



Review

Cobalt-catalyzed sulfate radical-based advanced oxidation: A review on heterogeneous catalysts and applications



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ABSTRACT

Recently sulfate radical-based advanced oxidation processes (SR-AOPs) attract increasing attention due to their capability and adaptability in decontamination. The couple of cobalt and peroxymonosulfate (PMS) is an efficient way to produce reactive sulfate radicals. This article reviews the state-of-the-art progress on various heterogeneous cobalt-based catalysts for PMS activation, including cobalt oxides, cobalt-ferrite and supported cobalt by diverse substrates. We summarize the intrinsic properties of these catalysts and their fundamental behaviors in PMS activation, as well as synthetic approaches. In addition, influencing factors and synergistic techniques of Co/PMS systems in organic degradation and possible environmental applications are also discussed. Finally, we propose perspectives on challenges related to cobalt-based catalysts, heterogeneous Co/PMS systems and their potential applications in practical environmental cleanup.

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1. Introduction

Organic contaminants in water remains being a great concern to the environment, especially those refractory and/or non-biodegradable pollutants that can hardly be treated by conventional methods. In recent decades, advanced oxidation processes (AOPs), which involve highly reactive oxygen species like hydroxyl radical ($\cdot\text{OH}$), have attracted increasing attention due to their potential capability in the removal of recalcitrant organic pollutants. Upon such strong oxidants, organic pollutants are destructed into innocuous or low toxic small compounds, or even thoroughly mineralized into carbon dioxide and water [1,2]. As typical $\cdot\text{OH}$ -generating AOPs, Fenton reaction and its derivative technologies, such as photo-Fenton [3], electro-Fenton [4,5], sono-Fenton [6] and sono-photo-Fenton [7,8], are most popular due to the production of strong oxidant $\cdot\text{OH}$ (oxidation potential is 1.8–2.7 V vs. normal hydrogen electrode (NHE)) [9]. However, these methods keep facing several drawbacks, including massive utilization of ferrous salts and H_2O_2 , chemical instability and difficulties in the storage and transport of the oxidant, low optimal reaction pHs (2–4), and subsequent separation and post-processing of huge amounts of sludge [10–13].

Advanced oxidation processes based on sulfate radical ($\text{SO}_4^{\bullet-}$) (SR-AOPs) have become to be a promising alternative owing to a series of merits that do not share with those $\cdot\text{OH}$ -generating methods: (a) $\text{SO}_4^{\bullet-}$ possesses an oxidation potential (2.5–3.1 V vs. NHE) comparable or even higher than $\cdot\text{OH}$ [14]; (b) $\text{SO}_4^{\bullet-}$ reacts more selectively and efficiently via electron transfer with organic compounds that contain unsaturated bonds or aromatic π electrons, while $\cdot\text{OH}$ may also react with diverse background constituents by hydrogen abstraction or electrophilic addition at high reaction rates [14–16]; (c) $\text{SO}_4^{\bullet-}$, as a dominant oxidizing species, would react efficiently with organic compounds over a wide pH range of 2–8 [17–19]; (d) The half-life period of $\text{SO}_4^{\bullet-}$ is generally supposed to be 30–40 μs , which enables $\text{SO}_4^{\bullet-}$ to have more stable mass transfer and better contact with target compounds than $\cdot\text{OH}$ (less than 1 μs) [20–22].

$\text{SO}_4^{\bullet-}$ can be produced by radiolysis, photolysis, pyrolysis or chemical activation of peroxymonosulfate (PMS, HSO_5^-) or persulfate (PS, $\text{S}_2\text{O}_8^{2-}$) [23–27]. The oxidation potential of PMS (1.82 V) is higher than H_2O_2 (1.76 V) but lower than PS (2.01 V) [28]. However, PMS displays a more efficient performance in organic degradation processes [29]. Oxone, a commercial name of potassium peroxymonosulfate ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), is a versatile and environmental friendly oxidant that has been widely utilized for bleaching, cleaning and disinfection and more importantly as a favorable source of PMS [30–32]. In fact, PMS can be activated by various transition metallic ions, such as Mn^{2+} , Ce^{3+} , Ni^{2+} , Fe^{2+} , V^{3+} , Ru^{3+} and so forth. Among them, the Co^{2+} /PMS system demonstrates the best performance that is even superior to traditional Fenton reaction at neutral pHs and with lower dosage of reagents [33,34].

Since catalytic decomposition of PMS using cobalt was first reported in 1958 [35], Co^{2+} /PMS system has successfully applied in chemiluminescent reactions [36,37], determination of trace Co^{2+} and PMS in aqueous solutions [38,39], modification of DNA [40] and SR-AOPs [30,41–43]. Cobalt-mediated activation of PMS can be illustrated as Fig. 1 [44]. It is apparent that the formation of CoOH^+ , which is regarded as the most effective species to activate PMS (Eq. (1)), is the rate-limiting step [45,46], while the regeneration of Co^{2+} by reducing from Co^{3+} (Eq. (2)) is the crucial step to maintain the reactions at a low dosage of cobalt [47,48].

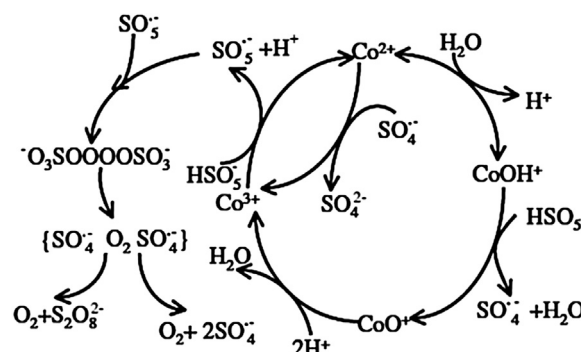
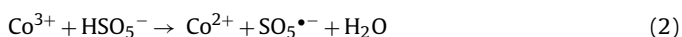
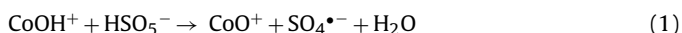


Fig. 1. Mechanism on $\text{SO}_4^{\bullet-}$ chain reactions.

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The average cobalt concentration in serum and urine of people are approximately $0.1\text{--}0.3 \mu\text{g L}^{-1}$ and $0.1 \mu\text{g L}^{-1}$, respectively [49]. Although cobalt is claimed not being a hazardous chemical, several researches showed that excessive cobalt ions are possibly toxic and carcinogenic, leading to serious health problems such as asthma, pneumonia and cardiomyopathy [48,50,51]. Homogeneous catalytic reactions of Co^{2+} /PMS system in aqueous solutions discharge cobalt ions containing water, which is a potential threat to human beings and increases the operation cost due to the loss of cobalt. PMS activation using cobalt containing materials as heterogeneous catalysts (Co /PMS) seems to be a promising strategy. Multifarious heterogeneous cobalt-based catalysts have been investigated so far, including cobalt oxides, spinel-type ferrite particles and immobilized cobalt catalysts [51–58]. This review aims to provide a latest summary of various heterogeneous cobalt-based catalysts for PMS activation and their synthetic strategies. The influencing factors in the decontamination reactions, advanced techniques of synergistic heterogeneous Co /PMS systems and possible environmental applications will also be introduced. Challenges confronted in the application of Co /PMS are discussed in the conclusion and outlook section.

2. Heterogeneous catalysts

2.1. Cobalt oxide

Cobalt oxide is versatile in various industrial sectors, such as rechargeable batteries [59], air pollution control [60], Fischer–Tropsch synthesis [61] and gas sensors [62]. Up to now five cobalt oxides, CoO , CoO_2 , Co_2O_3 , $\text{CoO}(\text{OH})$ and Co_3O_4 , have been reported. Among these species, CoO and Co_3O_4 are more frequently investigated while CoO_2 are thermally unstable [63–65]. Dionysiou's group first studied the heterogeneous activation of PMS by CoO or Co_3O_4 [66]. It was found that CoO /PMS system was inclined to be homogeneous because of significant dissolution of Co , which was attributed to the high solubility of CoO in water ($0.313 \text{ mg}/100 \text{ g H}_2\text{O}$) [49]. Chan et al. have found that even the filtrate of CoO possesses the ability to activate PMS [54]. However, in the form of Co_3O_4 , the leakage of cobalt ions is much suppressed due to the bound of CoO in the net of Co_2O_3 [66]. Yu et al. have proposed the mechanism of Co_3O_4 /PMS system, in which Co^{2+} ions are produced and participate in homogeneous redox reactions (Fig. 1), then Co^{3+} ions precipitate back into the crystal lattice of Co_3O_4 , so as to decrease the loss of cobalt [67]. As the relatively higher stability, Co_3O_4 based SR-AOPs have been extensively investigated.

Pleasant methods have been applied to synthesize Co_3O_4 nanoparticles, such as thermal decomposition [68], polymer combustion [69], hydrothermal treatment [70,71], and sol–gel synthesis [72]. Among them, direct thermal decomposition of inorganic

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