**Bicarbonate-activated persulfate oxidation of acetaminophen: Implications to
groundwater remediation by naturally occurring anions**

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Abstract

Persulfate (PS) is widely used as an oxidant for *in situ* chemical remediation of contaminated groundwater. In this study we demonstrated for the first time that PS could be activated by bicarbonate. Acetaminophen was used as the probe compound to examine the reactivity of PS/bicarbonate system. It was found that acetaminophen could be effectively transformed and the reaction rate appeared pseudo-first-order to the concentrations of both acetaminophen and PS. Radical scavenger tests indicated that neither free radicals ($\text{SO}_4^{\bullet-}$ and $\text{HO}\bullet$) nor superoxide ($\text{O}_2^{\bullet-}$) was responsible for acetaminophen transformation. Generation of singlet oxygen ($^1\text{O}_2$) was verified using furfuryl alcohol (FFA) as a probe. Formation of $^1\text{O}_2$ was further quantified in D_2O fortified solution based on kinetic solvent isotopic effect (KSIE) but it was found that $^1\text{O}_2$ contributed only 51.4% of the total FFA transformation. The other 48.6% was presumed to be ascribed to the reaction with peroxymonocarbonate (HCO_4^-). However, the transformation of acetaminophen was mostly due to the reaction with HCO_4^- but not $^1\text{O}_2$. Instead of degradation, HCO_4^- oxidized acetaminophen via a one-electron abstraction mechanism resulting in the generation of acetaminophen radicals which coupled to each other to form dimers and trimers. HCO_4^- also hydrolyzed rapidly to form hydrogen peroxide (H_2O_2) which led to the formation of $^1\text{O}_2$, during which $\text{O}_2^{\bullet-}$ was a key intermediates. Because bicarbonate is ubiquitously presented in groundwater, the findings of this research provide important insights into the fundamental processes involved in PS oxidation in subsurface.

Keywords: persulfate; acetaminophen; bicarbonate; peroxymonocarbonate; singlet oxygen

1. Introduction

Persulfate ($\text{S}_2\text{O}_8^{2-}$, PS) has attracted increasing attention for *in situ* chemical oxidation (ISCO) of contaminants in soil and groundwater (Peyton 1993). PS is a symmetrically substituted derivative of H_2O_2 by sulfonic moiety. The O-O distance in PS (1.497 Å) is similar to that in H_2O_2 (1.458 Å) but PS is more soluble and stable than H_2O_2 (Tsitonaki et al., 2010). The standard redox potential of PS is 2.01 V (vs. NHE), as compared to 1.78 V for H_2O_2 (House 1962; Lin and Pehkonen 1999; Wardman 1989). However, direct reaction between PS and most organic compounds is slow (Osgerby 2006; Tsitonaki et al., 2010). In aquifers, the half-life time of PS could be over 2 years while H_2O_2 decomposes rapidly to form O_2 (Johnson et al., 2008; Liu et al., 2014a; Petigara et al., 2002). Such stability in combination with the high solubility offers great advantage and flexibility in ISCO application in the subsurface, allowing PS being readily delivered and transported to the contaminants even in low permeable regions (Liang et al., 2008; Liang et al., 2007).

After appropriate activation, PS can be decomposed to generate more potent sulfate radical ($\text{SO}_4^{\cdot-}$, $E^0 = 2.7$ V, vs. NHE) (Neta et al., 1988; Tsitonaki et al., 2010). Sulfate radical is superior to hydroxyl radical ($\text{HO}^{\cdot}$) for ISCO applications because it maintains the high redox potentials over a wide pH range, while hydroxyl radical exhibits similar high redox potential only under acidic conditions that is unusually encountered in ISCO practices (Anipsitakis and Dionysiou 2003; Guan et al., 2011; Usman et al., 2012). Sulfate radical can oxidize a wide variety of organic contaminants, much like the hydroxyl radical. Common PS activators used for ISCO include heat, transient metals, base, carbon nanotube, graphene oxide, etc. (Adewuyi and Sakyi 2013; Duan et al., 2015; Furman et al., 2010; Liu et al., 2014b; Tsitonaki

et al., 2010). Sulfate radical-based ISCO for subsurface remediation usually involves the injection of both PS and activators to the contaminated zone. Nonetheless, all the activation approaches are suffered from certain limitations. For example, heating activation is energy intensive, especially for large subsurface region. Fe(II) can be rapidly oxidized by PS to insoluble Fe(III) which is unable to activate PS but clogs the pores therefore inhibits the transport of oxidants and activators. Efficiency of base activation is low at sites with strong natural buffering capacity.

In order to increase the cost-effectiveness of sulfate radical-based ISCO, attempts have been made to take the advantage of natural activators. It was found that PS could be activated by naturally occurring minerals, particularly those of iron and manganese forms (Lapworth et al., 2012; Liu et al., 2014a; Sra et al., 2010). Although such activation is less efficient, it results in the generation of sulfate radical in a more sustainable manner, making it an advantage for the remediation of dilute contaminants. In addition, high stoichiometric efficiency (i.e., the number of moles of contaminants transformed per mole of PS activated) can be achieved for PS oxidation activated by aquifer minerals (Liu et al., 2016; Sra et al., 2010).

Bicarbonate is inevitably encountered in natural environment. It provides the buffering capacity in natural waters. Its concentration is governed by pH and CO₂ partial pressure. In ground water, bicarbonate concentration varies from 0.7 to 10 mM, depending on the geological conditions (Abdelouas et al., 1998; Wilkin and Digiulio 2010). Bicarbonate was found to accelerate hydrogen peroxide (H₂O₂) decomposition (Bakhmutova-Albert et al., 2010; Flangan et al., 1986; Xu et al., 2011). Although the underlying mechanisms are not well

understood, it has been demonstrated that the reactions between H_2O_2 and HCO_3^- could lead to the formation of a series of reactive species such as peroxymonocarbonate (HCO_4^-), superoxide ($\text{O}_2^{\cdot-}$), and singlet oxygen ($^1\text{O}_2$) (Bakhmutova-Albert et al., 2010; Canonica et al., 2005; Li et al., 2011; Xu et al., 2011; Zhang et al., 2000). Bicarbonate activated H_2O_2 has been investigated as a water treatment technology to degrade organic pollutants such as azo dyes and chlorophenols (Cheng et al., 2014; Xu et al., 2011).

Considering the similarity between H_2O_2 and PS, we presume that PS can also be activated by bicarbonate. The objective of the present research was to test this hypothesis using acetaminophen, a widely prescribed nonprescription analgesic drug, as a probe compound. Acetaminophen has frequently been detected in groundwater and high concentration up to 15142 ng L^{-1} was reported (Lapworth et al., 2012). The key reactive species generated in PS/bicarbonate system were identified and their contributions to acetaminophen transformation were characterized. The kinetics and mechanisms of acetaminophen transformation were explored. The findings of this study provide more insights into the fundamental processes involved in PS oxidation in subsurface.

2. Experimental

2.1. Materials

All chemicals were of analytical grade or better. Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), sodium bicarbonate (NaHCO_3 , 99.8%) and sodium molybdate dihydrate ($\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$) were purchased from Aladdin (Shanghai, China). Acetaminophen (98%), furfuryl alcohol (FFA, 98%), superoxide dismutase (SOD, from bovine erythrocytes) were purchased from

Sigma-Aldrich (St. Louis, MO). Deuterium oxide (99.8%, D₂O) was purchased from J&K chemicals (Beijing, China). Methanol was of HPLC grade and obtained from Fisher (Waltham, MA). Stock solutions of acetaminophen, PS, and NaHCO₃ were prepared by dissolving the reagents in Milli-Q water (18.2 MΩ/cm) produced in a Millipore Super-Q Water Purification system. All solutions were used within a week.

2.2. Removal of acetaminophen in PS/bicarbonate system

Transformation of acetaminophen in PS/bicarbonate system was investigated in 42 mL EPA vials fitted with poly-tetrafluoroethylene lined caps as batch reactors at 25 °C. Initial concentrations of acetaminophen and NaHCO₃ were 10 μM and 25 mM, respectively. Unless otherwise mentioned, solution pH was adjusted to 8.3 by H₂SO₄ (0.1 M) or NaOH (0.1 M) before the reaction was initiated by adding appropriate amount of PS stock solution. At desired time intervals, 1.0 mL reaction solutions was withdrawn and immediately mixed with 40 μL ascorbic acid (250 mM) to quench the reaction. In addition, control experiments with PS alone were performed concurrently. The control samples were purged with N₂ for 10 min before PS was dosed and kept purging during the reaction in order to minimize CO₂ dissolution. All experiments were carried out in duplicates and data were averaged.

Methanol, SOD, and FFA were used to probe the formation of free radical (HO• and SO₄^{•-}), superoxide (O₂^{•-}), and singlet oxygen (¹O₂), respectively, in PS/bicarbonate system. The initial concentrations of acetaminophen, HCO₃⁻, and PS were 10 μM, 25 mM, and 5 mM, respectively. Each time a single probe species was added. The concentrations for methanol and FFA were 10 mM and 1 mM, respectively. The quantity of SOD was 1 kU. Other conditions and treatment were the same as described above. In order to further ascertain the

generation of $^1\text{O}_2$ in PS/bicarbonate system, the removal of acetaminophen and FFA were examined in solutions fortified with 50% D_2O . This approach was based on the fact that D_2O stabilizes $^1\text{O}_2$ thus facilitates $^1\text{O}_2$ -induced reactions (Wilkinson et al., 1995).

2.3. *Quantification of acetaminophen and FFA*

Concentrations of acetaminophen and FFA in the samples were analyzed by a Hitachi L-2000 high performance liquid chromatography (HPLC, Hitachi, Japan) equipped with an L-2455 diode array detector (DAD). The separation was performed on an Agilent ZORBAX Eclipse Plus C18 column (5 μm , 250 mm $\times$ 4.6 mm I.D.). Elution was performed at a flow rate of 1.0 mL min^{-1} with the mobile phase consisting 70% H_2O with 0.1% (v/v) formic acid and 30% MeOH with 0.1% (v/v) formic acid.

2.4. *Analysis of acetaminophen transformation products*

Solutions prepared as described above were allowed to react for 7 h before enriched by solid phase extraction (SPE) using HLB cartridge (WAT106202, Waters Oasis). The enriched samples were analyzed by an Agilent 6410 triple quadrupole mass spectrometer (MS) equipped with electrospray ionization interface (ESI) (Agilent Technologies, USA). The instrument was operated at negative ionization and full scan (50 - 500 m/z) mode. Products ion scan (MS/MS) was performed for suspected transformation products of acetaminophen. Detailed operational parameters were: capillary voltage, -3.5 kV; fragmentor voltage, 135 V; desolvation gas (nitrogen, $\geq 99.995\%$) flow rate, 10 L min^{-1} ; temperature, 350 $^\circ\text{C}$; nebulizer (nitrogen, $\geq 99.995\%$) pressure, 40 psi. The collision energy for MS/MS was optimized individually for each precursor ion.

Transformation products of acetaminophen in PS/bicarbonate system were compared with those in H_2O_2 /bicarbonate and H_2O_2 /NaMoO₄ systems which were known to generate HCO_4^- and $^1\text{O}_2$, respectively (Aubry 1985; Boehme and Brauer 2002; Nardello et al., 1995). For H_2O_2 /bicarbonate system, the reaction conditions were identical to those in PS/bicarbonate system except PS was replaced by equal concentration of H_2O_2 (5 mM). In addition, 1kU SOD was spiked to eliminate any transformation due to the reactions with $\text{O}_2^{\bullet-}$. For H_2O_2 /NaMoO₄ system, the concentrations of H_2O_2 and NaMoO₄ were 10 mM and 1 mM, respectively. The reaction time was 20 min. All the samples were enriched by SPE and analyzed by MS as described above.

3. Results and discussion

3.1. Removal of acetaminophen in PS/bicarbonate system

Acetaminophen was used as a probe compound to test the reactivity of PS/bicarbonate system. The reaction was performed at pH 8.3 in order to avoid the activation of PS by base. At this condition, bicarbonate species is dominant over carbonate ($\text{p}K_a = 10.3$). As shown in Figure 1, the concentration of acetaminophen decreased gradually in PS/bicarbonate solution. More than 50% of the acetaminophen was removed in 8 h with initial PS concentration of 5 mM. Although the reaction appeared slow compared with PS oxidation systems with other activators such as iron (Deng et al., 2014), the removal rate was remarkably higher than that in the control with bicarbonate minimized where less than 10% attenuation was observed (Figure S1). This indicates that PS can be activated by bicarbonate. Apparently, the removal of acetaminophen showed pseudo-first-order kinetics and the pseudo-first-order rate constant was linearly related to the initial concentration of PS in the solution (insert in Figure 1).

However, it should be noted that the equilibrium HCO_3^- concentration in aqueous solution is solely governed by pH and CO_2 partial pressure in an open system (Benjamin 2002). The value was approximately 1 mM at pH 8.3 despite that higher concentration of bicarbonate was added initially (before pH adjustment). Thus, as shown in Figure S1, the reaction rate only changed marginally at varying initial bicarbonate dose (before pH adjustment).

3.2. Identification of the reactive species

Data presented in Figure 1 indicate that reactive species responsible for acetaminophen removal were generated in PS/bicarbonate system. Generally, $\text{OH}\cdot$ and $\text{SO}_4^{\cdot-}$ are considered as the principal oxidizing species in activated PS oxidation processes. These radicals are extremely potent oxidants that react with a wide spectrum of compounds at second-order rate constants ranging from 10^6 to $10^9 \text{ M}^{-1}\text{s}^{-1}$ (Neta et al., 1977). To verify the formation of $\text{OH}\cdot$ and $\text{SO}_4^{\cdot-}$, methanol, a widely used radical scavenger (Buxton et al., 1988; Eibenberger et al., 1978), was added into the solution. However, it turned out that the removal of acetaminophen was little affected in the presence of 10 mM methanol as illustrated in Figure 2, indicating the removal of acetaminophen in PS/bicarbonate system was not ascribed to the reaction with $\text{OH}\cdot$ or $\text{SO}_4^{\cdot-}$. $\text{OH}\cdot$ and $\text{SO}_4^{\cdot-}$ are also known to react with bicarbonate to form carbonate radical ($\text{CO}_3^{\cdot-}$) (R3 and R4) which can serve as active species to degrade contaminants (Huang and Mabury 2000; Liang et al., 2006; Waldemer et al., 2007). However, degradation of acetaminophen by $\text{CO}_3^{\cdot-}$ was also unlikely. Otherwise, according to the reaction rate constants of bicarbonate oxidation, presence of 10 mM methanol was expected to pose a conspicuous inhibition effect on the formation of $\text{CO}_3^{\cdot-}$. Consequently, the transformation of acetaminophen would be affected markedly.

Previous studies reported that superoxide ($\text{O}_2^{\bullet-}$) could be generated in oxidation processes involving PS. For example, it was found that in base activated PS oxidation process, PS was initially decomposed to sulfate and hydroperoxide ion (HO_2^-) which reduced another PS molecule to give rise to $\text{SO}_4^{\bullet-}$ and $\text{O}_2^{\bullet-}$ (Furman et al., 2010). In this study, SOD was used as the scavenger of $\text{O}_2^{\bullet-}$. SOD catalyzes the dismutation of $\text{O}_2^{\bullet-}$ to form ground state molecular oxygen and H_2O_2 rapidly (Ines Dammak et al., 2009; Mcdj and Fridovich 1969). As shown in Figure 2, presence of 1 kU SOD showed no influence on acetaminophen degradation. Thus, the role of $\text{O}_2^{\bullet-}$ in acetaminophen degradation can also be reasonably ruled out.

Singlet oxygen ($^1\text{O}_2$) is another oxidizing species possibly formed in advanced oxidation processes. It was found that the formation of $^1\text{O}_2$ in benzequione activated peroxymonosulfate

(PMS) process (Zhou et al., 2015). It was also demonstrated that $^1\text{O}_2$ was the principal reactive species responsible for organic degradation in H_2O_2 /bicarbonate system (Zhou et al., 2013). Singlet oxygen as a selective oxidizing species shows high reactivity toward electron-rich compounds (e.g., phenols, sulfides, and amines) but negligible reactivity toward saturated alcohols (e.g., methanol) (Rodgers 2002). Furfuryl alcohol (FFA), which reacts with $^1\text{O}_2$ at a second-order rate constant of $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, is often used to probe the formation of $^1\text{O}_2$ (Haag and Hoigne 1986). The removal of acetaminophen in the presence of 1 mM FFA was shown in Figure 2. It can be seen that the reaction was conspicuously inhibited, implying the removal of acetaminophen could be attributed to the reaction with $^1\text{O}_2$. In order to further ascertain the role of $^1\text{O}_2$ in acetaminophen transformation, the reaction was examined in the solution containing 50% D_2O . Because $^1\text{O}_2$ exhibits kinetic solvent isotopic effect (KSIE), the quenching rate constants of $^1\text{O}_2$ by H_2O ($k_{\text{H}_2\text{O}}$) and D_2O ($k_{\text{D}_2\text{O}}$) are 2.5×10^5 and $1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Merkel et al., 1972; Wilkinson et al., 1995). In other words, $^1\text{O}_2$ induced reaction proceeds approximately 16 times slower in pure D_2O than in pure H_2O . As such, the reaction rate constant of targeted compound with $^1\text{O}_2$ in solution containing D_2O at molar fraction of x ($k_{\text{obs}, \text{H}_2\text{O}, \text{D}_2\text{O}_{\text{mix}}}$) can be computed according to the following equation (Eq. 1) (Cory et al., 2009; Wilkinson et al., 1995):

$$k_{\text{obs}, \text{H}_2\text{O}, \text{D}_2\text{O}_{\text{mix}}} = \frac{k_{\text{H}_2\text{O}} \cdot k_{\text{obs}, \text{H}_2\text{O}}}{x_{\text{H}_2\text{O}} \cdot k_{\text{H}_2\text{O}} + x_{\text{D}_2\text{O}} \cdot k_{\text{D}_2\text{O}}} \quad (\text{Eq. 1})$$

where $k_{\text{obs}, \text{H}_2\text{O}}$ represents the corresponding reaction rate constant in 100% H_2O . As illustrated in Figure 3a, when 50% H_2O was replaced by D_2O , the removal of acetaminophen was only slightly affected. In fact, there was little difference between the pure H_2O and D_2O

fortified solution during the first 4 h. This indicates that $^1\text{O}_2$, if present, was unlikely to contribute the removal of acetaminophen significantly, which seems inconsistent with the finding derived from the scavenger test (Figure 2). Figure 3b also presents the removal of FFA in the solution containing 50% D_2O . As expected, degradation of FFA was significantly enhanced compared with that in 100% H_2O , indicating $^1\text{O}_2$ was indeed formed and participated the degradation of FFA. The pseudo first-order rate constants in pure H_2O and 50% D_2O are determined to be 0.177 and 0.257 h^{-1} , respectively. However, according to Eq. 1, FFA degradation rate in 50% D_2O would be 0.333 h^{-1} if the degradation of FFA was solely attributed to $^1\text{O}_2$, suggesting there were other reactive species responsible for the degradation of FFA. Assuming the unknown species does not have KSIE, it can be computed that the first-order rate constant of FFA degradation due to the reaction with $^1\text{O}_2$ would be 0.091 h^{-1} in pure H_2O solution according to Eq. 1, corresponding to a steady-state concentration of 2.11×10^{-13} M for $^1\text{O}_2$ in this reaction solution. The overall FFA degradation rate constant was 0.177 h^{-1} . Thus, $^1\text{O}_2$ contributed approximately 51.4% of the total FFA degradation while the unidentified oxidative species contributed the rest 48.6%. Nonetheless, $^1\text{O}_2$ contributed very little to acetaminophen degradation. Instead, it was probably the unidentified species that played a central role. The inhibited acetaminophen transformation in the presence of FFA was due to the quenching of the unknown reactive species rather than $^1\text{O}_2$ by FFA (Figure 2). However, the reactivity of FFA to the unknown species is limited thus the degradation of acetaminophen was only partially quenched.

It was reported that H_2O_2 could react with bicarbonate to form peroxymonocarbonate (HCO_4^-) which is essentially a CO_2 adduct of the hydroperoxide anion (HO_2^-) (Richardson et

al., 2000; Yao and Richardson 2003). HCO_4^- can be classified as an anionic peracid. As an economic and environmental friendly oxidant, HCO_4^- is used in organic synthesis, bleaching, and chemical warfare agent decontamination (Yang 1995; Yang et al., 1992; Yang et al., 1990). Because PS is structurally similar to H_2O_2 , it may react in a similar way with bicarbonate to produce HCO_4^- . HCO_4^- has an oxidative potential of 1.8 ± 0.1 V (vs. NHE) at neutral to moderately basic conditions (Richardson et al., 2000), which is close to that of H_2O_2 (1.78 V vs. NHE). We postulate that the removal of acetaminophen in PS/bicarbonate system was mainly ascribed to the reaction with HCO_4^- .

3.3. Products of acetaminophen transformation

The reaction products of acetaminophen in PS/bicarbonate system were enriched and examined by MS with ESI interface operated at negative mode. Figure 4 presents the full scan MS of the reaction solution. The peak of m/z 150 corresponds to unreacted acetaminophen ($M_0 = 151$, Figure 4a). Its abundance was greatly reduced after reaction. In addition to this, peaks of m/z 299 and 448 were found (Figure 4b). Such a products profile is quite distinct from other oxidative degradation process where hydroxylation on the phenolic ring occurs followed by ring-cleavage (Li et al., 2015; Pozdnyakov et al., 2014; Zhang et al., 2008). Noted that, the spectrum profile was almost identical to what was found in an early study of using laccase to transform acetaminophen (Figure S2) (Lu et al., 2009). Laccase is an extracellular phenoxidase excreted by a lot of fungi, bacteria, and high plants. It catalyzes one-electron oxidation of acetaminophen to generate radical intermediates which couple to each other subsequently to form products with MW of $(n + 1)M_0 - 2n$ (Lu et al., 2009), where n is the number of coupling time. The peaks of m/z 299 and 448 in Figure 4b are supposed to

correspond to dimers and trimers of acetaminophen, respectively. This argument was further justified by the fact that the MS/MS of the peaks are almost identical to those of the dimer and trimer products of acetaminophen formed by laccase catalyzed oxidation (Figure S3). In summary, MS analysis indicates that acetaminophen underwent oxidative coupling reactions in PS/bicarbonate system. HCO_4^- reacted with acetaminophen via electron transfer mechanism, generating radical intermediates as laccase does. The oxidation could occur at either the hydroxyl oxygen or amide group. The unpaired electron then resonated to the respective conjugated sites at the benzene ring, leading to different radical intermediates. Thus, there could be multiple radical-radical coupling pathways depending on the sites where the unpaired electron resided, leading to several isomers (Lu et al., 2009). Further separation of the peak m/z 299 by HPLC revealed there were 2 dimers isomers, which is also identical to those found in the earlier study (Figure S4).

Oxidation of acetaminophen by HCO_4^- suggests that other phenolic compounds might undergo similar transformation to form phenoxy radicals in PS/bicarbonate system. Thus, if there is co-existence of additional phenolic compounds in the system, cross-coupling between different radical intermediates is expected just as what occurred in laccase catalyzed oxidation system (Lu and Huang 2009). This hypothesis was tested in the presence of guaiacol, a natural phenolic compound. The products were analyzed by MS (ESI+) and the spectrum was shown in Figure S5. A peak ($m/z = 274$) corresponds to a product that resulted from radical-radical coupling between guaiacol (MW = 124) and acetaminophen (MW = 151) can be found. The same product was also identified in laccase catalyzed oxidation of acetaminophen in the presence of guaiacol (Lu and Huang 2009). Its identity was confirmed

by a comparison of its MS/MS with that formed in laccase catalyzed system (Figure S5).

3.4. Mechanisms of PS activation by bicarbonate

The above analysis suggests that both HCO_4^- and $^1\text{O}_2$ could be formed in PS/bicarbonate system. But the transformation of acetaminophen was mostly due to the reactions with HCO_4^- . According to the molecular structures of the reaction products, HCO_4^- oxidized acetaminophen via single-electron abstract mechanism. We presume the formation of HCO_4^- was the result of direct oxidation of bicarbonate by PS (R6). However, HCO_4^- is unstable. It was rapidly hydrolyzed to form HCO_3^- and H_2O_2 (R7) (Richardson et al., 2000). In addition, HCO_4^- reacted with acetaminophen to form an acetaminophen radical and a carbonate radical (R8). The carbonate radical might also abstract an electron from acetaminophen molecule to give rise to an acetaminophen radical (R9). The acetaminophen radicals coupled to each other to form dimers.

Hydrolysis of HCO_4^- yields H_2O_2 that might lead to the formation of $^1\text{O}_2$, during which $\text{O}_2^{\bullet-}$ was a key intermediate. This can be rationalized by the observation of the inhibited FFA degradation in the presence of SOD. As shown in Figure 3b, the pseudo-first order rate constants of FFA degradation in the absence and presence of SOD were 0.177 and 0.076 h^{-1} , respectively, in PS/bicarbonate system. Assuming $\text{O}_2^{\bullet-}$ was completely quenched by SOD,

degradation due to the reaction with $^1\text{O}_2$ accounted for approximately 57% of the total degradation of FFA. The value is close to that (51.4%) estimated by KSIE approach. However, SOD had no influence on the degradation of acetaminophen because its transformation was mostly due to the reaction with HCO_4^- which preceded the formation of $\text{O}_2^{\bullet-}$.

Mechanism of $\text{O}_2^{\bullet-}$ formation is presumed to be same as in H_2O_2 /bicarbonate system (Lin and Liu 2009; Yao and Richardson 2003). H_2O_2 first reacted with $\text{CO}_3^{\bullet-}$ to form protonated superoxide ($\text{HO}_2^{\bullet}$) with a pK_a value of 4.8. (R10) $\text{HO}_2^{\bullet}$ deprotonated to generate $\text{O}_2^{\bullet-}$ (R11). $\text{O}_2^{\bullet-}$ reacted with additional H_2O_2 to generate $^1\text{O}_2$. The reaction process is described in R10 – R13 (Guo et al., 2015; Xu et al., 2011). It should be noted that formation of $^1\text{O}_2$ might be insignificant in the presence of acetaminophen because as an electron-rich compound it scavenger most of the $\text{CO}_3^{\bullet-}$. This also explains why acetaminophen degradation was not affected by SOD. However, FFA is less reactive to $\text{CO}_3^{\bullet-}$ thus favored the formation of $^1\text{O}_2$, making $^1\text{O}_2$ contributed significantly to the transformation of FFA.

3.5. Acetaminophen transformation kinetics

According to reactions R6 – R9, the equations for the reaction rates of acetaminophen, HCO_4^- and $\text{CO}_3^{\bullet-}$ can be written as:

$$\frac{dc_a}{dt} = -k_3 c_{HCO_4^-} c_a - k_4 c_{CO_3^{\bullet-}} c_a \quad (\text{Eq. 2})$$

$$\frac{dc_{HCO_4^-}}{dt} = k_1 c_{HCO_3^-} c_{PS} - k_2 c_{HCO_4^-} - k_3 c_{HCO_4^-} c_a \quad (\text{Eq. 3})$$

$$\frac{dc_{CO_3^{\bullet-}}}{dt} = k_3 c_{HCO_4^-} c_a - k_4 c_{CO_3^{\bullet-}} c_a \quad (\text{Eq. 4})$$

where c_a represents the concentration of acetaminophen. Supposing steady-state attained with the concentrations of both HCO_4^- and $CO_3^{\bullet-}$ remaining constant, the expression for the concentration of HCO_4^- can be obtained:

$$c_{HCO_4^-} = \frac{k_1 c_{HCO_3^-} c_{PS}}{k_2 + k_3 c_a} \quad (\text{Eq. 5})$$

$$k_4 c_{CO_3^{\bullet-}} c_a = k_3 c_{HCO_4^-} c_a \quad (\text{Eq. 6})$$

Combine Eq. 2 and Eq. 6, yielding:

$$\frac{dc_a}{dt} = -2k_3 c_{HCO_4^-} c_a \quad (\text{Eq. 7})$$

Substituting Eq. 5 to Eq. 7, yielding:

$$\frac{dc_a}{dt} = -\frac{2k_1 k_3 c_{HCO_3^-} c_{PS} c_a}{k_2 + k_3 c_a} \quad (\text{Eq. 8})$$

Supposing only a small amount of HCO_4^- was consumed by acetaminophen compared to its hydrolysis, i.e.:

$$k_3 c_a \ll k_2$$

Eq. (8) can be simplified as:

$$\frac{dc_a}{dt} = -\frac{2k_1k_3c_{HCO_3^-}c_{PS}c_a}{k_2} \quad (\text{Eq. 9})$$

Eq. 9 indicates the pseudo-first order rate constant of acetaminophen degradation is proportional to the concentration of PS, which is consistent with the data presented in Figure 1.

3.6. Comparison of H_2O_2 /bicarbonate and H_2O_2 /NaMoO₄ systems

The transformation of acetaminophen was further examined in H_2O_2 /bicarbonate system in which HCO_4^- was known to be generated (Bakhmutova-Albert et al., 2010; Lin and Liu 2009; Yao and Richardson 2003). SOD was spiked into solution in order to eliminate any reactions with 1O_2 which could be generated from $O_2^{\cdot-}$ (Lin and Liu 2009). Thus, the transformation of acetaminophen was presumed to be due to the reaction with HCO_4^- . The products were enriched and analyzed by MS (Figure 4c). It was evident that dimeric and trimeric acetaminophen were the main products in H_2O_2 /bicarbonate system. Overall, the MS of the products is almost identical to that in PS/bicarbonate system (Figure 4b). This serves evidence supporting the formation of HCO_4^- as the reactive species for acetaminophen transformation in PS/bicarbonate system.

HCO_4^- is a moderately reactive oxidant and it reacts with phenolic compounds via electron-abstracting mechanism leading to polymerized products with higher MW. This is apparently different from the degradation induced by free radicals which results in mineralization of the parent compound. The reactivity of HCO_4^- is also distinct from 1O_2 . Figure 4d shows the MS of acetaminophen transformation products in H_2O_2 /NaMoO₄ system which is known to generate 1O_2 (Aubry 1985; Boehme and Brauer 2002; Nardello et al., 1995).

It is evident that a dramatically different spectrum was obtained. Signatures of coupling products are absent in the MS of $^1\text{O}_2$ induced products. This also corroborates the finding that the removal of acetaminophen in PS/bicarbonate system was unlikely ascribed to $^1\text{O}_2$.

3.7. Environmental implications

Activated PS oxidation is a promising *in situ* remediation technology for contaminated soil/groundwater. The stability of PS in subsurface makes it a sustainable source of free radicals for contaminants degradation. In the absence of external activators, the half-life time of PS was estimated to be over 2 years in aquifers. PS decomposition can be accelerated in the presence of natural Fe/Mn minerals but the half-life time still ranges from months to a year (Liu et al., 2014a; Liu et al., 2016). At such conditions, formation of HCO_4^- due to HCO_3^- activation might be an important mechanism of PS decomposition. HCO_3^- is ubiquitously present. In open system, its concentration is approximately 0.05 mM at pH 7. Even higher concentration is expected at anaerobic conditions or sites with high CO_2 partial pressure and/or alkalinity. The findings of this study indicate HCO_4^- is a moderately oxidative species and selectively reacts with phenolic compounds. A wide spectrum of contaminants of concern falls into this category such as estrogens, halophenols, etc. Transformation due to the reactions with HCO_4^- may contribute significantly to the overall removal of such contaminants during the remediation.

4 Conclusions

PS can be activated by bicarbonate to form HCO_4^- which gives rise to $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ subsequently. Transformation of acetaminophen in PS/bicarbonate system was mostly

ascribed to its reaction with HCO_4^- . As a moderate oxidant, HCO_4^- reacted with acetaminophen via single-electron oxidation mechanism generating radical intermediates which coupled to each other to form dimers and trimers.

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Supporting Information

Supporting data associated with this article can be found in the online version.

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Figure captions

Figure 1 Kinetic plot of acetaminophen transformation in PS/bicarbonate system. Initial acetaminophen 10 μM ; CO_2 saturated, PS varied from 1 to 10 mM, pH 8.3. Solid points are experimental data; dash lines represent first-order fitting.

Figure 2 Effects of various scavengers on acetaminophen removal in PS/bicarbonate system. Initial acetaminophen was 10 μM , PS 5 mM, CO_2 saturated, pH 8.3, FFA 1 mM, MeOH 10 mM, SOD 1 KU.

Figure 3 Removal of (a) acetaminophen and (b) FFA in PS/bicarbonate system fortified with D_2O . Initial acetaminophen and FFA was 10 μM and 20 μM , PS 5 mM, CO_2 saturated, SOD 1KU, pH 8.3. Solid points are experimental data; dash lines represent first-order fitting.

Figure 4 Mass spectrum of acetaminophen transformation products in (a) PS as the control, (b) PS/bicarbonate (c) $\text{PS}/\text{H}_2\text{O}_2$ (d) $\text{H}_2\text{O}_2/\text{NaMoO}_4$ systems. Initial acetaminophen was 10 μM ; (a) PS 5 mM; (b) PS 5 mM, CO_2 saturated; (c) H_2O_2 5 mM, CO_2 saturated, SOD 1KU; (d) H_2O_2 10 mM, NaMoO_4 1 mM.

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Graphic Abstract