(^3\) low COD WW. \(^4\) medium COD WW. \(^5\) high COD WW. \(^6\) not reported.
4.2. PAA-Based AOPs

4.2.1. Homogeneous Catalysis

Catalysis in the homogeneous phase involves a homogeneous mixture of catalysts and reactants. The common homogeneous catalyst of PAA includes metal ions and inorganic anions. In Table 3, the transition metal ions that can be used to activate PAA are mainly Fe$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Ru$^{3+}$ and Mn$^{2+}$. Among them, Co$^{2+}$ has received wide attention due to its remarkable effect. Co$^{2+}$ showed superior removal in less time with fewer reagents and lower pH selectivity than Fe$^{2+}$ and Cu$^{2+}$ in removing bisphenol-A [72,77]. Kim et al. [77] also investigated the degradation of naproxen, sulfamethoxazole (SMX) and carbamazepine by the Co$^{2+}$/PAA process and confirmed the excellent performance of the process. However, some researchers found that the Co$^{2+}$/PAA process is still selective for pollutants. Zhao et al. [68] investigated the removal of nitrobenzene by the Co$^{2+}$/PAA process under the same conditions and found that the degradation rate was only 18.8%. In addition, there are still some controversies regarding the interpretation of the oxidation mechanism of the Co$^{2+}$/PAA process. Wang et al. [56] showed that R-O· is the main species in the process of Co(II)/PAA, while Zhao et al. [68] found the complex Co(II)-OO(O)CCH$_3$ with a stronger oxidizing ability to remove pollutants.

In contrast to toxic Co(II) and Mn(II), Fe(II) and Cu(II) are often considered ideal transition metal catalysts. However, the reaction is largely stopped when Fe(II) translate to Fe(III) [78]. Cu(II) is more soluble and less prone to generate sludge, but it is ineffective because of its lower reduction potential (E$_{Cu(II)/Cu(I)}$ = 0.167 V) [79]. In order to improve the Cu(II)/PAA, Wang [80] et al. added HCO$_3^-$ (CO$_3^{2-}$) to the Cu(II)/PAA process to form a highly reactive complex Cu(II)-HCO$_3^-$ (CO$_3^{2-}$). Instead of Cu(II), zero-valent copper has also been studied to activate PAA by generating low-valent copper ions (Cu(I)) under acidic conditions [81]. Furthermore, some scholars also used inorganic anions to activate PAA. Deng et al. [42] demonstrated that phosphate could activate PAA to produce HO· and R-O· by electron paramagnetic resonance and free radical scavenging experiments. Wang et al. [82] found that the Cl$^{-}$/PAA process removes Rhodamine B by producing R-O· and $^{1}$O$_2$ and showed high removal efficiency for Rhodamine B over a wide pH range.

### Table 3. Studies of activating PAA in homogeneous phase system.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$C_{Catalyst}$ (µM)</th>
<th>Contaminants</th>
<th>$C_0$ (µM)</th>
<th>$C_{PAA}$ (µM)</th>
<th>pH</th>
<th>Time (min)</th>
<th>Max. Removal Efficiency (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(VI)</td>
<td>200</td>
<td>SMX</td>
<td>10</td>
<td>100</td>
<td>9.0 ± 0.1</td>
<td>1</td>
<td>~100</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulfadimethoxine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>~100</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trimethoprim</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atenolol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;85</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Propranolol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;85</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Caffeine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Fe(II)</td>
<td>100</td>
<td>Methylene blue</td>
<td></td>
<td>60 mg L$^{-1}$</td>
<td>3.0~8.2</td>
<td>120</td>
<td>~90</td>
<td>[54]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Naproxen</td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td>&gt;80</td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td>0.4 mM</td>
<td>Bisphenol-A</td>
<td>60 mg L$^{-1}$</td>
<td>40 mg L$^{-1}$</td>
<td>3.5</td>
<td>10</td>
<td>100</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diclofenac</td>
<td>100</td>
<td>7</td>
<td>15</td>
<td>&gt;80</td>
<td>80</td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Caffeine</td>
<td>5</td>
<td>60</td>
<td>9.3</td>
<td>20</td>
<td>85</td>
<td>[80]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMX</td>
<td>10</td>
<td>100</td>
<td></td>
<td></td>
<td>~90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Carbamazepine</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
<td>&gt;80</td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td>15</td>
<td>Bisphenol-A</td>
<td>10</td>
<td>100</td>
<td>3.0~8.1</td>
<td>30</td>
<td>100</td>
<td>[77]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Naproxen</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
<td>88.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMX</td>
<td></td>
<td>15</td>
<td></td>
<td></td>
<td>87.7</td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td>0.8 µM</td>
<td>Acid orange 7</td>
<td>10</td>
<td>100</td>
<td>7</td>
<td>15</td>
<td>~90</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methylene blue</td>
<td></td>
<td>15</td>
<td></td>
<td></td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Congo red</td>
<td>0.05 mM</td>
<td>0.2 mM</td>
<td>7</td>
<td>60</td>
<td>52</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crystal Violet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMX</td>
<td></td>
<td>98</td>
<td></td>
<td></td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td>0.01 mM</td>
<td>Bisphenol-A</td>
<td>8.0</td>
<td>100</td>
<td>7</td>
<td>20</td>
<td>93.6</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SMX</td>
<td></td>
<td>99.3</td>
<td></td>
<td></td>
<td>66.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol</td>
<td></td>
<td>66.2</td>
<td></td>
<td></td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td>0.1~1 mg L$^{-1}$</td>
<td>Orange II</td>
<td>17.5 mg L$^{-1}$</td>
<td>36–3802 mg L$^{-1}$</td>
<td>9.5</td>
<td>n.r.</td>
<td>n.r.</td>
<td>[86]</td>
</tr>
<tr>
<td>phosphate</td>
<td>0.1 M</td>
<td>Diclofenac</td>
<td>5 µM</td>
<td>0.55 mM</td>
<td>7.4</td>
<td>45</td>
<td>~100</td>
<td>[42]</td>
</tr>
<tr>
<td>Cl$^{-}$</td>
<td>400 mM</td>
<td>Rhodamine B</td>
<td>10 mg L$^{-1}$</td>
<td>2.0 µM</td>
<td></td>
<td>n.r.</td>
<td>10</td>
<td>~100</td>
</tr>
</tbody>
</table>
### 4.2.2. Heterogeneous Catalysis

#### 1. Energy Catalysis

PAA can be activated by electric current, heat, microwave, ultraviolet light or sunlight. However, UV light is the most popular. Table 4 collects the results of different energy activations of PAA for the degradation of contaminants. Hollman et al. [36] used UV/PAA to produce R-O· to remove SMX, fluoxetine, carbamazepine and naproxen completely within 30 min under neutral conditions. However, electrochemistry and natural light need more time to remove pollutants effectively. The degradation rate of methylene blue under electrochemistry was reported to be 93.99% in 120 min [87], and venlafaxine was removed at 98.5% under natural light with 40 °C heating in 60 min [88]. PAA also releases more active substances when heated. Wang et al. [89] found that SMX was completely removed in 25 min under 60 °C/PAA. Energy activation has significant effects, but its high operating costs and low safety factor limit its further development.

The factors influencing the degradation effect of the energy/PAA process, such as energy intensity, pH, water quality, and PAA concentration on pollutants, also deserve to be studied [90]. The removal rate of the target pollutants generally increases and then decreases as the PAA concentration increases. Studies have shown that higher PAA concentrations improve the removal of organic pollutants by UV/PAA technology [63,64,91]. However, Hollman et al. and Li et al. [36,92] also found that too many dosages of PAA show a certain quenching effect on HO·. For the effect of pH, some studies have shown that PAA− has a stronger HO· scavenging effect in an alkaline environment, and the photolysis rate is higher than that of PAA0 [63]. Therefore, the higher the pH, the worse degradation. It can be concluded in Table 3 that the degradation rate is higher under neutral or acidic conditions. However, Daswat et al. found that alkaline conditions (optimum pH = 11) are most suitable for the UV/PAA process to treat chlorophenol industrial wastewater [90], which is probably attributed to the complex water quality conditions of industrial wastewater. Therefore, some coexisting substances in the water also have an impact on the degradation of organic pollutants. Chen et al. investigated the effect of CO32−/HCO3−, HA and Cl− common in water on the degradation of naphthalene (NAP) by the UV/PAA process and found that the effect of CO32−/HCO3− and Cl− was negligible and HA showed a significant inhibitory effect [64]. In addition, NO3−, as a photosensitive substance, has been shown to produce HO· under UV light, but the product NO2− is a strong HO· bursting agent and shows a slight increase in the overall degradation rate [93].

<table>
<thead>
<tr>
<th>Energy Activation</th>
<th>Contaminants</th>
<th>C0 (mg L−1)</th>
<th>C0 PAA (mmol L−1)</th>
<th>pH</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>Max. Removal Efficiency (%)</th>
<th>Free Radicals</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical oxidation</td>
<td>methylene blue</td>
<td>10</td>
<td>3.6</td>
<td>3</td>
<td>120</td>
<td>25 ± 2</td>
<td>93.99</td>
<td>HO· &gt; R-O·</td>
<td>[87]</td>
</tr>
<tr>
<td>Heat</td>
<td>SMX</td>
<td>5</td>
<td>0.025-0.2 mM</td>
<td>4-9</td>
<td>25</td>
<td>60</td>
<td>-100</td>
<td>R-O·</td>
<td>[89]</td>
</tr>
<tr>
<td>Microwave</td>
<td>thiophene sulfur</td>
<td>0.1%</td>
<td>0.50%</td>
<td>n.r.</td>
<td>3</td>
<td>n.r.</td>
<td>12.07</td>
<td>R-O·</td>
<td>[94]</td>
</tr>
<tr>
<td>Solar Radiation</td>
<td>Venlafaxine</td>
<td>5 mg L⁻¹</td>
<td>28.6 mmol⁻¹</td>
<td>2.3</td>
<td>60</td>
<td>40</td>
<td>98.5</td>
<td>n.r.</td>
<td>[88]</td>
</tr>
<tr>
<td>UV254</td>
<td>SMX</td>
<td>5 mg L⁻¹</td>
<td>0.5-100 mg L⁻¹</td>
<td>7 ± 0.2</td>
<td>30</td>
<td>n.r.</td>
<td>-100</td>
<td>R-O·</td>
<td>[36]</td>
</tr>
<tr>
<td>Fluoxetine</td>
<td>n.r.</td>
<td>7</td>
<td>14</td>
<td>20 ± 1</td>
<td>-80</td>
<td>n.r.</td>
<td>[64]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>n.r.</td>
<td>7</td>
<td>10</td>
<td>n.r.</td>
<td>&gt;90</td>
<td>n.r.</td>
<td>[64]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naproxen</td>
<td>n.r.</td>
<td>7</td>
<td>15</td>
<td>n.r.</td>
<td>&gt;90</td>
<td>n.r.</td>
<td>[64]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV254</td>
<td>Bezafibrate</td>
<td>1 µM</td>
<td>7.1</td>
<td>120</td>
<td>30</td>
<td>&gt;90</td>
<td>n.r.</td>
<td>[63]</td>
<td></td>
</tr>
<tr>
<td>Clofibric acid</td>
<td>10</td>
<td>&gt;90</td>
<td>n.r.</td>
<td>[64]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diclofenac</td>
<td>1 mg L⁻¹</td>
<td>10</td>
<td>&gt;90</td>
<td>n.r.</td>
<td>[64]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>10</td>
<td>&gt;90</td>
<td>n.r.</td>
<td>[64]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naproxen</td>
<td>10</td>
<td>&gt;90</td>
<td>n.r.</td>
<td>[64]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV254</td>
<td>methylene blue</td>
<td>10 mg L⁻¹</td>
<td>50 mg L⁻¹</td>
<td>7</td>
<td>0-120</td>
<td>n.r.</td>
<td>85%</td>
<td>n.r.</td>
<td>[91]</td>
</tr>
</tbody>
</table>

#### 2. Catalyst Catalysis

Although the activation of PAA by metal ions has the advantages of low energy consumption and high efficiency, the biological toxicity they bring will cause secondary
pollution to the environment, which limits their practical application. To overcome this drawback, researchers have investigated heterogeneous catalysts. In Table 5, the main heterogeneous catalysts for PAA are metal oxides, activated carbons and metal–carbon materials. Non-metallic carbonaceous catalysts have been extensively studied due to their large specific surfaces, lack of secondary contaminants and excellent chemical properties [95–97]. Water treatment processes have extensively investigated the use of carbon-based materials for activating peroxides. However, only one study has reported the use of carbon catalysts to activate PAA for the degradation of organic pollutants. Zhou et al. [48] investigated that 92.5% reactive brilliant red X-3B was degraded in 45 min under neutral conditions by ACF/PAA. In contrast, metal-based heterogeneous catalysts are more extensively studied and perform better. It has been reported that SMX and 2,4-dichloropheno can be removed completely by adding LaCoO$_3$ or Co@MXenes and PAA to the solution [55,58,74,77]. Co$_3$O$_4$ exhibited similar properties to LaCoO$_3$ properties [75]. However, metal-based catalysts loaded on carbon materials are more easily recovered. Wang et al. [98] activated PAA by Fe(II)-zeolite instead of Fe(II), which exhibited a solid–liquid interface reaction. The process can effectively degrade organic pollutants under neutral conditions and control the generation of iron sludge. Therefore, the heterogeneous catalysts not only have an excellent effect on the activation of PAA but also have the advantages of low toxicity and recyclability, which is an excellent catalyst method for the application of PAA in the treatment of wastewater.

Table 5. Studies of activating PAA in heterogeneous phase systems.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$C_{\text{Catalyst}}$ (g L$^{-1}$)</th>
<th>Contaminants</th>
<th>$C_0$</th>
<th>$C_{\text{PAA}}$ (mM)</th>
<th>pH</th>
<th>Time (min)</th>
<th>Max. Removal Efficiency (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasound/MnO$_2$</td>
<td>1</td>
<td>Phenol</td>
<td>98.8 mg L$^{-1}$</td>
<td>100</td>
<td>7</td>
<td>20</td>
<td>89</td>
<td>[99]</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>0.7</td>
<td>Phenol</td>
<td>n.r.</td>
<td>50 mg L$^{-1}$</td>
<td>9.5</td>
<td>120</td>
<td>n.r.</td>
<td>[100]</td>
</tr>
<tr>
<td>Co$\text{O}_3$</td>
<td>0.2</td>
<td>Orange G</td>
<td>n.r.</td>
<td>1</td>
<td>7</td>
<td>90</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>0.1</td>
<td>SMX</td>
<td>8 mg L$^{-1}$</td>
<td>0.4</td>
<td>n.r.</td>
<td>60</td>
<td>100</td>
<td>[74]</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>0.2</td>
<td>SMX</td>
<td>n.r.</td>
<td>0.2</td>
<td>7</td>
<td>30</td>
<td>74.7</td>
<td></td>
</tr>
<tr>
<td>ACF</td>
<td>2</td>
<td>SMX</td>
<td>n.r.</td>
<td>1</td>
<td>7</td>
<td>40</td>
<td>92.5</td>
<td></td>
</tr>
<tr>
<td>Co(II)/g-C$_3$N$_4$</td>
<td>0.1</td>
<td>SMX</td>
<td>10 µM</td>
<td>0.2</td>
<td>4.24</td>
<td>30</td>
<td>~100</td>
<td>[44]</td>
</tr>
<tr>
<td>Fe$^{3+}$-zeolite</td>
<td>0.8</td>
<td>SMX</td>
<td>5 µM</td>
<td>400 µM</td>
<td>7</td>
<td>50</td>
<td>~100</td>
<td>[101]</td>
</tr>
<tr>
<td>Co@MXenes</td>
<td>0.3</td>
<td>2,4-dichloropheno</td>
<td>20 µM</td>
<td>0.26</td>
<td>7</td>
<td>20</td>
<td>~100</td>
<td>[55]</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>0.3</td>
<td>SMX</td>
<td>10 µM</td>
<td>0.3</td>
<td>3</td>
<td>15</td>
<td>76.1</td>
<td>[102]</td>
</tr>
<tr>
<td>Phenol-AC</td>
<td>0.1-0.2</td>
<td>Orange G</td>
<td>n.r.</td>
<td>$2.6 \times 10^{-4}$-</td>
<td>7</td>
<td>n.r.</td>
<td>Effective degradation</td>
<td>[103]</td>
</tr>
<tr>
<td>N-rGO</td>
<td>0.75</td>
<td>SMX</td>
<td>0.15 mM</td>
<td>3</td>
<td>3</td>
<td>60</td>
<td>96</td>
<td>[43]</td>
</tr>
</tbody>
</table>

5. The Factors That Influence the Removal of Organic Pollutants in PAA-Based Processes

Through the above discussion, we learned that there are many ways to activate PAA and the PAA-based AOPs have strong oxidative properties. However, some factors, including PAA dosage, catalysts dosage, pH, temperature and water quality components, affect the degradation effect of the PAA system.

5.1. PAA Dosage

Generally, more oxidants can improve degradation efficiency. As the PAA concentration increases, more reactive radicals will be generated in the free radical pathway, but too much PAA will prevent it. Zhang et al. [55] found that with the increase in PAA concentration, the free radicals in the Co@MXenes/PAA process increased so that the reaction constant and degradation rate of 2,4-dichloropheno increased. Nevertheless, 2,4-dichloropheno degradation was inhibited when PAA concentrations exceeded 1.04 mM. Similarly, Kim et al. [54] also found that the degradation of methylene blue by the Fe(II)/PAA process was inhibited when the PAA concentration was increased to 1 mM. This may be attributed to the free radical scavenging effect of excess PAA. In addition, there are H$_2$O$_2$ in the PAA solution, which shows a scavenging effect on R-O· (Equations (34)–(36)). Furthermore, excess PAA absorbs UV light, reducing the number of target compounds that
are directly photolyzed [104]. However, the effect of PAA dosage on non-radical reactions has not been studied by scholars.

\[
\begin{align*}
H_2O_2 + CH_3C(O)OO & \rightarrow HO_2^- + CH_3C(O)OOH. \quad (34) \\
H_2O_2 + CH_3COO^- & \rightarrow HO_2^- + CH_3COOH. \quad (35) \\
O_2^- + CH_3C(O)OO & \rightarrow O_2 + CH_3C(O)OO^-. \quad (36)
\end{align*}
\]

5.2. Catalysts Dosage

Under the free radical pathway, the catalysts will promote the generation of more active radicals with the increase of the dosage. Kim et al. [77] found that increasing Co in the Co/PAA process accelerates the decomposition of PAA. Wang et al. [56] showed that as the initial concentration of Co increased from 0.2 to 3.2 \( \mu M \), the number of active radicals generated increased, and the degradative efficiency of SMX increased from 61.2% to nearly 100% within 15 min, which proved that Co\(^{3+}/Co^{2+}\) transformation occurred in Co/PAA through the redox cycle of Equations (37) and (38). Increased catalyst provides more active sites in heterogeneous catalysis. According to Zhang et al. [55], when Co@MXene was added to the reaction, the catalytic sites were increased, which speeds up the breakdown of 2,4-dichloropheno. The photocatalytic process also has a similar rule. By conducting experiments at different UV intensities of 0.65, 1.87 and 3.50 kW/m\(^3\), Hollman et al. [36] found that the increase in UV intensity accelerates the degradation of pollution.

\[
\begin{align*}
Co^{2+} + CH_3CO_3H & \leftrightarrow Co^{3+} + CH_3CO_2^- + OH^- \quad (37) \\
Co^{3+} + CH_3CO_3H & \leftrightarrow Co^{2+} + CH_3CO_3^- + H^+ \quad (38)
\end{align*}
\]

However, due to the limitation of oxidants in the system, too much catalyst cannot increase the degradation efficiency indefinitely and may also have a scavenging effect on free radicals. Kim et al. [54] found that Fe(II) dosage did not significantly affect the degradation rate of methylene blue in the initial stage but affected the second reaction stage.

5.3. pH

The pH of the reaction is one of the most important factors affecting the performance of PAA-based AOPs. First, pH affects the acid–base balance of PAA, which in turn affects the generation of free radicals. The pKa value of PAA was 8.2, and the PAA\(^0\) was dominant at pH 3–7 (neutral species fraction \( f_{PAA}^0 \) = 1~0.94). As the pH approached 8.2, \( f_{PAA}^0 \) decreased to 0.56, which suggested that under alkaline conditions, reactive radicals such as \( \cdot OH \) may be suppressed by their reduced redox potentials and competition with other compounds [104]. PAA\(^-\) is a weaker oxidant than PAA\(^0\) but reacts more readily with some radical species (\( \cdot OH \) reacts with PAA\(^-\) and PAA\(^0\) with second-order reaction rate constants of 9.97 \( \times 10^9 \) and 9.33 \( \times 10^8 \) M\(^{-1}\)·s\(^{-1}\), respectively). Kim et al. [54] investigated the catalytic effect of Fe\(^{2+}\) on PAA and found that at initial pH \( \leq 6.0 \), the PAA content decreased rapidly within 2 s while the pH value increased to 8.1, and the catalytic effect of Fe\(^{2+}\) on PAA was poor. In contrast, the molar absorption coefficient of PAA\(^-\) and PAA\(^0\) at 254 nm was higher for the photocatalytic process, resulting in a faster photolysis rate of PAA\(^-\) and PAA\(^0\). For example, Mukhopadhyay and Daswat [105] reported that the optimum pH for the degradation of 4-chlorophenol by the UV/PAA process was 9.5. The pH value also has an effect on the morphology of the metal. Fe(II) forms hydroxyl complexes at higher pH, and the catalytic activity is inhibited.

Fe\(^{2+}\) is oxidized by oxygen more readily as pH increases, decreasing the availability of Fe\(^{2+}\) reacting with PAA (or H\(_2O_2\)) at higher pH, while the Fe(III) generated during the reaction was precipitated at lower pH due to the complexation of hydroxide. In addition, pH also affects the surface charge of metal oxides during the heterogeneous activation of PAA. Zhang et al. [55] investigated the degradation of 2,4-dichloropheno by the Co\(_0@MXenes/PAA\) process and found that under neutral conditions, 2,4-dichloropheno
degraded faster. Furthermore, the activity of PAA and the surface properties of the catalyst are affected by pH. Under alkaline conditions, Co@MXenes has a negative charge, and there are mainly conjugated bases of PAA$^-$ in solution, which are attracted or suppressed by electrostatic repulsion. PAA is hydrolyzed more rapidly, and inactive cobalt hydroxide complexes are formed on the surface of Co@MXenes, reducing the efficiency of the system. Under acidic conditions, PAA mainly exists in the form of PAA$^0$, which is much more stable than PAA$^-$, inhibiting the generation of active free radicals. Similar conclusions remain in the non-radical pathway. Zhao et al. [68] found in the experiment of bisphenol A degraded by Co(II)/PAA that as the pH increased from 3.0 to 7.0, the degradation efficiency of bisphenol A gradually decreased, which is probably attributed to the protonation state of the Co(II)-OO(O)CCH$_3$ species was changed, while the fraction of Co$^{2+}$ decreased from 98.7% to 74.1% with the pH increased from 7.0 to 9.0, and there was no Co$^{2+}$ species but Co(OH)$_2$ with less reactive produced when pH reached 11.0.

5.4. Temperature

In practical applications, temperature is also an important factor affecting the efficiency of PAA-based AOPs. Zhang et al. [55] investigated the temperature dependence of 2,4-dichloropheno degradation in the Co@MXenes/PAA process and found that 2,4-dichloropheno was removed by 93.9% within 20 min at 10$^\circ$C, but the degradation rate reached 100% within 15 min when the temperature increased to 30$^\circ$C, and $k_{obs}$ increased from 0.1714 min$^{-1}$ increased to 0.3485 min$^{-1}$. The activation energy of 2,4-dichloropheno was 43.4 kJ/mol, lower than the reported Co(OH)F@MXenes/PMS system (57.32 kJ/mol) and Co$_3$O$_4$@MXenes/PMS system (54.4 kJ/mol), which indicates that the reaction energy barrier is lower in the Co@MXenes/PAA system.

5.5. Water Quality Components

There are various natural organic matters and dissolved inorganic anions in water and wastewater. Due to the special structures and properties of these substances, they become factors that cannot be ignored in the PAA process.

5.5.1. Anions

HCO$_3^-$/CO$_3^{2-}$ and Cl$^-$ are common inorganic anions in water. They can affect the treatment efficiency of PAA activation systems by competing with organic pollutants for free radicals. As shown in Equations (39)–(43) [46,82], the reaction of Cl$^-$ and HO$^-$ will generate HClO$^-$, which is mainly converted to HO$^-$ rather than Cl$^-$ under neutral conditions. At the same time, Cl$^-$ has the ability to react with R-O$^.$ to create Cl$_2$O$_2$. When the concentration of Cl$^-$ is very high, chlorine radicals including Cl$^.-$, Cl$_2$O$_2^.$ and OCl$^-$. are generated in the system. In contrast, when the concentration of Cl$^-$ is low, Cl$^-$ reacts with H$_2$O/OH$^-$ to generate HOCl$^-$. which is easily converted to HO$^-$ under acidic conditions. In addition, Cl$^.$ and Cl$_2$O$_2^.$ will further generate Cl$_2$ and HOCl. In spite of the high redox potentials ($E^0$(Cl$^-$/Cl$^-$) =2.5V, $E^0$(Cl$_2$O$_2^.$/Cl$^-$) = 2.2 V), these active chlorine species have stronger specificity. Therefore, when the target pollutants can be readily oxidized by active chlorine species, Cl$^-$ will improve the treatment efficiency in the PAA-based AOPs. Moreover, HOCl tends to be the dominant active species due to its longer lifetime than R-O$^.$ and HO$^-$ under high concentrations of Cl$^-$. Wang et al. [56] investigated that the addition of Cl$^-$ has minimal effects on the degradation of SMX in the Co/PAA system, showing that Cl$^-$ can scavenge R-O$^.$ as a by-product of SMX decomposition (Equation (16)). Wu et al. [75] observed that Cl$^-$ significantly inhibited the degradation of orange G in the Co$_3$O$_4$/PAA system and attributed it to the low reactivity of the generated active chlorine to orange G. Strong oxidizing properties of chlorine species coming from PAA-based AOPs have high selectivity, so it is confirmed that the reactions produced by Cl$^-$ affect the degradation of different organic pollutants in different ways.

$$\text{CH}_3\text{CO}_3^.- + \text{Cl}^- + \text{H}^+ \rightarrow \text{Cl}^.- + \text{CH}_3\text{CO}_3\text{H}. \quad (39)$$
\[ \text{Cl}^- + \text{HO} \cdot \rightarrow \text{HClO}^- \cdot \]  
\[ \text{HClO}^- \cdot + \text{H}^+ \rightarrow \text{Cl}^- + \text{H}_2\text{O}. \]  
\[ \text{Cl}^- + \text{Cl} \cdot \rightarrow \text{Cl}_2^- . \]  
\[ \text{Cl}^- + \text{Cl} \cdot \rightarrow \text{Cl}_2 \cdot \]  

The alkalinity of water is mostly affected by \( \text{HCO}_3^- / \text{CO}_3^{2-} \), which are known to scavenge free radicals. As shown in Equations (44) and (45), \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) can quench \( \cdot \text{OH} \), resulting in less reactive \( \text{CO}_3^- \) \cite{46,106}. At the same time, the combination of \( \text{HCO}_3^- \) and metal ions may form complexes. For example, Wang et al. \cite{56} examined the effect of \( \text{HCO}_3^- / \text{CO}_3^{2-} \) on the degradation of SMX by the Co/PAA process and found that though SMX degradation efficiency decreased with the increase of \( \text{HCO}_3^- / \text{CO}_3^{2-} \) concentration, the difference between \( \text{HCO}_3^- \) and \( R-O \cdot \) persisted. The Co/PAA reaction has a very low-rate constant, so the inability of this reaction would not primarily be due to the consumption of \( R-O \cdot \) through \( \text{HCO}_3^- \). However, \( \text{HCO}_3^- \) will form non-reactive \( \text{Co}^{2+} - \text{HCO}_3^- \) complexes during the reaction, which limits the activation of PAA and inhibits the degradation of SMX. Wang et al. \cite{47} studied the degradation process of SMX in a CoFe\textsubscript{2}O\textsubscript{4}/PAA system and found that the residual PAA content in the system with 2 mM \( \text{HCO}_3^- \) was higher than that without addition.

\[ \text{HCO}_3^- + \text{HO} \cdot \rightarrow \text{CO}_3^- + \text{H}_2\text{O}. \]  
\[ \text{CO}_3^{2-} + \text{HO} \cdot \rightarrow \text{CO}_3^- + \text{OH}^- . \]

5.5.2. Dissolved Organic Matter (DOM)

DOM reacts with \( R-O \cdot \) and \( \text{HO} \cdot \) (mainly \( R-O \cdot \)) to inhibit the degradation efficiency of PAA-based AOPs, and the higher the DOM concentration, the more obvious the inhibition. Wang et al. \cite{56} showed that when the HA concentration of the CoFe\textsubscript{2}O\textsubscript{4}/PAA system was increased from 0 to 10 mg L\textsuperscript{-1}, the SMX removal rate decreased from 74.7% to 5.8%, and the \( k_{\text{obs}} \) decreased from 0.047 to 0.002 min\textsuperscript{-1} in 30 min. In addition to adsorbing on the catalyst, some HA groups, such as phenolic hydroxyl and carboxyl groups, would inhibit PAA activation \cite{55}. Furthermore, HA may also scavenge free radicals. Zhao et al. \cite{68} evaluated the removal of bisphenol A in the Co(II)/PAA process and found that natural organic matter (NOM) significantly inhibited the removal efficiency, but PAA decomposition was only slightly inhibited, indicating that inhibition may be due to the competition between NOM and bisphenol A.

6. Conclusions and Future Prospects

The latest research on PAA-based AOPs for the removal of organic pollutants was reviewed in this paper. The methods principle and reactivity of activating PAA were discussed. Currently, the most prominent activation methods are energy radiation (UV, solar radiation, ultrasound, heating), transition metal and activated carbon material catalysis. Most studies showed that PAA attacked pollutants mainly by generating strong oxidative free radicals (\( R-O \cdot, \text{HO} \cdot \)), and \( R-O \cdot \) is dominant in most of the reactions. In recent years, some scholars have pointed out a non-radical pathway, which removes pollutants by generating complexes or high-valent metal species, and confirmed its key role in the degradation process. The removal effect of PAA-based AOPs is affected by various factors, such as PAA/catalyst dosage, \( \text{pH} \), temperature and water quality components (inorganic anions and DOM). PAA-based AOPs have gradually become a hot spot in the research of removing organic pollutants due to their excellent degradation effect.

However, PAA-based AOPs still face some challenges in removing organic pollutants. First, the activation mechanism of PAA is still controversial, especially since the emergence of non-radical pathways in recent years has broken people's potential awareness of radical pathways. Secondly, the reaction mechanisms, rate constants and identification methods of
organic radicals (R-O·) and non-radicals have not been systematically studied. Furthermore, transition metal catalysis will lead to metal leakage. Additionally, the toxicity assessment of by-products released from PAA activation of organic pollutants is an important research project, but there are few reports on it. Finally, the existing research is mainly aimed at small-scale laboratory experiments, and the technical development of its practical application is incomplete.

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