A FEASIBILITY STUDY ON SULFOLANE DEGRADATION IN GROUNDWATER USING NEUTRAL FENTON CATALYSTS

Linlong Yu
Postdoctoral Fellow, University of Calgary, Canada

Gopal Achari
Professor, University of Calgary, Canada

Cooper H. Langford
Professor, University of Calgary, Canada

Ian Keir
Senior Environmental Coordinator, Bonavista Energy Corporation, Canada

ABSTRACT

In this paper, degradation of sulfolane in an acidic or near neutral pH using Fenton or modified Fenton catalysts was investigated. The catalysts included nitrilotriacetic acid (NTA) iron complex and several commercially available products marketed as neutral pH catalysts. The experiments were conducted both in lab synthetic water and sulfolane contaminated groundwater. Our results showed that more than 99% of sulfolane can be removed by the classic Fenton-like reagent in acidic condition. At near neutral pH, 60% of sulfolane reduction in groundwater was achieved by adding NTA/Fe(III)/H$_2$O$_2$. Among the four commercially available products investigated, ethylenediaminetetraacetic acid (EDTA) chelated iron showed the most positive result in sulfolane degradation in the groundwater. Fifty percent of sulfolane in groundwater degraded when EDTA chelated iron was used with hydrogen peroxide. The decomplexation of chelated iron during reaction caused iron to precipitate and led to the cessation of the reaction.

Keywords: NTA, EDTA, Fenton, sulfolane, groundwater

1. INTRODUCTION

Sulfolane is an organic solvent which has been widely used in natural gas processing and petroleum refining operations as part of the Shell Sulfinol Process® for removal of polar compounds from sour gas streams (CCME 2006). Sulfolane is also used as extractive distillation solvent, polymer solvent, polymer plasticizer, in production of pesticides, polymerization solvent and in electronic/electric applications (Kirk-Othmer 1999). It has been found in groundwater around several gas processing plants in North America (Blystone 2011). This is due to leachates from disposal areas, leakage during processes and seepage from producing wells and unlined storage ponds. It is highly soluble in water and interacts minimally with soil organics (Luther et al. 1998). These properties make it mobile in the environment and result in offsite sulfolane contamination. Guidelines for sulfolane in environment have existed in Alberta (Canada), British Columbia (Canada), California (US), Delaware (US), Indiana (US), Texas (US) and Puerto Rico indicating its use and release to the environment in these jurisdictions and has been reported as detected in the environment in Australia, Louisiana (US), New Jersey (US) and North Carolina (US). As sulfolane is an emerging contaminant, so far, no comprehensive toxicology on sulfolane has been reported. However, the limited toxicological data has showed that sulfolane could be a potential hazard to human health and the ecosystem. Zhu et al. (1987) conducted toxicological studies of sulfolane on mammals such as mice and guinea pigs. The results showed that oral exposure to sulfolane at level of 500 mg/kg-day for 90 days can decrease serum alkaline phosphatase activity in rats and even a lower exposure dosage (55.5 mg/kg-day) can decrease serum alkaline phosphatase activity and white blood cell counts in guinea pigs.
Since 1980s, a number of sulfolane remediation strategies have been developed. Currently, the most common technique for sulfolane contaminated groundwater remediation is utilizing aerobic microbial bioremediation (Fedorak and Coy 1996; Greene et al. 1998). Aerobic microbial bioremediation requires suitable environmental conditions such as temperature, pH, nutrients, and oxygen. These requirements along with geological application challenges make microbial bioremediation difficult for in-situ application. Advanced oxidation processes (AOPs) (Agatonovic and Vaisman 2005) and activated carbon adsorption (Barr Engineering Company 2013) were also reported to degrade or remove sulfolane from water. Activated carbon adsorption cannot break down sulfolane but just transfer sulfolane from one phase to another phase. AOPs based on the generated hydroxyl radical or other equivalents have showed their capacities to decompose sulfolane in aqueous medium and could be a comprehensive solution for sulfolane remediation in groundwater. Among different AOPs, Fenton-like reagents (Fe(III)/H₂O₂) have been reported to degrade a number of industrial contaminants (Bautista et al. 2008). The reaction mechanisms for Fenton/Fenton-like reactions are very complex. The general accepted mechanism of Fe(III)/H₂O₂ process producing hydroxyl radicals are showed in Equations (1-2). Iron plays a role as catalyst to generate hydroxyl radicals.

\[
\begin{align*}
[1] \quad & \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+
\end{align*}
\]

\[
\begin{align*}
[2] \quad & \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}^- + \text{HO}^-
\end{align*}
\]

The success of classic Fenton based treatment technology relies on acidic conditions. At neutral and alkaline pH, Fe³⁺ precipitates out as hydrous oxyhydroxides, Fe₂O₃·nH₂O, resulting in a loss of reactivity (Sun and Pignatello 1993). The limited pH range has restricted the application of Fenton chemistry for treating neutral or alkaline water. The application of Fenton like reagents in these water require acidification and subsequent neutralization. The difficulty of application of Fenton chemistry on groundwater containing carbonate/bicarbonate is even higher as it is a good pH buffering system. At near neutral pH, Fe(III) can be solubilized by addition of chelates such as EDTA, NTA and others (Sun and Pignatello 1993). The solubilization of Fe(III) can keep Fe(III) catalytically active long enough in the water to carry out the Fenton reaction. A number of studies have been reported to use chelated iron with hydrogen peroxide for degrading organic compounds at near neutral pH (Canals et al. 2013; Lewis et al. 2009). Sun and Pignatello (1993) investigated fifty chelating agents with iron(III) and hydrogen peroxide to degrade 2,4-dichlophenoxyacetic acid (2,4-D) and found that NTA is one of the most promising chelating agent.

This research investigated the degradation of sulfolane at near neutral pH using the modified Fenton catalysts. The catalysts include lab prepared NTA iron complex and several commercially available products (EDTA chelated iron, Fe(II)DPTA, VTX and VTH). The experiments were conducted both in lab synthetic water and sulfolane contaminated groundwater.

2. METHODS AND MATERIALS

2.1 Chemicals

Sulfolane with 99% purity, nitritotriacetic acid disodium (NTA disodium) with 99% purity, ferric chloride with 97% purity, sodium thiosulfate with 99.5% purity, hydrogen peroxide (ACS grade, ~30 % in water) and sodium hydroxide with 98% purity were purchased from Sigma Aldrich, Canada. Sulfuric acid (ACS grade, ~18M) was obtained from VWR. EDTA chelated iron was obtained from Canadian Color Ltd. Fe(II)DPTA, VTX and VTH were obtained from Chemco Ltd. The composition of the catalysts VTX and VTH are confidential. Groundwater containing sulfolane was provided by Bonavista Energy Corporation.

2.2 Experimental procedure

Lab synthetic water containing 130 ppm (1.08mM) sulfolane was prepared by dissolving 130 mg of pure sulfolane in one liter of Milli-Q water. The groundwater containing 130 ppm sulfolane was directly tested as it was. All experiments were conducted in 250-ml glass jars with open cap. Each 100 ml of lab synthetic water or groundwater with a known amount of Fenton like reagents (H₂O₂ and iron catalysts) was placed in 250-ml glass jars. The initial concentration of H₂O₂ and NTA/Fe(III) were 15 mM and 1mM. NTA chelated iron was prepared by mixing NTA disodium with FeCl₃ at molar ratio=1:1 in the solution. The dosages of commercial catalysts added to water can be found in the caption of related figures.
The mixing of the solution was achieved by using a shaker. The glass jars containing the waters and Fenton reagents were placed in a shaker where the shaking speed was set at 200 rpm with a temperature of 23 °C. The details of each experiment can be found in the caption of each figure. For the experiments needing pH adjustment, diluted sulfuric acid (1mol/L) and sodium hydroxide (1mmol/L) was added drop wise to obtain the desired pH. For each experiment, one and half ml of water sample at different reaction time was collected in a 4-ml glass vial which contained 100 mg of sodium thiosulfate. The purpose of adding sodium thiosulfate to the water sample was to quench the Fenton reaction. The water samples were then filtered with a 0.22 micrometer filter and kept in a 4-ml glass vial.

2.3 Extraction and GC Analysis

Each 1mL of the filtered water sample was extracted with 1.5 mL of dichloromethane (DCM). The vials containing 1ml of filtered water sample and 1.5 mL of DCM were placed in the shaker (shaking speed=200 rpm) for half of an hour. The aqueous layer on the top was removed, and the DCM layer on the bottom of vial was transferred to 1 mL GC vial. The extraction efficiency using this method is about 70%. The extracts were then analyzed using an Agilent 6890 gas chromatograph (GC) equipped with auto-sampler and Flame Ionization Detector (FID). Chemstation software was used to perform data acquisition and analyses. A fused silica capillary column (ZB 5MSI, Phenomenex) was used to separate sulfolane and other compounds. High purity helium was used as the carrier gas with a head pressure of 300 kPa. The temperature of the injection port was set to 165°C and the injection was set on split less mode with 1.00 µL injection volume. The initial temperature was set to 120°C, which was ramped up to 300°C at a rate of 10°C/min where it was held for 3 min. The FID detector temperature was set to 330°C. External calibration was used to quantify the sulfolane in the sample. Detection limit for sulfolane analysis using this method was 1 ppm.

3. RESULTS AND DISCUSSIONS

3.1 Degradation of sulfolane in synthetic water

![Figure 1: Degradation of sulfolane using Fenton like reagent in synthetic water: [FeCl₃] =1mM; [H₂O₂] = 15mM; [NTA disodium] = 1mM.](image)

The degradation of sulfolane in the spiked water using Fenton-like reagents at different initial pH is shown in Figure 1. The pHs adjusted here were the ones of water before adding Fenton reagents. The change of normalized sulfolane concentration versus the reaction time is reported here. The results showed that sulfolane can be degraded by FeCl₃+H₂O₂ when initial pH of water was adjusted to be 3. Approximately 60% of sulfolane degraded after one hour and more than 95% of sulfolane degraded after three hours at pH = 3. The degradation of sulfolane is due to the generated hydroxyl radicals through Fenton-like reaction. No sulfolane degradation was observed at neutral pH using FeCl₃+H₂O₂. However, NTA chelated iron with hydrogen peroxide can degrade sulfolane without pH adjustment. The
degradation of sulfolane with NTA chelated iron + H₂O₂ is similar to the degradation of sulfolane at acidic condition with FeCl₃+H₂O₂.

3.2 Degradation of sulfolane in water collected from the field

To evaluate whether Fenton-like reagents can degrade sulfolane in the groundwater without pH adjustment, Fenton like reagents (FeCl₃/H₂O₂) and (NTA/Fe(III)/H₂O₂) were tested with sulfolane contaminated groundwater (see Table 1 for properties). The results (Figure 2) showed that sulfolane cannot degrade without pH adjustment using FeCl₃/H₂O₂. However, NTA/Fe(III)/H₂O₂ can degrade approximately 60% of sulfolane within 30 minutes. No further sulfolane degradation was observed after the initial 60% sulfolane reduction. As shown in Table 1, groundwater has high bicarbonate concentration indicating that the pH of water might be almost constant throughout the experiment. Compared to synthetic water, sulfolane degradation in groundwater by NTA/Fe(III)/H₂O₂ is less efficient. This can be explained by the complex composition of groundwater. De Laat et al. (2011) found that bicarbonates in water can act as hydroxyl radical scavengers and inhibit the Fenton reaction. De Laat (2001) also reported that the inhibiting effect of bicarbonate ion is less important than the one to tert-butanol, an organic compound. It was calculated that only 60% of dissolved organic carbon (DOC) in our groundwater comes from sulfolane and the rest of DOC may be contributed from humic materials or other organic compounds. These organic compounds can compete with sulfolane for hydroxyl radicals and inhibit the degradation of sulfolane. Furthermore, interferences in the groundwater may impact the stability of NTA/Fe(III) in the water and make them precipitate in the water. Orange precipitates were observed in this experiment which is hypothesized to be hydrous iron oxyhydroxides. The cessation of the reaction may due to two possible reasons: (a) hydrogen peroxide was consumed completely or (b) all catalytic active Fe (III) precipitated out.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfolane</td>
<td>mg/L</td>
<td>130</td>
</tr>
<tr>
<td>Hardness (CaCO₃)</td>
<td>mg/L</td>
<td>691</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>mg/L</td>
<td>726</td>
</tr>
<tr>
<td>Conductivity</td>
<td>µS/cm</td>
<td>1290</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.58</td>
</tr>
<tr>
<td>Dissolved Organic Carbon</td>
<td>mg/L</td>
<td>87.5</td>
</tr>
<tr>
<td>Alkalinity (Total as CaCO₃)</td>
<td>mg/L</td>
<td>641</td>
</tr>
<tr>
<td>Bicarbonate (HCO₃)</td>
<td>mg/L</td>
<td>782</td>
</tr>
<tr>
<td>Sulphate (SO₄)</td>
<td>mg/L</td>
<td>38.6</td>
</tr>
<tr>
<td>Chloride (Cl)</td>
<td>mg/L</td>
<td>32.5</td>
</tr>
<tr>
<td>Nitrate (NO₃)</td>
<td>mg/L</td>
<td>0.300</td>
</tr>
<tr>
<td>Nitrate plus Nitrite (N)</td>
<td>mg/L</td>
<td>0.068</td>
</tr>
<tr>
<td>Nitrite (N)</td>
<td>mg/L</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Dissolved Kjeldahl Nitrogen</td>
<td>mg/L</td>
<td>3.21</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>mg/L</td>
<td>197</td>
</tr>
</tbody>
</table>
Figure 2: Degradation of sulfolane using Fenton like reagents in groundwater, no pH adjustment: \([\text{FeCl}_3] = 1\text{mM}; [\text{H}_2\text{O}_2] = 15\text{mM}; [\text{NTA disodium}] = 1\text{mM}\).

Additional hydrogen peroxide was added into the system to see whether hydrogen peroxide was limited in the reaction and the result is reported in Figure 3. The results showed that the addition of hydrogen peroxide did not improve the degradation of sulfolane, which indicated that the cessation of the reaction was not due to the shortage of hydrogen peroxide. Therefore, the loss of catalytic activity due to precipitation of iron was the main reason for the cessation of reaction. NTA can be oxidized by hydroxyl radicals and form glycine, iminodiacetic acid, oxalic acid, ammonia and carbon dioxide (Chen et al. 1995). The oxidization of NTA led to a progressive decomplexation of NTA chelated iron and precipitation of Fe(III) after the complete depletion of free NTA in solution (De Laat et al. 2011). The results (Figure 3) also showed that addition of NTA disodium cannot convert iron in the form of precipitate to catalytically active iron in a short period. A higher concentration of NTA disodium was applied in the beginning to see whether it can improve the sulfolane degradation by NTA/Fe(III)/H$_2$O$_2$ in the water. The results (Figure 4) showed that an increase of initial NTA disodium concentration decreased the degradation rate. The excess of NTA disodium can act as hydroxyl radical scavengers (Chen et al. 1995) and compete hydroxyl radicals with sulfolane.

Figure 3: The effect of addition of hydrogen peroxide and NTA disodium after one hour: (a) control, \([\text{FeCl}_3] = 1\text{mM}, [\text{H}_2\text{O}_2] = 15\text{mM}, [\text{NTA disodium}] = 1\text{mM}\); (b) add more H$_2$O$_2$ after one hour; (c) add more NTA disodium after one hour.
3.3 Evaluation of four commercial catalysts

Four different commercially available products marketed as neutral pH catalysts including Fe(II)DTPA, EDTA chelated Iron, VTH and VTX were tested for the degradation of sulfolane in groundwater. The results (Figure 5) showed that Fe(II)DTPA/H$_2$O$_2$ can degrade 20% of sulfolane in groundwater and EDTA chelated iron /H$_2$O$_2$ can degrade approximately 50% of sulfolane. No significant degradation of sulfolane was observed when VTX or VTH was combined with H$_2$O$_2$ within two hours. Similar to NTA/Fe(III)/H$_2$O$_2$, EDTA chelated iron/H$_2$O$_2$ can degrade sulfolane but the reaction ceased at 50% of sulfolane degradation. Orange precipitate (probably hydrous iron oxyhydroxides) was observed for EDTA chelated iron/H$_2$O$_2$ experiments.

Figure 4: The effect of initial NTA disodium concentration: (a) [FeCl$_3$] =1mM, [H$_2$O$_2$] = 15mM, [NTA disodium] = 1mM; (b) [FeCl$_3$] =1mM, [H$_2$O$_2$] = 15mM, [NTA disodium] = 3mM.

Figure 5: Degradation of sulfolane using four different commercial catalysts with hydrogen peroxide: (a) [Fe(II)DPTA]=1mM, [H$_2$O$_2$] = 15mM; (b) [EDTA chelated iron]=1mM, [H$_2$O$_2$] = 15mM; (c) [VTH]=0.4% (w/w), [H$_2$O$_2$] = 15mM; (d)[VTX]=0.4% (w/w), [H$_2$O$_2$] = 15mM.
### 3.4 Batch mode vs semi-continuous mode

Two different modes of adding Fenton reagents were evaluated here. Table 2 summarizes the amount of chemicals added into water at different times for different modes. The total amount of Fenton reagents added were the same for both modes. The sulfolane degradation results with EDTA chelated iron/H$_2$O$_2$ or NTA chelated iron/H$_2$O$_2$ at different modes were reported in Figure 6. The results showed that the degradation of sulfolane in semi-continuous mode is slower than that in batch mode in the beginning, but in the end, similar percentage of sulfolane degradation was obtained for both.

<table>
<thead>
<tr>
<th>Time (minute)</th>
<th>Batch mode</th>
<th>Semi-continuous mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chelated iron added* (mmol)</td>
<td>H$_2$O$_2$ added (mmol)</td>
</tr>
<tr>
<td>0</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Volume of water is 100 ml.

![Graph](image)

Figure 6: Degradation of sulfolane with chelated iron/H$_2$O$_2$ using different modes: (a) NTA chelated iron + H$_2$O$_2$, semi-continuous mode; (b) EDTA chelated iron + H$_2$O$_2$, semi-continuous mode; (c) NTA chelated iron + H$_2$O$_2$, batch mode; (d) EDTA chelated iron + H$_2$O$_2$, batch mode.

### 4. CONCLUSIONS

The following conclusions are drawn from this research:

- NTA/Fe(III)/H$_2$O$_2$ can degrade sulfolane and achieve a significant reduction (60%) in groundwater.
- The initial concentration of chelating agents can impact the efficiency of sulfolane degradation.
- The mode of adding Fenton like reagents did not impact the overall sulfolane degradation efficiency.
- Among the commercial neutral catalysts investigated, EDTA chelated iron combined with hydrogen peroxide showed the most promising result in degrading sulfolane in groundwater.
- During the process of sulfolane degradation, the loss of catalytically active iron due to iron precipitation led to the cessation of the reaction.
ACKNOWLEDGEMENT

The authors acknowledge the financial support provided by Bonavista Energy Corporation to conduct this research.

REFERENCES


Barr Engineering Company. 2013. Revised point-of-entry treatment system feasibility study and design report, Prepared for Flint Hills Resources Alaska, LLC.


