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Activation of peroxymonosulfate by base: Implications for the degradation of organic pollutants

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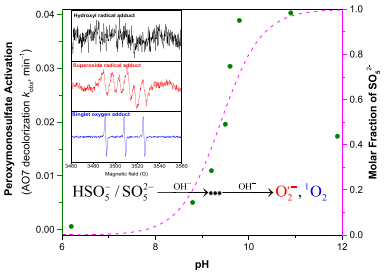
HIGHLIGHTS

- Base can activate peroxymonosulfate at a weakly basic environment.
- Base/peroxymonosulfate system is able to degrade a variety of organic pollutants.
- Superoxide radical and singlet oxygen may be the dominating reactive oxygen species.

GRAPHICAL ABSTRACT



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ABSTRACT

Increasing attention has been paid to environmentally friendly activation methods of peroxymonosulfate (PMS) in advanced oxidation processes (AOPs) for organic pollutant elimination. This work demonstrates that Base can be applied as a novel activator for PMS. The Base/PMS system, at ambient temperature, was able to degrade a variety of organic pollutants, including acid orange 7 (AO7), phenol and bisphenol A. In subsequent experiments with AO7, the decolorization rates for AO7 followed pseudo-first-order kinetics, with rate constant values ranging from 0.0006 to 0.1749 min^{-1} depending on the operating parameters (initial PMS, Base, AO7 concentrations and reaction temperature). Furthermore, the mechanism for PMS activation by the Base was elucidated by radical scavenger (*tert*–butyl alcohol, methanol, sodium azide and *p*–benzoquinone) and electron spin resonance trapping studies. The results revealed that superoxide anion radical and singlet oxygen other than sulfate radical were the primary reactive oxygen species in the Base/PMS system. The findings of this study present a new pathway for PMS activation and provide useful information for the treatment of wastewater.

1. Introduction

Advanced oxidation processes (AOPs), which are based on the generation of highly reactive oxygen species (e.g., hydroxyl radical, superoxide anion radical, sulfate radical, and singlet oxygen) have shown great potential for the removal of contaminants of emerging concern (Duan et al., 2015a, 2015b; Indrawirawan et al., 2015; Liu et al., 2015; Yan et al., 2015). Hydrogen peroxide and persulfates are common oxidizing agents used to generate reactive oxygen species in AOPs (Watts and Teel, 2006; Sun and Wang, 2015). In the past years, persulfates such as peroxymonosulfate (PMS, HSO_5^-) and peroxydisulfate (PDS, $S_2O_8^{2-}$), have attracted increasing attention because they are much more stable than hydrogen peroxide. Additionally, persulfates and their final product sulfate ion (SO_4^{2-}) have the least effect on native organisms (Tsitonaki et al., 2008). Furthermore, the sulfate radical (E^0 = 2.5–3.1 V) generated in

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activated persulfates processes is more selective than the hydroxyl radical (E^0 = 1.8–2.7 V) for the oxidation of compounds with carbon–carbon double bonds and benzene rings (Anipsitakis and Dionysiou, 2003, 2004; Huang et al., 2005). Thermal radiation (Eq. (1)) (Huang et al., 2005; Ghauch et al., 2015; Qi et al., 2015), UV light (Eqs. (1)–(2)) (Anipsitakis and Dionysiou, 2004; Antoniou et al., 2010), transition metals cation and zero valent metals (Eqs. (3)–(6)) (Anipsitakis and Dionysiou, 2003, 2004; Ghauch et al., 2013; Ayoub and Ghauch, 2014; Naim and Ghauch, 2016) are the main technologies for persulfates activation.

$$S_2O_8^{2-} + UV/Heat \rightarrow 2\ SO_4^{\cdot -} \quad (1)$$

$$HSO_5^- + UV \rightarrow SO_4^{\cdot -} + {}^{\cdot}OH \quad (2)$$

$$S_2O_8^{2-} + Me^{n+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Me^{(n+1)+} \quad (3)$$

$$HSO_5^- + Me^{n+} \rightarrow SO_4^{\cdot -} + OH^- + Me^{(n+1)+} \quad (4)$$

$$Fe^0 + O_2 + H_2O \rightarrow 2Fe^{2+} + 4\ OH^- \quad (5)$$

$$Fe^0 + H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \quad (6)$$

However, the high energy requirements for thermal and UV light irradiation, metal toxicity and risk of secondary pollution constrain further industrial application of these activation methods. Therefore, it is of great interest to develop a low–cost, high–efficiency method for the activation of persulfates for organic pollutant degradation.

Base–activated PDS technology has been successfully applied to destroy highly chlorinated methanes and ethanes in groundwater and soil systems (Block, 2004). Several mechanisms have been proposed for the Base activation of PDS (Kolthoff and Miller, 1951; House, 1962; Furman et al., 2010). Recently, a mechanism for the Base activation of PDS was proposed involving the Base-catalyzed hydrolysis of PDS to hydroperoxide anion and sulfate followed by the reduction of another PDS molecule by hydroperoxide. Reduction by hydroperoxide decomposes PDS into sulfate radical and sulfate anion, and hydroperoxide is oxidized to superoxide. The sulfate radical then oxidizes hydroxide, resulting in the formation of the hydroxyl radical (Eqs. (7)–(9)) (Furman et al., 2010).

$$S_2O_8^{2-} + 2H_2O \rightarrow HO_2^- + 2\ SO_4^{2-} + 3H^+ \quad (7)$$

$$S_2O_8^{2-} + HO_2^- \rightarrow SO_4^{\cdot -} + O_2^{\cdot -} + SO_4^{2-} + H^+ \quad (8)$$

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + {}^{\cdot}OH \quad (9)$$

PMS and PDS are similar in structure and both have an O–O bond. One hydrogen atom in H_2O_2 is replaced by SO_3 to generate HSO_5^-, and two hydrogen atoms in H_2O_2 are replaced by SO_3 to form $S_2O_8^{2-}$. Based on these facts, it was speculated that PMS could also be activated by Base.

The objective of the present study was to investigate the catalytic activity of the Base/PMS system for organic pollutants (tested mainly with Acid Orange 7) and the reaction kinetics under various experimental conditions. Furthermore, the dominant reactive oxygen species in the Base/PMS system were identified, the possible mechanism for the activation of peroxymonosulfate by Base and the possible pathways of AO7 degradation were elucidated.

2. Materials and methods

2.1. Reagents and materials

All chemical reagents and organic solvents were at least analytical grade and were used as received without further purification. PMS (commercially available as Oxone), 5,5–dimethyl–1–pyrrolidine N–oxide (DMPO), 2,2,6,6–tetramethyl–4–piperidone (TEMP), phenol, bisphenol A, furfuryl alcohol, sulfamethoxazole and 4-chlorophenol were obtained from Sigma–Aldrich (St. Louis, MO, USA). AO7, PDS, hydrogen peroxide, sodium hydroxide, sodium chloride, sodium carbonate, sodium nitrate, sodium hydrogen phosphate, sodium sulfate and sodium azide (NaN_3) were purchased from Sinopharm (Shanghai, China). Methanol (MeOH), dichloromethane, *tert*–butyl alcohol (TBA), ethanol and *p*–benzoquinone (BQ) were supplied by J&K Scientific (Beijing, China). All solutions were prepared using water with a resistance of 18.2 MΩ•cm from a Milli–Q Integral 5 system (EMD Millipore, Billerica, MA, USA).

2.2. Experimental methods

A stock solution of AO7 was freshly prepared with Milli–Q water, and the initial concentration (C_0) was fixed at 0.1 mM except for during experiments concerning the effect of initial AO7 concentration. Sodium hydroxide and PMS stock solutions (typically 60 mM) were also prepared before use in experiments. All experiments on the removal of AO7 were performed in a 250-mL glass flask with the temperature controlled at 25 °C except for the experiments concerning the effects of reaction temperature, which were performed in a constant–temperature water bath shaker unit (THZ–82A, Jiangsu, China). All reactions were initiated by immediately mixing appropriate amounts of AO7, NaOH, anions or scavengers (if necessary) and PMS in this order. During treatments, a rapid shaking (100 r min^{-1}) ensured a complete solution mixing state. At the given reaction time intervals, approximately 5 mL of sample was withdrawn and the AO7 content was determined immediately. For other analyses, the samples were quenched with an excess of 0.05 M H_2SO_4 (Ball and Edwards, 1956).

2.3. Analytical methods

The absorbance of the AO7 solution was generally measured immediately at the characteristic λ_{max} of 484 nm using a DR6000 UV–vis spectrophotometer (HACH, Loveland, CO, USA) except for several situations that were analyzed using ultra performance liquid chromatography (UPLC) (Text S1 and Fig. S1 and S2). The UV–vis spectra of selected samples were recorded between 200 and 600 nm using the same UV–vis spectrophotometer. Decolorization efficiencies and rate constant values were calculated according to Eqs. (10) and (11), respectively:

$$Decolorization(\%) = 100 \times (C_0 - C_t)/C_0 \quad (10)$$

$$\ln(C_0/C_t) = k_{obs}t \quad (11)$$

where C_0 is the initial AO7 concentration, C_t is the AO7 concentration at time t in the Base/PMS system, and k_{obs} is the pseudo–first–order constant (min^{-1}).

The concentrations of other organic pollutants (i.e., phenol, bisphenol A, furfuryl alcohol, sulfamethoxazole, and 4-chlorophenol) were measured using high-performance liquid chromatography (HPLC, Ultimate 3000, Dionex, Sunnyvale, CA, USA) equipped with a UV detector. Separation was performed on a Zorbax Eclipse Plus C18 column (150 mm × 4.6 mm, 5 μm, Agilent,