Combined treatment of organic material in oilfield fracturing wastewater by coagulation and UV/H₂O₂/ferrioxalate complexes process

Dan Ge

ABSTRACT

Organic material 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 organic material by coagulation and the UV/H₂O₂/ferrioxalate complexes process. Optimal reaction conditions are proposed based on the chemical oxygen demand (COD) removal efficiency. The overall removal efficiency of COD reached 83.8% when the dilution ratio of raw wastewater was 1:2, the pH was 4 and the FeCl₃ loading was 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⁻/C₀) was 3:1 and the pH was 4 in the UV/H₂O₂/ferrioxalate complexes process; the pH was adjusted to 8.5-9 with NaOH and then 2 mg/L of cationic polyacrylamide (CPAM) was added in the neutralization and flocculation process. The decrease in COD during the coagulation process reduced the required H₂O₂ dosage and improve efficiency in the subsequent UV/H₂O₂/ferrioxalate complexes process. Furthermore, there was a significant increase of 13.4% in the COD removal efficiency with the introduction of oxalate compared with UV/Fenton. Experimental results show that the coagulation and UV/H₂O₂/ferrioxalate complexes process could efficiently remove the organic material 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, oilfield fracturing wastewater, organic material, UV/H₂O₂/ferrioxalate complexes process

INTRODUCTION

Organic material is widely used in the hydraulic fracturing process. In the oilfield production process, large amounts of residual guar gum wastewater are generated (Nevin et al. 2013; Britt 2013; Hickenbottom et al. 2015). This oilfield fracturing wastewater (OFW) also contains various organics pollutants, impurities, solids, heavy metals, polymers, chemical additives, proppants, oil, etc (Chen et al. 2011; Stringfellow et al. 2014), significantly increasing the chemical oxygen demand (COD), chrominance and salinity, viscosity and strong acidity. Up to 15,140,000 litres 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 OFW contains high concentrations of potential organic pollutants 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. 2015). 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. 2013). With the improvement of environmental protection standards and the need to save energy and reduce emissions, an advanced treatment for OFW is necessary to satisfy the wastewater discharge quality or to reuse wastewater (Mehta & O’Sullivan 2015).

Currently, the treatment methods for OFW include the advanced oxidation process, chemical coagulation,
electrocoagulation, biological methods, activated carbon adsorption and solidification methods (Bagal & Gogate 2014; Akyon et al. 2015; Esmaeilrad et al. 2015; Benincá et al. 2016; Rosenbluma 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. 2013), while other methods can produce additional pollutants that do not meet national wastewater discharge standards (Hladik et al. 2014). 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 to treat high concentrations of toxic and hazardous biological emerging and promising oxidation process based on Fenton that removes contaminants in the liquid phase, and it usually causes shortfalls. For example, some methods require expensive equipment, while other methods can produce additional pollutants that do not meet national wastewater discharge standards (Kumar et al. 2019; Benincá et al. 2016; Riad et al. 2002). The UV/H₂O₂/ferrioxalate complexes method is not only less damaging to the environment but is also more economical compared to other advanced oxidation processes. Compared with traditional treatments, the method is advantageous because it has a wider range of applications, higher efficiency, produces little secondary pollution and the chemical reaction is completed during the treatment process (Yan et al. 2014).

As the aim of this work was to further improve the efficiency of wastewater treatment, the process of coagulation was used to pretreat the OFW for the removal/separation of organic/inorganics dissolved/suspended as colloids in water/solution (Zera et al. 2010). Then, the effectiveness of 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, low removal efficiency and easy onsite implementation.

**MATERIALS AND METHODS**

**Laboratory instruments and chemicals**

An ultraviolet spectrophotometer (UV-8000, Metash Instruments 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. 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 was generated using a UV lamp (500 W, Shanghai Metash Instruments Co., Ltd, China). A vacuum filtration device (FS3310, Shanghai Metash Instruments 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), 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.

Raw fracturing wastewater employed in this study was obtained from five different operating areas of CNOOC (China National Offshore Oil Corporation) in Tianjin province, China. The oil was skimmed before use. The wastewater was stored at 4°C until required. The main characteristics of sample wastewater are listed in Table 1. The value is the average value of five samples. As shown, the oilfield wastewater had high concentrations of COD, total dissolved solids and suspended solids (SS). Moreover, the oilfield wastewater had high color.

**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 400 mm x 500 mm x 1,500 mm cube 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 added to adjust the pH to 8.5–9. After precipitation, the supernatant was tested for each parameter.

**Coagulation experiments**

The 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. A large number of laboratory experiments found that ferric chloride is better than ferric sulphate as a coagulant, and ferric chloride is much cheaper, so the coagulant evaluated in this study was FeCl₃ (analytical grade). To determine the effective coagulant dose for the OFW treatment, a batch of jar-test 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. Before the UV/H₂O₂/ferrioxalate complexes experiments, I conducted several early experiments on the coagulant dosage and found a coagulant dosage in the range of 400–1,200 mg/L under the optimum pH condition better than others.

Immediately after adding the coagulant, the samples were rapidly mixed for 5 min at 150 rpm, 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 was adjusted to the desired levels by addition of appropriate amounts of H₂SO₄ (5%, v/v) or NaOH (5%, w/v).

**Table 1 | Characteristics of the raw oilfield wastewater**

<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 mg/L</td>
<td></td>
<td>4,069–4,386</td>
</tr>
<tr>
<td>BOD₅ mg/L</td>
<td></td>
<td>776</td>
</tr>
<tr>
<td>Suspended solids (SS) mg/L</td>
<td></td>
<td>562</td>
</tr>
<tr>
<td>Color</td>
<td></td>
<td>165 (turbid and light yellow)</td>
</tr>
<tr>
<td>Organic material mg/L</td>
<td></td>
<td>3,929–4,276</td>
</tr>
<tr>
<td>Alkalinity mg/L</td>
<td></td>
<td>5,126</td>
</tr>
<tr>
<td>Oil and grease mg/L</td>
<td></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.
Furthermore, in order to study the influence of the addition method (in one, two and three steps) on the removal of COD, the same dosage of coagulant was divided into one, two and three equal volumes, respectively. Then, they were evenly added into different water samples.

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 500 mL in a batch cylindrical glass photoreactor, a known volume of H₂O₂ (30%, v/v) solution, FeSO₄·7H₂O and H₂C₂O₄ 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.

Neutralization and flocculation experiments

After the coagulation/UV/H₂O₂/ferrioxalate complexes process, NaOH was added to the water to adjust the pH to 8.5–9. Then, adding an appropriate amount of CPAM (0.1% w/v) led to the formation of large precipitates immediately. After standing for 30 min, the water was filtered through 0.45 μm membrane by the vacuum filtration device.

All experiments in this study were performed in triplicate to get reliable data, 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 is cost-effective (Pliego et al. 2014). Furthermore, this process could considerably reduce the COD of the wastewater, thereby resulting in a lower H₂O₂ requirement in the subsequent UV/H₂O₂/ferrioxalate complexes process. Experiments were carried out to optimize the dilution ratio, pH and FeCl₃ dosage.

Effect of the dilution ratio

Using the dilution ratio is an important factor affecting the process, directly affecting the costs in water treatment and the purification efficiency. Therefore, the effect of OFW dilution ratio (namely initial COD of the wastewater) on the degradation efficiency was investigated at different dilution ratios (0, 1:1, 1:2, 1:3) and presented in Figure 2(b). 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 fact that the wastewater had a high...
organic content, which caused relatively high resistance to coagulation, leading to difficulty in floc formation, and thus leading to slow sedimentation and poor coagulation efficiency under the condition of 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. COD removal efficiency decreased after increasing or decreasing the pH value from pH 4. The same COD reduction phenomenon was observed when OFW effluent was subjected to the coagulation process. Therefore, the pH value of 4 was selected for the following experiments. FeCl₃ hydrolysis was performed and complex ions, such as Fe(OH)²⁺, Fe₂(OH)⁴⁺, Fe₃(OH)₆⁺ with high positive charge and a low degree of polymerization were formed at low pH; charge neutralization was selected as the main mechanism of the coagulant (Tatsi et al. 2009). FeCl₃ reduces coagulation efficiency by forming 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 3 shows the effect of FeCl₃ dosage on 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 the dissociation of FeCl₃. Meanwhile, a slow decrease in COD removal was observed when the FeCl₃ dosage exceeded 1,200 mg/L. Part of the reason may have been that negatively charged colloids were neutralized by the added coagulant, then gradually became positively charged when the optimum dosage was exceeded. They are thus mutually exclusive and not conducive to the aggregation of colloidal particles. Moreover, FeCl₃ addition was studied by comparing addition in one, two, and three steps. The total dosage of FeCl₃ remained the same. As shown in Figure 3, the COD removal increased with the increase in dosing steps and addition in three steps was significantly better than one and two steps. COD removal efficiency reached 48.2% when the FeCl₃ loading was 1,000 mg/L and added in three steps.

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

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

The pH effect was particularly studied through experiments. Figure 4 shows the COD removal from the OFW for different initial pH values. These results also revealed that the UV/Fenton system is a highly pH-sensitive process. Figure 4 shows that COD removal performance declined for pH values greater than 5. This occurs due to the formation of ferric hydroxocomplexes, 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 H$_2$O$_2$ to molecular oxygen and water, resulting in a decline of its oxidative capacity. When the pH is higher than 8.0 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 9.0. It is also possible that the precipitation occurs with Fe$^{3+}$ as oxy-hydroxide amorphous (Fe$_2$O$_3$·nH$_2$O) at pH greater than 3 (Kim et al. 1997). Conversely, for pH values lower than 2.0 the reaction of hydrogen peroxide with Fe$^{2+}$ is seriously affected due to the formation of the 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 concentration of H$^+$ ions to form the stable peroxide ion [H$_2$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 value of pH is 4, which is in agreement with previous results obtained in other studies using Fenton’s reagent (Peres et al. 2004).

**Effect of n(H$_2$O$_2$)/n(Fe$^{2+}$) on the UV/Fenton System**

A favorable n(H$_2$O$_2$)/n(Fe$^{2+}$) molar ratio is very important for researching the UV/Fenton process. In this work the molar ratios of n(H$_2$O$_2$)/n(Fe$^{2+}$) ranging from 1:1 to 6:1 were added to evaluate the COD removal and determine the FeSO$_4$ dosage during the UV/Fenton process. As shown in Figure 5, the COD removal efficiency was significantly influenced by various FeSO$_4$ dosages. When the molar ratio of n(H$_2$O$_2$)/n(Fe$^{2+}$) increased from 6:1 to 4:1, the COD removal efficiency increased slightly from 38 to 43%. Then, the increase of Fe$^{2+}$ concentration, the COD removal efficiency reached a maximum (47.8%) when the n(H$_2$O$_2$)/n(Fe$^{2+}$) increased from 3:1 to 2:1. Moreover, when the n(H$_2$O$_2$)/n(Fe$^{2+}$) was increased to 1:1, the removal efficiency decreased to 36.1%. The reason is mainly due to the relationship between the amount of free radicals generated and Fe$^{2+}$ content in the reaction system. The radical chain reactions in the Fenton process might be terminated with more Fe$^{2+}$ in the reaction system. This is because the HO$^*$ was produced as a result of the reaction (Equation (6)) then mainly reacts with Fe$^{2+}$ (Equation (7)) (Neyens & Baeyens 2003; Garrido-Ramírez et al. 2010). Taking the removal efficiency into consideration, the n(H$_2$O$_2$)/n(Fe$^{2+}$) ratio of 2:1 was selected for the UV/Fenton process.

$$
H_2O_2 + Fe^{2+} + OH^- + OH^- \rightarrow HO \cdot Fe^{3+} + OH^- \quad k_1 = 63\text{(L/mol.s)}$$

$$
HO \cdot \rightarrow Fe^{3+} + OH^- \quad k_2 = 3.2 \times 10^8\text{(L/mol.s)}$$

**Effect of H$_2$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 6 presents the effect of H$_2$O$_2$ dosage on COD removal with time under the conditions of n(H$_2$O$_2$)/n(Fe$^{2+}$) of 2 and pH 4. The figure shows that COD removal occurs principally in the initial period (0–30 min), and as the reaction time increased the COD removal approached a plateau under different H$_2$O$_2$ dosages. The maximum COD removal was achieved at an H$_2$O$_2$ dosage of 0.6% (v/v). Below the optimal H$_2$O$_2$ dosage, the oxidation removal efficiency increased with the increase of H$_2$O$_2$ dosage because of the increment of ·OH (Equation (6)). Then, continuously increasing the H$_2$O$_2$ dosage can reduce the COD removal efficiency, which could be attributed to the scavenger effect of excess H$_2$O$_2$. The degradation rate decreased as the H$_2$O$_2$ dosage continued to increase beyond the suitable level. The scavenging effect of ·OH by ·OH and the consumption of H$_2$O$_2$ by
The important elements (Equations (8) and (9)) were the important elements (Kuo 1992; Nguyen et al. 2014). The COD removal efficiency 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.

\[
\cdot \text{OH} + \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \quad k_5 = 5.3 \times 10^9 \text{/(L/mol.s)} \quad (8)
\]

\[
\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}^\cdot + \text{H}_2\text{O} \quad k_4 = 1.2 \times 10^7 \text{/(L/mol.s)} \quad (9)
\]

Furthermore, the H₂O₂ dosage can affect the UV/Fenton reaction. First, the form of hydrogen peroxide addition was studied by comparing addition in a single step to that in three steps (equal volumes) under the H₂O₂ dosage of 0.6% (v/v). As shown in Figure 6, COD removal with H₂O₂ dosage 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 reaction. 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 Figure 7(a), where the data derive from a sample at an initial pH of 4, H₂O₂ dosage of 0.6% n(H₂O₂)/n(Fe²⁺) of 2. The n(Fe²⁺)/n(C₂O⁴²⁻) was varied from 0 to 3:1. As shown in Figure 7(a), the COD removal efficiency of the UV/H₂O₂/ferrioxalate complexes system reached 55.2%, 13.4% higher than UV/Fenton when the n(Fe²⁺)/n(C₂O⁴²⁻) was 3:1. The main reason was that the...
ferrioxalate complexes could generate more hydroxyl radicals than the UV/Fenton process under UV irradiation and led to rapid oxidative degradation of various organic substances.

Under the UV/H₂O₂/ferrioxalate complexes system, -OH will be generated through the reaction shown in Equation (6) if the FeSO₄ and H₂O₂ are added first. On the other hand, the ferrioxalate complexes will be formed through the reaction of Fe²⁺ and C₂O₄⁻/C₀, then quickly react with H₂O₂ and generate -OH if the FeSO₄ and K₂C₂O₄ are added first. The form distribution of ferrioxalate complexes were determined as n(Fe²⁺ or Fe³⁺)/n(C₂O₄⁻/C₀), and different forms of photoactive ferrioxalate complexes will cause -OH to be generated at different rates. Furthermore, the amount of Fe(C₂O₄)₃⁻/C₀ produced will be reduced if the K₂C₂O₄ concentration is too low. On the other hand, if excessive, it will generate HCO₃⁻/C₀ and CO₃²⁻/C₀ in a concentrated K₂C₂O₄ solution, which have a scavenging effect on -OH. Through the reaction between HCO₃⁻/C₀, CO₃²⁻/C₀ and -OH, the secondary radical generation of HCO₃⁻ and CO₃⁻ will occur. The secondary radicals generated could react with organics at a relatively low speed. In addition, the photocatalytic decomposition reaction of Fe(C₂O₄)₃⁻/C₀ will be inhibited if the K₂C₂O₄ concentration is too high. Only if the n(H₂O₂)/n(Fe²⁺) and n(Fe²⁺)/n(C₂O₄⁻/C₀) are in a suitable range, will more -OH be obtained.

In this work, the n(Fe²⁺)/n(C₂O₄⁻/C₀) of 3:1 was selected as the optimum conditions for 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 wastewater to adjust the pH to 8.5–9, some Fe³⁺ will be converted into Fe(OH)₃, which is considered an excellent chemical coagulant. Then, adding an appropriate amount of CPAM led 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 7(b), the COD removal efficiency increased with the increase of CPAM dosage from 0 to 2 mg/L, and then decreased while the CPAM dosage exceeded 2 mg/L. The reason is that the reaction mechanisms of CPAM include the interaction of hydroxides, neutralization, precipitation and accumulation (Divakaran et al. 2001) at the suitable dosage, thus removed the COD. Nevertheless, CPAM itself acts as the organic matter, and in turn can increase the organic content when overused. So the optimal CPAM dosage obtained 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 initial OFW was first subjected to a coagulation process. Subsequently, the supernatant was withdrawn and subjected to the UV/H₂O₂/ferrioxalate complexes process. The experimental parameters were controlled under individual selected conditions. The characteristics of the coagulation and UV/H₂O₂/ferrioxalate complexes process and the overall treatment efficiency are summarized in Figure 8. A total of 48.2% COD could be removed in the coagulation process at pH 4, dilution ratio of raw OFW of 1 and FeCl₃ dosage of 1,000 mg/L, whereas 68.1% CO₃²⁻ 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(C₂O₄⁻/C₀) of 3:1. Furthermore, 30.4% COD was removed in the neutralization and flocculation process at pH 8.5–9 and CPAM dosage of

| Table 2 | Main parameters of the wastewater before and after the proposed treatment |
|-----------------|-----------------|-----------------|
| Parameter       | Before treatment | After treatment | Removal (%) |
| COD (mg/L)      | 1,440           | 233             | 83.8        |
| Suspended solids (mg/L) | 192          | 12.3            | 93.6        |
| Oil and grease (mg/L) | 19.2          | 4.7             | 75.5        |
| Color (°)       | 55              | 6.9             | 87.5        |

Figure 8 | Treatment efficiency of the coagulation and UV/H₂O₂/ferrioxalate complexes process.

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Table 3 | Comparison of COD removal from wastewater under different advanced oxidation processes

<table>
<thead>
<tr>
<th>Process/Fenton</th>
<th>COD (mg/L)</th>
<th>pH</th>
<th>Operating parameters</th>
<th>COD removal (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Floc/Fenton</td>
<td>9,360</td>
<td>6.35</td>
<td>[PAC] = 40 mg/L, [PAM] = 4 mg/L, dilution ratio = 1:2, stirring time = 30 min; [H2O2] = 2 mmol/L, [n(H2O2)/n(FeSO4)] = 2, reaction time = 60 min</td>
<td>76.6</td>
<td>Jin et al. (2015)</td>
</tr>
<tr>
<td>Oxone/Co2⁺/O3/PDS</td>
<td>1,116</td>
<td>8.17</td>
<td>[Oxone] = 4.5 mM, [Co2⁺] = 0.45 μM, pH₀ = 6.5, V = 0.1 L, 30 °C</td>
<td>57.5</td>
<td>Sun et al. (2009)</td>
</tr>
<tr>
<td>O3/H₂O₂/Fe₂⁺</td>
<td>2,180</td>
<td>8.5</td>
<td>[H₂O₂] = 50 mM, [Fe₂⁺] = 50 mM, [O₃] = 80 mg/L, pH₀ = 7, V = 2 L, 15 °C</td>
<td>65</td>
<td>Abu Amr et al. (2012)</td>
</tr>
<tr>
<td>Fenton</td>
<td>1,116</td>
<td>8.17</td>
<td>[H₂O₂] = 80 mM, [Fe₂⁺] = 40 mM, pH₀ = 2.5, V = 0.5 L, 25 °C</td>
<td>56</td>
<td>Shi et al. (2009)</td>
</tr>
<tr>
<td>UV/H₂O₂/Fe₂⁺</td>
<td>1,560</td>
<td>/</td>
<td>[H₂O₂] = 0.6 mol/L, [Fe₂⁺] = 3.0 mol/L, V = 0.5 L, 25 °C</td>
<td>73.3</td>
<td>Chen et al. (2014)</td>
</tr>
<tr>
<td>Floc/UV/H₂O₂</td>
<td>3,332</td>
<td>8.3</td>
<td>[FeCl₃] = 1,400 mg/L, pH = 4.0, rapid mixing at 100 W for 30 s; [H₂O₂] = 1,500 mg/L, pH = 4.0, UV = 25 W</td>
<td>71.9</td>
<td>Ana et al. (2014)</td>
</tr>
<tr>
<td>Coag/UV/H₂O₂/ferrioxalate complexes</td>
<td>4,069–4,386</td>
<td>6.5</td>
<td>[FeCl₃] = 1,000 mg/L, dilution ratio = 1:2, n(H₂O₂)/n(Fe₂⁺) = 4:0.6, n(Fe²⁺)/n(C₂O₄²⁻) = 1:1, [H₂O₂] = 2,500 mg/L</td>
<td>83.8</td>
<td>This study</td>
</tr>
</tbody>
</table>

2 mg/L, which lead to 83.8% overall COD removal efficiency. In addition, Table 2 also 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 turbidity in the OFW after coagulation and UV/H₂O₂/ferrioxalate complexes process treatment under the optimum conditions could satisfy the professional emission standard (level one) of the Petrochemical industry of PR China (GB 8978-1996: oil and grease < 10 mg/L, SS < 5 mg/L, color < 15). Furthermore, comparing this testing process with the other commonly used processes from Table 3, the coagulation and UV/H₂O₂/ferrioxalate complexes process proved to be an effective advanced treatment method for OFW.

CONCLUSIONS

On the basis of the experimental data obtained in this study, the degradation of organic material has been studied by applying coagulation and UV/H₂O₂/ferrioxalate complexes process 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 was 1.2, pH of 4 and the FeCl₃ loading of 1,000 mg/L. When the dosage of H₂O₂ was 0.6% and the n(H₂O₂)/n(Fe²⁺) was 2:1 and n(Fe²⁺)/n(C₂O₄²⁻) 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 CPAM (2 mg/L) was added. The COD value of the treated fracturing wastewater at room temperature was reduced to 233 mg/L, meeting the GB 8978-1996 ‘Integrated Wastewater Discharge Standard’ level III emission standard.

Therefore, coagulation and UV/H₂O₂/ferrioxalate complexes process may be a suitable advanced treatment method for OFW.

ACKNOWLEDGEMENTS

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

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First received 14 June 2017; accepted in revised form 20 November 2017. Available online 1 December 2017.