Supplementary Material for

Synthesis of ferrate (Fe(VI))-coated sand for stabilized reactivity and enhanced treatment of phenol

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12 pages
experimental description
1 table
13 figures
references

1 **Text S1. Synthesis of potassium ferrate**

2   The potassium ferrate (K_2FeO_4) solution was prepared via the wet oxidation process

3 following a method adapted from Guan et al.[1] A saturated solution of 13 M KOH was prepared,

4 chilled and stored at 4 °C throughout the synthesis to maintain cold temperature conditions.

5 Approximately 15 g of $CaOCl_2$ was added to 25 mL of the saturated KOH solution. The mixture

6 was stirred for 30-60 min and filtered using a Whatman glass microbore filter (grade GF/A)

7 paper to obtain a yellow solution of potassium hypochlorite. An additional 20 mL of the

8 saturated KOH was added to the yellow filtrate, and the mixture was placed in an ice bath for 20-

9 30 min to precipitate potassium chloride. The potassium chloride suspension was further filtered

10 with a GF/A filter paper. Then, 8 g of pulverized ferric nitrate was added slowly and in small

11 portions to the filtrate solution under cooling conditions (5 °C) to form K_2FeO_4. A VWR

12 recirculating chiller was used to maintain the temperature of the K_2FeO_4 throughout the

13 synthesis. The generated solution of K_2FeO_4 was stirred for an hour before the addition of 6 g of

14 KOH. The mixture was stirred for 20 min and left to cool for 40 min. Then the solution was

15 centrifuged at 4000 rpm for 10 min. The supernatant solid was discarded and the solid frozen at -

16 80 ˚C for 1 hr. The frozen solid was added to 50 mL of 3 M KOH solution pre-chilled at 4 ˚C.

17 The mixture was shaken until the K_2FeO_4 solid thawed and dissolved in the KOH solution. The

18 mixture was filtered into 150 mL of the saturated 13 M KOH solution and placed in an ice bath.

19 The filtrate solution was left in the ice bath until solid particles started precipitating, then the

20 filtrate was filtered. The solid K_2FeO_4 precipitate was washed subsequently with pentane (~250

21 mL), methanol (~ 100 mL) and dichloromethane (~20 mL). The final product was dried at 65 ˚C

22 for 4 hrs and stored in a desiccator for future uses. The purity of the Fe(VI) was determined as

23 described in Text S2 below.

24   Fe(VI) stock solution was freshly prepared in 10 mM borate buffer (pH 9) and used

25   within 15 min of preparation to minimize Fe(VI) self-decay.

26   **Text S2. Quantification of Fe(VI) purity**

27   The purity of Fe(VI) in the K2FeO4 powder was determined by measuring a K2FeO4 powder

28   and dissolving in 5 mM Na_2HPO_4/1 mM $Na_2B_4O_7$ solution (pH 9.25). The Fe(VI) concentration

29   was determined using the absorbance at 510 nm. This purity of Fe(VI) is then determined as the

30   ratio of calculated Fe(VI) concentration to the theoretical measured K_2FeO_4 powder

31   concentration. The purity of Fe(VI) in the K2FeO4 was estimated at approximately 88%.

32   The purity of Fe(VI) in the Fe(VI)-coated sand was also evaluated. This was achieved by

33   taking an aliquot of K_2FeO_4 slurry obtained prior to sand addition and freeze-drying it. The dry

34   product obtained was then used as K_2FeO_4 powder for purity calculation and the Fe(VI) purity

35   was estimated at 8-9%.

36   **Text S3. Quantification methods of aqueous Fe species**

37   Aqueous Fe(VI) was measured using the ABTS colorimetric method.[2] Fe(VI) samples

38   were reacted with 1.82 mM ABTS buffered at pH 4.2 with a 0.6 M acetate, 0.2 M phosphate

39   buffer.[2] The absorbance of the mixture was determined at 415 nm and used to calculate Fe(VI)

40   concentration.

41   Aqueous total Fe was determined using inductively coupled plasma – optical emission

42   spectrophotometer (ICP-OES). Samples taken throughout the study for total Fe analysis were

43   either in a buffer (i.e., 10 mM borate or phosphate) or in a 1% HNO_3 solution. The buffered

44   samples were acidified with 1% HNO_3 before analysis. An internal standard solution of 100 µg/L

45   yttrium in 1% HNO_3 was added to all samples before analysis to normalize changes in Fe signals

46   from the ICP-OES.

47   The measured aqueous Fe(II) concentration was determined using the colorimetric

48 ferrozine method.[3] Samples taken during Fe leaching tests and organic compound removal

49 experiments were reacted with 0.01 M ferrozine prepared in 0.1 M ammonium acetate. The

50 absorbance of the mixture was measured at 562 nm. Fe(III) can also react with ferrozine to form

51 the Fe-ferrozine complex with absorbance at 562 nm,[3,4] thus the samples were further reduced by

52 addition of 1.4 M hydroxylamine hydrochloride in 2 M HCl,[3] and buffered at pH 9.5 with 10 M

53 ammonium acetate[3] for accurate analysis of Fe(II).

54   The aqueous Fe(III) concentration was determined using the colorimetric KSCN method.

55 Fe(III) reacts with KSC to form a ferric thiocyanate complex.[5] Samples taken during Fe leaching

56 tests and organic compound removal experiments were reacted with 0.2 M KSCN and measured

57 at 476 nm with the UV-Vis spectrophotometer.

58 **Text S4. Choice of buffer**

59   The influence of buffering ions on the oxidation of PMSO by Fe(VI)-coated sand was

60 investigated using 10 mM Na_2HPO_4/NaH_2PO_4 and 10 mM $Na_2B_4O_7$ buffers at pH 9. A dose of 2

61 g/L Fe(VI)-coated sand was added to the buffer solutions containing PMSO (700-740 µg/L) and

62 the mixture was reacted for 1 hr. A 2 mL aliquot was taken at different sampling times and

63 quenched with 20 µL of 500 mM Na_2SO_3 then filtered with 0.2µm, 25 mm diameter cellulose

64 acetate (CA) syringe filters to measure residual PMSO and $PMSO_2$ using high performance

65 liquid chromatography (HPLC) methods.

66 **Text S5. HPLC Method**

67   The concentrations of phenol, PMSO and $PMSO_2$ were quantified using a Dionex

68 Ultimate 3000 HPLC equipped with a diode array detector and an Ascentis® C18 column (2.1

69 mm x 15 cm, 3 µm). The mobile phase was 0.1% formic acid in water (A) and acetonitrile (B).

70 The compounds were separated in an isocratic mode of elution at 75% of 0.1% formic acid in

71 water and 25% acetonitrile. The injection volume was 50 µL and the flow rate was 0.2 mL/min.

72 The wavelength for each compound is given below.

73 **Table S1.** Wavelengths used for HPLC analysis of organic compounds.

Compounds	Wavelength (nm)	Retention time (min)
Phenol	271	8.99±0.12
PMSO	230	4.46±0.01
$PMSO_2$	265	7.64±0.08

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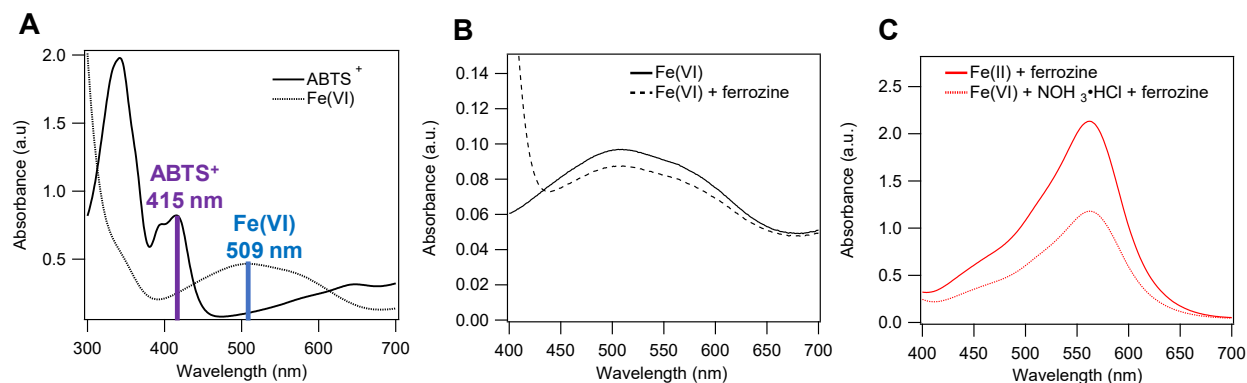
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76 **Figure S1.** Spectroscopic characterization of the Fe(VI)-coated sand. (**A**) UV-vis absorbance

77 spectra of Fe(VI) leached from the Fe(VI)-coated sand (dashed line) and reacted with ABTS

78 (solid line). (**B**) UV-vis absorbance of Fe(VI) leached from the media (solid line) and reacted

79 with ferrozine (dashed line). (**C**) UV-vis absorbance of Fe-ferrozine complex formed with Fe(II)

80 chloride (straight line) and with reduction of Fe(VI) (dashed line).

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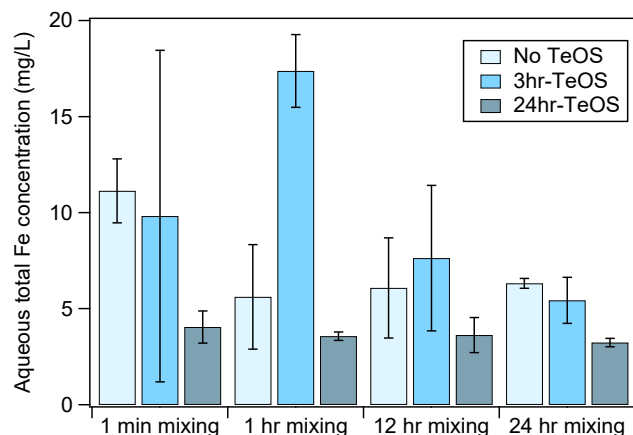
Figure S2. Total aqueous Fe concentration after 1 g/L Fe(VI)-coated sand was stirred in 1%

HNO$_3$ for 1 min, 1 hr, 12 hrs and 24 hrs. The Fe(VI)-coated sand was prepared with virgin sand

(no TeOS), 3hr-TeOS sand, and 24hr-TeOS sand.

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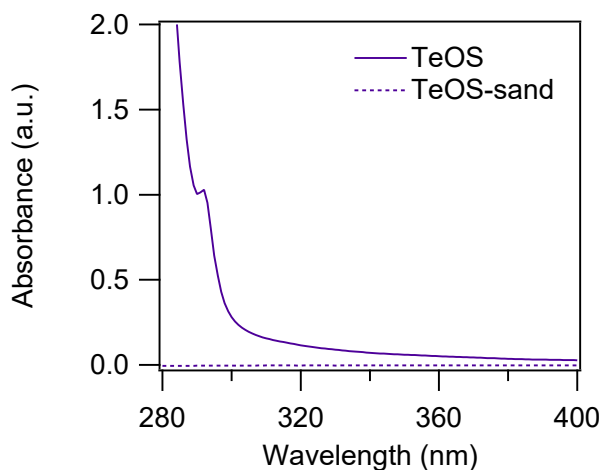
**Figure S3.** Spectroscopic analysis of TeOS stability on TeOS-coated sand. The UV-Vis

spectrum of the supernatant of 1 g/L TeOS-coated sand (dashed line) placed in 10 mM borate

buffer and sonicated was compared to the UV-Vis spectrum of TeOS (4 mL solution). The

absence of a peak at 292 nm in the spectrum of the TeOS-sand indicates that TeOS did not leach

from the TeOS-coated sand surface.

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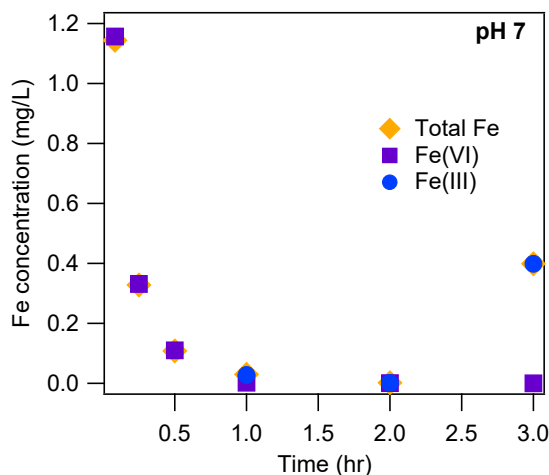
Figure S4. Kinetics of Fe(VI), Fe(III) and total Fe leached from 1 g/L Fe(VI)-coated sand into a
10 mM $Na_2B_4O_7$ solution at pH 7 as a function of time. Total Fe refers to the total Fe leached
into solution at a given time.

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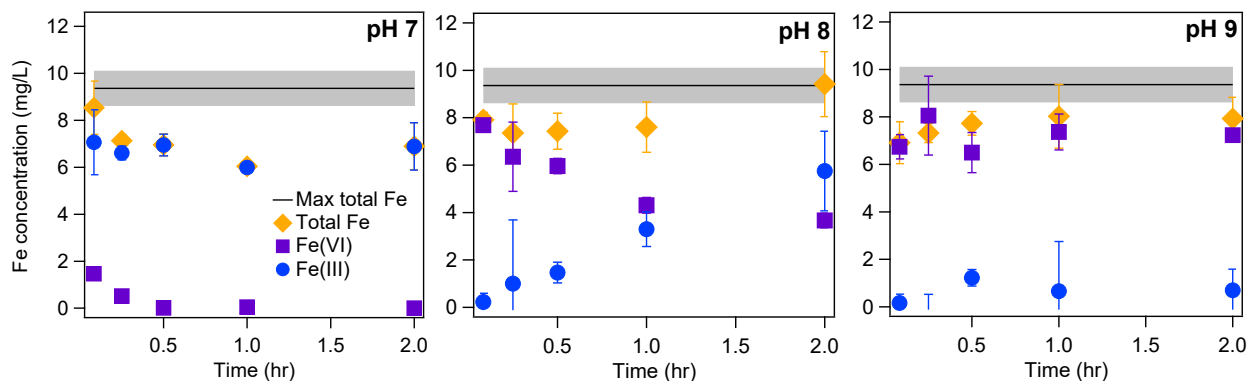
Figure S5. Kinetics of Fe(VI), Fe(III) and total Fe leached from 1 g/L Fe(VI)-coated sand with
3hr-TeOS sand modification into a 10 mM Na_2HPO_4/NaH_2PO_4 solution at pH 7, 8, 9 as a
function of time. Max total Fe refers to the maximum mass of Fe that would leach of the surface
of Fe(VI)-coated sand. This was determined by mixing 1 g/L Fe(VI)-coated sand into 1% HNO_3
and measuring total Fe in solution. Total Fe refers to the total Fe leached into solution at a given
time.

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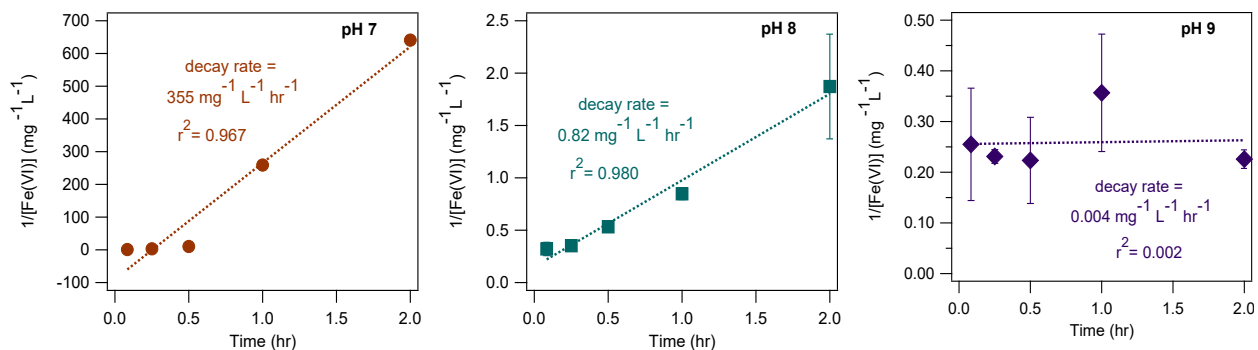
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107 **Figure S6.** Decay kinetics of aqueous Fe(VI) from 1 g/L Fe(VI)-coated sand in a 10 mM 10 mM

108 $Na_2B_4O_7$ at pH 7, 8, and 9. r^2 denotes the correlation coefficient of the fitted linear regression
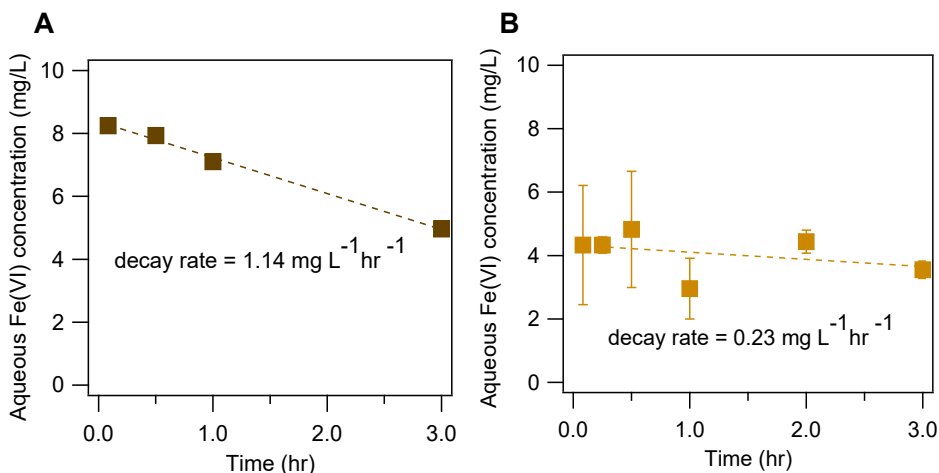
109 curve.

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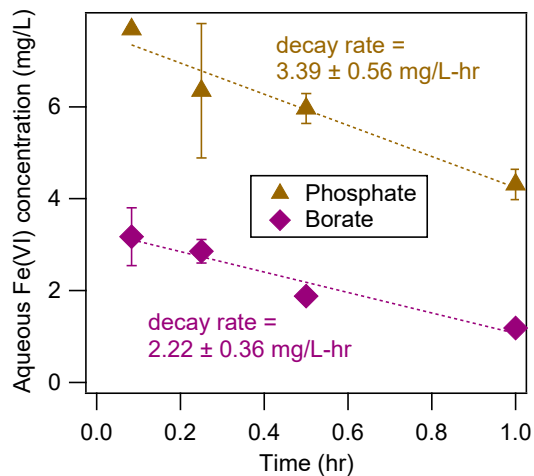
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112 **Figure S7.** Aqueous Fe(VI) concentration leached from 1 g/L Fe(VI)-coated sand in a 10 mM

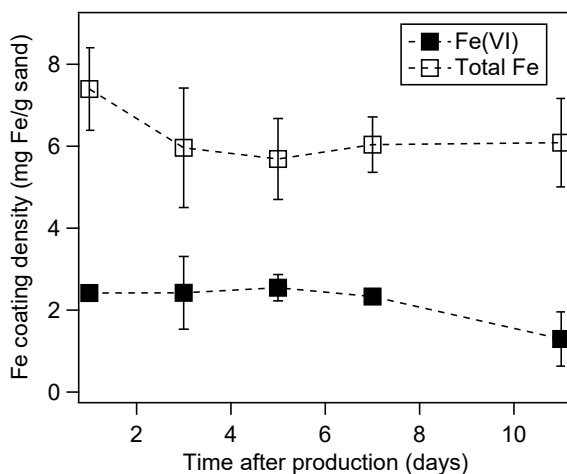113 Na_2HPO_4/NaH_2PO_4 and 10 mM $Na_2B_4O_7$ solution at pH 8.

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A

B

Figure S8. Decay of Fe(VI) in (A) 0.21 g/L K_2FeO_4 powder and (B) 1 g/L Fe(VI)-coated sand. The 0.21 g/L initial concentration of K_2FeO_4 was chosen to obtain a concentration of Fe(VI) that will be equivalent to the concentration of total Fe in the Fe(VI)-coated sand system.
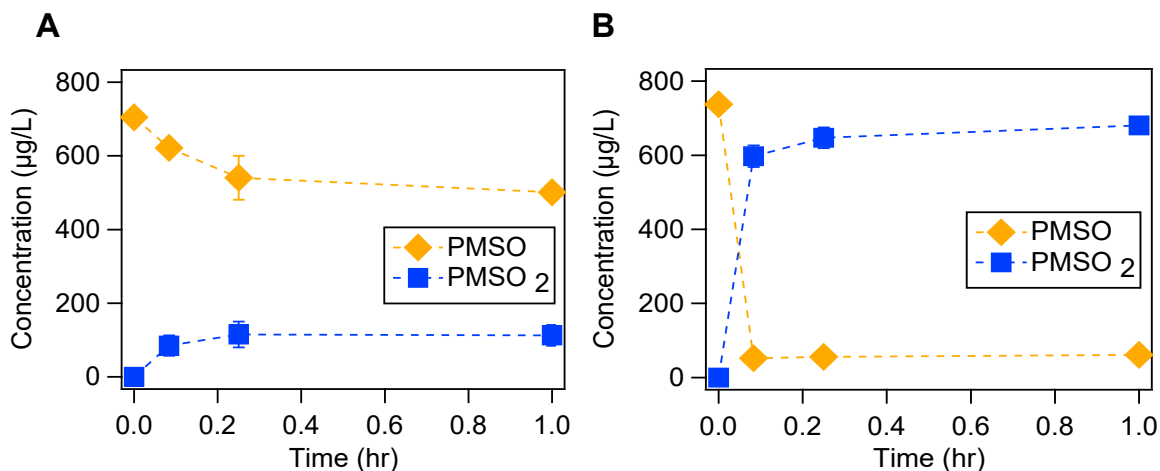

Figure S9. Total Fe and Fe(VI) coating mass leached from Fe(VI)-coated sand surface as a function of time. 3 g/L Fe(VI)-coated sand was mixed with 1% HNO_3 for the total Fe measurement. For the Fe(VI) coating mass determination, 3 g/L Fe(VI)-coated sand was mixed with 5 mM Na_2HPO_4/1mM NaB_4O_7 buffer.
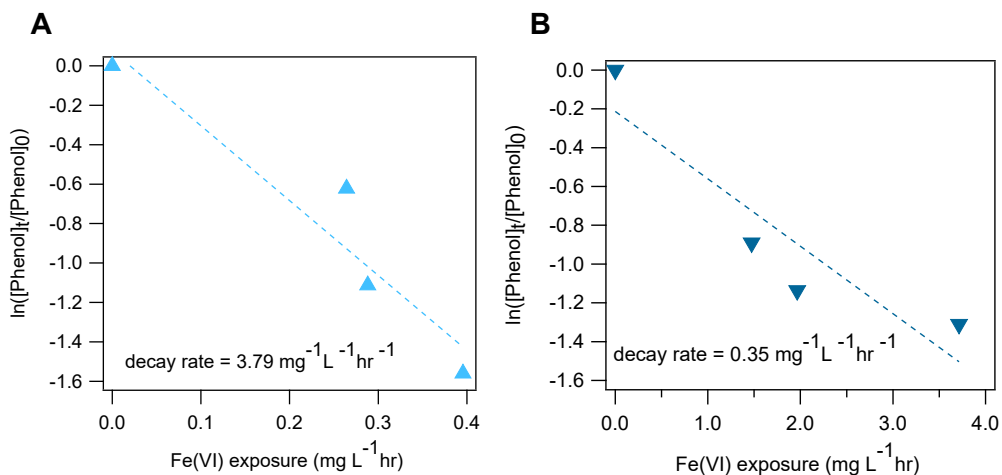
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Figure S10. Oxidation of PMSO to $PMSO_2$ by 2 g/L Fe(VI)-coated sand in (A) 10 mM phosphate buffer and (B) 10 mM borate buffer at pH 9. The initial PMSO concentration was 705±20 µg/L PMSO in the phosphate buffer and 738±14 µg/L PMSO in the borate buffer.
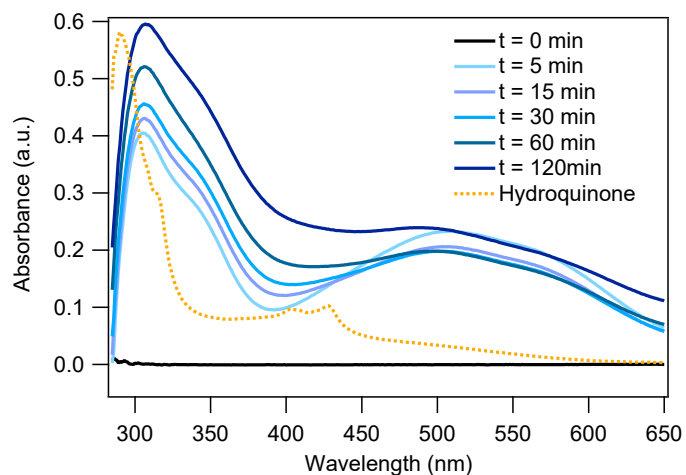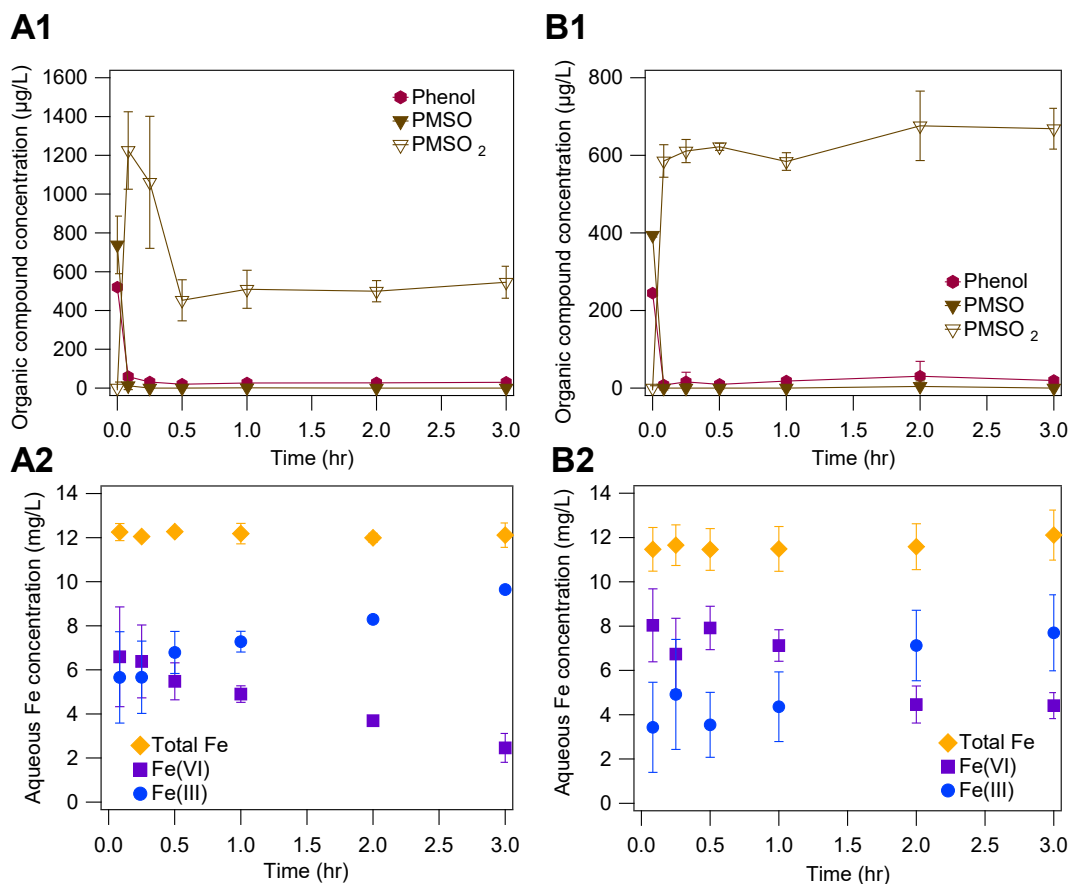

Figure S11. Linear fitting of the reaction kinetics of 219±12 µg/L phenol and (A) 12.6 mg/L Fe(VI) powder and (B) 2 g/L Fe(VI)-coated sand in 10 mM borate buffer pH 9.

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135 **Figure S12**. UV-Vis scans of 219±12 µg/L phenol reacted with 2 g/L Fe(VI)-coated sand in 10

136 mM borate buffer pH 9 measured at various time intervals within the 120-min and a

137 hydroquinone blank solution.

Figure S13. (**Row 1**) Degradation of phenol and oxidation of PMSO at different concentrations (**A**. 520±8.1 µg/L phenol and 739±148 µg/L PMSO; **B**. 245±3.0 µg/L phenol and 394±4.7 µg/L PMSO) by 2 g/L Fe(VI)-coated sand and (**row 2**) the corresponding changes in aqueous Fe concentrations.

References
1. W. Guan, Z. Xie and J. Zhang, *J. Spectro.*, 2014, **2014**, 1-8.
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