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Review

Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: Current development, challenges and prospects

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ABSTRACT

Sulfate radical-based advanced oxidation processes (SR-AOPs) employing heterogeneous catalysts to generate sulfate radical ($SO_4^{\bullet-}$) from peroxymonosulfate (PMS) and persulfate (PS) have been extensively employed for organic contaminant removal in water. This article aims to provide a state–of–the–art review on the recent development in heterogeneous catalysts including single metal, mixed metal, and nonmetal carbon catalysts for organic contaminants removal, with particular focus on PMS activation. The hybrid heterogeneous catalyst/PMS systems integrated with other advanced oxidation technologies is also discussed. Several strategies for the identification of principal reactive radicals in $SO_4^{\bullet-}$–oxidation systems are evaluated, namely (i) use of chemical probe or spin trapping agent coupled with analytical tools, and (ii) competitive kinetic approach using selective radical scavengers. The main challenges and mitigation strategies pertinent to the SR-AOPs are identified, which include (i) possible formation of oxyanions and disinfection byproducts, and (ii) dealing with sulfate produced and residual PMS. Potential future applications and research direction of SR-AOPs are proposed. These include (i) novel reactor design for heterogeneous catalytic system based on batch or continuous flow (e.g. completely mixed or plug flow) reactor configuration with catalyst recovery, and (ii) catalytic ceramic membrane incorporating SR-AOPs.

Contents

Abbreviations: AC, activated carbon; ACF, activated carbon fiber; CNT, carbon nanotube; DMPO, 5,5-dimethyl-1-pyrroline N-oxide; DMSO, dimethyl sulfoxide; DOM, dissolved organic matter; ESR, electron spin resonance; EtOH, ethanol; GO, graphene oxide; HDBP, halogenated disinfection byproduct; MeOH, methanol; MW, microwave; NB, nitrobenzene; NHE, normal hydrogen electrode; OMS, octahedral molecular sieves; PMS, peroxymonosulfate; PS, persulfate; rGO, reduced graphene oxide; SR-AOPs, sulfate radical-based advanced oxidation processese; $SO_4^{\bullet-}$, sulfate radical; TBA, tert-butyl alcohol; US, ultrasonic; ZVI, zero valent iron; 4-NB, 4-nitrobenzoic; $^{\bullet}OH$, hydroxyl radical.

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1. Introduction

In recent decades, environmental pollution by recalcitrant organics is increasingly becoming a challenging multidisciplinary problem as new chemicals are being introduced continuously into the environment. Water pollution due to recalcitrant organics particularly those classified as emerging contaminants (e.g. pharmaceuticals and their metabolites, endocrine disruptors, disinfection by-products, personal care products and illicit drugs) could lead to serious ecological impacts [1–3]. Many recalcitrant organics are toxic, biorefractory and difficult to be removed by the conventional treatment methods [4]. As such, advanced treatment techniques with chemical oxidation that offer remarkable treatment efficiency are highly desired.

Sulfate radical-based advanced oxidation processes (SR-AOPs) are increasingly gaining attention as effective solution to the destruction of recalcitrant organics in water. The SR-AOPs utilize highly–reactive sulfate radical ($SO_4^{\bullet-}$) to oxidize organic contaminants to innocuous CO_2 and H_2O. Recent studies have showed that SR-AOPs are effective in removing various types of recalcitrant contaminants such as volatile organic compounds [5,6], endocrine disruptors [7], pharmaceuticals and their metabolites [8,9], cyanotoxins [10,11] and perfluorinated compounds [12] in water. The SR-AOPs are also effective in many other applications including disintegration of activated sludge [13], disinfection [14] and decontamination of pool water [15].

Most commonly, $SO_4^{\bullet-}$ is generated *via* peroxymonosulfate (PMS) or persulfate (PS) activation. Various activation methods have been proposed which include the use of heat [16], chemicals [17,18], base [19], UV [20], transition metals [21–23] and ultrasound [24]. The transition metal activation method is less complex in reactor/system configuration and more economical compared to the energy-based activation methods (e.g. ultrasound, UV and heat etc.). The transition metal activation of PMS and PS can be achieved in the homogeneous and heterogeneous systems. The heterogeneous system is advantageous over the homogeneous system because (i) the solid heterogeneous catalyst can be easily separated from the treated water for reuse, (ii) secondary treatment to remove dissolved metals from the treated water is not required, and (iii) it is more tolerant towards extreme operating conditions [25]. The heterogeneous system is effective over a broader pH range including the common pH for natural water and wastewater (pH 2–9) whereas for the homogeneous system, the dissolved catalyst could precipitate at circumneutral and basic pH decreasing its performance [26,27]. Compared to PS, PMS is relatively easier to be activated with metal oxide catalysts due to the differences in their molecular structures (i.e. PMS is asymmetrical while PS is symmetrical) and bond dissociation energies. The PS activation by heterogeneous catalyst, most commonly Fe^0, consumes the catalyst through the irreversible conversion of Fe^0 to Fe^{3+}. On the other hand, the PMS catalysts have a relatively longer lifespan as they can potentially be regenerated through a redox cycle with PMS (e.g. Co^{2+} to Co^{3+} to Co^{2+}).

For activation of PMS by heterogeneous catalyst, many studies have adopted heterogeneous cobalt oxide catalysts for PMS activation because Co has been identified as the most efficient PMS activator [21,23,28–30]. To date, several review articles [31–33] and book chapter [34] have emerged to provide overviews of SR-AOPs involving the PMS activation by homogeneous and heterogeneous Co catalysts. However, Co leaching from heterogeneous Co catalysts during PMS activation poses a concern as Co is considerably toxic and potentially carcinogenic [35]. Dissolved Co concentration ranging from 0.002 to 0.107 mg L^{-1} has been detected in drinking water [36]. To avoid potential Co leaching, the research direction has shifted towards the use of other catalysts, namely metal (Mn-, Fe- and Cu- based) and nonmetal catalysts. To date, investigation of the nonmetal catalyst consists only of the carbon-based catalysts because they are relatively abundant and have tremendous potential for practical application. Considering that the SR-AOPs have been the subject of tremendous research interest due to their potential environmental applications, Mn-, Fe-, Cu- and carbon-based catalysts are extensively being investigated as PMS activators. To the best of our knowledge, there is no review on the development of heterogeneous catalysts as PMS activator other than those for heterogeneous Co catalysts.

This review aims to provide a timely overview on the development of metal- and nonmetal- based heterogeneous catalysts for the destruction of recalcitrant organics in water with particular focus on PMS activation. The heterogeneous transition metal-based catalysts can be classified into the single and mixed metal catalysts. The mixed metal catalysts have at least two different metal species in their metal framework. The topics discussed herein include a brief summary of the chemistry of $SO_4^{\bullet-}$, mechanisms of PMS activation, recent progresses in the development of single metal, mixed metal and nonmetal carbon catalysts for PMS activation, hybrid heterogeneous catalyst/PMS system integrated with other advanced