



Short Communication

Stability of dissolved percarbonate and its implications for groundwater remediation

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HIGHLIGHTS

- Although solid SPC is more stable than H₂O₂, dissolved SPC is less stable than H₂O₂.
- Compared to H₂O₂, SPC has higher oxidation efficiency of organic compounds.
- SPC decomposition and oxidation may be autocatalyzed by OH⁻ and CO₃²⁻/HCO₃⁻.
- SPC decomposition is first order and the reaction is promoted by high temperature.
- SPC decomposition reduces its oxidation efficiency of organic compounds.

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ABSTRACT

Efforts to improve the understanding of oxidant stability are of great practical significance to the design of an in-situ chemical oxidation (ISCO) system for soil and groundwater remediation. In this study, the stability of an emerging ISCO oxidant sodium percarbonate (SPC) was investigated. Although the dry solid form of SPC is relatively stable, dissolved SPC decomposes much faster than H₂O₂. SPC had higher oxidation efficiency for the dye Orange G than inactivated or alkaline-activated H₂O₂. Both OH⁻ and HCO₃⁻/CO₃²⁻, generated from SPC dissolution, activated the peroxide content of SPC and thus promoted its decomposition and pollutant oxidation. Higher incubation temperature and longer incubation period lead to faster SPC decomposition. Decomposed SPC had lower pollutant oxidation capability.

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1. Introduction

In situ chemical oxidation (ISCO) is a widely used technology for soil and groundwater remediation (Huling and Pivetz, 2006). Successful implementation of ISCO technology relies on successful delivery of the oxidant to the target zone (Huling and Pivetz, 2006; Baciocchi, 2013; Baciocchi et al., 2014). The stability of the oxidant determines the oxidant transport and delivery in the subsurface, thus it is critical for the lifetime and diffusion distance of the injected oxidant. Therefore, improved understanding of the oxidant stability in water is of great practical significance to the field-

application of ISCO technology (Johnson et al., 2008; Sra et al., 2010; Xu and Thomson, 2010). Since the stability of ISCO oxidants, including hydrogen peroxide (H₂O₂), persulfate, and permanganate, has been previously studied (Baciocchi et al., 2003; Mumford et al., 2005; Watts et al., 2007; Johnson et al., 2008; Xu and Thomson, 2008, 2009, 2010; Romero et al., 2009; Sra et al., 2010, 2014), any new oxidants require similar characterization before field application.

In recent years, sodium percarbonate (SPC, 2Na₂CO₃·3H₂O₂), a dry carrier of H₂O₂, has been increasingly used as an alternative for conventional H₂O₂. Compared to H₂O₂, SPC has advantages, such as higher safety for handling and transport, wider pH suitability, and higher pollutant removal efficiency. Laboratory studies have demonstrated the effectiveness of SPC in degrading various organic pollutants both in water (Fu et al., 2015, 2016; Miao et al., 2015a,

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2015b; Yang et al., 2016; Cui et al., 2017; Danish et al., 2017) and in soil (Cajal-Marinosa et al., 2012; de la Calle et al., 2012; Viisimaa and Goi, 2014; Apul et al., 2016).

Dry solid SPC is considered to be more stable than H_2O_2 . However, the stability of dissolved SPC has not been investigated despite its great importance for field implementation of SPC-based ISCO systems. To fill this important knowledge gap, batch experiments were conducted to compare the decomposition and pollutant oxidation kinetics of dissolved SPC and H_2O_2 .

2. Materials and methods

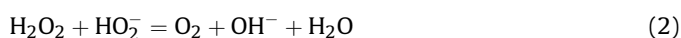
Batch experiments were conducted in 100 mL experimental vials incubating at desired temperature. The peroxide content of H_2O_2 and SPC was quantified by potassium permanganate titration. Detailed information on chemicals used, experimental procedure, and analytical methods can be found in the [Supplementary Materials](#).

3. Results and discussion

3.1. Decomposition of SPC and H_2O_2

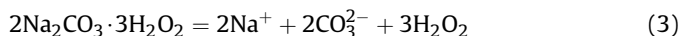
Although solid SPC is more stable than H_2O_2 , SPC becomes less stable than H_2O_2 after it is dissolved in water. This study explored the decomposition kinetics of 100 mM SPC and 300 mM H_2O_2 , both of which contained 300 mM peroxide. The pH of H_2O_2 and SPC solutions were 6.0 and 10.4, respectively. After 24 h of incubation, the peroxide content in the SPC solution declined by 79.1%, while the peroxide content of H_2O_2 did not change (Fig. 1a).

To eliminate interferences from differences in solution pH, the pH of H_2O_2 was adjusted to 10.4 by adding NaOH. Comparisons of H_2O_2 decomposition between pH 6.0 and 10.4 suggest that the alkaline conditions activated H_2O_2 and significantly ($p < 0.05$) promoted its decomposition (Fig. 1a). A similar phenomenon has also been reported by Arienzo (2000). The possible mechanism for alkaline-activated H_2O_2 decomposition is that H_2O_2 reacts with OH^- to form hydroperoxide ion (HO_2^-), which reduces another H_2O_2 to form O_2 and OH^- (Reactions (1) and (2)).



Further comparisons of H_2O_2 and SPC decomposition at pH 10.4 indicate that SPC decomposed much faster than H_2O_2 (Fig. 1a, $p < 0.05$). Fig. S1 shows that a plot of $\ln C/C_0$ versus time (t) results in linear correlations, suggesting that SPC and H_2O_2 decomposition followed pseudo-first-order patterns. Fitting $\ln C/C_0$ data gives the

pseudo-first-order rate constant for the decomposition of peroxide content (k_{peroxide}) (Table S1). The k_{peroxide} of SPC was about 4.2 times higher than that of H_2O_2 at pH 10.4 (Table S1). Dissolution of SPC forms Na^+ , CO_3^{2-} , HCO_3^- , OH^- , and H_2O_2 (Reactions (3) and (4)). Through a rough calculation based on equilibrium constant data ($\text{pK}_a(\text{HCO}_3^-) = 6.37$; $\text{pK}_a(\text{CO}_3^{2-}) = 10.33$; $\text{pK}_w(\text{H}_2\text{O}$ at $15^\circ\text{C}) = 14.346$), we determined that 100 mM SPC solution at pH 10.4 contained approximately 300 mM H_2O_2 , 100 mM HCO_3^- , 100 mM CO_3^{2-} and 0.11 mM OH^- , while 300 mM H_2O_2 solution at pH 10.4 contained 300 mM H_2O_2 and 0.11 mM OH^- . Faster peroxide decomposition in SPC than in H_2O_2 suggests that $\text{HCO}_3^-/\text{CO}_3^{2-}$ exerts supplementary promoting effects on peroxide decomposition, in addition to OH^- . To further confirm the influence of $\text{HCO}_3^-/\text{CO}_3^{2-}$, peroxide decomposition of a mixture of 300 mM H_2O_2 and 200 mM Na_2CO_3 ($\text{H}_2\text{O}_2 + \text{Na}_2\text{CO}_3$) was studied. The pH of $\text{H}_2\text{O}_2 + \text{Na}_2\text{CO}_3$ was also 10.4. The peroxide decomposition plots of $\text{H}_2\text{O}_2 + \text{Na}_2\text{CO}_3$ and SPC almost overlapped (Fig. 1a), thus confirming: 1) $\text{HCO}_3^-/\text{CO}_3^{2-}$ promoted peroxide decomposition; and 2) the chemical composition and behavior of dissolved SPC were the same as the mixture of $\text{H}_2\text{O}_2 + \text{Na}_2\text{CO}_3$.



3.2. Pollutant oxidation by SPC and H_2O_2

Orange G (OG) was not degraded by H_2O_2 at pH 6.0, while 74.7% of OG was degraded by H_2O_2 at pH 10.4 after 4 h (Fig. 1b), suggesting that the alkaline conditions activated H_2O_2 and enhanced its oxidation capacity. Previous studies also show that alkaline-activated H_2O_2 can react with organic compounds, notably dyes (Thompson et al., 1993a, 1993b; Brooks and Moore, 2000; Katafias et al., 2010; Yang et al., 2016). The active species responsible for OG oxidation by alkaline H_2O_2 was likely nucleophilic HO_2^- formed through Reaction (1) (Spiro and Griffith, 1997; Katafias et al., 2010; Yang et al., 2016). Compared to the H_2O_2 molecule, HO_2^- is a more powerful oxidant that can oxidize the double bonds of dye chromophoric groups (Thompson et al., 1993a, 1993b). Further studies are needed to reveal the underlying mechanisms.

SPC had much higher OG removal efficiency than H_2O_2 at pH 10.4 (Fig. 1b). OG degradation plots of SPC and $\text{H}_2\text{O}_2 + \text{Na}_2\text{CO}_3$ completely overlapped, which corroborates the peroxide decomposition data and confirmed our previous finding on the influence of $\text{HCO}_3^-/\text{CO}_3^{2-}$. $\text{HCO}_3^-/\text{CO}_3^{2-}$ -activated H_2O_2 has been used to oxidize a variety of compounds, including aryl sulfides (Richardson et al., 2000), water-soluble alkenes (Yao and Richardson, 2000), dyes

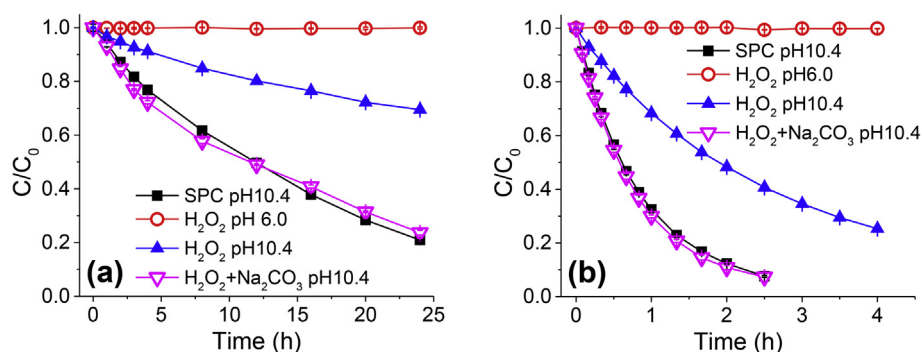


Fig. 1. (a): normalized peroxide content during SPC and H_2O_2 decomposition; (b): normalized Orange G (OG) concentration during OG oxidation.

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