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Activation of peroxymonosulfate by phenols: Important role of quinone intermediates and involvement of singlet oxygen

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ABSTRACT

In this study, the kinetics of reactions of peroxymonosulfate (PMS) with ten model phenols (including phenol, methylphenols, methoxyphenols, and dihydroxybenzenes) were examined. The oxidation kinetics of these phenols by PMS except for catechol and resorcinol showed autocatalysis in alkaline conditions (pH 8.5 and 10), due to the contribution of singlet oxygen ($^1O_2$) produced from PMS activation by quinone intermediates formed from their phenolic parents. The oxidation rates of ortho- and meta-substituted methylphenols and methoxyphenols by PMS were much higher than their para-substituted counterparts under similar conditions. This was attributed to the relatively low yields of quinone intermediates from para-substituted phenols. SMX could be efficiently degraded by PMS in the presence of phenols which showed great autocatalysis when they individually reacted with PMS, and the addition of methanol in excess had negligible influence suggesting that $^1O_2$ rather than hydroxyl radical and sulfate radical played an important role. Transformation of SMX by $^1O_2$ underwent three pathways including hydroxylation of aniline ring, oxidation of aromatic amine group to generate nitro-SMX, and oxidative coupling to generate azo-SMX and hydroxylated azo-SMX. These results obtained in this work improve the understanding of in situ chemical oxidation using PMS for remediation of subsurface, where phenolic and quinonoid moieties are ubiquitous.

1. Introduction

In recent years, the potential application of peroxymonosulfate (PMS) based chemical oxidation processes for in situ subsurface remediation (e.g., soli, sediment, and groundwater) and ex situ water/wastewater treatment has received increasing interests (Anipsitakis et al., 2008; Chesney et al., 2016; Cui et al., 2017; Do et al., 2009; Rastogi et al., 2009; Rodríguez-Chueca et al., 2017). Many studies have shown that transition metals (e.g., Fe^{2+} and Co^{2+}) and metal oxides (e.g., δ-MnO_2, CuO, and $CuFe_2O_4$) can efficiently decompose PMS to high reactive sulfate radical ($SO_4^{\bullet-}$, $E_H^0 = 2.5–3.1$ V) and/or hydroxyl radical (•OH, $E_H^0 = 1.9–2.7$ V) for the treatment of organic contaminants such as acetaminophen, iopamidol, and atrazine (Anipsitakis and Dionysiou, 2004; Buxton et al., 1988; Guan et al., 2013; Hu et al., 2017; Lutze et al., 2015; Tan et al., 2014; Zhang et al., 2016). The associated catalytic mechanisms mainly involve the reduction of PMS by free or surface bound metal ions (M^{n+}) to generate $SO_4^{\bullet-}$ (Eq. (1)).

$$M^{n+} + HSO_5^- \rightarrow M^{(n+1)+} + SO_4^{\bullet-} \quad (1)$$

Our recent study has reported a novel nonmetal based activation process of PMS by organic quinones, which are ubiquitous in the environments (Zhou et al., 2015). It was demonstrated that PMS could be activated by a model *p*-benzoquinone (*p*-BQ) for the degradation of sulfamethoxazole (SMX, a frequently detected sulfonamide antibacterial in the environment), and the degradation rate increased with solution pH from 7 to 10. Singlet oxygen

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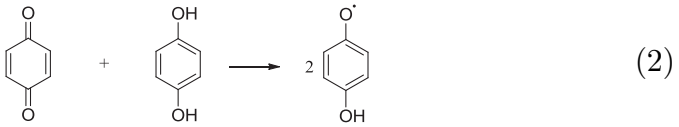
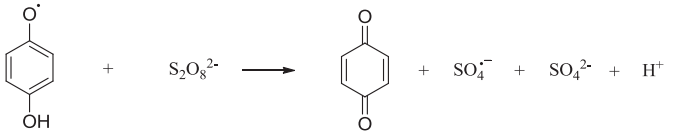
($^1O_2$) rather than •OH and $SO_4^{\bullet-}$ was generated in the PMS/*p*-BQ system via the nucleophilic addition of PMS (i.e., HSO_5^-) to the carbonyl groups of *p*-BQ with the formation of dioxirane intermediate. The increase of pH promoted the formation of the dioxirane intermediate and thus facilitated $^1O_2$ generation (see Text S1 for details). This mechanism can also account for the generation of $^1O_2$ in carbon materials catalyzed PMS oxidation processes, where carbonyl group (C═O, similar to quinonoid groups) are rich on the edging sites of these materials (Duan et al., 2016a,b; Li et al., 2017; Liang et al., 2017; Sun et al., 2017; Wang et al., 2017). As a moderately reactive electrophile, $^1O_2$ can effectively oxidize a variety of electron-rich pharmaceuticals, insecticides, and flame retardants such as ranitidine, fenthion, and tetrabromobisphenol A (Han et al., 2007; Hirahara et al., 2003; Kim et al., 2012). Compared with nonselective OH• and $SO_4^{\bullet-}$, $^1O_2$ is less susceptible to hindrance by background constituents in water (Rosado-Lausell et al., 2013).

Fang et al. (2013) found that quinones could activate peroxydisulfate (PDS) to generate $SO_4^{\bullet-}$ via a semiquinone radical-dependent Fenton-like reaction as shown in Eqs. (2) and (3): the comproportionation between *p*-benzoquinone (*p*-BQ) and its self-condensation or decomposition product hydroquinone generated benzosemiquinone radical (BSQ), and then BSQ activated PDS into $SO_4^{\bullet-}$.



(2)



(3)

Additionally, PDS can also be activated by phenols. Ahmad et al. (2013) studied the mechanism of PDS activation by model phenols and found that only the anionic form of phenols (i.e., phenoxide) could activate PDS via a one-electron reduction of PDS to produce $SO_4^{\bullet-}$, similar to a Fenton-like reaction (Eq. (4)).

$$PhO^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} + PhO_{ox} \quad (4)$$

Accordingly, the activation of PDS by phenols could be greatly enhanced when solution pH was increased over the *p*Ka values of phenols.

However, whether phenolic components could activate PMS or not is unknown so far and the underlying mechanisms have not been explored either. Similar to quinonoid groups, phenolic moieties are also widely distributed in the environments (Burges et al., 1964; Haumaier and Zech, 1995; Redman et al., 2002). In addition, some heterogeneous carbon materials, such as activated carbon and carbon nanotube, also contain phenolic moieties in their framework (Ago et al., 1999; Kostarelos et al., 2007; Seo et al., 2015). Hence, study on PMS activation by phenols may advance the understanding of in situ chemical oxidation (ISCO) using PMS for subsurface remediation as well as carbon materials based activation of PMS for water/waste water treatment. One possible mechanism for the activation of PMS by phenols may result from the reduction of PMS by phenoxide to generate $SO_4^{\bullet-}$ (Eq. (5)), similar to the case of PDS.

$$HSO_5^- + PhO^- \rightarrow OH^- + SO_4^{\bullet-} + PhO_{ox} \quad (5)$$

Another possible mechanism may involve the effect of quinone intermediates originated from phenols.

The main objective of this study was to investigate the underlying mechanism for the activation of PMS by phenols. For this purpose, ten model phenols [including phenol, methylphenols (MPs), methoxyphenols (MOPs), and dihydroxybenzenes] were selected, and the sulfonamide antibacterial SMX was used as a model contaminant. Firstly, reaction kinetics between PMS with phenol were investigated at pH 8.5 and 10. Primary oxidizing species produced therein were identified by chemical quenching and trapping methods and the involved mechanism was elucidated. Then, reaction kinetics of PMS with other nine substituted phenols were examined to explore the effect of substituent groups. Further, the potential of these phenols to activate PMS for the degradation of sulfonamide antibacterial SMX was explored and oxidation products of SMX were identified.

2. Material and methods

2.1. Chemicals and materials

Phenol, catechol, resorcinol, hydroquinone, 2-methylphenol (2-MP), 3-methylphenol (3-MP), 4-methylphenol (4-MP), 2-methoxyphenol (2-MOP), 3-methoxyphenol (3-MOP), 4-methoxyphenol (4-MOP), *p*-BQ, 2-methyl-*p*-benzoquinone (MBQ), and 2-methoxy-*p*-benzoquinone (MOBQ) with a purity of 97% or higher were purchased from J&K Scientific Ltd., and their chemical structures were shown in Table S1. PMS (available as Oxone® ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$)), SMX (99%), sulfanilamide (SA, 99%), 5-methylisoxazole (MI, 98%), 2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonic acid diammonium (ABTS, 99%), sodium azide (NaN_3, 99.5%), and 9,10-diphenylanthracene (DPA, 99%) were purchased from Sigma-Aldrich. Other chemicals of analytical grade or better were purchased from Aladdin (China) Reagent Co., Ltd. Stock solutions of PMS were prepared daily and standardized by an ABTS colorimetric method (Yang et al., 2015; Text S2). Stock solutions of phenols and quinones were freshly prepared before use. Due to the limited solubility, DPA stock solutions were made in acetonitrile:chloroform mixture (1:1, v:v) (Miyamoto et al., 2003a,b).

2.2. Experimental procedure

2.2.1. Kinetics

Experiments were conducted in 250 ml flasks on a reciprocating shaker in dark at 25 ± 1 °C. Sodium borate rather than phosphate was used as buffer reagent for pH 7–10 in this study, because the latter one can activate PMS as reported by Lou et al. (2014). Reactions were initiated by adding PMS in excess (0.2–0.8 mM) into pH-buffered solutions (20 mM sodium borate; pH 7, 8.5, or 10) containing a target phenolic compound (4–32 μM) and/or a constituent of interest (e.g., methanol, tert-butanol, NaN_3, or SMX) at desirable concentrations. Since strong reducing agents (e.g., ascorbic acid or thiosulfate) could destroy quinone intermediates that might be formed during the kinetic runs, formic acid was chosen as the quenching agent in this study, as its addition considerably decreased the solution pH (to 2.6–2.8) and thus passivated the reactions (Qin et al., 2010). Preliminary experiments confirmed that acidification by formic acid could maintain the stability of PMS, phenols, and quinones individually or together during high performance liquid chromatography