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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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S *Supporting Information*

ABSTRACT: Large volumes of oil sands process-affected water (OSPW) are produced during the extraction of bitumen from oil sands in Alberta, Canada. The degradation of a model naphthenic acid, cyclohexanoic acid (CHA), and real naphthenic acids (NAs) from OSPW were investigated in the presence of peroxydisulfate ($S_2O_8^{2-}$) and zerovalent iron (ZVI). For the model compound CHA (50 mg/L), in the presence of ZVI and 500 mg/L $S_2O_8^{2-}$, the concentration decreased by 45% after 6 days of treatment at 20 °C, whereas at 40, 60, and 80 °C the concentration decreased by 20, 45 and 90%, respectively, after 2 h of treatment. The formation of chloro-CHA was observed during ZVI/$S_2O_8^{2-}$ treatment of CHA in the presence of chloride. For OSPW NAs, in the presence of ZVI alone, a 50% removal of NAs was observed after 6 days of exposure at 20 °C. The addition of 100 mg/L $S_2O_8^{2-}$ to the solution increased the removal of OSPW NAs from 50 to 90%. In absence of ZVI, a complete NAs removal from OSPW was observed in presence of 2000 mg/L $S_2O_8^{2-}$ at 80 °C. The addition of ZVI increased the efficiency of NAs oxidation by $S_2O_8^{2-}$ near room temperature. Thus, ZVI/$S_2O_8^{2-}$ process was found to be a viable option for accelerating the degradation of NAs present in OSPW.

■ INTRODUCTION

In Northern Alberta, Canadian oil, in the form of bitumen, is extracted from oil sands using hot alkaline water.[1] The resulting oil sands process-affected water (OSPW) is highly saline and acutely toxic to aquatic organisms, primarily due to high concentrations of organic acids, termed naphthenic acids (NAs).[2,3] NAs is a general term used to describe a complex mixture of predominantly alicyclic carboxylic acids with smaller amounts of acyclic aliphatic (paraffinic or fatty) acids.[4,5] NAs have the general chemical formula of $C_nH_{2n+Z}O_2$, where n is the number of carbon atoms, and Z is zero or a negative even integer representing the number of hydrogen atoms lost as the structures become more cyclic, or form double bonds.[6]

NAs occur naturally in oil sands and may enter the environment through natural or anthropogenic sources. NAs present in OSPW are persistent and degrade very slowly in OSPW;[7] therefore, techniques for accelerating their degradation are now being investigated.

In a previous study on the decomposition of NAs, by vacuum UV (172 nm) and UV (254 nm)/H_2O_2, it was found that oxo- and hydroxynaphthenic acids could be formed during the reaction of hydroxyl radicals with NAs.[8] Oxygenated NAs (i.e., hydroxy- and oxo-NAs) may be partially responsible for the overall toxicity of OSPW,[2,3,9] thus warranting caution.

Recently, the oxidation of organic compounds by peroxydisulfate ($S_2O_8^{2-}$) has been studied as an alternative to advanced oxidation processes (AOPs). While AOPs make use of highly reactive hydroxyl radicals (E° = 2.7 V), peroxydisulfate decomposes to the sulfate anion radical by heat, UV, ultrasound, or during reaction with Fe^{2+}.[10,11] The sulfate anion radical is an equally powerful oxidant (E° = 2.5–3.1 V) and decomposes compounds which are not very reactive

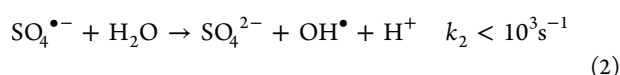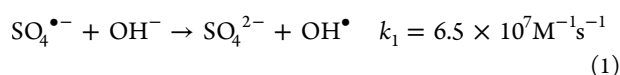with hydroxyl radical, for example, perflourooctanoic acid and cyanuric acid.[12,13] There is also a difference in the formation of byproducts during the reaction of sulfate anion radicals and hydroxyl radicals with aliphatic carboxylic acids. The hydroxyl radical reacts preferably with aliphatic carboxylic acids by H-abstraction at the α-position, whereas the sulfate anion radical leads to decarboxylation, yielding an aliphatic radical.[14] Thus, the sulfate anion radical is a more effective oxidant for oxidizing aliphatic acids as compared to the hydroxyl radical.[14] Despite this alternative mechanism, the sulfate anion radical can also react with hydroxide anion, or water, to form hydroxyl radical (reactions 1, 2), thereby increasing the oxidation potential through both the sulfate anion and hydroxyl radicals' pathways.[15−18]

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^\bullet \quad k_1 = 6.5 \times 10^7 M^{-1} s^{-1} \tag{1}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH^\bullet + H^+ \quad k_2 < 10^3 s^{-1} \tag{2}$$

OSPW contains a high concentration of chloride (around 600 mg/L),[1] which is a well-known hydroxyl radical and sulfate anion radical scavenger.[19] Nonetheless, the resultant chlorine radicals formed during these reactions can also be very effective oxidants of aliphatic carboxylic acids.[14,20]

The uncatalyzed decomposition of peroxidisulfate requires high temperature to rupture the 0−0 bond, with the activation energy being 140.25 kJ.[21] The rate constant for the degradation of peroxidisulfate decreases significantly with decreasing temperature.[22,23] Additionally, at any temperature the observed rate constant increases with decreasing peroxydisulfate concentration (decreasing effect of recombination of sulfate radical to peroxydisulfate) and with decreasing pH.[21] Moreover, the rate constant of the reaction of sulfate radicals with potential scavengers, such as chloride and carbonate, increases with increasing temperature.[22,24] Therefore, the reaction of peroxydisulfate with iron(II) for the generation of sulfate anion radicals is the most preferable for environmental protection applications.[10,25] OSPW is alkaline[1] and iron(II) forms insoluble iron(II) hydroxide under such conditions.[26] The process may show very low efficiency for organic pollutants removal under such conditions due to a very low concentration of available Fe^{2+}. The addition of chelating ligands to improve solubility of iron(II) and the efficiency of the process seems not to have a practical application for water treatment due to the need for the removal of the chelating agent from the treated water.[27]

Joo et al.[28] observed the oxidation of compounds in an aqueous solution when mixed with nanoscale zerovalent iron (ZVI, Fe(0)) particles in the presence of air, and without hydrogen peroxide (H_2O_2). Under oxygen-free conditions, ZVI is used for the reduction of organic compounds,[29] but here it was suggested that Fe^{2+} and H_2O_2 are generated from ZVI by O_2-induced surface corrosion.[30,31] The reaction between Fe^{2+} and H_2O_2 is the well-known Fenton reaction, commonly employed for generating hydroxyl radicals, whereas the oxidation of organic compounds by H_2O_2 in the presence of ZVI particles is an ineffective and slow process.[27] However, it was found that the oxidation of compounds by the use of peroxydisulfate in the presence of nanoscale ZVI particles may have a practical application for water treatment.[10,32,33]

Corrosion of zerovalent iron particles results in a decrease of pH, the formation of akaganeite and lepidocrocite, FeO(OH),

and the mixed Fe-oxide corrosion products, magnetite and maghemite.[29,34] The formation of such minerals facilitates the adsorption of anions on the surface of ZVI particles.[35] Carboxylic acids are also good chelating ligands of iron(II)[27] and the formation of iron−naphthenate complexes may increase the concentration of iron(II) in solutions with high, alkaline pH. Therefore, in the present study it is possible to hypothesize that ZVI may be used as a source of Fe(II) for the generation of sulfate anion radicals from persulfate under alkaline conditions in the presence of NAs. Furthermore, some iron naphthenates (mainly monocarboxylate) are not soluble in water[5,36,37] which may improve the adsorption of NAs on the surface of ZVI, leading to partial removal of NAs from the solution. The decrease of pH during the corrosion process may also reduce the solubility of NAs.[5]

The Fenton process is effective at low pH values (pH between 2 and 4). Hence, the process is inefficient in the pH range of OSPW (about 8.5).[1] Therefore, adjustment of the OSPW pH is required when using Fenton process. Moreover, NAs are mostly insoluble at acid conditions; therefore, the application of Fenton process is not suitable to treat OSPW, because NAs in such conditions will bind to the suspended solids. Additionally, NAs form insoluble salts with iron,[37] confirming the inefficiency of the Fenton process to treat OSPW.

Because OSPW is a very complex mixture of organic and inorganic compounds, model compounds are often used to investigate the degradation and/or removal of NAs under different treatment process.[5] In the present study, to evaluate the behavior of a saturated ring under different treatment processes without the interference of any NAs branching, CHA, which includes one ring and one carboxylic acid group, was used as model NA compound.[8,46] To our knowledge, this is the first study on the application of peroxydisulfate for the removal of NAs from OSPW. The aim of this investigation was to explore the feasibility of applying the $S_2O_8^{2-}$/ZVI process for the removal of NAs using cyclohexanoic acid (CHA). This study also explored the effect of chloride on the formation of byproduct. The results of the study using the model compound (CHA) were compared with those obtained after the treatment of NAs from OSPW by the $S_2O_8^{2-}$/ZVI process.

■ EXPERIMENTAL SECTION

Materials. CHA was of analytical grade purity (99+%) and was purchased from Sigma-Aldrich (Oakville, ON, Canada). All analyte solutions were prepared in ultrapure water (resistivity = 18 MΩ × cm and total organic carbon (TOC) content <0.1 mg/L) prepared with a Millipore ROMilli-Q system equipped with a UV lamp, adjusted to pH 9 with carbonate free 50% sodium hydroxide (ACS purity). ZVI powder was of analytical grade purity (99+%), purchased from Fisher Scientific (Ottawa, ON, Canada). The particle size was below 0.149 mm. Ammonium acetate and methanol were purchased from Fisher Scientific (LC-MS grade). Potassium peroxydisulfate was of analytical grade purity (99+%) and was purchased from Fisher Scientific.

OSPW was collected from an active settling basin on the site of Syncrude Canada Ltd. (Fort McMurray, AB, Canada), known as the West In-Pit (WIP). This tailing pond is constantly receiving process-affected waters, including water used during the bitumen extraction. OSPW contained 500 ± 0.5 mg/L of chloride and its alkalinity was 700 ± 10 mg/L as
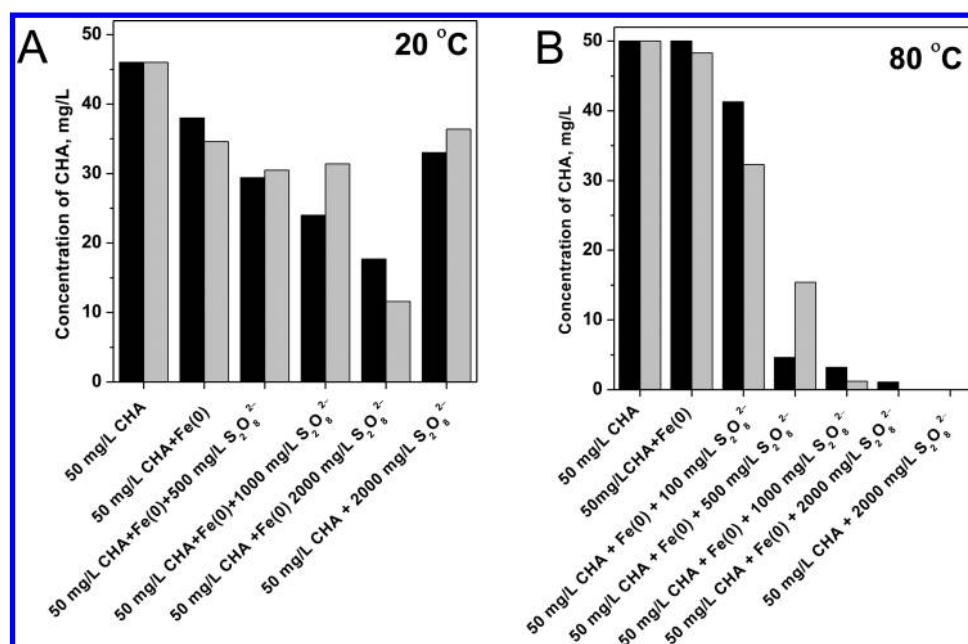
Figure 1. Removal of CHA after treatment with $S_2O_8^{2-}$/ZVI (A) for 6 days at 20 °C, (B) for 2 h at 80 °C, in absence (black bar) and presence of 500 mg/L chloride (gray bar).

calcium carbonate ($CaCO_3$) The pH value of the OSPW was 8.5.

The experiments, at 20 and 40 °C, were carried out in an incubated shaker (Excella, New Brunswick Scientific, Edison, NJ, USA). The investigated solutions were placed in 200-mL Winkler bottles with tight ground stoppers. The volume of the solutions was 100 mL and 20 g of ZVI was used in these experiments. The tests, at 60 and 80 °C, were carried out in a microwave oven (Ethos SEL, Milestone Inc., Shelton, CT, USA). The investigated solutions were placed in 100-mL Teflon bottles with tight screw caps. The volume of the solutions was 50 mL and 10 g of ZVI was used in these experiments.

The bottles used in the experiments were filled to half their nominal volume with sample solutions. To maintain constant oxygen supply, the sample bottles were vigorously shaken during the experiments. Because $S_2O_8^{2-}$/ZVI is a very slow process,[10] in the present study the amounts of reagents were used in excess in order to speed up the NAs oxidation by $S_2O_8^{2-}$/ZVI. Control experiments were conducted to determine the adsorption of CHA onto the surface of the test vessels. The results indicated that small amounts of CHA were lost due to its adsorption onto the vessel surface.

Analysis of CHA. For the analysis of CHA, a high-performance liquid chromatograph (HPLC) coupled to a triple quadrupole mass spectrometer (Varian 1200 L MS/MS) with unit mass resolution was used. The mass spectrometer was equipped with an electrospray interface operating in negative ion mode. The chromatographic conditions used in the study were described in an earlier paper.[8]

Analysis of NAs Using High-Resolution Mass Spectrometry (HRMS). An Acquity ultrapressure 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 TurboIon Spray source (Applied Biosystem/MDS Sciex, Concord, ON,

Canada). Detailed methodology for the analysis of NAs can be found in the Supporting Information (SI).

■ RESULTS AND DISCUSSION

Degradation of CHA by Peroxydisulfate in the Presence of ZVI at 20 and 40 °C. . In recent years, the most popular method for using peroxydisulfate in the presence of ZVI for in situ remediation is through the injection of peroxydisulfate solution to groundwater. The groundwater then flows through a semipermeable barrier made of iron powder, iron oxides, or, depending on the geology of the remediated site, natural iron ores or iron containing clays.[10] For our experiments conducted at 20 °C for 6 days, an incubated shaker was utilized to mimic the treatment conditions that could potentially be used for OSPW treatment in pump-and-treat systems. The degradation of 50 mg/L CHA by 500, 1000, and 2000 mg/L of $S_2O_8^{2-}$ (100 mL of solution) was investigated at pH 9 and in the presence of 20 g of ZVI powder. The use of pH 9 ensured that CHA was completely dissolved in the solution and further approximates the pH of OSPW.

The formation of black and brown deposits on the surface of the ZVI started after the first hour of contact with the solution containing peroxydisulfate. Therefore, the bottles were shaken vigorously to allow for contact of all ZVI particles with the solution. Deposit formation was not observed in the solution containing only CHA. However, it was observed that a certain amount of CHA (~10%) could be removed by ZVI alone (Figure 1A). This observation is supported by the formation of the byproducts, hydroxy- and oxo-CHA (Figure 2) suggesting that CHA was indeed oxidized during the corrosion of ZVI. Fe^{2+} and H_2O_2 are well-known byproducts of surface corrosion of ZVI particles.[28−31] The formation of hydroxyl radicals presumably resulted from the reaction (Fenton reaction) between Fe^{2+} and H_2O_2,[27] and the hydroxyl radical, in turn, reacted with CHA to form hydroxy- and oxo-CHA.[8] In Figure 2B, the strong peak (5 to 10 min) is due to the interference occurred when analyzing samples with high content of salts.
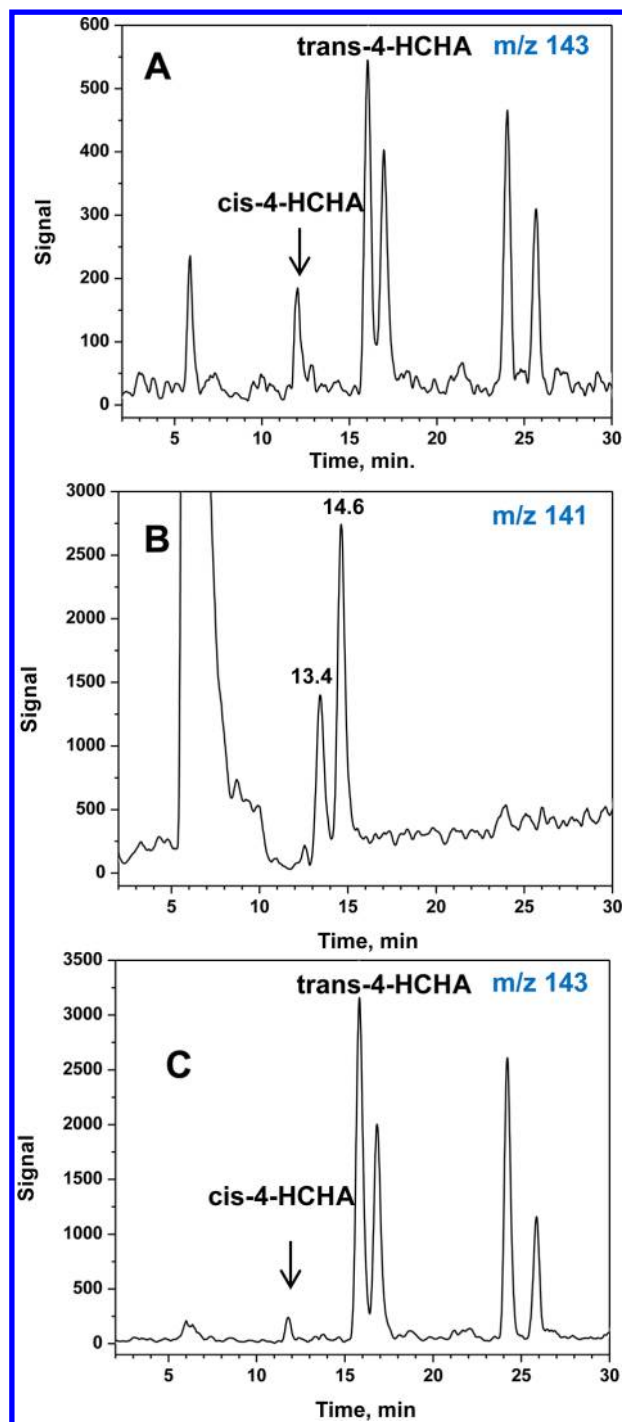
Figure 2. Formation of byproducts after the treatment with ZVI only for 6 days at 20 °C (A) in absence and (B), (C) in presence of 500 mg/L chloride. Chromatogram for m/z 143 is characteristic of hydroxy-CHA (HCHA), and for m/z 141 is characteristic of oxo-CHA.

In alkaline solution, peroxydisulfate decomposes to form sulfate anion and hydroxyl radicals.[38] The decomposition of CHA and the formation of hydroxy- and oxo-CHA were also observed in the solution containing 2000 mg/L $S_2O_8^{2-}$ without the addition of ZVI. However, peroxydisulfate induced the oxidation of CHA and the formation of the byproducts increased in the presence of ZVI. Hydroxyl radical formed in the presence of ZVI would react with CHA and the resulting

radical (reaction 3) may react with peroxydisulfate (reaction 4).[10]

$$R—H + OH^\bullet \rightarrow R^\bullet + H_2O \tag{3}$$

$$R^\bullet + S_2O_8^{2-} + OH^- \rightarrow R—OH + SO_4^{\bullet-} + SO_4^{2-} \tag{4}$$
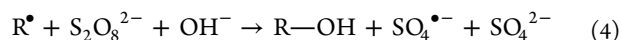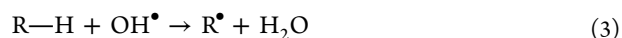
The results also indicated that the decomposition and oxidation of CHA was affected by the presence of 500 mg/L Cl^- (Figure 1A). Chloride anions are well-known scavengers of sulfate anion radicals and hydroxyl radicals.[19] The chlorine radical formed during the reaction of a hydroxyl radical with a chloride anion decomposed H_2O_2[19] and ceased the Fenton reaction. The presence of chloro-CHA (SI Figure S1) in the solution treated with 2000 mg/L $S_2O_8^{2-}$ in the presence of Fe(0) and 500 mg/L Cl^- strongly suggests the formation of chlorine radicals during the process, for example, following hydrogen abstraction (by hydroxyl radical or chlorine radical).[20,39] The resulting carbon centered radical may react with a chlorine radical or hypochlorite (a product of the reaction of H_2O_2 with a chlorine radical[39−41]) to form chloro-CHA (Figure 3).
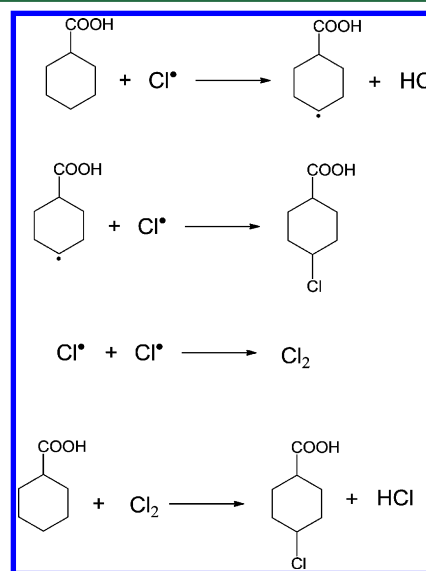
Figure 3. Proposed mechanism for the chlorination of CHA induced by chlorine radical formed during the reaction of sulfate anion radical with chloride.

Increasing the reaction temperature to 40 °C did not significantly improve the degradation of CHA in the presence of 2000 mg/L $S_2O_8^{2-}$ alone (SI Figure S2A). This suggests that the decomposition of peroxydisulfate by heat is not efficient despite increasing the temperature to 40 °C. However, it was observed that the addition of 20 g of ZVI to 2000 mg/L $S_2O_8^{2-}$ caused a 44% removal of CHA at 40 °C.

After the treatment at 20 and 40 °C, the pH of the solution decreased from 9 to 7 in the presence of ZVI alone, indicating the formation of iron hydroxide and the release of H^+ during corrosion.[29,31] A decrease in pH from 9 to 6 was also observed during the oxidation of CHA by 2000 mg/L $S_2O_8^{2-}$ alone at 20 and 40 °C. The decrease in pH may be explained by the reaction of the hydroxide anion with $S_2O_8^{2-}$ during the process.[38] After combined peroxydisulfate and ZVI treatment, the pH decreased from 9 to 5 at 20 and 40 °C. Additionally, the decrease in pH in the presence of ZVI may be explained by the
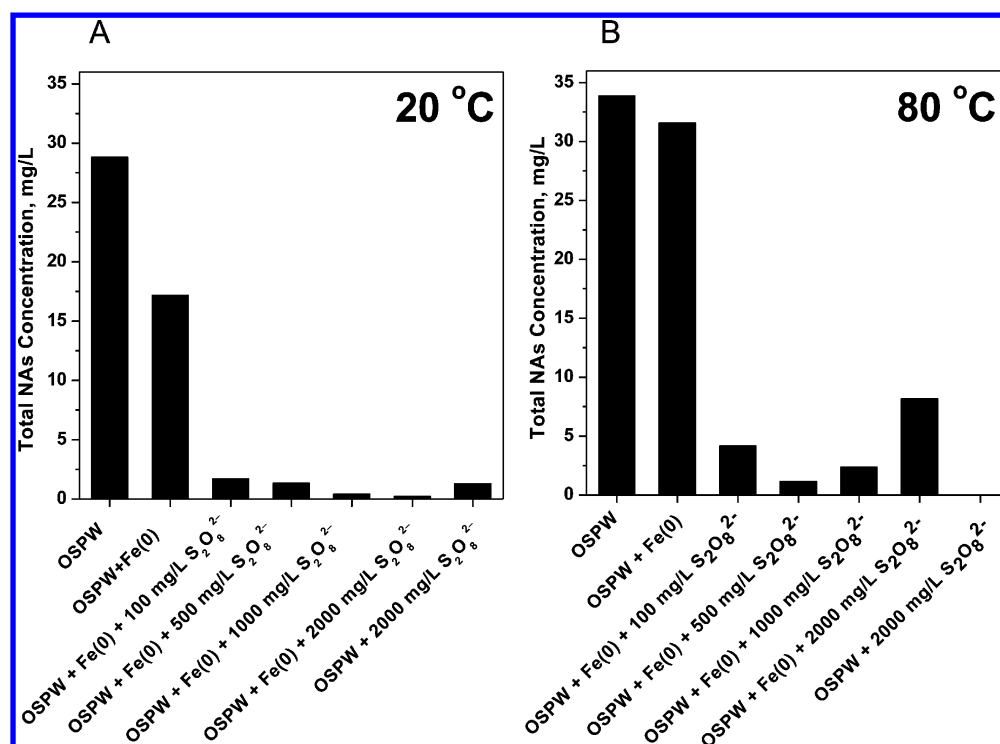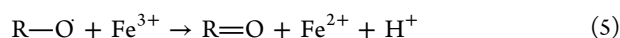
Figure 4. Removal of NAs from OSPW by $S_2O_8^{2-}$/ZVI after (A) 6 days at 20 °C and (B) 2 h at 80 °C.

reaction of Fe^{3+} with organic radicals formed during the CHA decomposition:[10]

$$R\!-\!\dot{O} + Fe^{3+} \rightarrow R\!=\!O + Fe^{2+} + H^+ \qquad (5)$$

A decrease in the pH of the solution during the treatment may facilitate the adsorption of CHA (i.e., the protonated acid species) on the surface of ZVI. Short-lived hydroxyl radical formed on the surface of ZVI would likely react preferentially with adsorbed CHA compared to CHA in bulk solution. Part of CHA may also be removed from solution due to the formation of poorly soluble iron-CHA salts formed with Fe^{2+}/Fe^{3+} present on the surface of ZVI. A control experiment showed that CHA was removed from solution after the addition of Fe^{2+}/Fe^{3+} at pH 9. However, further studies are required to explain the role of ZVI surface in the oxidation of CHA by $ZVI/S_2O_8^{2-}$.

Degradation of CHA at 60 and 80 °C. Microwave (MW) irradiation offers advantages over conventional heating, such as heating without physical contact, and instantaneous/rapid heating that results in a uniform heating.[42] The microwaves absorbed by a solution cause the polar molecules to rotate rapidly in the solution, bringing about a thermal effect, which reduces the activation energy of the system and weakens various chemical bonds.[43] Absorption of microwave energy by ZVI particles, in solution, causes the production of even more heating.[43] Therefore, MW heating was selected for studies of peroxydisulfate oxidation of CHA at elevated temperatures (>40 °C).

The degradation of 50 mg/L CHA by 500, 1000, and 2000 mg/L of $S_2O_8^{2-}$ (50 mL of solution) was investigated at pH 9 and in the presence of 10 g of ZVI powder over a 2 h period. Increasing the temperature to 60 °C improved the removal of CHA by peroxydisulfate (SI Figure S2B). In the presence of 2000 mg/L $S_2O_8^{2-}$ alone, CHA was degraded completely, whereas in the presence of ZVI, a dose of 1000 mg/L $S_2O_8^{2-}$

was enough to obtain 90% degradation of CHA. The presence of chloro-CHA was observed after treatment with 500 mg/L $S_2O_8^{2-}$, but there was no formation of chloro-CHA at higher concentration of $S_2O_8^{2-}$ in the presence of ZVI. In the presence of 2000 mg/L $S_2O_8^{2-}$ alone, chloro-CHA was not detected. After treatment with 2000 mg/L of $S_2O_8^{2-}$ at 60 °C, the pH decreased from 9 to 2 in the absence of ZVI and from 9 to 3 in the presence of ZVI.

At 80 °C, and in the presence of ZVI, the concentration of $S_2O_8^{2-}$ required for the 90% degradation of 50 mg/L CHA was 500 mg/L $S_2O_8^{2-}$ (Figure 1B). At 80 °C, ZVI did not participate in the decomposition of peroxydisulfate to a sulfate anion radical.[11] Because the increase of the CHA oxidation was insignificant when the $S_2O_8^{2-}$ concentration increased from 500 to 1000 mg/L, it may be assumed that 500 mg/L $S_2O_8^{2-}$ is the highest dose required to achieve the almost complete degradation of 50 mg/L CHA in the absence of ZVI at this temperature and under the experimental conditions used in the present study. Additional tests are required to estimate the optimum $S_2O_8^{2-}$ dose.

At 60 and 80 °C, and in the presence of 500 mg/L Cl^-, the surface of ZVI was covered with "green rust" after the process carried out at 60 and 80 °C. Chloride may have an effect on the corrosion and deactivation of the surface of ZVI.[44] In the presence of a high concentration of chloride, green ferrous chloride, $FeCl_2$, embedded in the lattice of iron hydroxides and oxides may form on the surface of ZVI.[44] High concentration of sulfate formed from the degradation of peroxydisulfate may also have an effect on the formation of green deposit of melanterite, $FeSO_4 \cdot 7H_2O$, on the surface ZVI.[44] It is likely that elevated temperature and high salinity, especially high chloride concentration, increase the formation of iron salt deposit and cause the surface deactivation of ZVI. However, further study is required to explain the effect of surface deactivation process on the mechanism of CHA oxidation by $S_2O_8^{2-}$/ZVI.
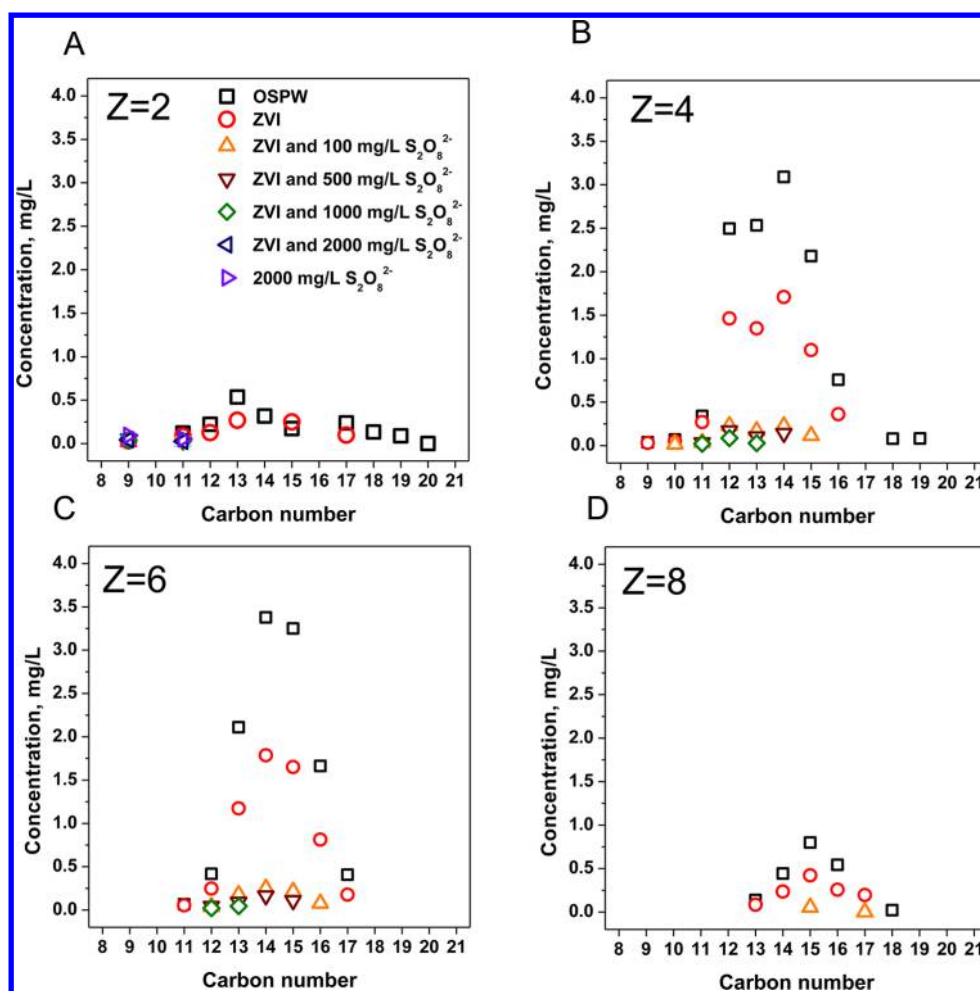
Figure 5. NAs signatures before and after the treatment of OSPW with $S_2O_8^{2-}$/ZVI for 6 days at 20 °C. Z is a number of rings or double bonds equivalents in the structure. (A) NAs $Z = 2$, (B) NAs $Z = 4$, (C) NAs $Z = 6$, and (D) NAs $Z = 8$.

Decomposition of Naphthenic Acids in OSPW by $S_2O_8^{2-}$/ZVI at 20 and 40 °C. The degradation of NAs in OSPW by 100, 500, 1000, and 2000 mg/L of $S_2O_8^{2-}$ (100 mL of solution) was investigated at 20 °C in presence of 20 g of ZVI. The bottles with the solutions were shaken vigorously for 6 days. The corrosion of ZVI started immediately after placing it in the OSPW (see X-ray Photoelectron Spectroscopy (XPS) Surface Analysis of ZVI section in SI). Corrosion of ZVI was probably induced by the high pH of OSPW (8.5) and the high contents of chloride (500 mg/L). The occurrence of a corrosion process was indicated by an increase in pH to 10.4 presumably due to the reduction of oxygen to H_2O_2 and the formation of hydroxide anions during the process.[29,31]

$$O_2 + 2H_2O + 2e \rightarrow 2OH^- + H_2O_2 \qquad (6)$$

$$Fe(0) - 2e \rightarrow Fe^{2+} \qquad (7)$$
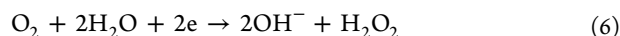
ZVI alone removed almost 50% of NAs from OSPW after 6 days at 20 °C (Figure 4A). Formation of an insoluble salt of NAs with iron cations on the surface of ZVI may be an explanation for this.[5,36] Higher removal efficiency was observed for cyclic NAs with Z number 4 and 6 (Figures 5B and 5C). In analogy to CHA, the adsorption of NAs on iron surface may facilitate their subsequent oxidation. The addition of 100 mg/L $S_2O_8^{2-}$ to OSPW containing a 20 g ZVI suspension increased the removal of NAs to 90%. A further increase in the

peroxydisulfate concentration did not increase the removal of NAs more than 90%.

After the addition of 100 mg/L $S_2O_8^{2-}$ to the OSPW containing 20 g of ZVI, the pH of the solution decreased from 10.4 to 9, and further decreased to 6 after the addition of 2000 mg/L $S_2O_8^{2-}$. The lower pH after the addition of $S_2O_8^{2-}$ to OSPW containing a ZVI suspension may be explained by the aforementioned reactions of peroxydisulfate and sulfate anion radicals with hydroxide anions and the formation of iron hydroxide and oxides on the surface of ZVI. The declining of pH during the treatment may facilitate the adsorption of NAs on the surface of ZVI and the formation of poorly soluble iron-NAs salts. Traces of organic compounds which were likely NAs and/or their oxidation byproducts, were found on the surface of ZVI by XPS analysis (see X-ray Photoelectron Spectroscopy (XPS) Surface Analysis of ZVI section in SI). The adsorbed NAs likely underwent further oxidation processes induced by hydroxyl radical formed on the surface of ZVI.

The addition of ZVI increased the utilization of $S_2O_8^{2-}$ in the process at 20 and 40 °C. In case of treatment with ZVI and 100 mg/L $S_2O_8^{2-}$, increasing the temperature to 40 °C resulted in 88% removal of NAs after 2 h, whereas, at 20 °C, the same removal was obtained after 6 days of the treatment (SI Figure S3A).

Degradation of Naphthenic Acids in OSPW at 60 and 80 °C. NAs naturally present in OSPW are poorly dissociable

and are low polar compounds; hence, MW irradiation improves heat transfer to the solution rather than the reactivity of the compounds. The degradation of NAs in OSPW by 100, 500, 1000, and 2000 mg/L of $S_2O_8^{2-}$ was investigated at 60 and 80 °C in presence of 10 g of ZVI. The solutions (50 mL) were heated for 2 h in a microwave oven.

Increasing the reaction temperature to 60 °C did not bring any improvement in the degradation level in comparison to 40 °C (SI Figure S3B). There was no difference in the removal of NAs with various ring numbers (SI Figure S5) suggesting their removal presumably by the formation of insoluble salts with Fe^{2+}/Fe^{3+} present on the surface of ZVI. Further oxidation, however, might be hindered by the deactivation of ZVI due to the formation of iron salt deposits.

The formation of green rust, deposit of iron salt, on the surface of ZVI was observed only at 80 °C. Therefore, ZVI did not participate in the decomposition of NAs due to surface deactivation. Moreover, thermolysis of persulfate to sulfate anion radical is a very fast process at this temperature.[22] Taken together, thermolysis of peroxidisulfate is the only source of sulfate anion radical available for the decomposition of NAs.

It was observed that the concentration of NAs in OSPW did not decrease in the presence of ZVI alone. The addition of 100 mg/L of peroxidisulfate decreased the concentration of NAs by 90%. A further increase in the concentration of $S_2O_8^{2-}$, by more than 500 mg/L, did not improve the removal of NAs from the OSPW. It was found that the removal of NAs depended on the number of rings in their structure, contrary to what was observed at lower temperature (SI Figures S4, S5, and S6). The reactivity of NAs with hydroxyl radicals has previously been shown to have a structure-reactivity (reactivity increased with the number of rings)[45] whereas the solubility of iron salt is likely independent of the NA structure. Therefore, the structure dependence of NAs removal suggests that ZVI was not involved in the oxidation of NAs at 80 °C.

At 60 and 80 °C, in the presence of ZVI alone, the pH of the OSPW increased from 8.3 to 9 after treatment, whereas, in the combined $S_2O_8^{2-}$/ZVI process, the pH decreased to 6. The pH of the OSPW decreased to 2 after treatment with $S_2O_8^{2-}$ alone. This may indicate the reaction of a sulfate anion radical with a hydroxide anion and chloride during which a hydroxyl radical and chlorine are formed, respectively.

At 80 °C, NAs were completely removed from OSPW at 80 °C after 2 h treatment with 2000 mg/L $S_2O_8^{2-}$ alone (Figure 4). This indicated that 80 °C was the best condition for the uncatalyzed decomposition of peroxidisulfate to sulfate anion radical and the removal of NAs by $S_2O_8^{2-}$ alone.

Environmental Significance. The $S_2O_8^{2-}$/ZVI process can be successfully applied for the removal of NAs from OSPW at room temperature. Operational and capital cost of OSPW treatment could decrease with a decrease of the process temperature. On the other hand, peroxydisulfate alone can be applied to hot extraction water after the bitumen extraction process in order to remove organic pollutants. After that process, residual $S_2O_8^{2-}$ left in the treated OSPW can be removed using ZVI at room temperature. Iron(II) and iron(III) can be recovered for reuse by using chemical reduction with borohydride[47] and ZVI can be regenerated by using acid washing.[48] The $S_2O_8^{2-}$/ZVI process is promising for real applications in OSPW remediation and may be competitive with other processes due to its low energy requirements near room temperature. The disadvantage of the process is that a long time is needed for the removal of organic pollutants

without significant addition of heat. Therefore, the assessment of process fundamentals and process optimization including the impacts of exposure time, temperature, and amount of peroxydisulfate and ZVI on the treatment performance, as well as the determination of the levels of ZVI recovery, will be conducted in future studies. Because OSPW contains thousands of organic acids[49,50] that have not been identified, comprehensive research is ongoing to characterize the organic fraction of OSPW as well as to identify the byproduct generated by the $S_2O_8^{2-}$/ZVI process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures presenting chromatograms of CHA byproduct and the structure dependence of NAs degradation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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■ REFERENCES

(1) Allen, E. W. Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. *J. Environ. Eng. Sci.* **2008**, 7 (2), 123−138.

(2) He, Y. H.; Wiseman, S. B.; Zhang, X. W.; Hecker, M.; Jones, P. D.; Gamal El-Din, M.; Martin, J. W.; Giesy, J. P. Ozonation attenuates the steroidogenic disruptive effects of sediment free oil sands process water in the H295R cell line. *Chemosphere* **2010**, 80 (5), 578−584.

(3) Martin, J. W.; Barri, T.; Han, X. M.; Fedorak, P. M.; Gamal El-Din, M.; Perez, L.; Scott, A. C.; Jiang, J. T. Ozonation of oil sands process-affected water accelerates microbial bioremediation. *Environ. Sci. Technol.* **2010**, 44 (21), 8350−8356.

(4) Whitby, C. Microbial naphthenic acid degradation. *Adv. Appl. Microbiol.* **2010**, 70, 93−125.

(5) Brient, J. A.; Wessner, P. J.; Doyle, M. N. Naphthenic acids. *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc., 2000.

(6) Fan, T. P. Characterization of naphthenic acids in petroleum by fast-atom-bombardment mass-spectrometry. *Energy Fuels* **1991**, 5 (3), 371−375.

(7) Han, X. M.; MacKinnon, M. D.; Martin, J. W. Estimating the in situ biodegradation of naphthenic acids in oil sands process waters by HPLC/HRMS. *Chemosphere* **2009**, 76 (1), 63−70.

(8) Drzewicz, P.; Afzal, A.; Gamal El-Din, M.; Martin, J. W. Degradation of a model naphthenic acid, cyclohexanoic acid, by vacuum UV (172 nm) and UV (254 nm)/H_2O_2. *J. Phys. Chem. A* **2010**, 114 (45), 12067−12074.

(9) He, Y. H.; Wiseman, S. B.; Hecker, M.; Zhang, X. W.; Wang, N.; Perez, L. A.; Jones, P. D.; Gamal El-Din, M.; Martin, J. W.; Giesy, J. P. Effect of ozonation on the estrogenicity and androgenicity of oil sands

process-affected water. *Environ. Sci. Technol.* **2011**, *45* (15), 6268–6274.

(10) Tsitonaki, A.; Petri, B.; Crimi, M.; Mosbaek, H.; Siegrist, R. L.; Bjerg, P. L. In situ chemical oxidation of contaminated soil and groundwater using persulfate: A review. *Crit. Rev. Environ Sci. Technol.* **2010**, *40* (1), 55–91.

(11) Oh, S. Y.; Kim, H. W.; Park, J. M.; Park, H. S.; Yoon, C. Oxidation of polyvinyl alcohol by persulfate activated with heat, Fe^{2+}, and zero-valent iron. *J. Hazard. Mat.* **2009**, *168* (1), 346–351.

(12) Manoj, P.; Varghese, R.; Manoj, V. M.; Aravindakumar, C. T. Reaction of sulphate radical anion (SO$_4^{\bullet-}$) with cyanuric acid: A potential reaction for its degradation? *Chem. Lett.* **2002**, *1*, 74–75.

(13) Hori, H.; Yamamoto, A.; Hayakawa, E.; Taniyasu, S.; Yamashita, N.; Kutsuna, S. Efficient decomposition of environmentally persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant. *Environ. Sci. Technol.* **2005**, *39* (7), 2383–2388.

(14) Madhavan, V.; Levanon, H.; Neta, P. Decarboxylation by SO$_4^{\bullet-}$ radicals. *Radiat. Res.* **1978**, *76* (1), 15–22.

(15) Criquet, J.; Nebout, P.; Leitner, N. K. V. Enhancement of carboxylic acid degradation with sulfate radical generated by persulfate activation. *Water Sci. Technol.* **2010**, *61* (5), 1221–1226.

(16) Herrmann, H.; Reese, A.; Zellner, R. Time-resolved UV/Vis diode-array absorption-spectroscopy of SO$_x^-$ (X=3, 4, 5) radical-anions in aqueous-solution. *J. Mol. Struct.* **1995**, *348*, 183–186.

(17) Tang, Y.; Thorn, R. P.; Mauldin, R. L.; Wine, P. H. Kinetics and spectroscopy of the SO$_4^-$ radical in aqueous solution. *J. Photochem. Photobiol. A* **1988**, *44* (3), 243–258.

(18) McElroy, W. J.; Waygood, S. J. Kinetics of the reactions of the SO$_4^-$ radical with SO$_4^{\bullet-}$, S$_2$O$_8^{2-}$, H$_2$O, and Fe^2. *J. Chem. Soc. Faraday T.* **1990**, *86*, 2557–2564.

(19) Neta, P.; Huie, R. E.; Ross, A. B. Rate constants for reactions of inorganic radicals in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027–1247.

(20) Buxton, G. V.; Wang, J. Q.; Salmon, G. A. Rate constants for the reactions of NO$_3^{\bullet-}$, SO$_4^{\bullet-}$ and Cl$^{\bullet-}$ with formate and acetate esters in aqueous solution. *Phys. Chem. Chem. Phys.* **2001**, *3* (13), 2618–2621.

(21) Kolthoff, I. M.; Miller, I. K. The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium. *J. Am. Chem. Soc.* **1951**, *73* (7), 3055–3059.

(22) House, D. A. Kinetics and mechanism of oxidations by peroxydisulfate. *Chem. Rev.* **1962**, *62* (3), 185–203.

(23) Johnson, R. L.; Tratnyek, P. G.; Johson, O. R. Persulfate persistence under thermal activation conditions. *Environ. Sci. Technol.* **2008**, *42*, 9350–9356.

(24) Huie, R. E.; Clifton, C. L. Temperature dependence of the rate constants for reactions of the sulfate radical, SO$_4^{\bullet-}$ with anions. *J. Phys. Chem.* **1990**, *94*, 8561–8567.

(25) Siegrist, R. L.; Crimi, M.; Simpkin, T. J. *In Situ Chemical Oxidation for Groundwater Remediation*; Springer, 2011.

(26) Appelo, C. A. J.; Postma, D. *Geochemistry, Groundwater and Pollution*; Taylor & Francis, 2005; pp 415–487.

(27) Pignatello, J. J.; Oliveros, E.; MacKay, A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit. Rev. Environ Sci. Technol.* **2006**, *36* (1), 1–84.

(28) Joo, S. H.; Feitz, A. J.; Sedlak, D. L.; Waite, T. D. Quantification of the oxidizing capacity of nanoparticulate zero-valent iron. *Environ. Sci. Technol.* **2005**, *39* (5), 1263–1268.

(29) Noubactep, C. The fundamental mechanism of aqueous contaminant removal by metallic anion. *Water SA* **2010**, *36*, 663–670.

(30) Shi, Z. Q.; Nurmi, J. T.; Tratnyek, P. G. Effects of nano zero-valent iron on oxidation reduction potential. *Environ. Sci. Technol.* **2011**, *45* (4), 1586–1592.

(31) Lin, X. Q.; Elliot, D. W.; Zhang, W. X. Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. *Crit. Rev. Solid State Mater. Sci.* **2006**, *31* (4), 111–122.

(32) Liang, S. H.; Kao, C. M.; Kuo, Y. C.; Chen, K. F.; Yang, B. M. In situ oxidation of petroleum-hydrocarbon contaminated groundwater using passive ISCO system. *Water Res.* **2011**, *45* (8), 2496–2506.

(33) Rastogi, A.; Ai-Abed, S. R.; Dionysiou, D. D. Sulfate radical-based ferrous-peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems. *Appl. Catal., B* **2009**, *85* (3–4), 171–179.

(34) Dickinson, M.; Scott, T. B. The application of zero-valent iron nanoparticles for the remediation of a uranium-contaminated waste effluent. *J. Hazard. Mater.* **2010**, *178* (1–3), 171–179.

(35) Sun, Y. P.; Li, X. Q.; Cao, J. S.; Zhang, W. X.; Wang, H. P. Characterization of zero-valent iron nanoparticles. *Adv. Colloid Interface Sci.* **2006**, *120* (1–3), 47–56.

(36) Ronzio, A. R. Metal loaded scintillator solutions. *Int. J. Appl. Radiat. Isot.* **1959**, *4*, 196–200.

(37) Pourrezaei, P.; Drzewicz, P.; Wang, Y.; Gamal El-Din, M.; Perez-Estrada, L. A.; Martin, J. W.; Anderson, J.; Wiseman, S.; Liber, K; Giesy, J. P. The impact of metallic coagulants on the removal of organic compounds from oil sands process-affected water. *Environ. Sci. Technol.* **2011**, *45* (19), 8452–8459.

(38) Furman, O. S.; Teel, A. L.; Ahmad, M.; Merker, M. C.; Watts, R. J. Effect of basicity on persulfate reactivity. *J. Environ. Eng.-ASCE* **2011**, *137* (4), 241–247.

(39) Oliver, B. G.; Carey, J. H. Photochemical production of chlorinated organics in aqueous-solutions containing chlorine. *Environ. Sci. Technol.* **1977**, *11* (9), 893–895.

(40) Liao, C. H.; Kang, S. F.; Wu, F. A. Hydroxyl radical scavenging role of chloride and bicarbonate ions in the H$_2$O$_2$/UV process. *Chemosphere* **2001**, *44* (5), 1193–1200.

(41) Yu, X. Y. Critical evaluation of rate constants and equilibrium constants of hydrogen peroxide photolysis in acidic aqueous solutions containing chloride ions. *J. Phys. Chem. Ref. Data* **2004**, *33* (3), 747–763.

(42) Mudhoo, A.; Sharma, S. K. Microwave irradiation technology in waste sludge and wastewater treatment research. *Crit. Rev. Environ Sci. Technol.* **2011**, *41* (11), 999–1066.

(43) Lee, C. L.; Jou, C. J. G.; Wang, H. P. Enhanced degradation of chlorobenzene in aqueous solution using microwave-induced zero-valent iron and copper particles. *Water Environ. Res.* **2010**, *82* (7), 642–647.

(44) Gilberg, M. R.; Seeley, N. J. The identity of compounds containing chloride ions in marine iron corrosion products: A Critical review. *Stud. Conserv.* **1981**, *26* (2), 50–56.

(45) 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.

(46) Afzal, A.; Drzewicz, P.; Martin, J. W.; Gamal El-Din, M. Decomposition of cyclohexanoic acid by the UV/H$_2$O$_2$ process under various conditions. *Sci. Total Environ.* **2012**, *426*, 387–392.

(47) Wang, C. B.; Zhang, W. X. Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environ. Sci. Technol.* **1997**, *31*, 2154–2156.

(48) Ruiz, N.; Seal, S.; Reinhart, D. Surface chemical reactivity in selected zero-valent iron samples used in groundwater remediation. *J. Hazard. Mater.* **2000**, *80* (1–3), 107–117.

(49) Grewer, D. M.; Young, R. F.; Whittal, R. M.; Fedorak, P. M. Naphthenic acids and other acid-extractables in water samples from Alberta: What is being measured? *Sci. Total Environ.* **2010**, *408*, 5997–6010.

(50) Headley, J. V.; Barrow, M. P.; Peru, K. M.; Fahlman, B.; Frank, R. A.; Bickerton, G.; McMaster, M. E.; Parrott, J.; Hewitt, L. M. Preliminary fingerprinting of Athabasca oil sands polar organics in environmental samples using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Commun. Mass Spectrom.* **2011**, *25*, 1899–1909.