

SUPPORTING INFORMATION SECTION

**In Situ Chemical Oxidation of Contaminated Groundwater by Persulfate:  
Decomposition by Fe(III)- and Mn-Containing Oxides and Aquifer Materials**

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# Table of Contents

Procedure to prepare minerals of iron and manganese oxides.....	4
Table S1 Characterization of aquifer materials, clay materials and pure minerals.....	5
Table S2 Chemical composition of synthetic groundwater used in this study.....	6
Table S3 Comparison of pseudo first-order reaction rates of persulfate decomposition in synthetic groundwater and in MQ water.....	7
Table S4 Reaction Rate Constants Used in Branching Ratio Calculations.....	8
Figure S1 XRD spectra of synthesized goethite $\alpha$ -FeOOH. The XRD spectra confirmed that the synthesized particles are pure goethite. ....	8
Figure S2 Stability of persulfate in the presence of different mass loadings of silica. ....	9
Figure S3 Persulfate loss in homogeneous system. ....	10
<b>Figure S4 (A)</b> Formation of sulfate during the activation of persulfate by aquifer solid and the mass balance on sulfate species. <b>(B)</b> Comparison of persulfate consumption rate during pyrolusite activation both in the presence and absence of oxygen. ....	11
Figure S5 Correlation between dissolved oxygen generation and persulfate consumption during activation by pyrolusite in anaerobic condition.....	12

### **Procedure to prepare minerals of iron and manganese oxides**

Four types of pure minerals were employed in this study, *i.e.*, amorphous ferrihydrite ( $\text{Fe}(\text{OH})_{3(s)}$ ), goethite ( $\alpha\text{-FeOOH}_{(s)}$ ), pyrolusite ( $\beta\text{-MnO}_{2(s)}$ ) and silica ( $\text{SiO}_2$ ). Pyrolusite and ferrihydrite were directly obtained from Sigma-Aldrich. Pyrolusite was used without further processing. Ferrihydrite was aged in deionized water buffered at pH 8.0 with 50 mM borate for 2 weeks prior to experiments, with daily pH adjustment to 8.0 by adding 1 mM NaOH. After that, ferrihydrite suspension was centrifuged and the particles were washed three times with deionized water before finally dried with a freeze dry system. Silica obtained as pure sand (ACROS Organics) was rinsed in 0.1 M  $\text{HClO}_4$  at a concentration of 300 g/L. After 24 hours, the solution was decanted and replaced. This step was repeated for 3 consecutive days. After that, silica particles were freeze-dried. Goethite was synthesized by aging freshly made ferrihydrite in a concentrated NaOH solution at 70 °C for 60 hours.

**Table S1** Characterization of aquifer materials, clay materials and pure minerals.

<b>Material Type</b>	<b>Material Name</b>	<b>BET Surface area (m<sup>2</sup>/g)</b>	<b>Total Fe (wt %)</b>	<b>Total Mn (wt %)</b>	<b>Sand (wt %)</b>	<b>Silt (wt %)</b>	<b>Clay (wt%)</b>
<b>Aquifer Material</b>	CADOU	3.9	0.77%	0.01%	84%	16%	4%
	CAROL	39.8	2.49%	0.02%	63%	18%	19%
	AWBPH	14.3	1.67%	0.03%	82%	10%	8%
	AFTCS	27.7	1.44%	0.03%	60%	22%	18%
	AMTAL	16.2	1.85%	0.12%	64%	22%	14%
<b>Clay Material</b>	Nontronite	69.0	26.2%	0.01%	--	--	100%
	Montmorillonite	32.0	2.6%	0.05%	--	--	100%
<b>Pure Mineral</b>	Goethite $\alpha\text{-FeOOH}_{(s)}$	37.1	62.9%	--	--	--	--
	Ferrihydrite $\text{Fe}(\text{OH})_{3(s)}$	180.1	52.3%	--	--	--	--
	Pyrolusite $\beta\text{-MnO}_{2(s)}$	0.11	--	62.8%	--	--	--
	Silica $\text{SiO}_{2(s)}$	27.0	--	--	--	--	--

**Table S2** Chemical composition of synthetic groundwater used in this study.

<b>Chemical parameter</b>	<b>Concentration</b>
Na <sup>+</sup>	23 mg/L
Ca <sup>2+</sup>	20 mg/L
Mg <sup>2+</sup>	5 mg/L
SO <sub>4</sub> <sup>2-</sup>	20 mg/L
Cl <sup>-</sup>	35.5 mg/L
Br <sup>-</sup>	0.1 mg/L
NO <sub>3</sub> <sup>-</sup>	1 mg/L
HCO <sub>3</sub> <sup>-</sup>	1 mM
TDS	166 mg/L
Suwannee River NOM	1 mg C/L
pH	8

The solution was buffered at pH 8.0 with 50 mM borate. The use of high buffer concentration was necessary to maintain a constant pH throughout the experiment.

- Experimental condition is with 50 g/L of minerals, initial persulfate concentration 1 mM and pH 8. In experiments with benzene, the initial concentration of benzene was 1 mM.

**Table S3** Comparison of pseudo first-order reaction rates of persulfate decomposition in synthetic groundwater and in MQ water.

Type of mineral	Pseudo 1 <sup>st</sup> -order reaction rate (d <sup>-1</sup> )*			
	Without benzene		With benzene	
	Synthetic groundwater	MQ water	Synthetic groundwater	MQ water
Goethite	$5.4 \times 10^{-3}$	$3.1 \times 10^{-3}$	$9.4 \times 10^{-3}$	$1.0 \times 10^{-2}$
Ferrihydrite	$3.2 \times 10^{-3}$	$4.3 \times 10^{-3}$	$3.4 \times 10^{-2}$	$3.9 \times 10^{-2}$
Pyrolusite	$1.3 \times 10^{-3}$	$4.2 \times 10^{-3}$	$3.0 \times 10^{-3}$	$8.2 \times 10^{-3}$

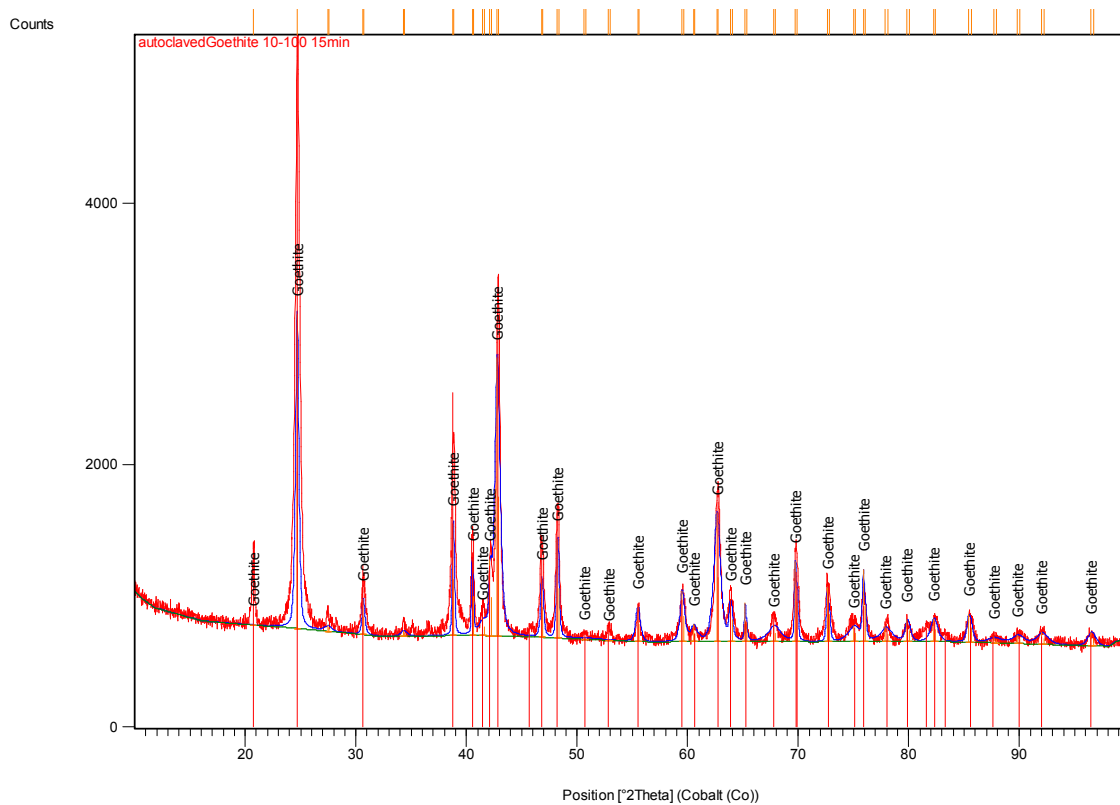
\* Experimental condition is with 50 g/L of minerals, initial persulfate concentration 1 mM and pH 8. In experiments with benzene, the initial concentration of benzene was 1 mM. In both synthetic groundwater and MQ water matrix, 50 mM borate was added as pH buffer.

**Table S4** Reaction Rate Constants Used in Branching Ratio Calculations.

	<b>Reaction</b>	<b>Rate Constant</b>	<b>Units</b>
5.	$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-}$	$6.3 \times 10^5$	$M^{-1}s^{-1}$
7.	$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + HO^{\bullet} + H^+$	660	$s^{-1}$
8.	$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + HO^{\bullet}$	$4.6 \times 10^7$	$M^{-1}s^{-1}$
13.	$SO_4^{\bullet-} + \text{C}_6\text{H}_6 \dashrightarrow SO_4^{2-} + \text{C}_6\text{H}_6^{\bullet+}$	$3 \times 10^9$	$M^{-1}s^{-1}$
14.	$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet}$	$3.0 \times 10^8$	$M^{-1}s^{-1}$
15.	$SO_4^{\bullet-} + Br^- \rightarrow SO_4^{2-} + Br^{\bullet}$	$3.5 \times 10^9$	$M^{-1}s^{-1}$
16.	$SO_4^{\bullet-} + HCO_3^- \rightarrow CO_3^{\bullet-} + SO_4^{2-} + H^+$	$2.8 \times 10^6$	$M^{-1}s^{-1}$
17.	$CO_3^{\bullet-} + S_2O_8^{2-} \rightarrow CO_3^{2-} + S_2O_8^{\bullet-}$	$3.0 \times 10^7$	$M^{-1}s^{-1}$

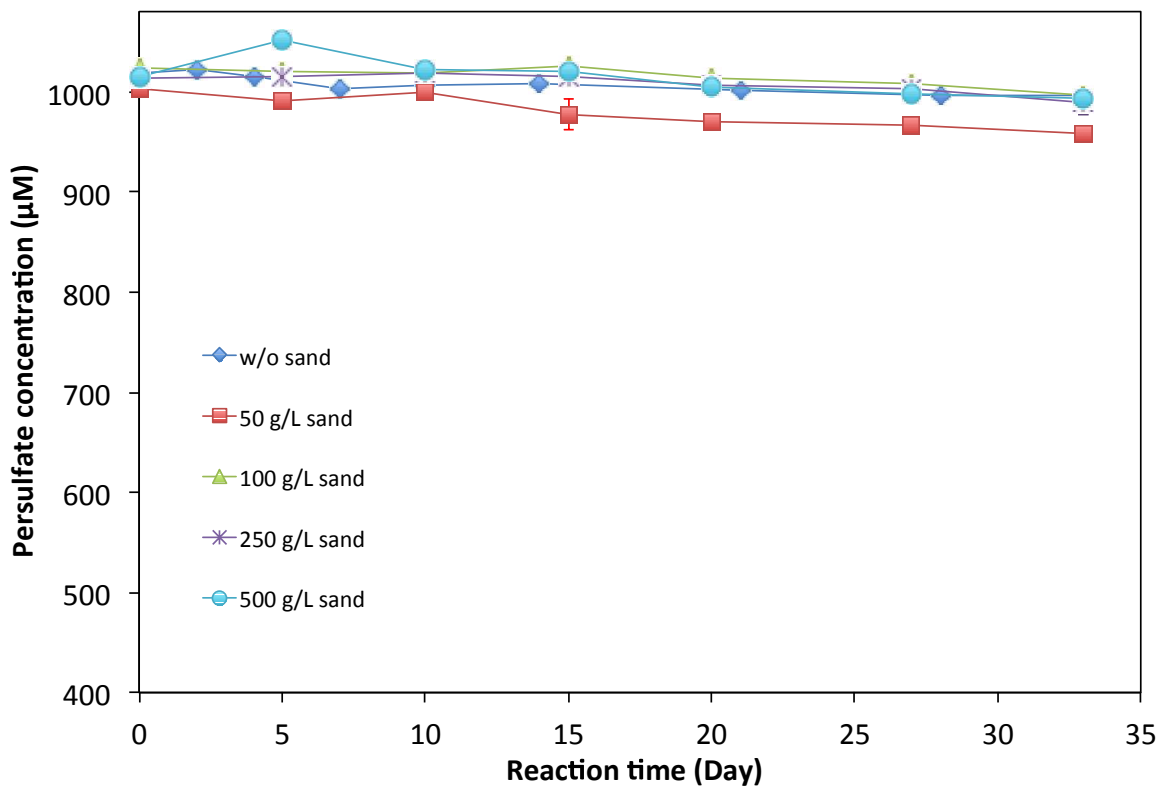
The solution was buffered at pH 8.0 with 50 mM borate. The use of high buffer concentration was necessary to maintain a constant pH throughout the experiment.

- Experimental condition is with 50 g/L of minerals, initial persulfate concentration 1 mM and pH 8. In experiments with benzene, the initial concentration of benzene was 1 mM.



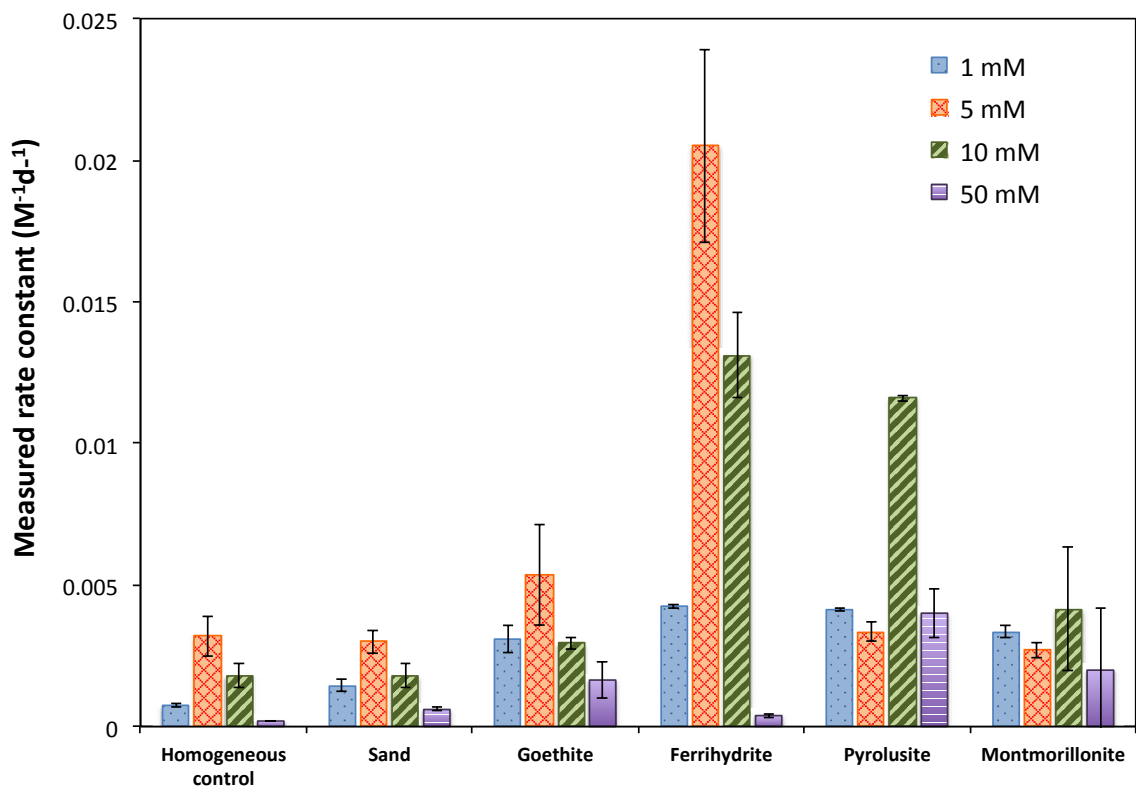
**Figure S1** XRD spectra of synthesized goethite  $\alpha$ -FeOOH. The XRD spectra confirmed that the synthesized particles are pure goethite.



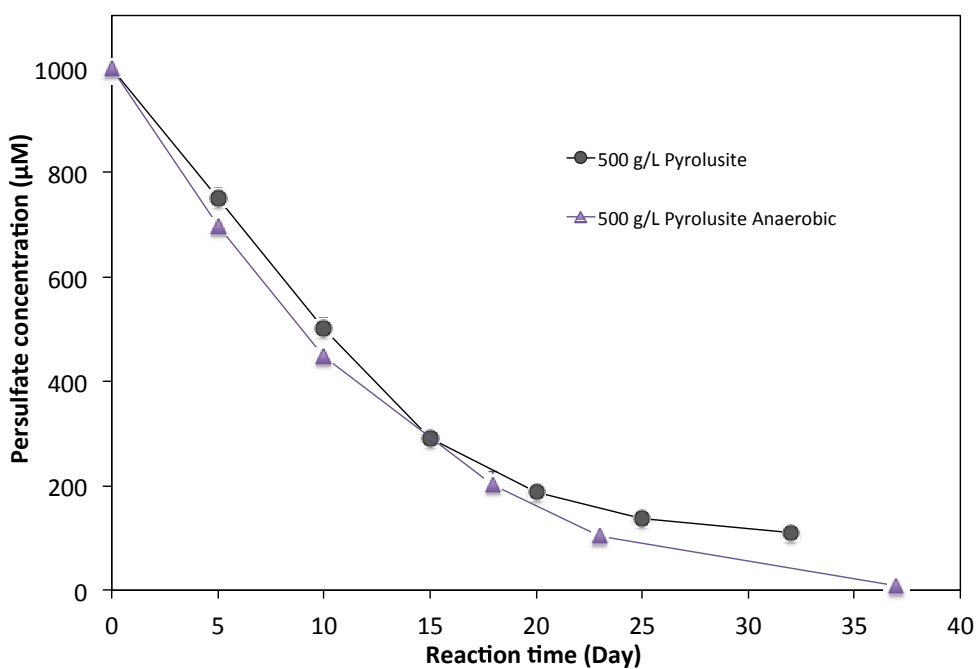
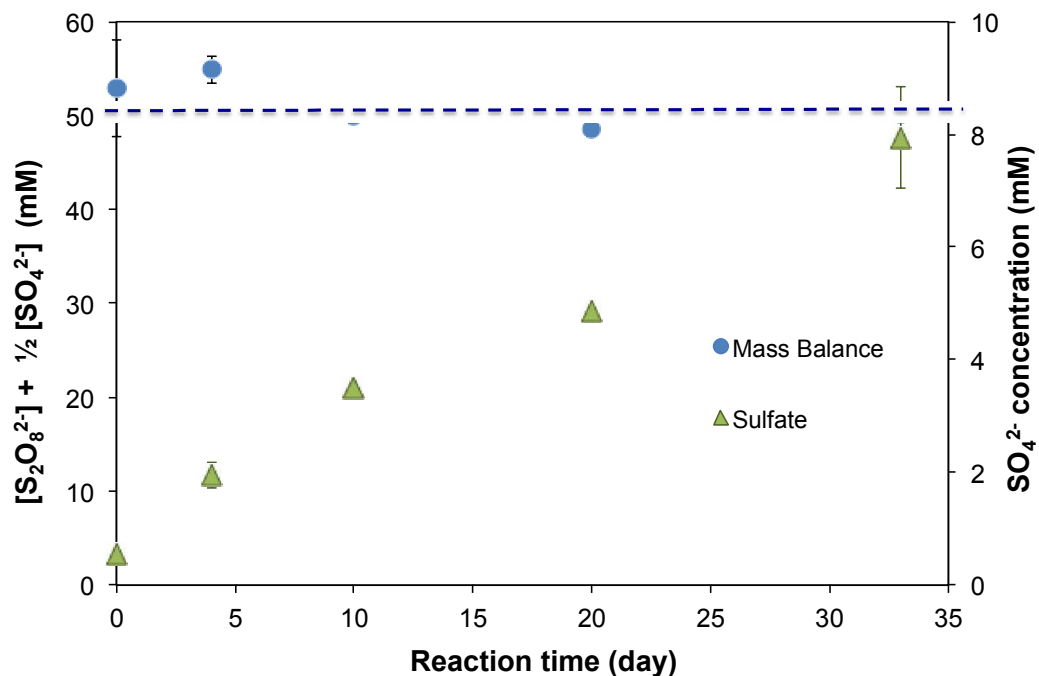


**Figure S2** Stability of persulfate in the presence of different mass loadings of silica. In contrast to accelerated persulfate decomposition with increasing Fe- and Mn-containing minerals, persulfate was stable in the presence of silica at varying mass loadings.

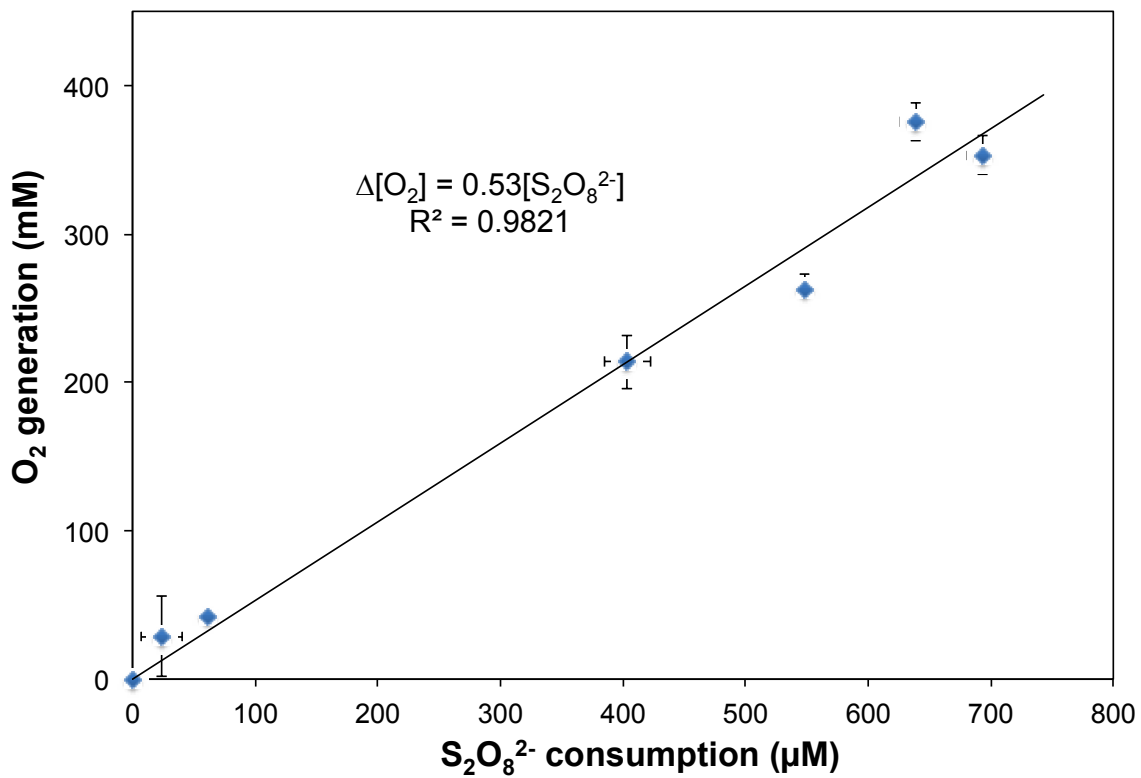
Persulfate 1 mM, pH 8.0, ionic strength 55 mM.



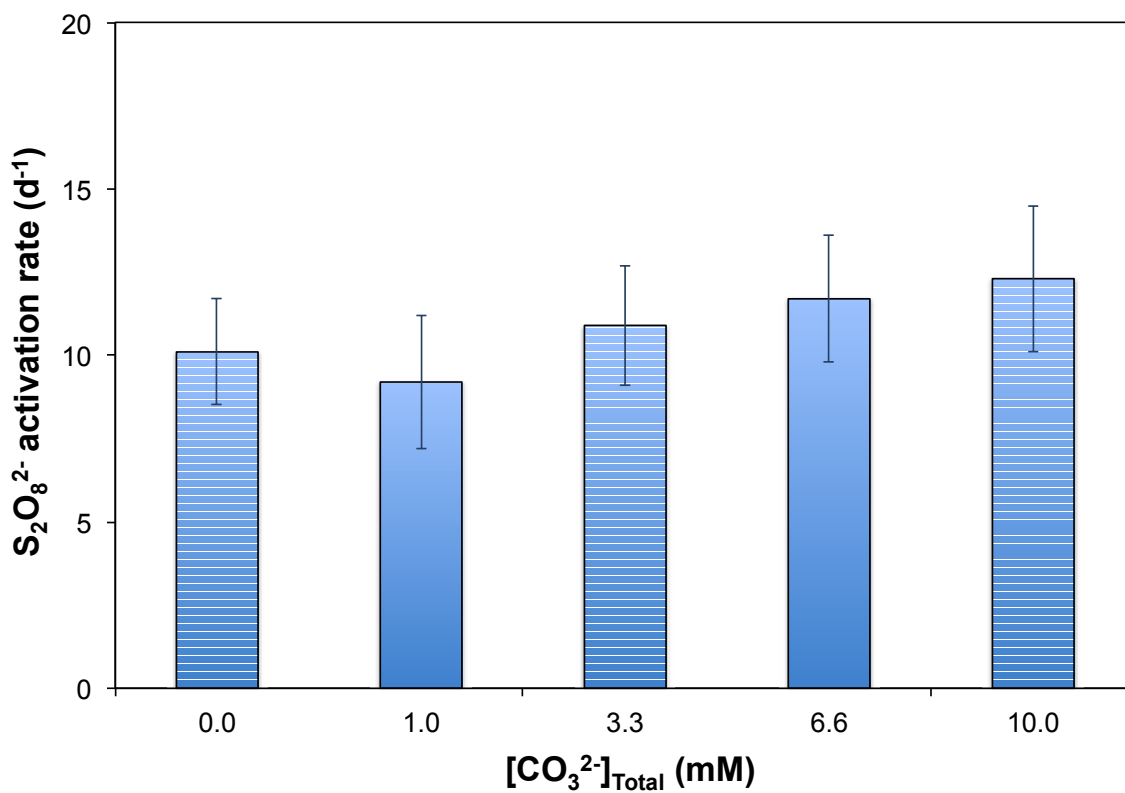
**Figure S3** Persulfate loss in homogeneous system. Solid mass loading is 50 g/L, pH 8.0.



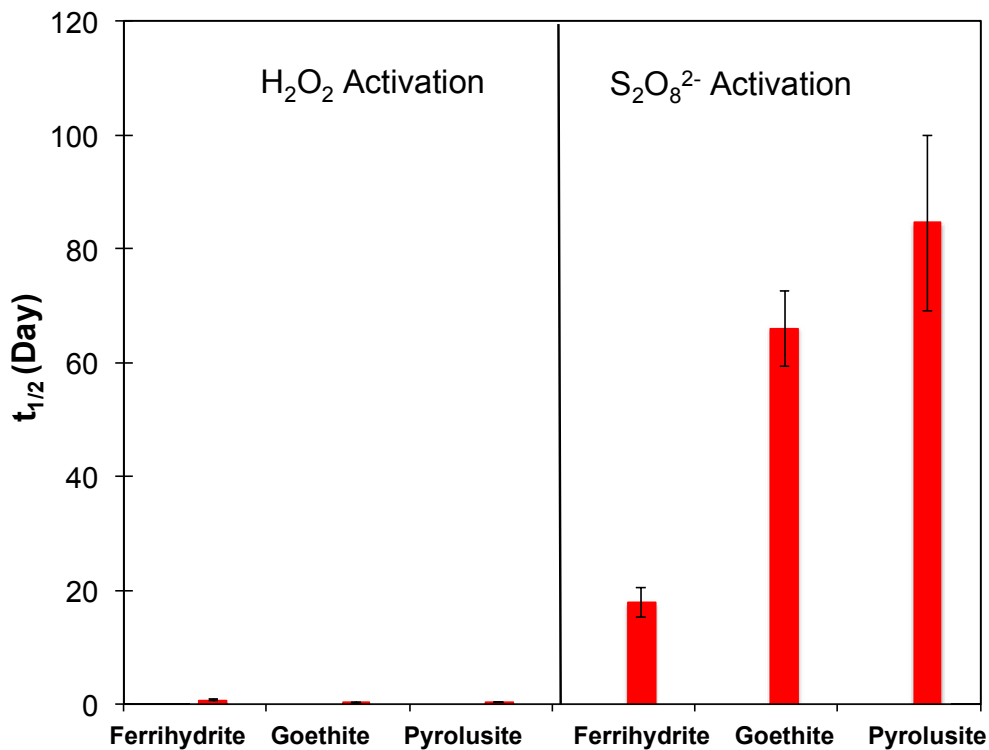
**Figure S4** (A) Formation of sulfate during the decomposition of persulfate by aquifer solids and the mass balance on sulfate species. Initial persulfate concentration 50 mM, aquifer solid concentration 500 g/L, pH 8.0. (B) Comparison of persulfate decomposition rate during pyrolusite activation both in the presence and absence of oxygen.



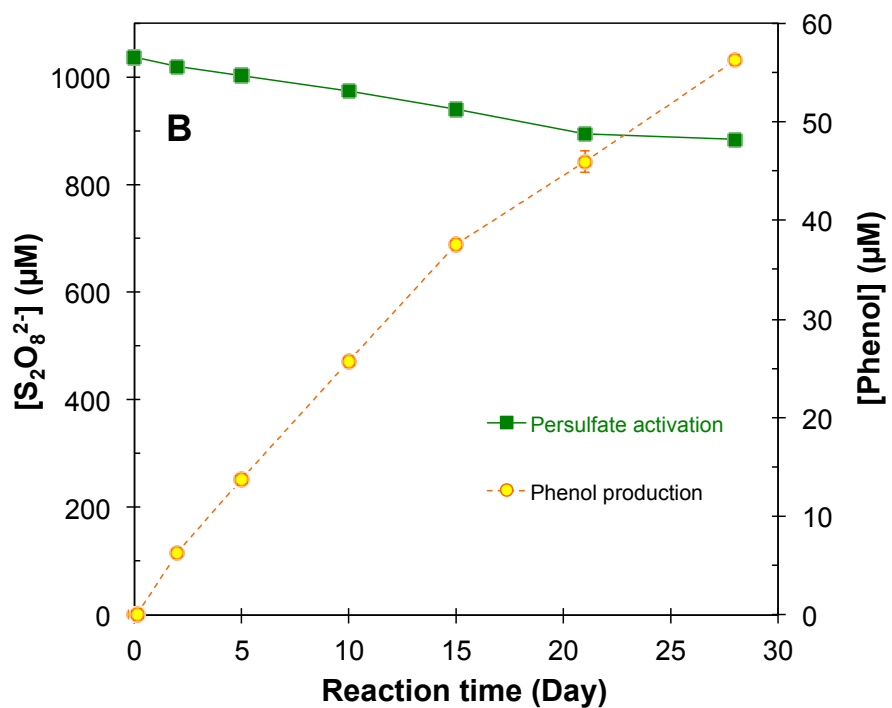
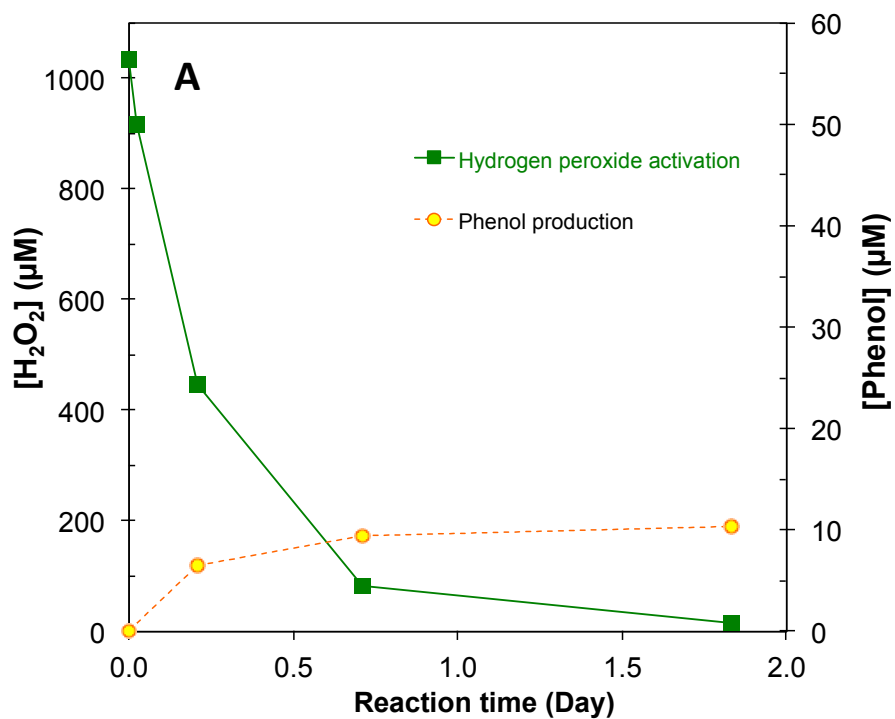
**Figure S5** Correlation between dissolved oxygen generation and persulfate consumption during decomposition by pyrolusite under anaerobic conditions.



**Figure S6** Impact of carbonate concentration on persulfate stability and reaction rate in pyrolusite system. Initial persulfate concentration 1 mM, initial benzene concentration 1 mM, pyrolusite 50 g/L, pH 8.0.



**Figure S7** Comparison of half-lives of persulfate vs. hydrogen peroxide (Fenton system) in the presence of different pure minerals. Initial persulfate or hydrogen peroxide concentration was 1 mM. Initial benzene concentration=1 mM. Mineral concentration=50 g/L, pH=8, with 50 mM borate buffer.



**Figure S8** Formation of phenol in systems with hydrogen peroxide and persulfate, respectively. Initial oxidant concentration 1 mM; initial benzene concentration 1 mM; pH 8.0. (A) Hydrogen peroxide; (B) persulfate.