

SUPPORTING INFORMATION

The Impact of Peroxydisulfate in the Presence of Zero Valent Iron on the Oxidation of Cyclohexanoic Acid and Naphthenic Acids from Oil Sands Process-Affected Water

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Environmental Science & Technology

Date: July 13, 2012

Number of Pages (including cover page): 11

Number of Figures: 7

Analysis of NAs using High-Resolution Mass Spectrometry (HRMS)

An Acquity ultra-pressure liquid chromatography (UPLC) System (Waters, MA, USA) was used for the analysis of NAs from OSPW. The UPLC system was coupled with a high-resolution mass spectrometer (~ 10,000 resolutions) QSTAR Pulsar equipped with a Turbolon Spray source (Applied Biosystem/ MDS Sciex, Concord, ON, Canada) operating in negative mode.

Before analysis, samples were centrifuged at 10,000 RPM (9600 RCF) for 5 min to separate the suspended solids. After that, supernatant was diluted at a 1:1 ratio in methanol. Tetradecanoic acid-1-¹³C (C₁₄H₂₈O₂) was added to each sample (0.2 µg/mL) as an internal standard in order to correct for drift of sensitivity and retention time.

An Acquity UPLC phenyl BEH column (150×1 mm, 1.7 µm) was used for the separation of OSPW NAs. The mobile phase consisted of 10 mM ammonium acetate in a 50% methanol and 50% acetonitrile solution (A) and 10 mM ammonium acetate in an aqueous solution (B). The initial concentration of solution A was 1%, and after 2 min it was rapidly ramped to 60% A over 3 min, then to 70% A over 7 min, and finally to 95% A over 13 min. The 95% concentration of A was held for the next 14 minutes. The column was equilibrated in 1 % A for 5.8 minutes before the next injection. The flow was 0.100 mL/min and the column temperature was 50 °C. During the analysis, blank samples were injected to assess the background as well as any carry-over. The concentration of NAs was determined based on the relation of the relative chromatographic peak area of each analyte to the internal standard by single point calibration. Detailed methodology for the analysis of NAs can be found in an earlier publication¹.

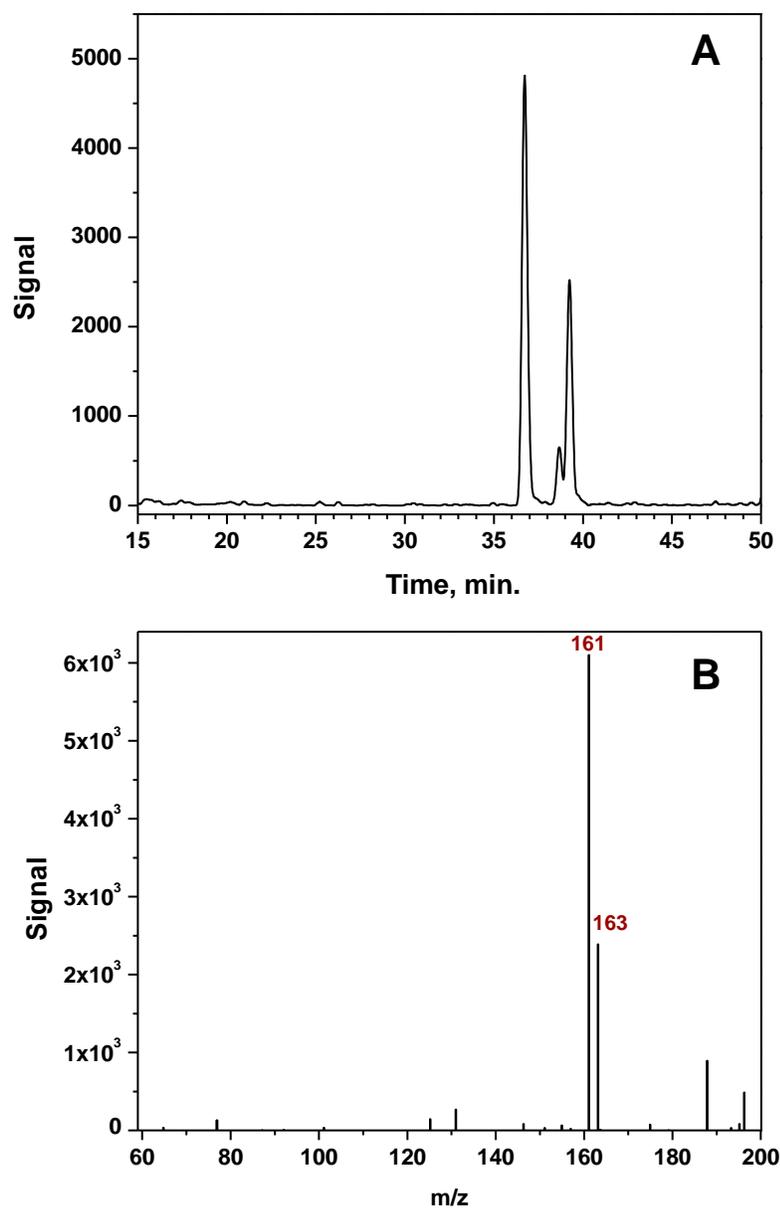


Figure S1. Formation of chloro-CHA after treatment with ZVI and 2000 mg/L $S_2O_8^{2-}$ in the presence of 500 mg/L chloride for 6 days at 20 °C. (A) chromatogram of by-products at m/z 161, (B) spectrum of chloro-CHA.

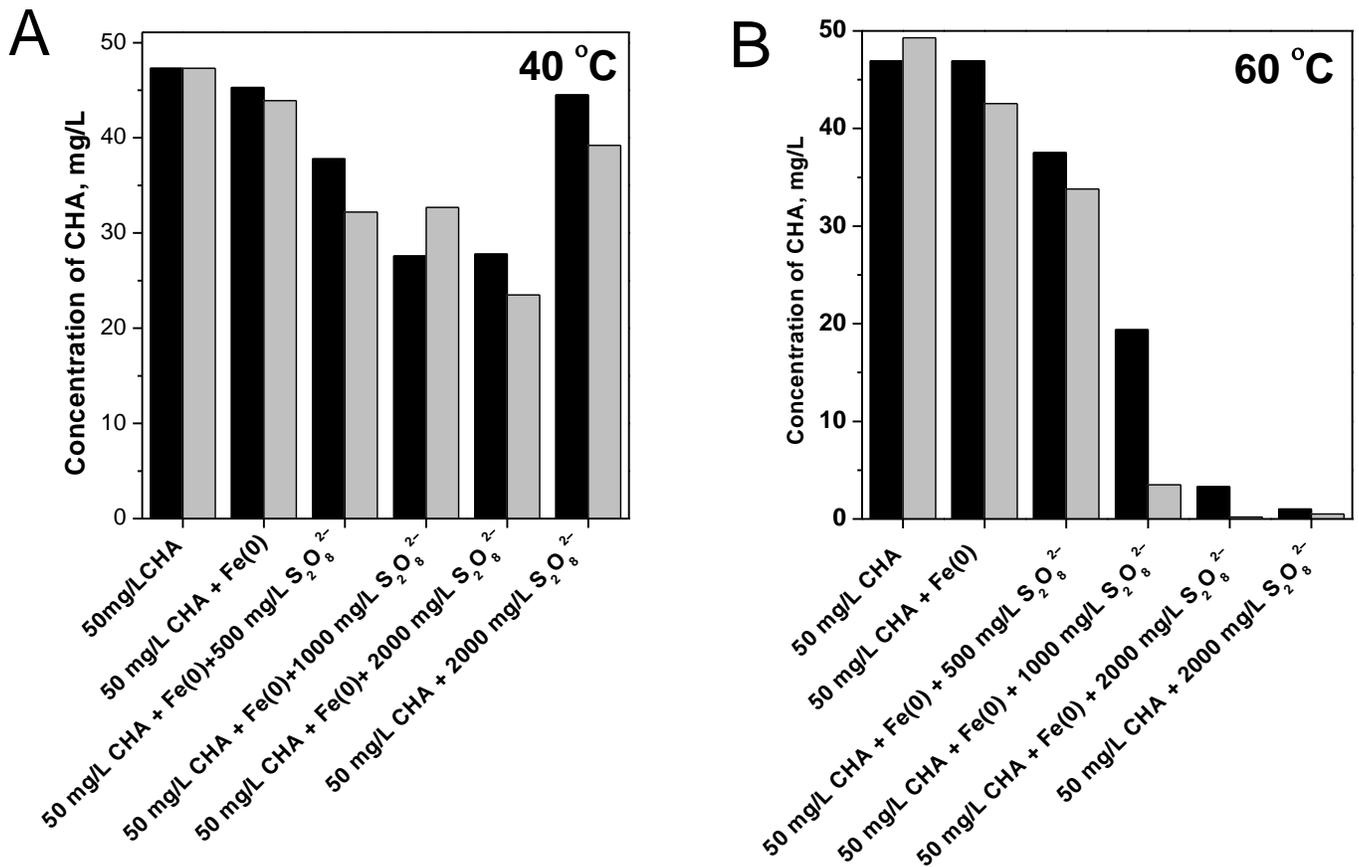
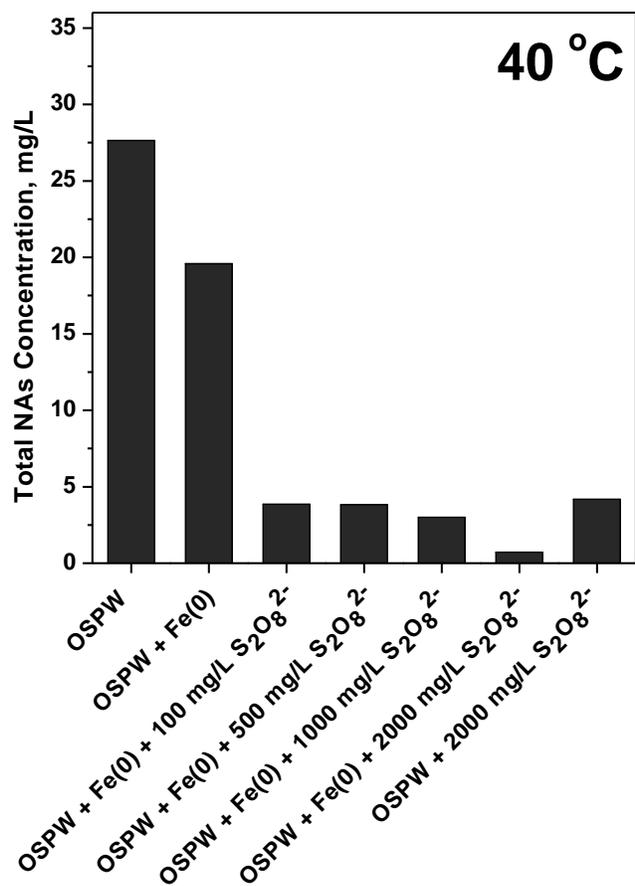


Figure S2. Removal of CHA after treatment with S₂O₈²⁻/ZVI for 2h at (A) 40 °C and (B) 60 °C, in absence (black bar) and presence of 500 mg/L chloride (grey bar).

A



B

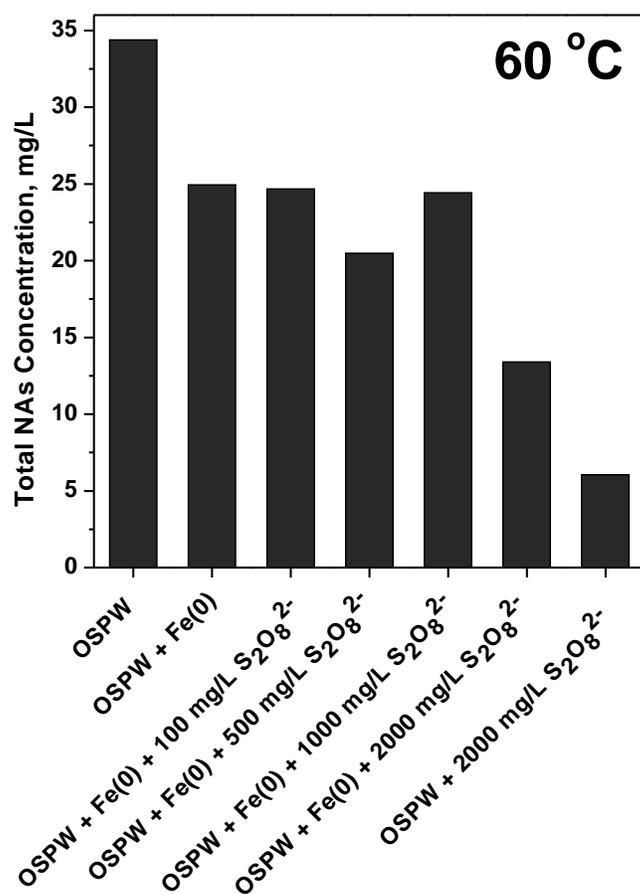


Figure S3. Removal of NAs from OSPW by S₂O₈²⁻/ZVI after 2 hours at (A) 40 °C and (B) 60 °C.

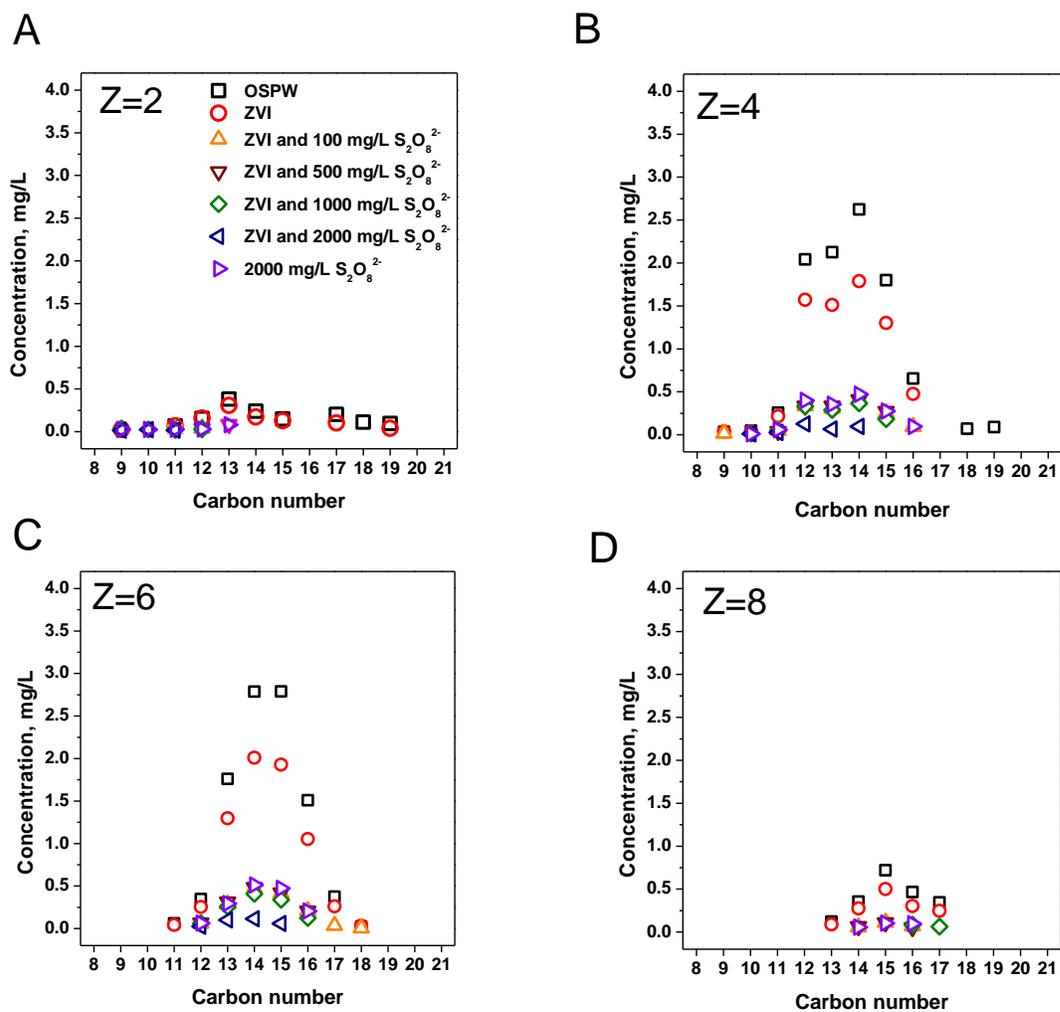


Figure S4. NAs signatures before and after the treatment of OSPW with $S_2O_8^{2-}$ /ZVI for 2 hours at 40 °C. Z is the number of rings in the structure.

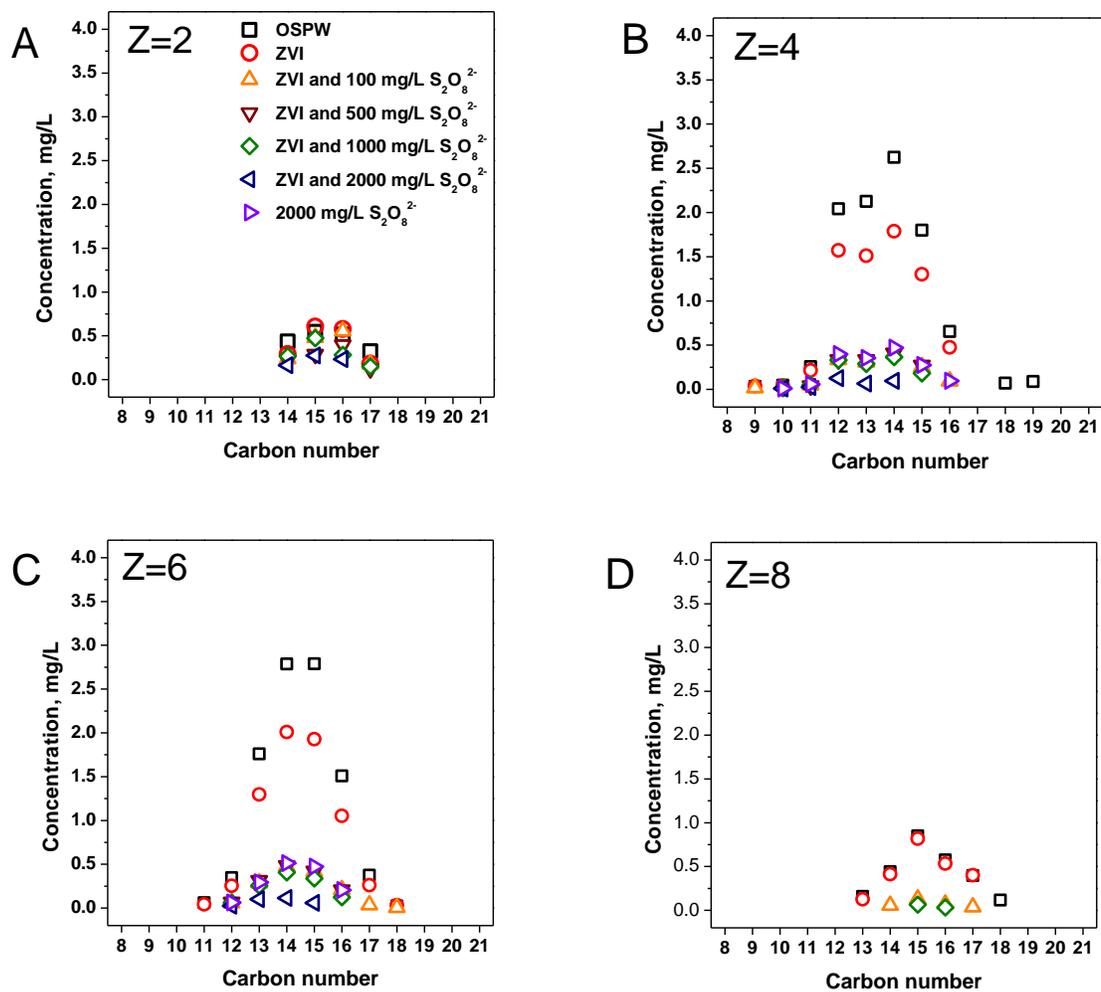


Figure S5. NAs signatures before and after the treatment of OSPW with $S_2O_8^{2-}$ /ZIV for 2 hours at 60 °C. Z is the number of rings in the structure.

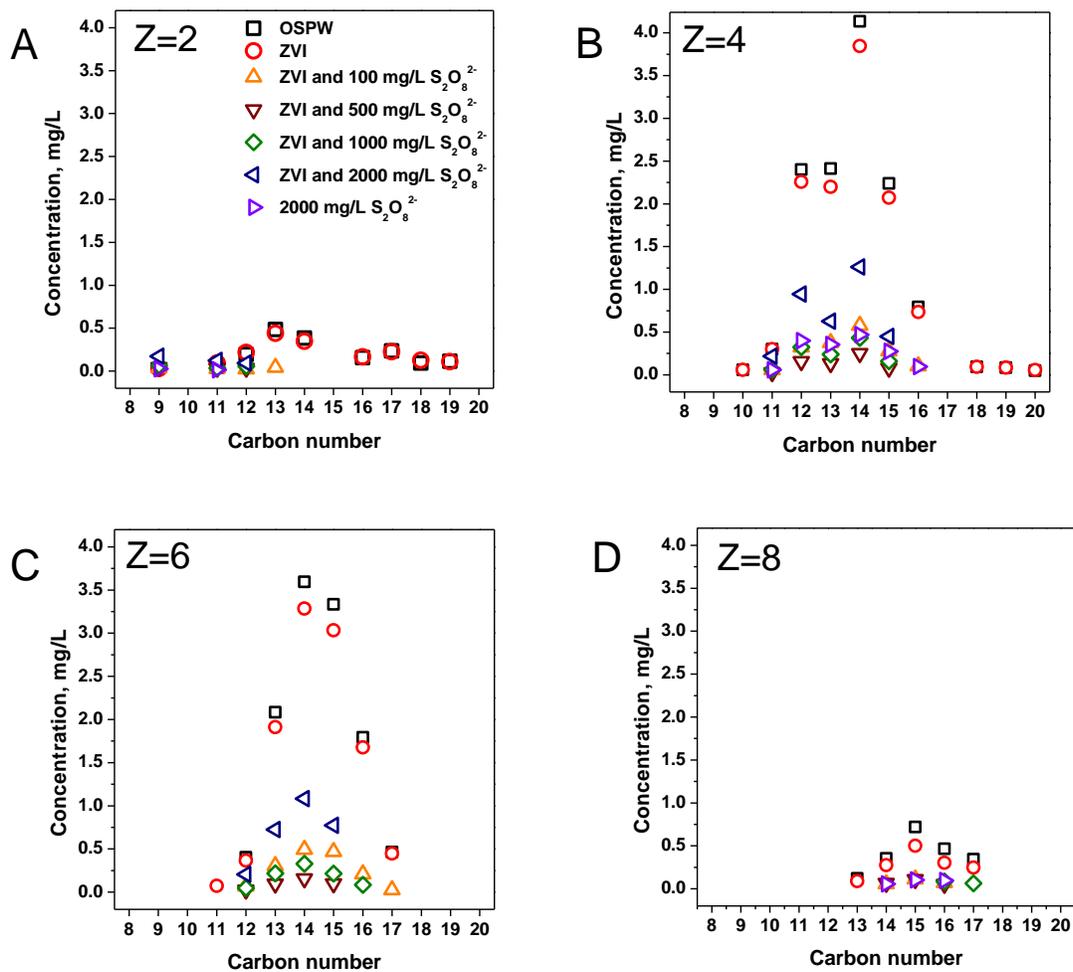


Figure S6. NAs signatures before and after the treatment of OSPW with $S_2O_8^{2-}$ /ZIV for 2 hours at 80 °C. Z is the number of rings in the structure.

X-Ray Photoelectron Spectroscopy (XPS) Surface Analysis of ZVI after the Process

The elemental composition of ZVI surface layer after the treatment at 20 °C was determined by an X-ray photoelectron spectrometer (XPS) (Kratos Axis 165, Kratos Analytical, Japan) equipped with a monochromatic AlK α source ($h = 1486.6$ eV) operating at below 3×10^{-8} Pa. ZVI was filtered out from solution on 0.45 μm nylon filter (Supelco, Massachusetts, USA), and then dried completely by washing with anhydrous ethanol. The ZVI samples were stored in anhydrous ethanol prior analysis. The data were further analyzed using CasaXPS software (Ver. 2.3.15, Casa Software Ltd.) and the determined binding energies (E_b) were compared with the referenced E_b from the National Institute of Standards and Technology database (NIST) database².

The XPS spectrum revealed the presence of Na, Fe, O, and C atoms with the atomic concentrations of 1.28%, 27.13%, 49.95%, and 21.64%, respectively. The survey XPS spectrum on Fe2p region (Figure S7A) showed that the main peak with the E_b of 710.5 eV was attributed to Fe (III). The broad peak at 723.7 eV suggested the presence of FeOOH and/or Fe₂O₃. The characteristic peak of metallic iron at 707.2 eV was not found on the spectrum.

In C1s region were found three carbon peaks (Figure S7B). The peak at E_b of 284.8 eV was attributed to the single bond between carbons. The peak at E_b of 286.5 eV was attributed to C-O bond. The peak at the E_b of 289.0 eV was attributed to C in carboxyl group and/or carbonate.

The spectrum of O1s region was resolved into four individual peaks. The first peak at 529.4 eV was assigned to O in O₂⁻. The second peak at 531.5 eV was assigned as O in hydroxides. The third peak at 532.3 eV was assigned to C=O bond in carboxyl group and/or carbonate. The fourth peak at 533.3 eV was assigned to C-O bond.

Together, the results indicated the occurrence of iron oxides and hydroxides, carboxylates and/or carbonates on the surface of ZVI which suggested that the surface of iron particles was extensively oxidized. The results also suggested the occurrence of trace of organic compounds containing aliphatic and carboxylic groups, likely aliphatic carboxylic acids, on the surface.

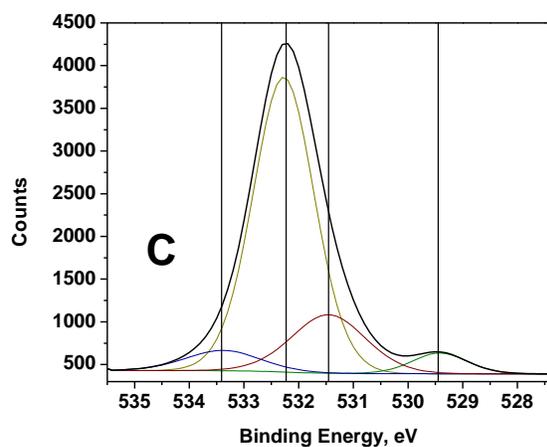
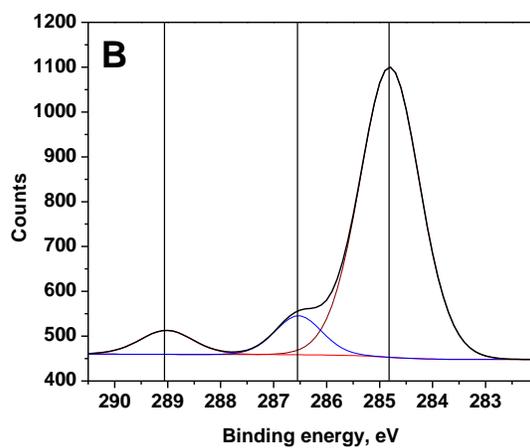
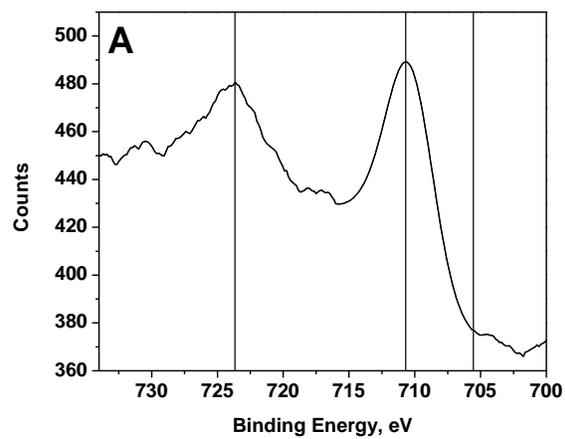


Figure S7. XPS survey spectra on (A) Fe2p, (B) C 1s, and (C) O 1s regions.

References

(1) Pérez-Estrada, L.A.; Han, X.; Drzewicz, P.; Gamal El-Din, M.; Fedorak, P.M.; Martin, J.W. Structure-reactivity of naphthenic acids in the ozonation process. *Environ Sci Technol.* **2011**, *45* (17), 7431-7437.

(2) NIST Standard Reference Database 20 (2012), Version 3.5 C.D. Prepared by Wagner, A. V. Naumkin, A. Kraut-Vass, J. W. Allison, C. J. Powell, and J. R. Rumble: <http://srdata.nist.gov/xps/Default.aspx>