Extended Fenton’s process: toward improving biodegradability of drilling wastewater

Ran Ding, Yanming Wang, Xing Chen, Yingxin Gao and Min Yang†

ABSTRACT

In this study, an extended Fenton process was used to improve biodegradability of the waste drilling mud containing bio-refractory polymers. Variation of biodegradability and organics with different molecular weights with the oxidation time were investigated during the Fenton oxidation process. Although the residual total organic carbon (TOC) arrived at a stable level soon after oxidation reaction, organics with the lower molecular weight increased and its biodegradability was improved significantly in the extended oxidation process, which originated from decomposition of residual H2O2 catalyzed by transformation of the Fe3+/Fe2+ and organoradicals. Under the conditions that follow: pH 3.0, H2O2 500 mg L−1, Fe2+ 250 mg L−1, oxidation time 120 min, further TOC removal of 35.9% and biochemical oxygen demand and total organic carbon (BOD/TOC) ratio of 0.83 was achieved. At the biological test, a substantial increase in TOC degradation by biological treatment with extension of Fenton oxidation time was observed. Finally, more than 90% biological removal of the TOC was achieved for the 120 min oxidation treatment. The experimental results highlight that an extended process can be adopted to improve the biodegradability of wastewater by utilization of the slow reaction of hydrogen peroxide with Fe3+/ and organoradicals.

Key words | adsorption removal, bio-refractory organics, extended Fenton oxidation, improvement of biodegradability, waste drilling mud

INTRODUCTION

With the large demand of oil and natural gas in modern civilization, more and more wastewater is generated during the drilling process. The drilling wastewater contains organic pollutants with high chemical oxygen demand (COD) level and low biodegradability, which can cause serious environmental and ecological impacts (Bakke et al. 2013; Dos Santos et al. 2014; Changmai et al. 2019). Typically, there are still some refractory organic pollutants in the effluent after conventional coagulation, including some chemical agents with large molecular weight usually adopted as additives to drilling mud, such as ammonium polyacrylonitrile (NH4-HPAN), sulfonated phenolic resin (SMP), silicon stabilization agent (SSA), and acrylonitrile-acrylamide-potassium (FKP), etc. (as shown in Figure 1).

Various advanced oxidation methods were applied to remove the pollutants directly, or enhance their biodegradability (Wang et al. 2004; Chen et al. 2016; Xu et al. 2017; Zhang et al. 2017; Tian et al. 2019). Chen et al. had reported a modified UV-Fenton process with addition of carboxymethyl-beta-cyclodextrin for treatment of phenolic contaminants at neutral pH (Chen et al. 2016). Patino et al. had used a combination of ozone oxidation and membrane separation to treat oil drilling wastewater, and effectively reduced COD Cr from 7,838 mg L−1 to 77 mg L−1 (Patino 1999). Yanming Wang had improved the biodegradability of oil field drilling wastewater using ozone oxidation. The minimum biochemical oxygen demand and total organic carbon (BOD/TOC) ratio (0.4 g/g) was observed when wastewater was treated with ozone continuously for 15 min (Wang et al. 2004). However, the high costs, and high energy consumption of ozone or UV-aided oxidation process limited its wide applications.

As one of the most promising advanced oxidation processes, Fenton’s reagent can be used for effective oxidation based on the production of highly reactive hydroxyl radical (-OH) through decomposition of H2O2 catalyzed by Fe2+/ (Xu et al. 2017; Uman et al. 2018). Up to now, Fenton...
oxidation process has been well used in wastewater treatment for improving its biodegradability (Mater et al. 2007; Khan et al. 2009; Sanchis et al. 2013; Wildea et al. 2017). Sanchis et al. have evaluated the feasibility of Fenton’s oxidation as a pretreatment or tertiary treatment following the activated sludge process in the pigment wastewater. It was found that the removal efficiency of COD was 54.2%, the removal efficiency of the color was 91.2% and BOD5/COD ratio was increased from 0.04 to 0.36 under conditions: H2O2/COD = 1.85 (w/w), H2O2/Fe2+ = 10 (molar), HRT = 0.5 h (Sanchis et al. 2013). Kitis et al. have studied the effectiveness of Fenton’s reagent pretreatment on the biodegradability of selected nonionic surfactants. Their results demonstrated Fenton’s reagent can enhance the biodegradability significantly for some compounds. As to polypropylene glycol (PPG), after the application of 1,750 mg L−1 H2O2 (H2O2/Fe2+ molar ratio of approximately unity, pH of 3, and oxidation time of 10 min), the biodegradable fraction of PPG increased from 2% to 90% (Kitis et al. 1999). Martins et al. have studied the effect of Fenton’s peroxidation on the biodegradability of phenol wastewater. The Fenton reagents with certain ratio injected in the wastewater each 30 min during 6 h of reaction reached optimal efficiencies. The analysis of BOD5/COD ratio obtained a high improvement of the treated wastewater biodegradability from 0.30 to 0.80 after Fenton oxidation (Martins et al. 2010). Xu et al. have investigated the effects of Fenton reaction parameters on COD removal, the dissolved organic matter (DOM) removal and the transformation and migration of typical organic matters during the treatment of petrochemical wastewater. The highest COD removal efficiency of 61.9% can be achieved under the optimized condition (Xu et al. 2017). Most of these studies focused on the effect of Fenton’s oxidation on the toxic organics removal and variations of biodegradability during the Fenton oxidation.

It should be noted that the value of COD stabilized in the short time during the common Fenton oxidation process, which was usually considered as one of the important indicators of Fenton’s oxidation process related to the enhancement of biodegradability (Sanchis et al. 2013; Xu et al. 2016). However, the reactions during the ‘stable’ stage and its impacts on the biodegradability have not been well investigated, especially in the drilling wastewater treatment process. In this study, we mainly focus on the reactions after the COD got ‘stable’, the so-called ‘extended Fenton process’. Herein, the effects of whole Fenton’s oxidation process on the improvement of biodegradability were systematically investigated for treatment of the drilling wastewater, containing the BOD/TOC ratio and the batch experiment. Furthermore, the distributions of molecular weight were also adopted to uncover the inherent mechanism of biodegradability enhancement during the whole Fenton oxidation process.
FENTON'S PROCESS MATERIALS AND METHODS

Materials and wastewater

Stock solutions of H2O2 (1%) and FeSO4 (1,000 mg L\(^{-1}\)) were prepared from hydrogen peroxide (30%) and reagent grade granular ferrous sulfate respectively diluted by deionized water. Polyalumium chloride (PAC, Al2O3 content: 30%) was obtained from the First Chemical Plant of Dagang Oilfield in China. All other chemicals and solvents were analytical grade and used without further purification.

The drilling wastewater was taken from a wastewater pit in Jidong Oilfield located in Tangshan City, Hebei Province. The main chemical additives, such as NH4-HPAN, SMP, PAC-141, silicon stabilization agents and FPK were injected into oil wells (3,200 m in depth) during the drilling process.

Experimental methods

The drilling wastewater was firstly treated by coagulation process with PAC dose of 1,000 mg L\(^{-1}\), pH of 4.6–4.8. Then, Fenton’s oxidation process was performed in a 2.0 L glass jar with a sample port located 3 cm below the water surface under vigorous magnetic stirring. The solution temperature was controlled at 25 °C by a thermostatic jacket, and the initial pH was adjusted to 3.0 ± 0.1 using H2SO4 or NaOH solutions (Wu et al. 2011). The effect of H2O2 and Fe\(^{2+}\) dosages on removal efficiency was investigated for a H2O2 concentration range between 200 and 1,000 mg L\(^{-1}\) and the molar ratio of Fe\(^{2+}\)/H2O2 between 0.1 to 0.5.

Batch biological treatment was performed for Fenton’s process treated wastewater in 500 L Erlenmeyer flasks on the shaking table with shaking at 160 rpm under the temperature of 20 ± 1 °C. 300 L Fenton’s process treated supernatants were added to the flasks in which seed sludge was inoculated (the seed sludge was collected from a municipal wastewater treatment plant in Beijing, acclimated with drilling wastewater for one week, and the concentration of sludge was about 2,200 mg L\(^{-1}\)). The initial pH of 7.0 (±0.2) was controlled for batch aerobic bioassay. Samples were periodically taken from the flasks to remove the biomass by centrifugation for TOC analysis. The effects of biosorption were verified by using mercuric nitrate to inhibit biological activity in control tests (Swisher 1987).

All the experiments were conducted three times.

Analytical methods

The TOC of liquid samples and solid samples were measured on a TOC-500 analyzer (Shimadzu Co., Japan) and Apollo-9000 (Tekmar-Dohrmann Co., USA), respectively. A slight excess of sulfite was added to quench H2O2 and terminate the Fenton reactions for TOC measurement.

The BOD\(_5\) analysis were conducted on a manometric BOD analyzer (Oxi Top IS6, Germany). For the determination of BOD\(_5\), the pH of samples was adjusted to 7, and then the residual H2O2 was quenched through aeration for 12 h.

H2O2 was measured by potassium iodide-sodium thiosulfate titration (Kitis et al. 1999). The concentrations of Fe\(^{2+}\) were determined by using the o-phenanthroline colorimetric method at 510 nm. COD, total nitrogen (TN), total phosphorus (TP), Cl\(^-\) and SS were measured according to the Standard Methods of Water and Wastewater Monitoring of China (fourth edition).

For determination of molecular weight distribution of organics in wastewater, a membrane filtration unit was used. Ultrafiltration membranes (acetate fiber) with different molecular weight cut-offs (60,000 Daltons, 10,000 Daltons, and 3,000 Daltons MWCOs) were mounted on the bottom of a transparent plastic cell (effective volume, 1.5 L) connected to a nitrogen gas cylinder. The membranes were produced by the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, and the working pressure was set to 0.3 MPa.

The Fenton oxidation reaction was quenched with sulfite, and iron ions were removed by precipitation with adjusting pH to 7.0. Before TOC measurements, all the samples were filtered through a 0.22 μm membrane filter. To discriminate the contributions of Fenton oxidation and iron sludge adsorption toward pollutant removal, TOC of iron sludge precipitates were also measured by using the solid-module analyzer.

RESULTS AND DISCUSSION

The characteristics of the drilling wastewater from Jidong Oilfield are listed in Table 1. The BOD\(_5\)/COD is as low as 0.02, indicating that the biodegradability of drilling wastewater

<table>
<thead>
<tr>
<th>Items</th>
<th>COD (mg L(^{-1}))</th>
<th>TOC (mg L(^{-1}))</th>
<th>BOD(_5) (mg L(^{-1}))</th>
<th>TN (mg L(^{-1}))</th>
<th>TP (mg L(^{-1}))</th>
<th>Cl(^-) (mg L(^{-1}))</th>
<th>SS (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>5,800 ± 107</td>
<td>1,850 ± 20.4</td>
<td>126 ± 15.5</td>
<td>135.6 ± 5.23</td>
<td>22.6 ± 2.20</td>
<td>9,160 ± 28.6</td>
<td>1,400 ± 65.3</td>
</tr>
</tbody>
</table>
was poor. This might be attributed to the chemical additive agents with large molecular weight. The total TOC is 1,850 mg L$^{-1}$. The molecular weight distribution analysis results indicate that organic substances with molecular weight over 60,000 Daltons exceeded 83.5% in the drilling wastewater.

Conventional coagulation was performed as the pretreatment process, for that it was one of the cheapest, and most efficient method for wastewater treatment. After coagulation with PAC dose of 1,000 mg L$^{-1}$ and pH of 4.6–4.8, TOC of the supernatant reduced to 168.5 mg L$^{-1}$. Although approximately 91% of the organic pollutants were removed, the outlet water still contained high concentration of TOC that cannot reach the industrial discharge standard.

Figure 2(a) shows the effects of concentration of H$_2$O$_2$ on the TOC removal at a constant Fe$^{2+}$/H$_2$O$_2$ molar ratio during Fenton oxidation process. As Fe$^{2+}$/H$_2$O$_2$ molar ratio was 0.1, the TOC value decreased quickly in no more than 10 min, and then got nearly ‘stable’. To be well discussed, the process was divided into two stages at 10 min: ‘reactive’ stage and ‘stable’ stage. After 120 min, the TOC got to 135.2 mg L$^{-1}$, 124.3 mg L$^{-1}$, and 109.6 mg L$^{-1}$, respectively, when the H$_2$O$_2$ dosages were 200 mg L$^{-1}$, 500 mg L$^{-1}$, and 1,000 mg L$^{-1}$. Obviously, the TOC removal ratio was dependent on H$_2$O$_2$ dosage. This indicated that more reactive hydroxyl radicals (·OH) were produced with increase of H$_2$O$_2$ dosage, and hydroxyl radicals reacted with the easily oxidized groups or small molecules quickly, leading to the sharp decrease of TOC. The same phenomenon can be observed when the Fe$^{2+}$/H$_2$O$_2$ molar ratio was improved to 0.5 as shown in Figure 2(b). However, the effect of H$_2$O$_2$ dosage on TOC removal was not so significant. It might be attributed to the reactions of Fe$^{2+}$ during the Fenton process. On the one hand, Fe$^{2+}$ takes part in the reactions of ·OH production. On the other hand, overdosed Fe$^{2+}$ can scavenge ·OH (Joseph et al. 2000). Additionally, Fe$^{2+}$ would be transformed into Fe$^{3+}$ or other forms of iron complexes, which can absorb pollutants in the solution, especially after adjusting the pH from acidic to neutral.

In order to study the mechanism of TOC removal during Fenton oxidation treatment, the concentrations of H$_2$O$_2$ and Fe$^{2+}$ over time were also plotted as shown in Figures 3 and 4. Similar to the TOC results, concentrations of H$_2$O$_2$ and Fe$^{2+}$ also have two stages.

In the ‘reactive’ stage, a rapid decomposition of H$_2$O$_2$ occurred in Figure 3, and more than 98% of Fe$^{2+}$ was transformed into Fe$^{3+}$ by H$_2$O$_2$ in this stage.
previous study, a quick reaction rate at the start of the reactions (Equation (1)) led to rapid decrease of H$_2$O$_2$, Fe$^{2+}$, and TOC within 10 min. Interestingly, a maximum residual Fe$^{2+}$ began to occur after about 10 min reaction in Figure 4. This result is similar to previous research findings that reductive intermediates of the hydroxylation of pollutants, such as hydroquinone (and benzoquinone) catalyze the redox reactions through an electron-shuttle (Chen & Pignatello 1997; Pignatello et al. 2006). It was speculated that similar mechanisms were likely present in this system that reductive intermediates reduces Fe$^{3+}$ by successive electron-transfer, which resulted in the increase of residual Fe$^{2+}$ level.

$$
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot \text{OH} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \cdot \text{O}_2\text{H}^+ + \text{H}^+ \tag{2}
$$

In the ‘stable’ stage, it was found that the residual H$_2$O$_2$ was still quite high, that is, the slow decomposition of hydrogen peroxide was observed and the residual Fe$^{2+}$ decreased to a stable level with time. The residual Fe$^{2+}$ varied in a range between 4 and 21 mg L$^{-1}$, depending on the Fe$^{2+}$/H$_2$O$_2$ molar ratio and initial H$_2$O$_2$ dose. Obviously, properties of the organic substances in drilling wastewater affect the Fenton reactions. The high residual hydrogen peroxide occurs just after the initial decrease of hydrogen peroxide, since the reaction of RH with ·OH (Equation (3)), overwhelms the reaction of hydrogen peroxide with ·OH (Equation (4)) (Neyens & Baeyens 2005). The possible reason was proposed that the oxidation of Fe$^{2+}$ by H$_2$O$_2$ (Equation (1)) counterpoised with the reduction of Fe$^{3+}$ by H$_2$O$_2$ and organoradicals (Equations (2) and (5)), which resulted in the stable level of Fe$^{2+}$, and then highly reductive organic intermediates were oxidized with extension of oxidation time. However, generation rate of Fe$^{2+}$ from the reduction of Fe$^{3+}$ by H$_2$O$_2$ (Equation (2)) and organoradicals (Equation (5)) was much lower than consumption rate of Fe$^{2+}$ (Equation (1)), so the high-level residue of hydrogen peroxide occurred.

$$
\text{RH} + \cdot \text{OH} \rightarrow \text{R} + \text{H}_2\text{O} \tag{3}
$$
$$
\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2 \cdot + \text{H}_2\text{O} \tag{4}
$$
$$
\text{R} \cdot + \text{Fe}^{3+} \rightarrow \text{R}^+ + \text{Fe}^{2+} \tag{5}
$$

In order to further investigate the removal mechanism during the Fenton process, the contribution of mineralization by Fenton oxidation and adsorption by hydrolyzed iron ions (mainly Fe$^{3+}$) were tested as shown in Table 2. On the one hand, the amount of TOC removed by oxidation remained almost unchanged (from 22.9 mg to 23.8 mg) when the Fe$^{2+}$/H$_2$O$_2$ ratio was increased from 0.1 to 0.5 under the given H$_2$O$_2$ dose (500 mg L$^{-1}$), indicating that the oxidation reaction was mainly determined by the H$_2$O$_2$ dose. On the other hand, the contribution of adsorption to TOC removal increased from 42.7% to 55.3% when the Fe$^{2+}$/H$_2$O$_2$ molar ratio was increased from 0.1 to 0.5. The result demonstrated that the increased TOC removal upon the increased Fe$^{2+}$/H$_2$O$_2$ molar ratio mainly resulted from the increased Fe$^{3+}$ adsorbent. Gao et al. also reported

![Figure 4](https://iwaponline.com/wst/article-pdf/79/9/1790/575793/wst079091790.pdf)

Table 2 | Contributions of adsorption and oxidation to TOC removal

<table>
<thead>
<tr>
<th>Items</th>
<th>1*</th>
<th>2*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial TOC (mg)</td>
<td>134.8 ± 2.45</td>
<td></td>
</tr>
<tr>
<td>TOC of reaction after 120 min (mg)</td>
<td>94.8 ± 2.04</td>
<td>81.5 ± 1.84</td>
</tr>
<tr>
<td>Removed TOC (mg)</td>
<td>40.0 ± 0.41</td>
<td>53.3 ± 0.20</td>
</tr>
<tr>
<td>Adsorbed TOC (mg)</td>
<td>17.1 ± 1.39</td>
<td>29.5 ± 0.20</td>
</tr>
<tr>
<td>Oxidation TOC (mg)</td>
<td>22.9 ± 0.98</td>
<td>23.8 ± 0.41</td>
</tr>
<tr>
<td>Adsorption ratio (%)</td>
<td>42.7 ± 0.03</td>
<td>55.3 ± 0.58</td>
</tr>
<tr>
<td>Oxidation ratio (%)</td>
<td>57.3 ± 0.03</td>
<td>44.7 ± 0.58</td>
</tr>
</tbody>
</table>

*Fenton condition: 500 mg L$^{-1}$ H$_2$O$_2$, Fe$^{2+}$/H$_2$O$_2$ = 0.1, pH = 3.0.

*Fenton condition: 500 mg L$^{-1}$ H$_2$O$_2$, Fe$^{2+}$/H$_2$O$_2$ = 0.5, pH = 3.0.
that the contribution of mineralization to TOC removal increased with the increase of H$_2$O$_2$ dosage and under an high Fe$^{2+}$/H$_2$O$_2$ molar ratio, nearly 80% of TOC removal was caused by adsorption for the total TOC removal of 49% (Gao et al. 2004). It was proven that the hydrolysis rate of Fe$^{3+}$ species in the Fenton process was faster and more complicated than that in the ferric sulphate system. The generated Fe$^{3+}$ species had a larger polymerization degree, which was helpful to the adsorption removal of organic pollutants (Gao et al. 2009). Therefore, the proper Fe$^{2+}$ dosages might be beneficial for TOC removal in Fenton treatment of drilling wastewater.

Figure 5 shows the variation of biodegradability of organic compounds in Fenton oxidation over a period of 150 min with the addition of 500 mg L$^{-1}$ H$_2$O$_2$ at the Fe$^{2+}$/H$_2$O$_2$ molar ratio of 0.5. In the first 10 min, a significant increase of the BOD/TOC ratio from 0.19 to 0.48 was observed, accompanied by the TOC decrease from 168.5 mg L$^{-1}$ to 122 mg L$^{-1}$ by oxidation. Interestingly, the BOD and BOD/TOC ratio increased gradually from 50 mg L$^{-1}$ to 100 mg L$^{-1}$ and from 0.48 to 0.95, respectively, though the TOC almost changed a little during the following 140 min. It can be speculated that the improved biodegradability was mainly attributed to the oxidation reactions.

To testify the hypothesis above, changes of molecular weight distribution over time were measured as shown in Figure 6. With extension of reaction time, TOC of all fractions with molecular weights above 3,000 Daltons decreased markedly, and the components with molecular weights under 3,000 Daltons increased to over 90% of total TOC after 60 min. This demonstrated that the extension of Fenton reaction did not apparently make an increase in total TOC removal, but organic compounds with molecular weights under 3,000 Daltons produced significantly during Fenton oxidation treatment, resulting in biodegradability improvement of the drilling wastewater. It can be found that the extension of Fenton reaction time without improving the dosages of H$_2$O$_2$ and Fe$^{3+}$ enhance the biodegradability of drilling wastewater. Considering the slow reaction of hydrogen peroxide with Fe$^{3+}$ in the second stage, the oxidation reactions were still occurring based on not only -OH radicals, but also the organoradicals produced from organics in drilling wastewater by Fenton oxidation.

Batch biodegradation test was performed to investigate the practical application of extensive Fenton oxidation treatment. In the batch biodegradation test, samples were withdrawn at different oxidation times (10 min, 30 min, 60 min, 120 min) to be measured as shown in Figure 7. By treating drilling wastewater under an H$_2$O$_2$ dose of

![Figure 6](https://iwaponline.com/wst/article-pdf/79/9/1790/575793/wst079091790.pdf)
500 mg L\(^{-1}\) at Fe\(^{3+}\)/H\(_2\)O\(_2\) molar ratio of 0.5, when the oxidation time was extended from 10 min to 120 min, the removal efficiency of TOC could increase from 50\% to 90\% in biological treatment. A high COD removal occurred after biological treatment for 13 h, beyond which COD of the oxidized wastewater was removed slowly. It can be seen that the above result of batch biodegradation tests verified the improvement of biodegradability with the increase of oxidation time, which originated from the more biodegradable organic substances produced by the slow reaction of hydrogen peroxide with Fe\(^{3+}\) and organoradicals.

**CONCLUSION**

An extended Fenton process was investigated as a key technique for improving biodegradability of the drilling wastewater containing mainly bio-refractory polymers. The effective improvement of biodegradability of drilling wastewater was achieved by utilization of the slow reaction of hydrogen peroxide with Fe\(^{3+}\) and organoradicals at relatively low H\(_2\)O\(_2\) and Fe\(^{2+}\) doses, which produced more biodegradable organic substances. The ratio of BOD to TOC approached 1.0, and components with molecular weights under 3,000 Daltons reached over 90\% of the total TOC under an H\(_2\)O\(_2\) dose of 500 mg L\(^{-1}\) at Fe\(^{3+}\)/H\(_2\)O\(_2\) molar ratio of 0.5 for 150 min. More than 90\% of the TOC can be biologically removed when drilling wastewater was oxidized for 150 min by Fenton oxidation. In light of this finding, we believed that extended Fenton’s process coupled with biodegradation process would be one of the most promising methods for treatment of drilling wastewater.

**ACKNOWLEDGEMENTS**

The authors acknowledge the financial support from National Natural Science Foundation of China (Grant No. 21777164) and Fundamental Research Funds for the Central Universities (Grant No. PA2019GDQT0019).

**REFERENCES**


Sanchis, S., Polo, A. M., Tobajas, M., Rodriguez, J. J. & Mohedano, A. F. 2013 Degradation of chlorophenoxy herbicides by...


First received 8 January 2019; accepted in revised form 16 May 2019. Available online 24 May 2019