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Review

Metal-free carbon materials-catalyzed sulfate radical-based advanced oxidation processes: A review on heterogeneous catalysts and applications

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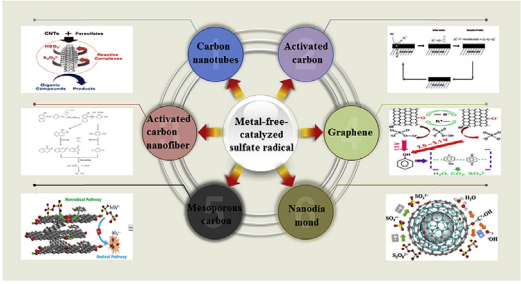
HIGHLIGHTS

- Heterogeneous sulfate radical-based advanced oxidation processes were introduced.
- Strategies of metal-free catalyst for PMS/PS activation were overviewed.
- Knowledge gaps and research needs related to this systems were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

In recent years, advanced oxidation processes (AOPs), especially sulfate radical based AOPs have been widely used in various fields of wastewater treatment due to their capability and adaptability in decontamination. Recently, metal-free carbon materials catalysts in sulfate radical production has been more and more concerned because these materials have been demonstrated to be promising alternatives to conventional metal-based catalysts, but the review of metal-free catalysts is rare. The present review outlines the current state of knowledge on the generation of sulfate radical using metal-free catalysts including carbon nanotubes, graphene, mesoporous carbon, activated carbon, activated carbon fiber, nanodiamond. The mechanism such as the radical pathway and non-radical pathway, and factors influencing of the activation of sulfate radical was also be revealed. Knowledge gaps and research needs have been identified, which include the perspectives on challenges related to metal-free catalyst, heterogeneous metal-free catalyst/persulfate systems and their potential in practical environmental remediation.

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Contents

1. Introduction

Nowadays, the researches focusing on the advanced oxidation processes (AOPs) have been published wildly because of the enormous potential capability in the removal of organic and inorganic micropollutants (Gogate and Pandit, 2004). In AOPs systems, recalcitrant organic pollutants can be destructed into innocuous or low toxic compounds, or even mineralize into CO_2 and H_2O. In the last few decades, the hydroxyl radical (•OH) based AOPs including photo-Fenton (Lan et al., 2015), electro-Fenton (Kourdali et al., 2014; Olvera-Vargas et al., 2014), photo-sono-Fenton (Vaishnave et al., 2014; Giannakis et al., 2015), photo-electro-Fenton, sono-Fenton (Wang and Shih, 2015) were most popular because of the generating of relatively strong oxidant •OH (oxidation potential: 1.8–2.7 V). Nevertheless, huge amount of sludge, low optimal reaction pH, difficulties in the storage and transport of H_2O_2 are remaining (Dhakshinamoorthy et al., 2012; Luo et al., 2014; Messele et al., 2015).

1.1. Sulfate radical-based advanced oxidation processes

Compared with AOPs based on •OH, AOPs based on sulfate radical (SR-AOPs) have some unique superiorities: (a) through electronic exchange of organic compounds with unsaturated bonds or aromatic π electrons, the reaction of $SO_4^{\bullet-}$ has exhibit selectivity and effectiveness, however, under different background, by hydrogen abstraction or electron addition, •OH may also achieve relatively high reaction efficiency (Antoniou et al., 2010); (b) sulfate radical ($SO_4^{\bullet-}$) is provided with higher oxidation potential (2.5–3.1 V vs. NHE) that may be higher than •OH; (c) Because the half-life of the $SO_4^{\bullet-}$ (30–40 μs) is generally longer than that of the hydroxyl radical (less than 1 μs)), it can be more stable and better mass transfer and contact with the target compound; (d) $SO_4^{\bullet-}$ could react with organic compounds in a wide range of pH values from 2.0 to 8.0 when it is the main oxide species (Yang et al., 2008; Huang and Huang, 2009).

Recent years, it was proven that emerging pollutants from environmental aqueous matrices, such as pro-gesterone (Mezyk et al., 2011), ciprofloxacin (An et al., 2010), ethynilestradiol, estradiol, triclosan (Nfodzo and Choi, 2011), carbamezepine (Matta et al., 2011), and antibiotic (Rickman and Mezyk, 2010; Su et al., 2011), can be eliminated by SR-AOPs. Peroxymonosulfate (PMS) or persulfate (PS) as the precursor of $SO_4^{\bullet-}$ are monosubstituted or symmetrically substituted hydrogen peroxide derivative by sulfo moiety. The structure of the PMS anion is $HOOSO_3^-$, it is similar to those in $S_2O_8^{2-}$, and its bond lengths is the three terminal S–O and an internal S–O (peroxo) bonds lengths, and the O–O distance similar to that of H_2O_2 in X-ray analyses (Zhang et al., 2008; Zhang and Lin, 2010). Among the PS and PMS, sodium persulfate is the first choice of application in the decontamination technologies due to high stability and water solubility (Liang et al., 2003). The $SO_4^{\bullet-}$ reacts in the following three different ways (Chawla and Fessenden, 1975; Neta et al., 1977; Huie et al., 1991): (i) Hydrogen abstraction: the main reaction of $SO_4^{\bullet-}$ with organic compounds is hydrogen abstraction. For instance, alkanes, alcohols, organic acids, ethers, lipids and so on. The main mode of action of sulfate and organic matter is to hold hydrogen, which is proven by Khusan S.L. being used to calculate $SO_4^{\bullet-}$ with different organic reactions under different activation energies of hydrogen; (ii) Electron transfer: organic reactions of $SO_4^{\bullet-}$ with benzene and aromatic are principally affected by electron transfer. Free radicals attack the aromatic substance ring opening is mainly pass through the $SO_4^{\bullet-}$ using strong oxidation of aromatic compounds to capture electron. And destroy the original sharing electrons, the electron transfer occurs on the structure. It is proved by principle storage process of tyrosine and high sulfate free radicals, and with different radiation and laser photolysis; (iii) Addition: for olefin unsaturated compounds as alkynes organic or C=C including double bond, $SO_4^{\bullet-}$ is usually deemed to the major process, this reaction is the addition of $SO_4^{\bullet-}$ to single electron, it can attack the unsaturated bond actively, after the bond breaks, and organics and sulfate generate addition reaction, and then $SO_4^{\bullet-}$ and fracture formation of electronic.

1.2. Metal-free catalysts

$SO_4^{\bullet-}$ can be produced by many methods, i.e., illumination, ultrasonic activation, thermal activation, transition metal activation, microwave activation, nonmetal catalyst activation (Shao et al., 2017). For the moment, the catalysts used in chemical industries are mainly metal based catalysts (*e.g.*, precious metals and metal oxides) (Guo et al., 2016). However, they are often not highly selective, and will cause the waste of resources, energy consumption and greenhouse gases. Metal-free carbonaceous materials have attracted considerable interests as heterogeneous catalysts, due to its physical and chemical properties compared to the metal based catalyst has more advantages (*e.g.*, no pollution, low cost, thermal