

Activation of Persulfate by Quinones: Free Radical Reactions and Implication for the Degradation of PCBs

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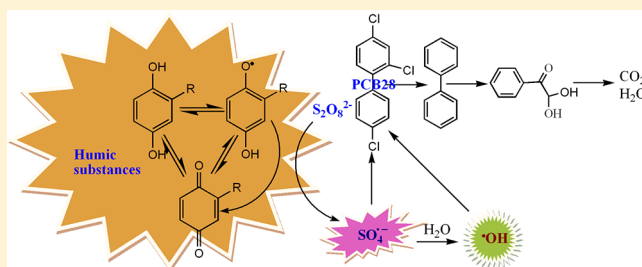
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S Supporting Information

ABSTRACT: There has been considerable interest in the use of persulfate for *in situ* chemical oxidation of organic contaminants in soils, sediments, and groundwater. Since humic acid (HA) exists ubiquitously in these environmental compartments, its redox active functional moieties, such as quinones, may play an important role in the oxidation processes of persulfate treatments. Understanding the effects of HA, especially the quinone functional groups on the degradation of pollutants by persulfate and the production of sulfate radicals ($\text{SO}_4^{\bullet-}$) from persulfate, is beneficial for devising effective and economically feasible remediation strategies. In this study, the effects of model quinone compounds and HA on the degradation of 2,4,4'-trichlorobiphenyl (PCB28) by persulfate and the production of $\text{SO}_4^{\bullet-}$ from persulfate were investigated. It was found that quinones and HA can efficiently activate persulfate for the degradation of PCB28. The mechanism of persulfate activation was elucidated by quenching and electron paramagnetic resonance (EPR) studies. The results indicated that production of $\text{SO}_4^{\bullet-}$ from persulfate and quinones was semiquinone radical-dependent. The effects of quinone concentrations were also studied. The findings of this study elucidated a new pathway of persulfate activation, which could degrade environmental contaminants efficiently and provide useful information for the remediation of contaminated soil and water by persulfate.



INTRODUCTION

In situ chemical oxidation (ISCO) technologies based on persulfate for the remediation of contaminated soils, groundwater, and sediments have received considerable attention in recent years.^{1,2} Activation of persulfate by UV, heat, base, or transition metals is commonly used to generate sulfate radical ($\text{SO}_4^{\bullet-}$), which is a strong oxidant with a redox potential of 2.5–3.1 V, depending on the solution pH.^{3–6} Sulfate radical can degrade a wide range of organic contaminants, including chlorinated ethylene, chlorophenols, polycyclic aromatic hydrocarbons, perfluorinated compounds, and numerous volatile organic compounds.^{6–12} Recently, naturally occurring metal oxides have also been identified to be able to activate persulfate for the degradation of contaminants.^{13,14} Comparatively, little is known about the activation of persulfate by natural organic compounds.

Quinone are a group of highly reactive organic compounds widely distributed in soils, surface water, and even in atmospheric aerosols,^{15–17} which can act as electron-shuttle in chemical and biochemical processes occurring in the environment.^{18–21} Several previous studies reported that the quinone moieties in humic acid (HA) can reductively degrade chlorinated compounds.^{22–25} The reactivity of quinone (or quinone moieties on HA) is related to its redox cycling, a

process that involves reversible reduction of quinones to semiquinone anion radical ($\text{SQ}^{\bullet-}$) or hydroquinone.²⁶ It has been well established that $\text{SQ}^{\bullet-}$ can transfer electrons to molecular oxygen to produce superoxide in living cells,^{27,28} and, abiotically, the redox cycle of quinones and their corresponding semiquinone radicals occurs spontaneously in various environmental compartments, such as airborne particulate matter, surface water, and soils.^{29–32}

Recently, Zhu et al.³³ found that hydroxyl radical ($\bullet\text{OH}$) was produced from hydrogen peroxide (H_2O_2) in the presence of chloroquinones, and the reaction is semiquinone radical-dependent, which was consistent with Koppenol and Butler's study.³⁴ Similarly, molecular oxygen can also be activated by semiquinone radicals to form reactive oxygen species on the surface of CuO/silica particles.^{35,36} Both H_2O_2 and O_2 can be activated by a semiquinone radical to produce highly reactive radical oxidants, which are critical for the effective remediation of contaminants using ISCO techniques.⁸ However, it is unclear whether a semiquinone radical can react in a similar way with

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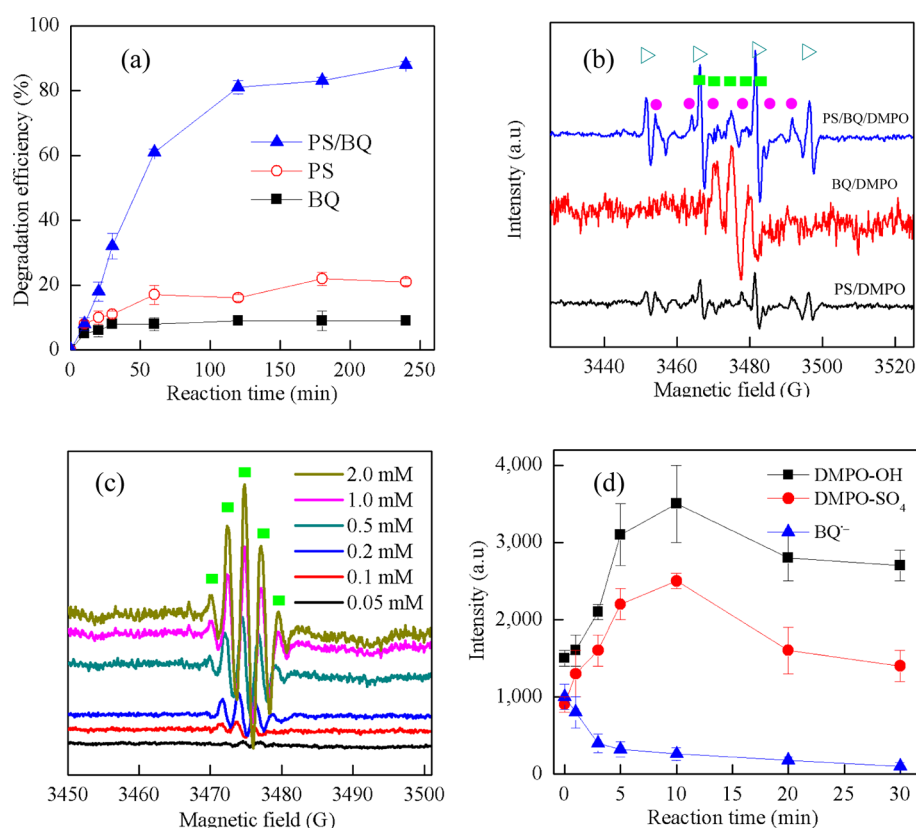


Figure 1. Effects of quinones on the degradation of 2,4,4'-CB (PCB28) and the production of sulfate and hydroxyl radicals by persulfate (PS). (a) degradation of PCB28 by PS with and without 1,4-benzoquinone (BQ); (b) EPR spectra of persulfate with and without BQ at 10 min; (c) EPR spectra of BQ at varied concentrations (0.05–2.0 mM); (d) changes in the intensities of DMPO–SO₄, DMPO–OH, and BQ•⁻ in PS/BQ system. Reaction condition: initial concentrations [BQ]₀ = 0.1 mM; [DMPO]₀ = 0.1 M; [PS]₀ = 5.0 mM; [PCB28]₀ = 0.5 mg L⁻¹; T = 25 °C; pH = 7.4 (10 mM phosphate buffer (PBS)). ■ (green): BQ•⁻ radical; ● (purple): DMPO–SO₄; △ (pointing to the right): DMPO–OH.

persulfate to produce SO₄•⁻. To the best of our knowledge, there have been no investigations concerning the effects of quinones or HA quinone moieties on the degradation of pollutants by persulfate and the production of SO₄•⁻ from persulfate, which could be beneficial for devising effective and economically feasible remediation strategies.

The primary concerns of this study were to verify the following questions: (i) can persulfate be activated by quinones or HA quinone moieties to produce SO₄•⁻; (ii) can the activation be efficient for the degradation of pollutants; and (iii) what is the underlying mechanism of the activation process. In this study, 2,4,4'-trichlorobiphenyl (PCB28) was chosen as the target contaminant, since PCBs are an important group of persistent contaminants and the mechanism of PCB28 degradation by SO₄•⁻ has been clearly elucidated in our previous studies.³⁷ The 1,4-benzoquinone (BQ), 2-methyl-1,4-benzoquinone (MBQ), and 2-chloro-1,4-benzoquinone (CBQ) were selected since the corresponding semiquinone radicals are relatively stable under the environmentally relevant conditions and easily detectable by electron paramagnetic resonance (EPR). They were used as model compounds in combination with a sample of humic acid to better elucidate the role of SQ•⁻ in persulfate activation by natural quinones and quinone moieties in natural organic matter.

MATERIALS AND METHODS

Materials. Details of all chemicals used in this study are included in the Supporting Information (Text S1).

Degradation Experiments. Batch experiments were conducted in 40-mL brown serum bottles capped with Teflon mininerts; each reaction was performed in 20 mL of solution in the dark. A brief description of the procedure is as follows: first, 1.0 mL of 2.0 mM quinones stock solution was added into 18.9 mL of 0.5 mg L⁻¹ PCB28 aqueous solution at pH 7.4 with 10 mM phosphate buffer; after complete mixing, 0.1 mL of 1.0 M persulfate solution was quickly added; then the bottles were sealed and kept shaking at 150 rpm on a reciprocating shaker at 25 °C. Separate control experiments were also performed under the same conditions with only persulfate or quinones added to PCB28 solutions. At each sampling event, 2.0 mL aliquots of reaction solution were taken into an 8-mL serum bottle, and 1.0 mL of ethanol was immediately added to quench the reaction. The solution was subsequently extracted by 2.0 mL of hexane and shaken for 1 h with a reciprocal shaker (the recovery of PCB28 was approximately 90–110%). The supernatant after extraction was analyzed by a gas chromatograph (GC/μECD, Agilent7890, USA) equipped with ⁶³Ni electron capture detection (ECD) and autosampler.³⁷ Another 1.0 mL aliquot was taken to determine the concentration of persulfate remaining in solution using the colorimetric method developed by Liang et al. (Text S2).³⁸ All experiments were carried out in triplicates, and average values and the standard deviations were presented in the Results and Discussion. Details of analysis are shown in Text S2.

Electron Paramagnetic Resonance Studies. Experiments were conducted in a mixed solution of 0.1 mM different quinones (BQ, MBQ, and CBQ), 5.0 mM persulfate, and 0.1 M

spin trapping agent 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) in 10 mM phosphate buffer at pH 7.4. Quinones were dissolved in acetone, and the final concentration of acetone in the experiments was less than 2.4 mM,¹¹ which had negligible effects on the formation of sulfate radical ($\text{SO}_4^{\bullet-}$) or hydroxyl radical ($^{\bullet}\text{OH}$) from persulfate.³⁷ All these solutions were prepared freshly and stored in the dark at 4 °C less than 1 day before analysis. The EPR spectra were obtained at room temperature on a Bruker EMX 10/12 spectrometer (Germany) with a resonance frequency of 9.77 GHz, microwave power of 19.97 mW, modulation frequency of 100 kHz, modulation amplitude of 2.0 G, sweep width of 100 G, time constant of 40.96 ms, sweep time of 83.87 s, and receiver gain of 2.0×10^4 . The EPR spectra of quinones at various concentrations (BQ, 0.05–2.0 mM; MBQ and CBQ, 0.1, 0.2 mM) were acquired; the EPR spectra of persulfate or quinones alone in the presence of different concentrations of radical scavengers (ethanol, desferrioxamine (DFO)) were obtained at pH 7.4. The formation of DMPO-CH(CH₃)OH in persulfate/BQ solution with the presence of 2 mM ethanol and 0.05 mM DFO was also detected by EPR. It was difficult to determine the concentrations of sulfate radicals ($\text{SO}_4^{\bullet-}$) in the presence of coexisting hydroxyl radicals ($^{\bullet}\text{OH}$) in the reaction mixture. Thus, the changes of peak intensities of DMPO adducts and semiquinone radical were used to indicate concentration changes of free radicals, and the level of background noise was corrected by measuring the main low field peak height (in arbitrary units).^{31,32}

RESULTS AND DISCUSSION

Effects of Quinones on PCB28 Degradation and Sulfate Radical Production by Persulfate. To explore the possibility of persulfate activation by quinones, the effects of quinones on the degradation of PCB28 by persulfate and the production of $\text{SO}_4^{\bullet-}$ from persulfate were investigated. Figure 1a shows 88% of 0.5 mg L⁻¹ PCB28 was degraded by 5.0 mM persulfate in the presence of 0.1 mM BQ at pH 7.4 and 25 °C, while separately only 20% or 9% of PCB28 was degraded by persulfate or BQ. The results indicated that PCB28 degradation by persulfate was greatly enhanced in the presence of BQ.

It has been reported that $\text{SO}_4^{\bullet-}$ was the dominant radical species in the persulfate solution at pH 7.4.^{12,37} From EPR spectra (Figure 1b), mixing of 5.0 mM persulfate and 0.1 M DMPO could form the typical DMPO- SO_4 and DMPO-OH signals based on their hyperfine splitting constants (DMPO-OH: $a_{\text{H}} = a_{\text{N}} = 14.9$ G; DMPO- SO_4 : $a_{\text{N}} = 13.2$ G, $a_{\text{H}} = 9.6$ G, $a_{\text{H}} = 1.48$ G, and $a_{\text{H}} = 0.78$ G). This result indicated that $\text{SO}_4^{\bullet-}$ and $^{\bullet}\text{OH}$ were produced during persulfate decomposition. The production of $^{\bullet}\text{OH}$ was pH-dependent in reaction solution, and at pH 7.4 the concentration of $^{\bullet}\text{OH}$ was approximately 5% of $\text{SO}_4^{\bullet-}$ as estimated by kinetic modeling.^{7,37} However, since the second-order reaction rate constants of PCB28 with $\text{SO}_4^{\bullet-}$ was smaller than that with $^{\bullet}\text{OH}$,³⁷ both the $\text{SO}_4^{\bullet-}$ and $^{\bullet}\text{OH}$ contributed to the oxidative degradation of PCB28.

Compared with EPR spectra of persulfate in the absence of BQ, the peak intensities of DMPO- SO_4 and DMPO-OH in the presence of BQ were significantly higher, which indicated that BQ might activate persulfate to produce more $\text{SO}_4^{\bullet-}$. Furthermore, a typical five-line EPR spectrum was obtained for BQ solutions with an intensity ratio of 1:4:6:4:1 and hyperfine splitting constants of $a_{\text{H}} = 2.36$ G, $g = 2.0045$ (Figure 1c), which indicated the existence of 1,4-benzosemiquinone anion radicals ($\text{BQ}^{\bullet-}$).³⁹ With the increase of BQ concentration from

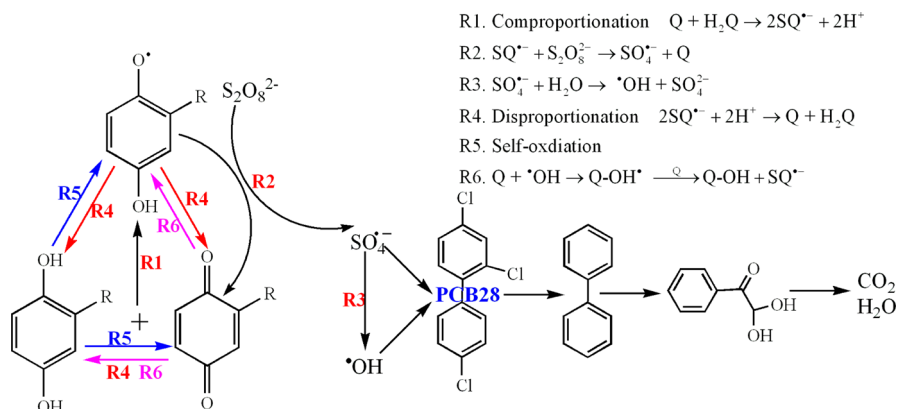
0.05 to 2.0 mM, the peak intensity of $\text{BQ}^{\bullet-}$ radical increased from 500 to 5500 a.u. rapidly, which indicated that $\text{BQ}^{\bullet-}$ was produced in solution. The results were consistent with those obtained in previous studies and verified as the “spontaneous” formation of semiquinone radicals in quinone systems.^{33,39–43}

The $\text{BQ}^{\bullet-}$ signal was dramatically reduced from 1000 to 100 a.u. within 30 min after adding 5.0 mM persulfate into BQ solutions (Figure 1b) in the presence of DMPO. In contrast, in the absence of persulfate the $\text{BQ}^{\bullet-}$ signal was relatively stable (Figure S1a), even for up to 2 h ($p > 0.05$, data not shown). As the reaction of BQ and persulfate underwent, the peak intensity of $\text{BQ}^{\bullet-}$ decreased monotonically, while the peak intensities of DMPO- SO_4 and DMPO-OH first increased and then decreased rapidly after 10 min (Figure 1d). In the absence of BQ, the peak intensities of DMPO- SO_4 and DMPO-OH produced from persulfate solution, however, were markedly lower (Figure S1a).

The activations of persulfate by MBQ and CBQ were also examined (Figure S1b). The peak intensities of DMPO- SO_4 and DMPO-OH increased from 1000 to 2100 a.u. and 1500 to 3100 a.u. or from 1000 to 1600 a.u. and from 1500 to 2600 a.u. in the presence of 0.1 mM MBQ or 0.1 mM CBQ, respectively, while the peak intensities of the corresponding semiquinone radicals decreased significantly (Figures S1c and S2a). These results clearly indicated that semiquinone radicals formed in the MBQ and CBQ reaction solution, which activated persulfate to produce $\text{SO}_4^{\bullet-}$. The addition of MBQ or CBQ also enhanced PCB28 degradation by persulfate (Figure S2b and Table S1). If it was assumed that the degradation of PCB28 by persulfate followed the pseudo-first-order reaction kinetics, the PCB28 degradation rate constant k_{obs} increased from 0.034 to 0.31, 0.20, and 0.58 h⁻¹, and the decomposition rate constant of persulfate $k_{\text{obs,ps}}$ increased from 0.046 to 0.32, 0.22, and 0.14 h⁻¹ with the addition of 0.1 mM of MBQ, CBQ, and BQ, respectively (Table S1). These results suggested that quinones accelerated the PCB28 degradation by activating persulfate to produce $\text{SO}_4^{\bullet-}$ radicals.

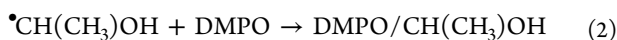
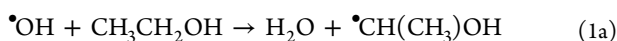
Possible Mechanism of Persulfate Activation by Quinones. Quinones undergo self-redox cycling to produce semiquinone radicals under environmentally relevant conditions, while the concentration of semiquinone radicals decreased, and the concentration of $\text{SO}_4^{\bullet-}$ increased as persulfate was added to the system (Figure 1). Therefore, it was hypothesized that semiquinone radicals played an important role in the production of $\text{SO}_4^{\bullet-}$ from persulfate (Figure 1). It has been reported that the production of $^{\bullet}\text{OH}$ from H_2O_2 and quinones was semiquinone radical-dependent,³³ which suggested the activation of persulfate by quinones might follow a similar pathway. The semiquinone radical might be formed from the comproportionation reaction between the quinone and hydroquinone, while the latter is commonly produced during the self-condensation or decomposition of quinones.^{44,45} The results of HPLC analysis show that approximately 5.0, 9.0, and 1.2 μM corresponding hydroquinone existed in 0.1 mM of BQ, CBQ, and MBQ solutions, respectively. When persulfate was mixed with BQ solutions in the presence of DMPO, the peak intensity of DMPO- SO_4 increased rapidly from 900 to 4500 a.u., while the peak intensity of $\text{BQ}^{\bullet-}$ decreased from 1000 to 200 a.u. with persulfate concentration changes from 0 to 20 mM (Figures S3a and 3b). Although the peak intensities of DMPO- SO_4 and DMPO-OH also increased with increasing persulfate concentration in the absence of BQ, the changes were markedly smaller than

Scheme 1. Proposed Pathways for the Formation of Semiquinone and Sulfate Radicals in the Persulfate/Quinones System



those with BQ. These results suggested that BQ would activate persulfate to produce $SO_4^{\bullet-}$ via a pathway as depicted in Scheme 1. The comproportionation reaction (reaction R1) between quinone and hydroquinone forms two semiquinone radicals, which activates persulfate ion ($S_2O_8^{2-}$) to produce $SO_4^{\bullet-}$ (reaction R2). The increases of the concentration of persulfate could produce more $SO_4^{\bullet-}$.

To further verify this hypothesis, quenching studies were employed to examine the reaction between $S_2O_8^{2-}$ and $BQ^{\bullet-}$. Ethanol is an efficient scavenger of $\bullet OH$ and $SO_4^{\bullet-}$, and the rate constant of reaction between ethanol and $\bullet OH$ or ethanol and $SO_4^{\bullet-}$ to produce $\bullet CH(CH_3)OH$ radicals was 10^9 or 10^8 $M^{-1} s^{-1}$ at 25 °C, respectively (eqs 1a and 1b).¹⁰



At higher concentrations of $SO_4^{\bullet-}$ and $\bullet OH$, more $\bullet CH(CH_3)OH$ was produced, and thus the peak intensity of $DMPO-CH(CH_3)OH$ ($a_H = 22.7$ G, $a_N = 15.7$ G) detected by EPR was also stronger.⁴⁸ The production of $\bullet CH(CH_3)OH$, therefore, can be used to obtain the trends of concentration changes of $SO_4^{\bullet-}$ and $\bullet OH$. As shown in Figure 2a, the peak intensities of $DMPO-SO_4$ and $DMPO-OH$ decreased, while the peak intensity of $DMPO-CH(CH_3)OH$ increased rapidly, and the peak intensity of $BQ^{\bullet-}$ remained unchanged ($p > 0.05$) with ethanol concentration increased from 0.001 to 0.05 M. These results indicated that ethanol efficiently quenched $SO_4^{\bullet-}$ and $\bullet OH$ but did not affect $BQ^{\bullet-}$.

It has been proved that DFO is an effective scavenger of semiquinone radical.^{33,46,47} Figure S3c shows the peak intensity of $BQ^{\bullet-}$ in BQ solution decreased rapidly from 1000 to 100 a.u. within 10 min after adding 0.05 mM DFO. Moreover, the peak intensities of $DMPO-SO_4$ and $DMPO-OH$ also dropped dramatically as 0.05 mM DFO added into the persulfate solution. Figure S3d shows the peak intensity of $DMPO-CH(CH_3)OH$ changed negligibly as DFO concentration increased from 0 to 0.2 mM in the presence of 2.0 mM ethanol, which indicated that $SO_4^{\bullet-}$ and $\bullet OH$ hardly reacted with DFO in the presence of 2.0 mM ethanol. Therefore, 0.05 mM DFO and 2.0 mM ethanol were applied to identify the formation of $SO_4^{\bullet-}$ from the reaction between $S_2O_8^{2-}$ and $BQ^{\bullet-}$ (Figure 2b). The peak intensity of $DMPO-CH(CH_3)OH$ in persulfate/BQ/ethanol solution increased from 4200 to 8300

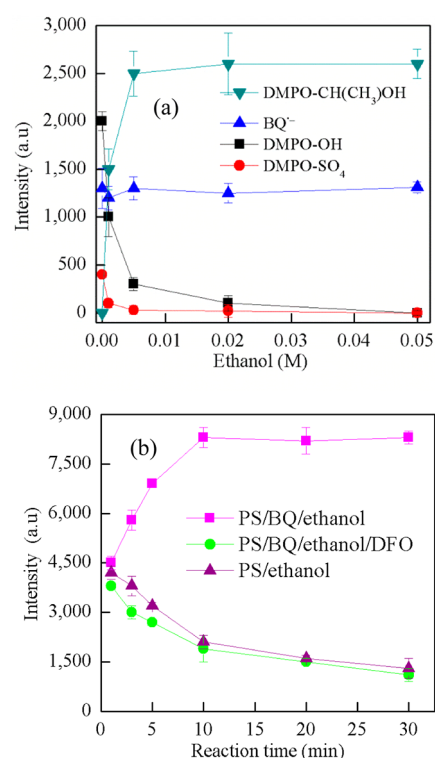


Figure 2. Effects of DFO and ethanol on the formation of $DMPO-SO_4/OH/CH(CH_3)OH$. (a) changes in the intensities of $DMPO-SO_4$, $DMPO-OH$, and $BQ^{\bullet-}$ in the presence of ethanol with different concentrations in PS or BQ solution; (b) change in the intensity of $DMPO-CH(CH_3)OH$ in PS/BQ system in the presence of 2.0 mM ethanol and 0.05 mM DFO. Reaction conditions: initial concentration $[PS]_0 = 5.0$ mM; $[BQ]_0 = 0.1$ mM; $[ethanol]_0 = 0.001-0.05$ M; $T = 25$ °C; $[DMPO]_0 = 0.1$ M; pH = 7.4 (10 mM PBS).

a.u. within 30 min in the absence of DFO, but it decreased from 4000 to 1100 a.u. within 30 min in the presence of 0.05 mM DFO, which indicated that the formation of $\bullet CH(CH_3)OH$ radical was greatly inhibited in the presence of DFO. This is due to the fact that DFO quenched $BQ^{\bullet-}$, which inhibited the formation of $SO_4^{\bullet-}$ by R2 in Scheme 1. Thus, the production of $\bullet CH(CH_3)OH$ radical was decreased based on eq 1. The results presented in Figure 2 clearly indicated that the production of $SO_4^{\bullet-}$ from persulfate and quinone was semiquinone radical-dependent.

The source of electron to reduce quinone in the reaction was hydroquinone (Scheme 1). Thus, the concentration of

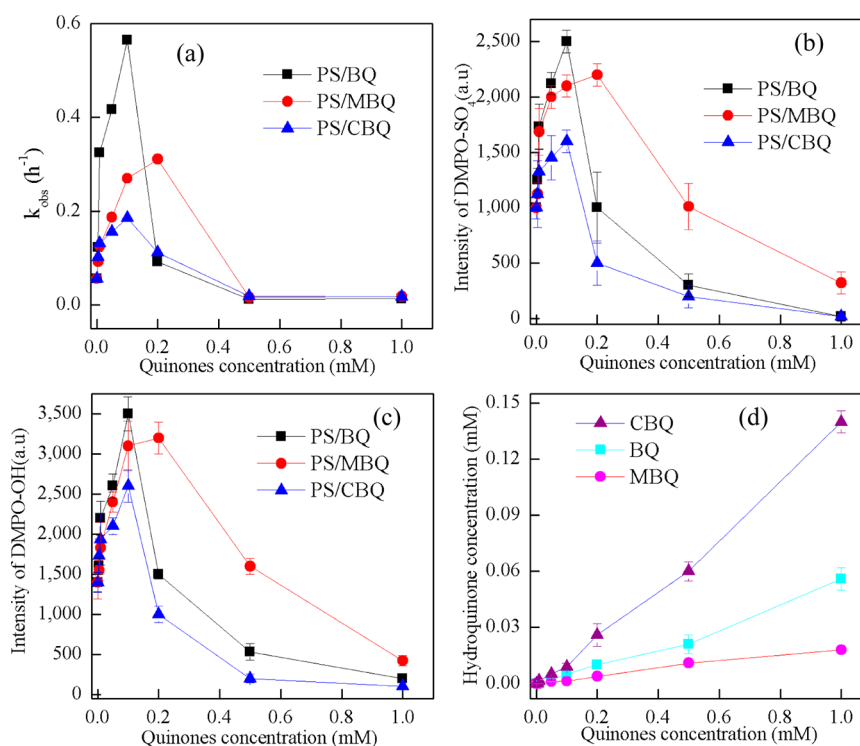


Figure 3. Effects of quinone concentration on k_{obs} of PCB28 degradation, and the formation of DMPO-SO₄ and DMPO-OH by persulfate. Effects of BQ, MBQ, and CBQ concentrations on k_{obs} of PCB28 degradation within 4 h (a), on changes in the intensities of DMPO-SO₄ and DMPO-OH (b and c), and on the production of corresponding hydroquinones (d). Reaction conditions: initial concentration [BQ]₀ = [MBQ]₀ = [CBQ]₀ = 0.005–1.0 mM; [PS]₀ = 5.0 mM; [PCB28]₀ = 0.5 mg L⁻¹; T = 25 °C; [DMPO]₀ = 0.1 M; pH = 7.4 (10 mM PBS).

hydroquinone would affect the formation of semiquinone radical and the activation of persulfate. In order to examine hydroquinone effects on DMPO-SO₄ and DMPO-OH, EPR spectra were obtained from 5.0 mM persulfate solution by adding only hydroquinones at pH 7.4 and 25 °C (Figure S4). The results indicated that hydroquinone significantly inhibited the production of SO₄^{•-} and [•]OH from persulfate, which was consistent with the fact that hydroquinone was an effective scavenger of sulfate radical.⁴⁹ The results showed that sulfate radical was not from the reaction between hydroquinone and persulfate ion.

Quinone Concentration on Persulfate Activation. As shown in Figure 3a, the degradation rate constant of PCB28 k_{obs} increased from 0.034 to 0.58, 0.31, and 0.20 h⁻¹ with BQ, MBQ, and CBQ concentration increased from 0 to 0.1, 0.2, and 0.1 mM, respectively. The most possible explanation was that SQ^{•-} formation increased with an increase in quinone concentration (Figure 1c), which would activate more S₂O₈²⁻ to produce SO₄^{•-} (R2 in Scheme 1) and induced more PCB28 degradation. However, the value of PCB28 degradation rate constant k_{obs} decreased rapidly to 0.013, 0.017, and 0.018 h⁻¹ with further increasing BQ, MBQ, and CBQ concentration up to 1.0 mM. One likely reason was that increasing quinone concentration would increase the formation of SO₄^{•-} by persulfate, but the competitive reaction of quinone/hydroquinone with SO₄^{•-} was also enhanced. It has been reported that the reaction of quinones and [•]OH produces hydroquinone (R4 and R6 in Scheme 1),⁵⁰ where the [•]OH came from the reaction between SO₄^{•-} and OH⁻. Therefore, the degradation of PCB28 was inhibited in the presence of relatively high quinone concentrations.

Figures 3b and 3c showed the peak intensities of DMPO-SO₄ increased from 1000 to 2500, 2200, and 1600 a.u., and the peak intensities of DMPO-OH increased from 1400 to 3500, 3200, and 2600 a.u., with BQ, MBQ, and CBQ concentrations increased from 0 to 0.1, 0.2, and 0.1 mM, respectively. With further increases of quinone concentrations up to 1.0 mM, the peak intensities of DMPO-SO₄ and DMPO-OH decreased rapidly. Figure 3d showed that increasing the concentration of quinone produced more semiquinone radical (reaction 1 in Scheme 1) and hydroquinone (reaction 4 in Scheme 1), which was consistent with the previous study by Taguchi et al.²⁷ Because hydroquinone effectively quenched sulfate radicals (Figure S5),⁴⁶ the degradation of PCB28 was inhibited.

Effects of Humic Acids on Persulfate Activation. Humic acids (HA) are often used as model compounds to study the role of natural organic matter (NOM) in the environmental systems. The typical concentration of HA ranges from 1 to 50 mg L⁻¹ (carbon) in soils and groundwater.⁵¹ Ten mg L⁻¹ HA (5.28 mg L⁻¹ carbon, Text S1) was selected for studying the effects HA on the degradation of PCB28 and formation of sulfate radicals by persulfate (Figure S6). The results indicated that persulfate was activated by HA for the degradation of PCB28. The EPR peak intensities of DMPO-SO₄ and DMPO-OH increased with the addition of HA. Furthermore, the semiquinone type radicals in HA solution were detected, and their EPR signal intensities were reduced with the addition of persulfate. These results were consistent with those obtained in the studies dealing with the persulfate activation by simple quinones, which would suggest a similar pathway involving the reactive quinone moieties on HA molecules.

Environmental Implications. Recently, the activation of persulfate has been intensively studied and used for the

remediation of contaminated soils, groundwater, and sediments. Quinones and quinone functional moieties in soil organic matter are naturally abundant in the soils and waters, which can undergo self-redox cycles.^{15–17} In the comproportionation reaction between quinone and hydroquinone, semiquinone radical was produced, which induced persulfate activation to produce $\text{SO}_4^{\bullet-}$. The findings of this study elucidated a new pathway of persulfate activation and efficient degradation technique for environmental contaminants, which may provide useful information for developing *in situ* remediation strategy of contaminated soils and waters. It was demonstrated that both model quinones and 10 mg L^{-1} humic acids activated the persulfate efficiently for the degradation of PCB28. However, to better understand the molecular mechanism of the reaction between persulfate ion and semiquinone radical, further studies are warranted to identify the reaction intermediate products of persulfate ion and semiquinone radical. The effects of semiquinone radical on the formation of $\bullet\text{OH}$ by H_2O_2 for the degradation of contaminants is also an interesting topic and deserves further investigation.

■ ASSOCIATED CONTENT

● Supporting Information

Additional data including EPR spectra and changes in the intensities of DMPO-SO_4 , DMPO-OH , and semiquinone radical in different reaction systems can be found in this section. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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