Treatment of oilfield wastewater by combined process of micro-electrolysis, Fenton oxidation and coagulation

Zhenchao Zhang

ABSTRACT

In this study, a combined process was developed that included micro-electrolysis, Fenton oxidation and coagulation to treat oilfield fracturing wastewater. Micro-electrolysis and Fenton oxidation were applied to reduce chemical oxygen demand (COD) organic load and to enhance organic components gradability, respectively. Orthogonal experiment were employed to investigate the influence factors of micro-electrolysis and Fenton oxidation on COD removal efficiency. For micro-electrolysis, the optimum conditions were: pH, 3; iron-carbon dosage, 50 mg/L; mass ratio of iron-carbon, 2:3; reaction time, 60 min. For Fenton oxidation, a total reaction time of 90 min, a H2O2 dosage of 12 mg/L, with a H2O2/Fe2+ mole ratio of 30, pH of 3 were selected to achieve optimum oxidation. The optimum conditions in coagulation process: pH, cationic polyacrylamide dosage, mixing speed and time is 4.3, 2 mg/L, 150 rpm and 30 s, respectively. In the continuous treatment process under optimized conditions, the COD of oily wastewater fell 56.95%, 46.23%, 30.67%, respectively, from last stage and the total COD removal efficiency reached 83.94% (from 4,314 to 693 mg/L). In the overall treatment process under optimized conditions, the COD of oily wastewater was reduced from 4,314 to 637 mg/L, and the COD removal efficiency reached 85.23%. The contribution of each stage is 68.45% (micro-electrolysis), 24.07% (Fenton oxidation), 7.48% (coagulation), respectively. Micro-electrolysis is the uppermost influencing process on COD removal. Compared with the COD removal efficiency of three processes on raw wastewater under optimized conditions: the COD removal efficiency of single micro-electrolysis, single Fenton oxidation, single coagulation is 58.34%, 44.88% and 39.72%, respectively. Experiments proved the effect of combined process is marvelous and the overall water quality of the final effluent could meet the class III national wastewater discharge standard of petrochemical industry of China (GB8978-1996).

Key words | COD removal efficiency, Fenton oxidation-coagulation, fracturing wastewater, micro-electrolysis, orthogonal experiment

INTRODUCTION

Oilfield fracturing wastewater is a by-product of various processes in oil and gas production. During the production stage, large amounts of wastewater are generated during hydraulic fracturing to recover oil from deep shale formations (Aguilera 1980; Neghaban et al. 1998; Hickenbottom et al. 2015). This fracturing wastewater contains various impurities solids, heavy metals, polymers, chemical additives, proppants, oil, etc. (Olsson et al. 2015). The wastewater is characterized by high chemical oxygen demand (COD), chrominance and salinity, strong acidity and viscosity, which has become one of the main sources of water pollution in oilfields and can increase considerable environmental hazards if discharged without effective treatment (Chase et al. 1997). At this time, disposal of fracturing wastewater constitutes one of the most significant waste discharges associated with oil well drilling (Yang et al. 2014).

Usually, fracturing wastewater is often treated by using coagulation, neutralization, oxidation, activated carbon adsorption alone or their integration in Chinese (Divakaran & Pillai 2001; Chen et al. 2011). The effectiveness and applicability of a physicochemical coagulation/flocculation process for the pretreatment of textile industry discharges...
containing Hydron blue dye using Al₂(SO₄)₃ as a destabilizing agent was studied. The process was effective with a maximum yield of 77% under optimized conditions (Chenna et al. 2016). Suspended matter and fluoride are simultaneously eliminated by combining coagulation and electroflotation. The electroflotation cell was equipped with DSA titanium coated with ruthenium oxide (Ti/RuO₂) as anode and stainless steel as cathode. Under optimum conditions, the solid-liquid separation efficiency is about 97% which corresponds to a residual turbidity of 4.4 NTU (Aoudj et al. 2015). Evaluation of modified Algerian clay as a mineral adsorbent was done for its adsorbing capacity on copper and zinc cations. Biological flocculant (chitosan) was employed to speed up the settling of generated clay suspensions. The results show a rapid kinetic adsorption for both metals following the pseudo-second-order model with high elimination rates of 67.2% and 61.8% for Cu and Zn, respectively (Ferhat et al. 2018). However, the treatment effect is not ideal, which causes limitation for field application.

Micro-electrolysis and Fenton oxidation has been used to pretreat industrial wastewater widely due to extensive adaptability to wide variations of compositions of wastewater (Wang et al. 2006). Especially, it has been studied on treatment of poor biodegradable wastewater, including pesticide wastewater (Wu et al. 2005), pharmacy wastewater (Wang & Zhang 2001; Liu et al. 2005) and dye wastewater (Li & Xia 2003; Cheng et al. 2005). From a chemical point of view, waste iron chips containing a lot of carbon form numerous galvanic cells between iron and carbon in wastewater, which results in galvanic cell reaction in the electrical flow. Products released from galvanic cell reaction include hydroxyl, atomic hydrogen and Fe²⁺. Those free radicals have a strong ability of oxidation and are easy to react with contaminants (Santos et al. 2006). Furthermore, those high activated products and numerous galvanic cell reactions lead to redox electro-flocculation and consequently remove contaminants (Glaze 1987; Wang et al. 2006; Yang et al. 2009; Hörsing et al. 2012). The electrode reaction mechanism has taken place as follows (Neyens & Baeyens 2003; Janda et al. 2004).

Anode reaction: \( Fe - 2e^- \rightarrow Fe^{2+} \) \( E^0_{Fe^{2+}/Fe} = -0.44 \text{V} \)  \( (1) \)

Cathode reaction: \( 2H^+ + 2e^- \rightarrow 2[H] \)
\( \rightarrow H_2 \uparrow E^0_{H^+/H_2} = 0.00 \text{V} \)  \( (2) \)

In the condition of full oxygen, the cathode reaction can change as follows:

With oxygen attended: \( O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{acid solution} \) \( E^0_{O_2} = 1.23 \text{V} \)  \( (3) \)

Neutral and alkaline solution: \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{acid solution} \) \( E^0_{OH} = 0.40 \text{V} \)  \( (4) \)

By contrast, chemical oxidation may not only decompose target contaminants but also reduce toxicity associated with formulation ingredients and active agents through the generation of extremely reactive hydroxyl radical (·OH) in the acid condition. What is more, the process does not produce secondary pollution. So it can be an effective pretreatment step for recalcitrant wastewater (Bagal & Gogate 2014). If the flocculation method was used alone to treat wastewater, the removal efficiency of COD can reach 68.6% which is not meeting the effluent discharge standard. Fenton oxidation method was used alone to treat the mid-stage pulping effluent, the removal efficiency of COD and chrominance can reach 77% and 98% respectively, which is a perfect result in some senses and the effluent can be reused but the cost is too high (Yoon et al. 2001). By contrast, micro-electrolysis method can treat wastewater with processes of wastes against one another because its raw material is abandoned scrap iron. The generated Fe²⁺ in the micro-electrolytic process can act as the raw material of the Fenton oxidation process and the pH requested by micro-electrolysis process and Fenton oxidation process are almost the same, thus the collo-cational method of the two methods can save the acid and alkali used in the adjustment process of pH (Chen et al. 2014). The abundant Fe³⁺ generated in the Fenton oxidation process is a kind of efficient flocculant, therefore the method of micro-electrolysis couples with Fenton oxidation-flocculation technology used for the treatment of oilfield fracturing wastewater. This cannot only enhance the treatment efficiency greatly but also decrease the treatment cost (Wilén et al. 2004; Gao et al. 2005). Lan and Wu (Lan et al. 2013) applied the integration of micro-electrolysis and Fenton Oxidation process to treat oilfield wastewater, and a total COD removal efficiency of 96.98% was obtained and the quality of sewage treatment is greatly enhanced. Atmaca also discussed the feasibility of using electro-Fenton to treat the landfill leachate and the results show that the removal of COD can reach 72% under the conditions of cast-iron anode and cathode plates, 58.82 mM of H₂O₂, 15.6 mM of Fe²⁺ and pH 3.0 (Atmaca 2009).
In this present work, the oilfield fracturing wastewater was treated sequentially by using micro-electrolysis, hydrogen peroxide oxidation and coagulation. The experimental conditions of micro-electrolysis and Fenton oxidation were optimized by the orthogonal array.

**MATERIALS AND METHODS**

**Chemicals**

The hydrogen peroxide (H₂O₂, 30%, v/v), sodium hydroxide (NaOH), hydrochloric acid (HCl), ferrous sulfate heptahydrate (FeSO₄·7H₂O), potassium dichromate (K₂Cr₂O₇), cationic polyacrylamide (CPAM) were of analytical grade, and other chemicals used were analytical reagent grade. All solutions were prepared with distilled water.

Activated carbon (nutshell-based, high-grade, carbon content ≥21%, average particle size 3 mm). Iron scraps (C45E4 steel, scraps of steel-tubes processing, carbon content 0.42–0.50%, particle size 3–5 mm).

**Fracturing wastewater**

Raw fracturing wastewater employed in this study was obtained from CNOOC (China National Offshore Oil Corporation). The oil was skimmed before being used and determined. The wastewater was stored at 4°C until required. The main characteristics of the fracturing wastewater are listed in Table 1. As shown, the fracturing wastewater had high concentrations of COD, total dissolved solids and suspended solids (SS). In addition, the fracturing wastewater had high chroma.

**Micro-electrolysis design**

The micro-electrolysis experiments were carried out in a rectangular reactor with 1,000 mL working volume. The micro-electrolysis cell was equipped with iron scraps (C45E4 steel) as anode and activated carbon as cathode. The reactor was immersed in an ice-water bath to keep the temperature constant at 20°C. A magnetic stirrer (Model DW-3, Yingyu Yuhua Instrument Plant, China) provided mixing of the solution in the reactor. The initial pH value of the wastewater was adjusted using concentrated sulfuric acid and sodium hydroxide before the wastewater was transferred to the reactor. At the pre-selected time interval, 500 mL samples were withdrawn from the reactor and neutralized by sodium hydroxide to precipitate iron ions. The neutralized samples were centrifuged for 10 min at 2,000 rpm using a centrifuge (TDL-5Z, Hunan Xingke, China). The COD value of the supernatant indicated the residual COD in the effluent after the overall process (Wu et al. 2012). The optimum micro-electrolysis conditions were determined by the application of the orthogonal experimental design L₉(4)⁵. The five factors were iron-carbon mass ratio, iron-carbon dosage, reaction time and pH. The five levels of each factor and the arrangements of orthogonal experiments are listed in Table 2.

**Fenton oxidation design**

Fenton oxidation experiment has been carried out in a standard agitated reactor provided with a six blade turbine and four equally spaced baffles to avoid vortex formation. A 300 mL wastewater based on the optimum conditions of electrolytic experiment was investigated in the 500 mL flask. The Fenton process consists of four stages: pH adjustment, oxidation, neutralization and sedimentation. Firstly, the pH of the treated wastewater was adjusted to 3.0 with sulphuric acid. Immediately, a known volume of H₂O₂ was added. All these operations were carried with 800 rpm agitation speed to provide rapid mixing of reagents. In the case of experiments at acidic conditions, Fe²⁺ was oxidized by H₂O₂ to ferric ion by dissolved oxygen. After the desired duration of oxidation, calcium oxide was added to adjust the pH to 8.0–9.0. The solution was allowed to settle for 1 h, the supernatant collected and its COD measured. The optimum oxidation conditions were determined by using the orthogonal experimental design L₁₆(4)⁵. The four factors were pH, H₂O₂ dosage, H₂O₂/Fe²⁺ mole ratio and reaction time. The five levels of each factor and the arrangements of orthogonal experiments are listed in Table 3.

**Coagulation treatment**

Based on the optimum conditions of Fenton oxidation and micro-electrolysis experiment, subsequent coagulation
experiment were performed in the same 500 mL flask. First, add 250 mL wastewater into the flask, then add the CPAM and stir the mixture by an electronic stirrer at 150 rpm, which was maintained at room temperature. After 10 min of stirring, the mixture was allowed to stand for 1 h, and then the supernatant was taken for characterization.

COD was analyzed according to the potassium dichromate standard method (Cao 2009), the chroma was measured using UV-Vis spectrophotometry, and the pH value using a digital pH (pHS-25, Shanghai Leici Instrument Factory, China).

**Data analysis**

All experiments in this study were performed in triplicate to ensure a repeatability error less than 5%, and the results presented here represent the average values of three independent measurements. The results for all orthogonal experiments were fed in statistical software SPSS 13.0 for the analysis of variance.

### RESULTS AND DISCUSSION

#### Effect of micro-electrolysis conditions

The micro-electrolysis results were closely related with micro-electrolysis conditions, such as iron-carbon dosage, reaction time, pH, etc. To obtain the optimum micro-electrolysis conditions, the orthogonal experiments of five levels and four factors were performed. Because the content of COD was much higher than that of others in this kind of wastewater (Table 1), the selection of micro-electrolysis conditions was based on COD removal.

The experimental results are listed in Table 2. K₁, K₂ and K₃ were the average value of COD removal of level 1, level 2, and level 3, respectively, for each factor; R was the difference between the maximum and the minimum of the average values of the experimental results, under different levels of the same factor or the range. The higher the value of R was, the larger the effect of the factor was on the COD removal. It can be obtained from Table 2 that

<table>
<thead>
<tr>
<th>No.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Reaction time (min)</td>
<td>Iron-carbon mass ratio</td>
<td>Iron-carbon dosage (g/L)</td>
<td>COD removal (%)</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>20</td>
<td>1:2</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>40</td>
<td>1:2</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>60</td>
<td>1:2</td>
<td>70</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>90</td>
<td>1:2</td>
<td>90</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>40</td>
<td>2:3</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>20</td>
<td>2:3</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>90</td>
<td>2:3</td>
<td>70</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>60</td>
<td>2:3</td>
<td>90</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>60</td>
<td>1:1</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>90</td>
<td>1:1</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>20</td>
<td>1:1</td>
<td>70</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>40</td>
<td>1:1</td>
<td>90</td>
<td>3</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>90</td>
<td>3:2</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>14</td>
<td>2</td>
<td>60</td>
<td>3:2</td>
<td>50</td>
<td>4</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>40</td>
<td>3:2</td>
<td>70</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>4</td>
<td>20</td>
<td>3:2</td>
<td>90</td>
<td>2</td>
</tr>
<tr>
<td>K₁</td>
<td>34.833</td>
<td>32.775</td>
<td>39.993</td>
<td>26.483</td>
<td>40.820</td>
</tr>
<tr>
<td>K₂</td>
<td>43.558</td>
<td>35.680</td>
<td>44.718</td>
<td>43.515</td>
<td>38.288</td>
</tr>
<tr>
<td>K₃</td>
<td>40.313</td>
<td>43.278</td>
<td>40.025</td>
<td>42.685</td>
<td>38.535</td>
</tr>
<tr>
<td>K₄</td>
<td>35.710</td>
<td>42.680</td>
<td>29.678</td>
<td>41.730</td>
<td>36.770</td>
</tr>
<tr>
<td>R</td>
<td>8.725</td>
<td>10.503</td>
<td>15.040</td>
<td>17.032</td>
<td>4.050</td>
</tr>
</tbody>
</table>

**Table 2** Orthogonal experiment design and result of iron-carbon micro-electrolysis
the influence of the coefficients of micro-electrolysis conditions on the COD removal was in the following decreasing order: iron-carbon dosage > iron-carbon mass ratio > reaction time > pH. Then the optimum conditions were obtained as follows: iron-carbon dosage, 90 g/L; iron-carbon mass ratio, 2:3; reaction time, 60 min and pH, 3.

Table 2 demonstrates that iron-carbon dosage was the most dominant factor influencing COD removal efficiency. This may be because when the iron-carbon dosage was small, iron was less than carbon and the amount of dissolution leaching was small, relatively. The anode material was insufficient, so it could not provide sufficient electronics to cathode and the electrode reaction was blocked and affected the treatment of organic pollutants (Yang et al. 2015). With the iron-carbon dosage increasing, the situation of inadequate supply of electronics improved gradually. When continuing to increase iron-carbon dosage, iron becomes overloaded. It could cause local density of new hydrogen in solution to be too large when they react with hydrogen ions (Solano et al. 2015). It would interact quickly and release produced hydrogen before reaction of organic pollutants. It was not beneficial to the removal of organic matter and reflected on the quick decrease of COD removal efficiency. To check the results obtained above, under the optimum micro-electrolysis conditions, a series of experiments were conducted separately on the wastewater and the results are shown in Figure 1. As shown, the COD removal efficiency significantly as the iron-carbon dosage increased up to 50 g/L, when the iron-carbon dosage varied from 50 to 90 g/L. However, the COD removal efficiency only slightly increased from 56.95% to 59.69%. Thereupon, in engineering, iron-carbon dosage is too small, the amount of used carbon is large, and then the cost is high. The system's power loss will increase and the dose of active drug will increase if iron-carbon dosage is too large and not economical. Taking it into consideration, the optimum iron-carbon dosage is 50 g/L in actual production process.
Effect of Fenton oxidation conditions

Under the optimum micro-electrolysis conditions, the COD of the wastewater decreased from 4,314 to 1,857 mg/L (Table 4). This indicates that the fracturing wastewater contained a large amount of dissolved recalcitrant organic components, which were not effectively removed by the micro-electrolysis treatment. Thereupon, Fenton oxidation aimed at enhancing degradation of the organic wastewater was required.

Based on a five-level factorial experiment and the results of orthogonal experiments, factors influencing the efficiency of the H₂O₂ oxidation were analyzed with the range method. As shown in Table 3, the factor most influential on COD removal efficiency was pH, followed by H₂O₂ dosage, reaction time and H₂O₂/Fe²⁺ mole ratio, and their optimum conditions were obtained as follows: 3, 12 mg/L, 50 min and 30, respectively. In the oxidation process, COD removal efficiency has reached 46.23% and the supernatant has a COD of 999 mg/L (Table 4).

Because of the amount of Fe²⁺ in the solution after micro-electrolysis experiments, it can be used as a catalyst for sufficient degradation of H₂O₂. In this process, the Fe²⁺ is made good use of without being added. Table 5 shows the evolution of remaining concentration of COD and COD removal based on the optimum conditions except the variation pH. The importance of pH on Fenton oxidation of organic compounds in water has been shown in previous studies with different conclusions. Sedlak and Andern (Sedlak & Ander 1991) reported that pH values between 3 and 5 were most effective for oxidation. So we choose the condition of acidity and found that when the pH was lower than 3, removal efficiency of COD was increasing with the increase of pH. When pH was 3, the removal efficiency of COD reached 45.5% in the oxidation process. That could be explained by the mechanism of the Fenton oxidation reaction (Pan et al. 2008):

$\text{Fe}^{2+} + \text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}_2^-$  \hspace{1cm} (5)

$\text{Fe}^{2+} + \text{HO}_2^- \rightarrow \text{Fe}^{3+} + \text{HO}_2$  \hspace{1cm} (6)

$\text{HO}_2 + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+$  \hspace{1cm} (7)

According to this mechanism, ferrous and ferric irons compete for the hydroperoxide radical through reactions (5) to (7). However, at pH higher than 3, Fe³⁺ exists mostly as hydroxy complex like Fe(OH)²⁺ or Fe(OH)₃⁺ or as insoluble oxygen-hydroxide like Fe₂O₃ or Fe(OH)₃. In addition, since the rate of Fe²⁺ oxidation of with oxygen is proportional to the square of the hydroxyl ion concentration, C₂OH⁻, while that with H₂O₂ is only proportional to C₀OH⁻, at high pH formation of Fe³⁺ complex or hydroxides are favored and generation of hydroxyl radicals under the mild conditions (Kang et al. 2002; Martínez et al. 2003; Sanz et al. 2003; Heredia et al. 2004) through the reaction (8) or (9) diminishes. Thus, reactions like (7) predominate at high pH:

$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}$ \hspace{1cm} (8)

$\text{H}_2\text{O}_2 + \text{Fe(OH)}^+ \rightarrow \text{Fe(OH)}_2^+ + \cdot\text{OH}$ \hspace{1cm} (9)

$\text{Fe(OH)}_2 + 0.5\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3$ \hspace{1cm} (10)

So that the removal of COD of wastewater oxidation are inhibited.

### Table 4 | Changes in water quality parameters during micro-electrolysis and Fenton treatment under their respective optimum conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw wastewater</th>
<th>After micro-electrolysis</th>
<th>After Fenton oxidation</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>4,314</td>
<td>1,857</td>
<td>999</td>
<td>76.84</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>586</td>
<td>73</td>
<td>35</td>
<td>94.03</td>
</tr>
<tr>
<td>Oil and grease (mg/L)</td>
<td>4.31</td>
<td>3.18</td>
<td>1.95</td>
<td>54.76</td>
</tr>
<tr>
<td>Chroma (0)</td>
<td>165</td>
<td>76</td>
<td>18</td>
<td>89.09</td>
</tr>
</tbody>
</table>

Figure 1 | Effect of the dosage of iron-carbon on COD removal during micro-electrolysis. The experimental conditions: iron-carbon mass ratio, 2:3; reaction time, 60 min; pH, 3 and room temperature.
Subsequent coagulation process

Coagulation and flocculation process can reduce the fraction of recalcitrant organic matter present in wastewater, particularly humic substances, which can be verified by COD reduction. Meanwhile, the coagulation results were closely related with coagulation conditions (Pliego et al. 2014) such as dosage of flocculent, stirring time and pH, etc. After being treated by micro-electrolysis and Fenton oxidation, the fracturing wastewater contains large quantities of ferric ion that can be used as the coagulant in this paper. Experimental results indicate that COD removal was most effective at pH 4 under acidic conditions (Cheibub et al. 2014). Under which the ferric ions could hydrolyze and form polynuclear cation, such as Fe(OH)²⁺, Fe₂(OH)₄²⁻, Fe₃(OH)₅⁵⁺, and other species with positive charges, especially when using ferric chloride as the coagulant. In addition, rapid mixing of 150 rpm for 30 s achieved the highest extent of COD removal and was chosen for process optimization. In this paper, under the condition of the pH 4.3, mixing at 150 rpm for 30 s, and the effect of CPAM on the COD was investigated as flocculant. The results were shown in Figure 2.

As shown in Figure 2, increasing the dosage of the CPAM favored COD removal. A dosage of less than 2 mg/L flocculant did lead to a significant reduction in the COD. However, when the dosage exceeded 2 mg/L, the COD began to increase gradually. The coagulation mechanisms of CPAM include the interaction of hydroxides, neutralization, precipitation and accumulation (Divakaran & Pillai 2001) in the suitable dosage, thus can remove the COD. Nevertheless, when it acts as the organic matter, in turn, can increase the organic content when overused. So the optimal CPAM dosage obtained was 2 mg/L, with a 30.67% reduction in the COD and the COD of the wastewater decreased to 693 mg/L.

Based on the above results, the 2 mg/L dosage of CPAM was considered adequate for this coagulation treatment. After the micro-electrolysis/Fenton/coagulation treatment, the total COD removal was 83.94%. The COD of the effluent could satisfy the professional emission standard (grade three) (COD <1,000 mg/L) of petrochemical industry of PR China (GB8978-1996).

Overall treatment under optimized conditions

The whole treatment was performed in just one experiment and described straightforwardly step by step, based on the results and optimal conditions obtained before. A fresh 200 mL sample of fracturing wastewater was used. The analysis of the sample indicated that it contained 4,314 mg/L COD and 586 mg/L SS, and pH lower than 7. Table 5 shows the initial and final values of selected parameters.

The steps for the treatment were the following (Figure 3):

1. Sulfuric acid was added to obtain pH 3 (2.8% v/v). This acidification condition promoted an efficient micro-electrolysis environment to degrade of organic substances.
2. Iron and carbon were added to the wastewater, and the conditions were: iron-carbon dosage, 50 mg/L; iron-carbon mass ratio, 2:3; reaction time, 60 min. The solution gradually turned into black with a large amount of SS.
3. The micro-electrolysis solid was filtered, and in the solution, COD dropped to 1,797 mg/L.
4. H₂O₂ was added to the filtered solution in steps under the optimum conditions (dosage, 12 mg/L; reaction time, 50 min). When Fenton process has basically reached equilibrium, the residual COD is about 912 mg/L.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before treatment</th>
<th>After treatment</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>4,314</td>
<td>637</td>
<td>85.23</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>586</td>
<td>20.46</td>
<td>96.51</td>
</tr>
<tr>
<td>Oil and grease (mg/L)</td>
<td>4.31</td>
<td>1.06</td>
<td>75.41</td>
</tr>
<tr>
<td>Chroma (°)</td>
<td>165</td>
<td>6.9</td>
<td>95.82</td>
</tr>
</tbody>
</table>

Figure 2 | The effects of CPAM on the COD.
After Fenton treatment, the CPAM was added into the solution. Because the effluent retains a large number of iron ions, it can be a good coagulant and the coagulation mixed better with CPAM. After coagulation, a large number of alum flocc and iron mud deposited on the bottom. Meanwhile, the supernatant turned bright yellow, caused by residual iron ions. The COD drastically diminished to 637 mg/L.

At the end of the coagulation step, neutralization was performed by adding calcium oxide up to pH 8.5. The iron precipitated immediately, with an excellent settlement after approximately 1 h. In this step, iron ions were removed in the form of ferric hydroxide.

After neutralization, the effluent was filtered (Figure 3, treated wastewater). The obtained concentrations of COD, SS, oil and grease, and chroma are shown in Table 5. In addition, iron ions (0.67 mg/L) remaining after the treatment was in agreement with local regulations, and with H$_2$O$_2$, no regulations for discharge have been found in the literature. However, it would be advisable to use a lower amount than in the present work in the last addition before calcium oxide precipitation. The addition of a quenching agent to destroy H$_2$O$_2$ excess could be another alternative.

The effectiveness of each stage is shown in Figure 4. In the overall treatment process under optimized conditions, the COD of oily wastewater was reduced from 4,314 mg/L to 637 mg/L, and the COD removal efficiency reached 85.23%. Therefore, the contribution of micro-electrolysis process, Fenton oxidation process, coagulation process on the COD removal is 68.45%, 24.07%, 7.48%, respectively. It indicates that micro-electrolysis is the uppermost influencing process on COD removal, followed by Fenton oxidation and coagulation process.

The effectiveness of the integration of advanced oxidation and coagulation processes for treating recalcitrant wastewater, including oily wastewater, has been extensively reported by many researchers (Li et al. 2012; Ying et al. 2013). The first step aimed to simplify the chemical structure of recalcitrant organic substances for enhancing their
degradability. For fracturing wastewater, it has been demonstrated that no single technology can meet suitable effluent characteristics, and two or more treatment systems are required in series operation (Olsson et al., 2015). Micro-electrolysis can be used to remove dissolved refractory organics and colloidal particles but have many limited problems. For instance, some constituents are not completely degraded, galvanic reaction can easily be blocked due to surface passivation prone and generate more iron mud, etc. Thus, micro-electrolysis is usually combined with other treatment processes. In a laboratory-scale study of the combined micro-electrolysis/Fenton oxidation adsorption process, COD and chrominance of produced wastewater were reduced to 217 and 40.8 mg/L from 1,360 and 240 mg/L, respectively (Lan et al., 2015). In this process, operational conditions for the process were as follows: aeration was 6 L/min, the mass ratio of iron-carbon was 4:1, the addition of iron was 1,500 mg/L, pH was 4, and reaction time was 30 min, the addition of H₂O₂ (concentration is 50%) was 3 mg/L, pH was 4, and oxidation reaction time was 15 min. Coagulation and flocculation is the usual method for treating wastewater to further remove what has not been degraded or degraded incompletely macromolecular organic matter. Meanwhile, the COD removal efficiency for the effluent is also increased. In the present study, by using the combination of micro-electrolysis/Fenton/coagulation treatment, the total COD removal was 85.23% (initial value 4,314 mg/L) and neutralization and sedimentation was required for the filter process. This demonstrated the salient features of the present work.

**Process comparison**

Comparison of the COD removal efficiency under three different conditions:

1. Single micro-electrolysis: pH, reaction time, iron-carbon mass ratio and iron-carbon dosage is 3, 60 min, 2:3 and 50 g/L, respectively.
2. Single Fenton oxidation: pH, reaction time, H₂O₂/Fe²⁺ mole ratio and H₂O₂ dosage is 3, 50 min, 30 and 12 mg/L, respectively.
3. Single coagulation: pH, CPAM dosage, mixing speed and time is 4.3, 2 mg/L, 150 rpm and 30 s, respectively.

The results are shown in Figure 5. The COD removal efficiency of three process is 58.34%, 44.88% and 39.72%, respectively. Micro-electrolysis process has a greater effect on COD removal efficiency than the other two processes. Compared with single micro-electrolysis, single Fenton oxidation and single coagulation, a relatively higher COD removal efficiency can be achieved in the combined process. Under the experimental conditions, the effect of the combined process is marvelous.

**CONCLUSIONS**

In this work, an integrated process, including micro-electrolysis, Fenton and coagulation showed excellent performance in the removal efficiency of COD, oil and grease, SS and chroma of oilfield fracturing wastewater. The experimental conditions of micro-electrolysis and Fenton oxidation were
optimized by the orthogonal array. For micro-electrolysis, the optimum conditions were: pH 3; iron-carbon dosage, 50 mg/L; mass ratio of iron-carbon, 2:3; reaction time, 60 min. For Fenton oxidation, a total reaction time of 90 min, a H$_2$O$_2$ dosage of 12 mg/L, with a H$_2$O$_2$/Fe$^{2+}$ mole ratio of 30, pH of 3 were selected to achieve optimum oxidation. The optimum conditions in coagulation process: pH, CPAM dosage, mixing speed and time is 4.3, 2 mg/L, 150 rpm and 30 s, respectively. In the continuous treatment process under optimized conditions, the COD of oily wastewater fell 56.95%, 46.23%, 30.67%, respectively, from last stage and the total COD removal efficiency reached 85.94% (from 4,314 mg/L to 693 mg/L). In the overall treatment process under optimized conditions, the COD of oily wastewater was reduced from 4,314 mg/L to 637 mg/L, and the COD removal efficiency reached 85.23%. The contribution of each stage is 68.45% (micro-electrolysis process), 24.07% (Fenton oxidation process), 7.48% (coagulation process), respectively. The micro-electrolysis is the uppermost influencing process on COD removal. Comparing the COD removal efficiency of three processes on raw wastewater under optimized conditions: the COD removal efficiency of single micro-electrolysis, single Fenton oxidation, single coagulation is 58.34%, 44.88% and 39.72%, respectively. Experiments proved the water quality of the effluent could meet the professional discharge standard (grade three) set forth by China’s EPA and the combined treatment method offers an attractive alternative in disposing of the recalcitrant petrochemical waste stream.

ACKNOWLEDGEMENTS

The authors thank the kind help of China National Offshore Oil Corporation in Tianjin for providing water samples.

REFERENCES


Bagal, M. V. & Gogate, P. R. 2014 Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review. Ultrasoundics Sonochemistry 21 (1), 1–14.

Cao, Q. 2009 The uncertainty analyze of determination of the chemical oxygen demand in water by potassium dichromate method. Pollution Control Technology 3, 95–98.


