Combined treatment of hydroxypropyl guar gum in oilfield fracturing wastewater by coagulation and the UV/H₂O₂/ferrioxalate complexes process

Zhenchao Zhang

ABSTRACT

Hydroxypropyl guar gum is considered to be a main component of oilfield fracturing wastewater (OFW). This work is intended to optimize the experimental conditions for the maximum oxidative degradation of hydroxypropyl guar gum by the coagulation and UV/H₂O₂/ferrioxalate complexes process. Optimal reaction conditions were proposed based on the chemical oxygen demand (COD) removal efficiency and UV-vis spectra analysis. The overall removal efficiency of COD reached 83.8% for a dilution ratio of raw wastewater of 1:2, pH of 4 and FeCl₃ loading of 1,000 mg/L in the coagulation process; the dosage of H₂O₂ (30%,v/v) was 0.6% (v/v) and added in three steps, the n(H₂O₂)/n(Fe²⁺) was 2:1, n(Fe²⁺)/n(C₂O₄²⁻) was 3:1 and pH was 4 in the UV/H₂O₂/ferrioxalate complexes process; pH was adjusted to 8.5–9 by NaOH and then cationic polyacrylamide (CPAM) of 2 mg/L was added in the neutralization and flocculation process. The decrease in COD during the coagulation process reduced the required H₂O₂ dosage and improved efficiency in the subsequent UV/H₂O₂/ferrioxalate complexes process. Furthermore, COD removal efficiency significantly increased by more than 13.4% with the introduction of oxalate compared with UV/Fenton. The UV-vis spectra analysis results indicated that the coagulation and UV/H₂O₂/ferrioxalate complexes process could efficiently remove the hydroxypropyl guar gum dissolved in OFW. An optimal combination of these parameters produced treated wastewater that met the GB8978-1996 Integrated Wastewater Discharge Standard level III emission standard.

Key words | coagulation process, hydroxypropyl guar gum, oilfield fracturing wastewater, UV/H₂O₂/ferrioxalate complexes process, UV-vis spectra analysis

INTRODUCTION

Hydroxypropyl guar gum is widely used in the hydraulic fracturing process. In the oilfield production process, large amounts of residual guar gum wastewater are generated (Wan et al. 2011; Britt 2012; Hickenbottom et al. 2013). This oilfield fracturing wastewater (OFW) contains various organic pollutants, impurities, solids, heavy metals, polymers, chemical additives, proppants, oil, etc (Chen et al. 2011; Stringfellow et al. 2014; Yang et al. 2014) that significantly increase the chemical oxygen demand (COD), colour and salinity, viscosity and strong acidity. Up to four million gallons of water-based fluid could be injected into a single drilled well to both initiate and expand fractures during hydraulic fracturing, and act as proppant transport, of which 10–70% is subsequently recovered as flowback (Lester et al. 2015). This wastewater contains high concentrations of potentially polluting organic and inorganic constituents and it requires some degree of treatment. However, hydraulic fracturing in underground gas and oil operations produces contaminated wastewater that is difficult to treat (Chapman et al. 2012; Vengosh et al. 2013). Furthermore, OFW has become one of the main sources of water pollution in oilfields and can considerably increase environmental hazards if discharged without effective treatment (Olsson et al. 2015). With the improvement of environmental protection standards and the need for energy saving and reducing emissions, an advanced treatment for OFW is necessary to satisfy wastewater discharge quality or to reuse wastewater (Mehta & Sullivan 2015).
Currently, the treatment methods of OFW include the advanced oxidative process, chemical coagulation, electrocoagulation, biological methods, activated carbon adsorption and solidification methods (Bagal & Gogate 2014; Hao et al. 2014; Akyon et al. 2015; Esmaeilirad et al. 2015; Benincà et al. 2016; Rosenblum et al. 2016), all of which have various shortcomings. For example, some methods require high processing costs, complex processing equipment, or a large amount of oxidizing agents (Rahm et al. 2015), while other methods can produce additional pollutants that do not meet national wastewater discharge standards (Hladik et al. 2013). Treatment processes that address all types of wastewater have not yet been developed and they must be refined and improved to increase the efficiency and reduce the economic costs of hydraulic fracturing.

The UV/H2O2/ferrioxalate complexes method is an emerging and promising oxidation process based on Fenton to treat high concentrations of toxic and hazardous biological materials in refractory wastewater. It is a chemical process that removes contaminants in the liquid phase, and it usually requires UV radiation and an agent to oxidize organic pollutants to CO2, water, and inorganic or small organic molecules. It not only has a strong ability to make full use of ultraviolet and visible light, but the hydroxyl radical (OH) production rate is high for the oxidative degradation of organic matter (Nogueira & Guimarães 2000; Salem et al. 2009; Li et al. 2015). The reaction of ferric ions with C2O42− generates Fe(C2O4)33− ferrioxalate complexes under UV irradiation, which has great potential photochemical activity. Fe(C2O4)33− has a high molar absorption coefficient when the wavelength is higher than 200 nm and even absorbs 500 nm visible light to generate Fe2+. The photolysis mechanism of Fe(C2O4)33− is as follows (Safarzadeh-Amiri et al. 1996; Xie et al. 2000; Lehoczki et al. 2013; Schenone et al. 2013):

\[
\text{Fe(C2O4)3}^{3−} + \text{hv} \rightarrow \text{Fe}^{2+} + 2\text{C2O2}^{4−} + \text{C2O4}^{−}
\]  \hspace{1cm} (1)

\[
\text{C2O4}^{−} + \text{Fe(C2O4)}_{3}^{3−} \rightarrow \text{Fe}^{2+} + 3\text{C2O4}^{2−} + 2\text{CO2}
\]  \hspace{1cm} (2)

\[
\text{C2O4}^{−} \rightarrow \text{CO2} + \text{CO2}^{·}
\]  \hspace{1cm} (3)

In the air-saturated solution, C2O4· and CO2· will further react with O2 to generate H2O2 in acidic conditions.

\[
\text{C2O4}^{−} + \text{CO2}^{·} + \text{O2} \rightarrow \text{O2}^{·} + 2\text{CO2}/\text{CO2}
\]  \hspace{1cm} (4)

\[
2\text{O2}^{·} + 2\text{H}^{+} \rightarrow \text{H2O2} + \text{O2}
\]  \hspace{1cm} (5)

Thus, it can offer enough reagents to the traditional Fenton reaction under photolysis of ferric oxalate complexes into Fe2+ and H2O2. In addition, the dose of H2O2 also decreases with the addition of C2O42− (Safarzadeh-Amiri et al. 1996; Zhang et al. 2002). The UV/H2O2/ferrioxalate complexes method is not only less damaging to the environment but it is also more economical compared with other advanced oxidation processes that often use harmful and/or expensive oxidizing agents, such as ozone (Pu et al. 2015). Compared with traditional treatments, the method is advantageous because it has a wider range of application, higher efficiency, produces little secondary pollution and the chemical reaction is completed during the treatment process (Yao et al. 2012).

The aim of this work is to further improve the efficiency of wastewater treatment. The process of coagulation is used in the pretreatment of OFW as well as in industrial processes for the removal/separation of organics/inorganics dissolved/suspended as colloids in water/solution (Verma et al. 2010). The effectiveness of the UV/H2O2/ferrioxalate complexes process in treating OFW was explored. Experiments were conducted to explore the effects of various operating conditions using a laboratory-scale reactor. The merits of the physicochemical method employed for the pretreatment of wastewater are primarily due to the method’s simplicity, high removal efficiency and easy onsite implementation.

MATERIALS AND METHODS

Laboratory instruments and chemicals

An ultraviolet spectrophotometer (UV-8000, Metash instrument Co., Ltd, China) and quartz cuvettes were used for measurements of absorbance analysis and COD using a dichromate solution as the oxidant in strong acid media. The pH values were determined by using an acidometer (PHS-3C, INESA Scientific Instrument Co., Ltd, China). Oxidation experiments were conducted with a six-joint heat-collection temperature magnetic stirrer (HJ-6, Changzhou ZOJE Experimental Instruction Manufacturing Co., Ltd, China). Ultraviolet light was generated using a UV lamp (300 W, Metash instrument Co., Ltd, China). A vacuum filtration device (FS3310, Shanghai collar Germany Instrument Co., Ltd, China) was also needed for treating the effluent.

The hydrogen peroxide (H2O2, 30%, w/w), sodium hydroxide (NaOH), hydrochloric acid (HCl), ferrous
sulfate heptahydrate (FeSO₄·7H₂O), ferric chloride (FeCl₃), oxalic acid (H₂C₂O₄), cationic polyacrylamide (CPAM), potassium dichromate (K₂Cr₂O₇) were of analytical grade, and other chemicals used were analytical reagent (AR) grade. All solutions were prepared with distilled water.

The raw OFW employed in this study was obtained from CNOOC (China National Offshore Oil Corporation) in Tianjin province, China. The oil was skimmed before being used and analysed. The wastewater was stored at 4 °C until required. The main characteristics of the OFW are listed in Table 1. As shown, the OFW had high concentrations of COD, total dissolved solids and suspended solids (SS). Moreover, the OFW had an intense colour.

**Experimental setup**

The experimental setup is shown in Figure 1. The coagulation and UV/H₂O₂/ferrioxalate complexes reactor designed was used batch-wise in all experiments and was a cube of 400 mm × 500 mm × 1,500 mm, with a working volume of 250 L. Pharmaceuticals were added to the reactor according to need, and circulating cooling water was used to keep the reaction system at 25 °C. A 300 W Hg lamp in a quartz sleeve was placed in the middle of the reactor. After completion of the reaction, NaOH solution was applied to adjust the pH to 8.5–9. After precipitation, the supernatant was tested for each parameter.

**Coagulation experiments**

Coagulation process was carried out with 1 L water samples at 25 °C in a jar test apparatus. The following conditions were evaluated: pH, mixing time and coagulant dosages. The coagulant evaluated in this study was FeCl₃ (analytical grade). To determine the effective coagulant dose for the OFW treatment, a bench-scale jar-testing apparatus equipped with six glass beakers (1 L) was used to conduct the coagulation experiments. A coagulant dosage in the range of 400–1,200 mg/L under the optimum pH condition was studied.

Immediately after adding the coagulant, the samples were rapidly mixed for a preestablished period of time, followed by a slow mixing stage for 20 min at 15 rpm and subsequent settling of the sludge sediment for 30 min. After the settling period, the supernatant was withdrawn from the beakers and used for analysis. Meanwhile, the pH value of the samples were adjusted to the desired levels by addition of appropriate amounts of H₂SO₄ (5%, v/v) or NaOH (5%, w/v).

Furthermore, in order to study the influence of the adding method (in one, two and three steps) on the removal of COD, the same dosage of coagulant was divided into equal volumes, as necessary. Then they were added into different water samples at intervals of 2 min.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>6.5</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>4,069–4,386</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mg/L</td>
<td>776</td>
</tr>
<tr>
<td>Suspended solids (SS)</td>
<td>mg/L</td>
<td>562–588</td>
</tr>
<tr>
<td>Colour</td>
<td></td>
<td>165 (turbid and light yellow)</td>
</tr>
<tr>
<td>Hydroxypropyl guar gum</td>
<td>mg/L</td>
<td>3,929–4,276</td>
</tr>
<tr>
<td>Total salinity</td>
<td>mg/L</td>
<td>5,126</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>mg/L</td>
<td>37</td>
</tr>
</tbody>
</table>

**Figure 1** | Schematic diagram of the experimental setup. (1) pH adjusting tank; (2) pH meter; (3) stirrer; (4) heating/cooling unit; (5) condensate outlet; (6) reaction vessel; (7) stent; (8) condensate imports; (9) UV irradiation system; (10) effluent; (11) sludge precipitation; (12) peristaltic pump.
UV/H₂O₂/ferrioxalate complexes experiments

The UV/H₂O₂/ferrioxalate complexes experiments were carried out after coagulation. The oxidative treatment of the OFW was performed at 25°C and atmospheric pressure. Operating parameters including initial pH, H₂O₂ dosage, the n(H₂O₂)/n(Fe²⁺) and n(Fe²⁺)/n(C₂O₄²⁻) were investigated.

The experiments were performed using a laboratory-scale batch reactor composed of a 500 mL cylindrical glass photoreactor. A known volume of H₂O₂ (30%, v/v) solution, FeSO₄.7H₂O and H₂C₂O₄ were loaded into the reactor under vigorous magnetic stirring and UV irradiation, respectively. The supernatant was withdrawn for COD analysis after allowing the treated wastewater to stand for 30 min.

Analytical methods

The colour value was measured using ultraviolet spectrophotometer (UV-8000, Metash instrument Co., Ltd, China). The pH values were measured using a digital pH meter (pHS-25, Shanghai Leici Instrument Factory, China). The organic matter was characterized using UV-Vis spectrophotometer (UV-2550, Shimadzu Co., Ltd, Japan). COD was analyzed according to the potassium dichromate standard method (Hach DR2800, USA) (Water Environment Federation & American Public Health Association 2005). COD removal was calculated according to the following equation (Zhang et al. 2014):

\[
\text{COD removal} (%) = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100
\]

where COD₀ and CODₜ are the COD values of the sample at time 0 and t min, respectively.

All experiments in this study were performed in triplicate to ensure repeatability error of less than 5%, and the results presented here represent the average values of three independent measurements.

RESULTS AND DISCUSSION

Coagulation process studies

Using the coagulation process to remove dissolved organic matter, SS and other colloidal solids in wastewater was cost-effective (Pliego et al. 2014). Furthermore, this process could considerably reduce the COD of the wastewater, thereby resulting in lower a H₂O₂ requirement in the subsequent UV/H₂O₂/ferrioxalate complexes process. Experiments were carried out on the dilution ratio, pH and FeCl₃ dosage.

Effect of the dilution ratio

Usually, it is important from an application point of view to study the dependence of the pollutant. Therefore, the effect of the OFW dilution ratio (namely the initial COD of the wastewater) on the degradation efficiency was investigated at different dilution ratios (relative to raw water) and presented in Figure 2(a). It can be observed that the COD removal increased significantly as the dilution ratio increased up to 1:2. When the dilution ratio increased from 1:2 to 1:3, however, the COD removal efficiency only slightly increased from 44.5% to 46.1%. This may be due to the wastewater having a high organic content, which caused relatively high resistance to coagulation, leading to difficulty in floc forming, and thus slowing sedimentation and poor coagulation efficiency under the conditions of the low dilution ratio. Therefore, the raw OFW should be diluted twice before the coagulation process.

Effect of pH

The pH value is an important parameter that affects coagulation efficiency (Wang et al. 2013). Figure 2(b) shows the efficiency of coagulation with FeCl₃ at different pH values. The maximum COD removal (43.6%) was observed at pH 4. The COD removal efficiency decreased after increasing or decreasing the pH value from pH 4. The same COD reduction phenomenon was observed when the OFW effluent was subjected to the coagulation process. Therefore, the pH value of 4 was selected for subsequent experiments.

FeCl₃ hydrolysis was performed and complex ions, such as Fe(OH)²⁺, Fe₂(OH)₄²⁺, Fe₃(OH)₅⁴⁺ with high positive charge and low polymerization were formed at low pH; charge neutralization was selected as the main mechanism of the coagulant (Tatsi et al. 2005). FeCl₃ reduces coagulation efficiency by forming the free iron ions at extremely low pH levels. The coagulation function will decrease because of the reduction of the degree of FeCl₃ depolymerization when the pH is too high.

Effect of FeCl₃ dosage

Figure 2(c) shows the effect of dosage when FeCl₃ is added for COD removal during coagulation. COD reduction
increased with increasing FeCl₃ dosage. According to the adsorption and charge neutralization theory, the negatively charged colloids in wastewater are adsorbed by the positively charged colloids of dissociated FeCl₃. Meanwhile, a slow decrease of the COD removal was observed when FeCl₃ dosage exceeded 1,200 mg/L. It might be that negatively charged colloids were neutralized with the addition of coagulant, then gradually changed to having a positive charge when the optimum dosage was exceeded. This would not be conducive to the aggregation of colloidal particles. In addition, the form of FeCl₃ addition was studied by comparing addition in one, two and three steps (with equal volumes). As shown in Figure 2(c), the COD removal increased with the increase in steps, and adding in three steps is significantly better than in one and two steps. COD removal efficiency reached 48.2% when the FeCl₃ loading was 1,000 mg/L and it had been added in three steps.

**UV/H₂O₂/ferrioxalate complexes process studies**

**Effect of initial pH on the UV/Fenton system**

Figure 3 shows the COD removal of OFW for different initial pH values. These results also reveal that the UV/Fenton system is a highly pH-sensitive process. Figure 3 shows that COD removal performance declined for pH values greater than 5. This occurs due to the formation of ferric hydroxo-complexes, namely the precipitation of Fe³⁺ as Fe(OH)₃, hindering the reaction between Fe³⁺ and H₂O₂, and therefore the regeneration of Fe²⁺. Besides, Fe(OH)₃ catalyzes the self-decomposition of H₂O₂ to oxygen molecule and water, resulting in a decline of its oxidative capacity. When the pH is higher than 8 the ferric complexes would further form [Fe(OH)₄]⁻ with the generation of flocs and consequent precipitation (Kuo 1992; Bigda 1995). This formation of flocs contributes to a small reduction of COD which occurs at pH 9. It is also possible that precipitation occurs with Fe⁵⁺ as oxy-hydroxide amorphous (Fe₂O₃·nH₂O) at a pH greater than 5 (Kim et al. 1997). On the other hand, for pH values lower than 2 the...
reaction of hydrogen peroxide with Fe\(^{2+}\) is seriously affected due to the formation of complex species [Fe(H\(_2\)O\(_6\))]\(^{2+}\), which reacts more slowly with peroxide compared to [Fe(OH)(H\(_2\)O\(_5\))]\(^{2+}\). In addition, peroxide gets solvated in the presence of high concentrations of H\(^+\) ions to form the stable peroxide ion [H\(_3\)O\(_2\)]\(^+\). The peroxide ion leads to an electrolytic behaviour on the part of hydrogen peroxide, improving its stability and substantially reducing the reactivity with ferrous ion (Bautista et al. 2007).

Therefore, the initial pH value has to be in the acidic range (3–5) to generate the maximum amount of HO\(^-\) and oxidize the organic compounds. In particular the optimal pH value is 4, which is in agreement with previous results obtained in other studies using Fenton’s reagent (Peres et al. 2007).

Effect of n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)) on the UV/Fenton system

A favourable n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)) molar ratio is worth researching in the UV/Fenton process. In this work, the molar ratios of n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)) ranged from 1:1 to 6:1 were used to evaluate the COD removal and determine the FeSO\(_4\) dosage during the UV/Fenton process. As shown in Table 2, the COD removal efficiency was significantly influenced by the addition of various FeSO\(_4\) dosages. When the molar ratio of n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)) increased from 1:1 to 6:1, the COD removal efficiency increased slightly from 42.5% to 44.2%. Then with the increase of Fe\(^{2+}\) concentration, the COD removal efficiency reached its maximum (47.8%) when the n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)) was increased to 1:1, the removal efficiency was 36.1%. This is mainly due to the relationship between the amount of free radicals generated and the Fe\(^{2+}\) content of the reaction system. The radical chain reactions in the Fenton process might be terminated when more Fe\(^{2+}\) exists in the reaction system. This is because the HO\(^-\) was produced as a result of reaction (Equation (7)) (Neyens & Baeyens 2003; Garrido-Ramírez et al. 2010). Taking the removal efficiency into consideration, the n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)) of 2:1 was selected for UV/Fenton process.

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{OH}^- \quad k_1 = 63(\text{L/mol} \cdot \text{s}) \\
\cdot\text{OH} + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad k_2 = 3.2 \times 10^8(\text{L/mol} \cdot \text{s})
\end{align*}
\]

Effect of \(\text{H}_2\text{O}_2\) dosage on the UV/Fenton system

Hydrogen peroxide plays a very important role as a source of hydroxyl radicals in the UV/Fenton process. Figure 4 presents the effect of \(\text{H}_2\text{O}_2\) dosage on COD removal with time under the condition of n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)) of 2:1 and pH 4. The figure shows that COD removal occurs principally at initial period (0–30 min) and as the reaction time increased the COD removal approached a plateau under different \(\text{H}_2\text{O}_2\) dosages. The maximum COD removal was achieved at a \(\text{H}_2\text{O}_2\) dosage of 0.6% (v/v). Below the optimal \(\text{H}_2\text{O}_2\) dosage, oxidation removal efficiency increased with the increase of \(\text{H}_2\text{O}_2\) dosage because of the increment of ·OH (Equation (7)). Then, continuous increase \(\text{H}_2\text{O}_2\) dosage can reduce the COD removal efficiency, which could be attributed to the scavenger effect of excess \(\text{H}_2\text{O}_2\). The degradation rate decreased as the \(\text{H}_2\text{O}_2\) dosage continued to increase beyond the suitable level. The scavenging effect of ·OH by ·OH and the consumption of \(\text{H}_2\text{O}_2\) by ·OH were the important elements (Equations (9) and (10)) (Kuo 1992; Nguyen et al. 2012). The COD removal efficiency

```latex
\begin{table}
\centering
\begin{tabular}{|c|c|}
\hline
n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)) & COD removal rate \\
\hline
1:1 & 36.1\% \\
2:1 & 47.8\% \\
3:1 & 46.8\% \\
4:1 & 44.2\% \\
5:1 & 41.9\% \\
6:1 & 42.5\% \\
\hline
\end{tabular}
\caption{Effect of n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)) on COD removal rate (experimental conditions: \(\text{H}_2\text{O}_2\) dosage, 0.6%; pH, 4)}
\end{table}
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Figure 4 | Effect of \(\text{H}_2\text{O}_2\) dosage (%, v/v) of OFW on COD removal treated with UV/Fenton system; (experimental conditions: n(H\(_2\)O\(_2\))/n(Fe\(^{2+}\)), 2; pH, 4).
reached 48.7% when the H2O2 dosage and reaction time were 0.6% and 80 min, respectively. In this study, 0.6% was selected as the suitable H2O2 dosage for the UV/Fenton process.

\[
\text{HO}^\cdot + \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \quad k_3 = 5.3 \times 10^9 (\text{L/mol} \cdot \text{s}) \quad (9)
\]

\[
\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2 \cdot + \text{H}_2\text{O} \quad k_4 = 1.2 \times 10^7 (\text{L/mol} \cdot \text{s}) \quad (10)
\]

Furthermore, the dosage in which H2O2 is added can affect the UV/Fenton reaction. First, the form of H2O2 addition was studied by comparing addition in single step to that in three steps (with equal volumes) under the H2O2 dosage of 0.6% (v/v). As shown in Figure 4, COD removal with addition in three steps (47.8%) is better than in one step (43%). The main reason is that multiple additions can make the reagent dispersion more uniform and lead to more complete reactions. Therefore, the H2O2 ought to be added in three steps.

**Effect of n(Fe²⁺)/n(C₂O₄²⁻) on the UV/H₂O₂/ferrioxalate complexes system**

The effect of the n(Fe²⁺)/n(C₂O₄²⁻) on the removal efficiency of COD is shown in Table 3, where the data derive from samples at an initial pH of 4, H₂O₂ dosage of 0.6%, n(H₂O₂)/n(Fe²⁺) of 2:1. The n(Fe²⁺)/n(C₂O₄²⁻) was varied from 0 to 3:1. As shown in Figure 8, the COD removal of the UV/H₂O₂/ferrioxalate complexes system reached 55.2%, 13.4% higher than for UV/Fenton when the n(Fe²⁺)/n(C₂O₄²⁻) was 3:1. The main reason was that ferrioxalate complexes could generate more hydroxyl radicals than in the UV/Fenton process under UV irradiation and rapidly oxidative degradation of various organic substances.

**Table 3** Effect of n(Fe²⁺)/n(C₂O₄²⁻) on COD removal rate (experimental conditions: H₂O₂ dosage, 0.6%; n(H₂O₂)/n(Fe²⁺), 2:1; pH, 4)

<table>
<thead>
<tr>
<th>n(Fe²⁺)/n(C₂O₄²⁻)</th>
<th>COD removal rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>41.1%</td>
</tr>
<tr>
<td>1:1</td>
<td>49.9%</td>
</tr>
<tr>
<td>2:1</td>
<td>47.8%</td>
</tr>
<tr>
<td>3:1</td>
<td>55.2%</td>
</tr>
<tr>
<td>1:2</td>
<td>32.9%</td>
</tr>
<tr>
<td>1:3</td>
<td>26.5%</td>
</tr>
</tbody>
</table>

Under the UV/H₂O₂/ferrioxalate complexes system, ·OH will be generated through the reaction shown in Equation (7) if the FeSO₄ and H₂O₂ are added first. On the other hand, the ferrioxalate complexes will be formed through the reaction of Fe²⁺ and C₂O₄²⁻, then quickly react with H₂O₂ and generate ·OH if the FeSO₄ and K₂C₂O₄ are added first. The form distribution of ferrioxalate complexes are determined by n(Fe²⁺) or Fe²⁺)/n(C₂O₄²⁻) and different forms of ferrioxalate complexes photoactive will cause ·OH to be generated at different rates. Furthermore, the amount of Fe(C₂O₄)³⁻ produced will be reduced if the K₂C₂O₄ concentration is too low. On the other hand, if excessive, it will generate amounts of HCO₃⁻ and CO₃⁻ under the high concentration K₂C₂O₄ solution which have a scavenging effect on ·OH. Through the reaction between HCO₃⁻, CO₃⁻ and ·OH, the secondary radicals HCO₅⁻ and CO₅⁻ will be generated. The secondary radicals generated could react with organics at relatively low speed. In addition, the photocatalytic decomposition reaction of Fe(C₂O₄)³⁻ will be inhibited if the K₂C₂O₄ concentration is too high. Only if n(H₂O₂)/n(Fe²⁺) and n(Fe²⁺)/n(C₂O₄²⁻) are in a suitable range will more ·OH will be obtained.

In this work, the n(Fe²⁺)/n(C₂O₄²⁻) of 3:1 was selected as the optimum conditions of OFW treated by the UV/H₂O₂/ferrioxalate complexes process.

**Neutralization and flocculation studies**

After the coagulation/UV/H₂O₂/ferrioxalate complexes process, a large number of iron ions dissolved in the wastewater. When NaOH was added to the water to adjust the pH to 8.5–9, an amount of Fe³⁺ will be converted into Fe(OH)₃, which is considered an excellent chemical coagulant. Then, adding an appropriate amount of CPAM leads to the formation of large precipitates immediately. After standing for 30 min, the water was filtered through a membrane (0.45 μm) using vacuum suction filter. As shown in Figure 5, the COD removal efficiency increased with the increase of CPAM dosage from 0 to 2 mg/L, and then decreased when the CPAM dosage exceed 2 mg/L. The reason is that the reaction mechanisms of CPAM include the interaction of hydroxides, neutralization, precipitation and accumulation (Divakaran & Pillai 2001) in the suitable conditions. Nevertheless, it acts as the organic matter and, in turn, can increase the organic content when overused. So the optimal CPAM dosage was 2 mg/L, with a 30.2% reduction in the COD during the single process.
Coagulation and UV/H₂O₂/ferrioxalate complexes process

Based on the optimization of the coagulation and UV/H₂O₂/ferrioxalate complexes process, the OFW was initially subjected to a coagulation process. Subsequently, the supernatant water was withdrawn and subjected to the UV/H₂O₂/ferrioxalate complexes process. Experimental parameters were controlled under individual selected conditions. The characteristics of the coagulation and UV/H₂O₂/ferrioxalate complexes process treated effluent and the overall treatment efficiency are summarized in Figure 6. A total of 48.2% COD could be removed in the coagulation process at pH 4, dilution ratio of raw OFW of 1:2 and dosage of FeCl₃ of 1,000 mg/L, whereas 55.1% COD was removed in the UV/H₂O₂/ferrioxalate complexes process at pH 4, at H₂O₂ dosage of 0.6% (v/v), n(H₂O₂)/n(Fe²⁺) of 2:1 and n(Fe²⁺)/n(C₂O₄²⁻) of 3:1. Furthermore, 50.4% COD was removed in the neutralization and flocculation process at pH 8.5–9 and CPAM dosage of 2 mg/L, which lead to 83.8% the overall COD removal efficiency. In addition, Table 4 lists the changes in other water quality parameters after coagulation and oxidation treatment under their respective optimum conditions. The levels of oil and grease, SS as well as colour in OFW after coagulation and the UV/H₂O₂/ferrioxalate complexes process treatment under the optimum conditions could satisfy the professional emission standard (grade one) of the petrochemical industry of the PR China (GB4287-92) (oil and grease < 10 mg/L, SS < 50 mg/L, colour < 10⁶). Furthermore, compared this testing process with the other commonly used processes from Table 5, the coagulation and UV/H₂O₂/ferrioxalate complexes process proved to be an effective advanced treatment for wastewater.

UV-vis spectra analysis

Figure 7 shows the UV–vis spectra for pre-treatment and post-treatment OFW. Different absorption peaks were observed when the wavelength range from 190 to 460 nm. The main reason is that OFW contains a large amount of guar gum, surfactants, defoamers, fungicides, drainage aids and other organic additives, thus these substances’ ultraviolet absorption peak were superimposed. Comparison of pre-treatment and post-treatment UV-vis absorbance spectra showed the absorption peak decreased significantly after treatment. The results show that through coagulation and UV/H₂O₂/ferrioxalate complexes oxidation, OFW organic macromolecules underwent rapid oxidative degradation, and mostly oxidized to CO₂ and H₂O. In addition, Figure 7 also shows that there has always been a lower peak near 200 nm ultraviolet region during degradation and also indicates for generating a number of small molecule compounds in the degradation process. So there is still some absorption in the near-ultraviolet region. As indicated by the UV–vis spectra analysis,

<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>1,440</td>
<td>233</td>
<td>83.8</td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>192</td>
<td>12.3</td>
<td>93.6</td>
</tr>
<tr>
<td>Oil and grease (mg/L)</td>
<td>19.2</td>
<td>4.7</td>
<td>75.5</td>
</tr>
<tr>
<td>Colour (°)</td>
<td>55</td>
<td>6.9</td>
<td>87.5</td>
</tr>
</tbody>
</table>
the degradation performance of the coagulation and UV/ H2O2/ferrioxalate complexes process improved the effluent water quality of the OFW.

**CONCLUSIONS**

On the basis of the experimental data obtained in this study, the degradation of hydroxypropyl guar gum has been studied by applying the coagulation and UV/H2O2/ferrioxalate complexes process, which has proved to be an effective advanced treatment method for OFW. By the coagulation pretreatment process, 48.2% of COD could be reduced under optimal conditions, as follows: dilution ratio of 1:2, pH of 4 and FeCl3 loading of 1,000 mg/L. When the dosage of H2O2 was 0.6%, n(H2O2)/n(Fe2+) was 2:1 and n(Fe2+)/n(C2O42-/C02-) was 3:1, the maximum COD reduction (55.1%) was obtained via the UV/H2O2/ferrioxalate complexes process at pH 4. In addition, the solution was adjusted to 8.5-9 using NaOH after oxidation and the COD removal efficiency reached 30.4% when the CPAM (2 mg/L) was added. The COD value of the treated OFW at room temperature was reduced to 233 mg/L, meeting the GB 8978-1996 ‘Integrated Wastewater Discharge Standard’ level III emission.

Furthermore, the UV-vis spectra analysis results indicated that the coagulation and UV/H2O2/ferrioxalate complexes process could efficiently remove the hydroxypropyl guar gum dissolved in OFW. Therefore, coagulation and UV/H2O2/ferrioxalate complexes process may be a suitable advanced treatment method for OFW standard.

**ACKNOWLEDGEMENTS**

The authors thank the China National Offshore Oil Corporation in Tianjin for kindly 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. Ultrasonics Sonochemistry 21 (1), 1–14.


