Naval derusting wastewater containing high concentration of iron, treated in UV photo-Fenton-like oxidation

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Abstract

The UV photooxidation with Fe(III) and H₂O₂ was employed to treat a naval derusting wastewater, which contains the high COD (chemical oxygen demand) and various metal concentrations exceptionally with high concentrations of citric acid and iron. Because of its iron containment, the Fenton-like reaction automatically took place with the added amount of H₂O₂ and various metal concentrations exceptionally with high concentrations of citric acid and iron. Normally, two wastewater streams are generated during the derusting operation of ship bilge, naval shipyards generate the derusting wastewater containing highly concentrated citric acid and triethanolamine (TEA). In addition to these, the rust, predominantly oxidized iron, is high in Fe(III) concentration in the derusting wastewater. Both citric acid and TEA are strong chelating agents, so they are specialized in chelating metals in the wastewater. Their optimal chelation-forming pH range varies. Citric acid prefers a lower pH while TEA prefers a more alkaline range. Therefore, the mixture of two chelating agents consequently may limit interferences such as the surface acidity and the presence of other oxides during the derusting operation (Perrin, 1970). Basically, TEA functions as a corrosion inhibitor. It had been reported that the optimal ratio of citric acid to TEA for the rust removal was 1:2.5 (V/V) (Antonov and Pchelintsev, 1974). In fact, the naval derusting wastewater has a similar ratio.

During the derusting operation of ship bilge, naval shipyards generate the derusting wastewater containing highly concentrated citric acid and triethanolamine (TEA). In addition to these, the rust, predominantly oxidized iron, is high in Fe(III) concentration in the derusting wastewater. Both citric acid and TEA are strong chelating agents, so they are specialized in chelating metals in the wastewater. Their optimal chelation-forming pH range varies. Citric acid prefers a lower pH while TEA prefers a more alkaline range. Therefore, the mixture of two chelating agents consequently may limit interferences such as the surface acidity and the presence of other oxides during the derusting operation (Perrin, 1970). Basically, TEA functions as a corrosion inhibitor. It had been reported that the optimal ratio of citric acid to TEA for the rust removal was 1:2.5 (V/V) (Antonov and Pchelintsev, 1974). In fact, the naval derusting wastewater has a similar ratio.

Normally, two wastewater streams are generated during the ship cleaning process; the rust removal (acid) solution and the passivation solution. The rust removal acid solution containing up to 10% citric acid and 4% TEA (volume ratio of citric acid to TEA = 1:2.5) is sprayed onto the bilge or tank walls that are manually cleaned off paint. The citric acid preferentially chelates the oxidized iron form, although some base metals are also lost in the process. As a result, the difficult rust deposits are dissolved, along with the thin film of rust that covers the entire bare surface. This solution is then flushed out of the structure being derusted with water, and subsequently collected for the disposal. The passivation solution containing up to 10% citric acid and 4% TEA is immediately sprayed onto the derusted surface, protecting it until a primer can be applied. The excess passivation solution which drains from the structure being derusted is then collected for the disposal. Therefore, the derusting wastewater consists of these two wastewaters with the rinsing water.

Typical naval derusting wastewater has 8%–10% citric acid, 4% TEA, 10,000 mg/L of chemical oxygen demand (COD), and pH 2.5. The shipyard wastewater including Navy’s is generated in the enormous amount of gallons (Pan et al., 1990). Conventional method practiced is the chemical oxidation using potassium permanganate solution. Drawbacks encountered in this treatment include the unnecessary heat production, lengthy treatment duration, and the generation of hazardous brown MnO₂ precipitates which are difficult to dispose of.

The use of UV in conjunction with H₂O₂ and Fe(II) is well known as Fenton oxidation and a proven method as one of AOPs (advanced oxidative processes). The OH radical generated from hydrogen peroxide (H₂O₂) is a strong oxidant and its wide application is well known in the treatment of recalcitrants which are difficult to remove. The process involving the highly reactive hydroxyl radical.
can mineralize almost all the organic molecules owing to its high oxidation potential (\(E = +2.8 \text{ V}\)) (Legrini et al., 1993). Also, the Fenton oxidation process utilizing the activation of \(\text{H}_2\text{O}_2\) by iron catalyst and the generation of strong iron oxidant is effective in the destruction of hazardous substances, such as phenols, chlorinated compounds, pesticides, as well as in the reduction of COD in municipal waste. The process with \(\text{H}_2\text{O}_2\) alone or Fenton alone can be improved in the combination with UV (Primo et al., 2008; Saritha et al., 2007; Catalkaya and Kargi, 2007; Kusic et al., 2006; Neyens and Baeyens, 2003). The importance of this study is that the derusting wastewater can be feasibly treated in the method of UV/\(\text{H}_2\text{O}_2\) and Fe(III), which benefits from iron metals already exiting in the derusting wastewater. This process is so-called Fenton-like oxidation. The ions from the process perform Fenton-like oxidation. According to a research (Lee et al., 2009), heterogeneous Fenton (Fenton-like) systems offer significant advantages as well as solving problems (e.g., sludge production) that Fenton oxidation causes. Heterogeneous iron makes the catalytic ion in solution, which properly generates the Fenton reaction without the formation of sludge. In other words, this metal containment in the wastewater may allow the Fenton-like reaction to take place in the removal system. In this sense, the experiment was designed to decompose the synthetic citric acid as a model compound and to observe the effects of OH radical, the Fenton-like reaction and its associated iron catalyst. The comparative study of UV/\(\text{H}_2\text{O}_2\)/Fenton reaction/Fenton-like reaction, was performed to see the optimum combinational method in the decomposition of the citric acid and the naval derusting wastewater as a practice. Since this study is dependent on \(\text{H}_2\text{O}_2\), the difference between the single point and multiple-point injections of \(\text{H}_2\text{O}_2\) was evaluated for finding the higher removal efficiency. The degradation degree was estimated measuring COD reduction with ion chromatography (IC) and using a UV-Vis spectrophotometer. The aims of this study are to address the environmental issue of the derusting wastewater from shipyard and to implement the UV photolysis and Fenton-like reaction using radicals.

1 Experimental

1.1 Derusting wastewater characterization

Derusting wastewater samples (A, B, C, and D) were obtained from Long Beach Naval Shipyard. The citric acid, TEA, and metal concentrations are shown in Table 1. The derusting wastewater is low in \(pH\) and extremely high in COD. Most derusting wastewater does not show alkalinity due to a low \(pH\). The contents of citric acid and TEA vary in different samples as well as does COD. The concentrations of heavy metals such as Cd, Cr, Cu, Pd, Ni, Se, and Zn, are varied. The iron concentrations of samples used in this study ranged from 710–1500 mg/L, which is one of the important characteristics of the derusting wastewater. The average iron concentration of the derusting wastewater, 2000 mg/L, exceeds that of acid mine drainage, 1000 mg/L (Twort et al., 1974). The derusting wastewater is highly colorful due to this high iron content which will form a complex with the citric acid and TEA. Therefore, this high content of iron can play an essential role in the carboxylic type acid photooxidation.

1.2 UV photolysis and analysis

The complete photolysis assembly was purchased from ACE Glass Inc. (USA). The UV lamp is made of quartz and mercury-vaporized with a 450-W in medium pressure. Of total energy radiated, ultraviolet is approximately 40%–48%, visible light is 40%–43%, and the rest is infrared. The UV radiation covers far, middle, and near UV but not the extreme (vacuum) UV that is responsible for the water dissociation. The lamp is inserted into a water-cooled (4 L/min) quartz immersion, and the whole unit is fitted to a 1 L glass reactor. The assembly also includes a stirrer bar and thermometer. The system is an open unit to prevent any gas generated and to allow for the expansion of the exothermic reaction.

The citric acid was purchased from Pfizer (USA) and 30% strength of \(\text{H}_2\text{O}_2\) solution was obtained from Fisher Scientific (USA). The synthetic citric acid was freshly prepared in certain molarity before being placed under the UV irradiation. The \(\text{H}_2\text{O}_2\) solution was made in di-water. The lamp is inserted into a water-cooled (4 L/min) quartz immersion, and the whole unit is fitted to a 1 L glass reactor. The assembly also includes a stirrer bar and thermometer. The system is an open unit to prevent any gas generated and to allow for the expansion of the exothermic reaction.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid (%)</td>
<td>7.06</td>
<td>1.48</td>
<td>0.90</td>
<td>1.00</td>
</tr>
<tr>
<td>TEA (%)</td>
<td>4.25</td>
<td>1.57</td>
<td>0.03</td>
<td>0.00</td>
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<tr>
<td>Alkalinity</td>
<td>2.5</td>
<td>4.26</td>
<td>2.64</td>
<td>5.53</td>
</tr>
<tr>
<td>(as CaCO₃ mg/L)</td>
<td></td>
<td></td>
<td></td>
<td>600</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>140,000</td>
<td>60,000</td>
<td>46,700</td>
<td>51,200</td>
</tr>
<tr>
<td>Mercury (mg/L)</td>
<td>7.10</td>
<td>1052</td>
<td>1042</td>
<td>1456</td>
</tr>
<tr>
<td>Lead (mg/L)</td>
<td>24.0</td>
<td>2.30</td>
<td>2.24</td>
<td>8.32</td>
</tr>
<tr>
<td>Nickel (mg/L)</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Copper (mg/L)</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.14</td>
</tr>
<tr>
<td>Zinc (mg/L)</td>
<td>0.00</td>
<td>77.3</td>
<td>76.9</td>
<td>200</td>
</tr>
</tbody>
</table>

\[ \text{CaCO}_3 = \text{CO}_2 + \text{H}_2\text{O} \]

\[ \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 \]
spectrophotometer (UV-25, Beckman, USA) was used to quantify the decomposition of Fe(III) and citrate complex. Ferrous sulfate was purchased from J.T. Baker (USA) to make 20 mg/L solution and ferric chloride was purchased from Mallinkrodt (USA) to make 20 mg/L and 2000 mg/L solutions.

1.3 Single point and multiple points H₂O₂ injection in citric acid photodegradation

For the single point H₂O₂ injection, 300 mL of 30% strength of H₂O₂ was added in 800 mL of 8% synthetic citric acid right before the UV irradiation begun. For the multiple injection points, three 100 mL solutions of 30% H₂O₂ were added at 20, 50, and 80 min of UV times. The H₂O₂ consumption, COD reduction, and citric acid decomposition were evaluated. In the experiment of the real naval desusting wastewater, the multiple H₂O₂ injections were also carried out. Every two hours for the entire UV irradiation time (18 hr), 35 mL of 30% H₂O₂ was added. COD was monitored for the citric acid decomposition throughout the UV irradiation.

2 Results and discussion

2.1 Photodegradation of citric acid by UV/H₂O₂

Under the UV irradiation, the photooxidation of citric acid was observed. Approximately 30% of citric acid was decomposed (Fig. 1a). On the other hand, when H₂O₂ was added, the removal rate of citric photooxidation went up to 95% after 90 min of UV irradiation. If putting in kinetics, the citric photooxidation with UV/H₂O₂ is a first order reaction ($k = 0.0199 \text{ min}^{-1}; R = 0.9999$). The degradation of the citric acid can be increased by diluting the citric solution (Fig. 1b). The weaker concentrations of citric acid such as 0.2% and 0.08% were degraded at a relatively faster rate. Within 60 min of the UV irradiation, 0.08% concentration of the citric acid was completely decomposed in the UV photolysis with H₂O₂.

2.2 Photo and Fenton-like degradation of citric acid by UV/H₂O₂ and Fe(III)

In the citric acid solution, Fe(III) tends to make the citrate organic complex. When it comes to the citric acid photooxidation, the photodegradation of the organic complex starts from the cleavage of a metal-organic complex, which essentially requires the OH radical oxidation and Fenton-like reaction with the preference of an enhanced electronegativity on the reactive site of the Fe(III)-citrate complex.

The OH radical is naturally electrophilic (Walling, 1975; Ikekizu et al., 1987). The complex degradation is carried out in a highly selective way, based upon the kinetic order of entire reaction, and the oxidative electron transfer is precisely guided by the coordination bond from ligand to metal. The complex photodegradation virtually stops after the electron transfer occurs. The oxidative electron transfer in the OH radical oxidation is induced by the collision between the OH radical and the organic compound. The OH radical can directly attack the Fe(III)-citrate complex and its decomposed products indirectly. In order to increase the possibility of the collision between the OH radical and the organic compound, an OH radical concentration level exceeding the stoichiometric ratio may be needed.

The reactions involving UV, H₂O₂, and Fe(III) are quite complicated. The citric acid and its decomposed products are oxidized in a chain reaction spurred by the UV irradiation and strong radicals. The decomposition of the metal-organic complex is also facilitated by the presence of iron. Citric acid solutions with 20 and 2000 mg/L of Fe(III) were prepared to form the Fe(III)-citrate complex prior to the addition of H₂O₂ and the UV irradiation. Another set of Fenton experiment containing 20 mg/L of Fe(II) but without UV was prepared to determine the effectiveness of UV photolysis. The initial concentrations of the citric acid and H₂O₂ were 0.3 and 2.4 mol/L, respectively. Without the UV irradiation, the citric acid concentration was only 10% reduced all the way during the Fenton reaction, while, under the UV irradiation with H₂O₂, up to 50% of citric acid was removed (Fig. 2). As mentioned by Neyens and Baeyens (2003), Fenton reaction limitedly works for the lower concentration of organic compounds, although its extensive application was successful in degrading the organic toxics. In addition to the drawbacks of Fenton reaction, Fe²⁺ and H₂O₂ must be added continuously to keep the reaction proceed (Chiou et al., 2006). This may cause another big precipitation problem to further produces
a large volume of iron hydroxide sludge. However, introducing the UV light to a Fenton-like process will overcome this problem by helping regenerate Fe$^{2+}$ for the continuous Fenton reaction as follows:

$$\text{Fe(OH)}_3^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \text{OH}^- \quad (1)$$

$$\text{Fe(OH)}_3^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \text{OH}^- + \text{H}^+ \quad (2)$$

In this mechanism, the occurrence of the increased concentration of Fe$^{2+}$ may be explained, as illustrated in Fig. 4a. Fenton reaction consumes the most amount of Fe$^{2+}$ species existing in the solution at the initial stage of reaction and when the added amount of H$_2$O$_2$ was used up in Fenton reaction, Fe$^{2+}$ shows in the later part of the UV reaction.

As noted in Reactions (6) and (7), Fe$^{3+}$ is abundant species right after the organic complex (RH) is dissociated by UV or OH radical. Therefore, the reduction of Fe$^{3+}$ to Fe$^{2+}$ is somewhat advantageous to make the Fenton reaction repeatedly proceed without the continuous addition of Fe$^{2+}$ as in Reactions (11), (12), and (13) (Chiou et al., 2006). Fenton reaction is a progressive way to Fenton-like reaction. In Fig. 2, a drastic reduction of the citric acid concentration was observed when Fe$^{3+}$ was added. More than 65% of citric acid was decomposed in the method of UV/H$_2$O$_2$/Fe(III) of 2000 mg/L within 60 min. Fe(III) is capable of forming a complex with the citric acid and is also used to dissociate H$_2$O$_2$ in the formation of the OH radicals. In Fig. 3, the UV spectra exhibit the reduction of the Fe(III)-citrate complex as the UV/H$_2$O$_2$ with 2000 mg/L of Fe(III) was applied. Around 260–270 nm, Fe(III)-citrate complex was found (see 0 min). After 5 min, the UV peak at 260 nm disappeared and a new broad peak showed at 280 nm, which indicates for the photodegradation of the Fe(III)-citrate complex. The Fe(III)-citrate complex yields 1,3-ADCA and Fe(II) after the degradation. The reduced Fe(II) is quickly reoxidized to Fe(III) when the addition of H$_2$O$_2$ is present, which is repeatedly occurring in terms of a chain reaction, presented as Reactions (3) and (4). This reaction basically ended up with the OH radical generation.

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \quad (3)$$

$$k_1 = 76 \text{ (mol/L)}^{-1}\text{sec}^{-1}$$

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad (4)$$

$$k_2 = 0.02 \text{ (mol/L)}^{-1}\text{sec}^{-1}$$

After the decomposition of the Fe(III)-citrate complex, the reoxidized Fe(III) cannot form a complex with the remaining citric acid, and therefore after 5 min of the UV irradiation, the complex peak disappeared in the UV spectra and Fe(III) is available in the solution. Fe(III) is a quite strong oxidizer that can be used to directly attack the organic compound as does the OH radical. Fe(III) is initially bound to the citric acid and could not catalyze H$_2$O$_2$ as significantly as Fe(II) could. However, Fe(II) surpasses Fe(III) as to consume H$_2$O$_2$ (Kusic et al., 2006; Chiou et al., 2006).

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \quad (3)$$

$$k_1 = 76 \text{ (mol/L)}^{-1}\text{sec}^{-1}$$

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad (4)$$

$$k_2 = 0.02 \text{ (mol/L)}^{-1}\text{sec}^{-1}$$

Apparantly the reoxidized Fe(III) cannot form a complex with the remaining citric acid, and therefore after 5 min of the UV irradiation, the complex peak disappeared in the UV spectra and Fe(III) is available in the solution. Fe(III) is a quite strong oxidizer that can be used to directly attack the organic compound as does the OH radical. Fe(III) is initially bound to the citric acid and could not catalyze H$_2$O$_2$ as significantly as Fe(II) could. However, Fe(II) surpasses Fe(III) as to consume H$_2$O$_2$ (Kusic et al., 2006; Chiou et al., 2006).
be explained as follows.

\[
\begin{align*}
\text{H}_2\text{O}_2 + h\nu & \rightarrow 2\text{OH}^- \quad (5) \\
\text{RH} (\text{Fe}^{3+} - \text{Citrate}) + h\nu & \rightarrow \text{RH}^- + \text{Fe}^{3+} \\
& \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \quad (7) \\
\text{OH}^- + \text{RH} & \rightarrow \text{RH}^- + \text{H}_2\text{O} \quad (8) \\
\text{OH}^- + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (9) \\
\text{OH}^- + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (10) \\
\text{Fe}^{3+} + \text{RH} & \rightarrow \text{RH}^- + \text{Fe}^{2+} \quad (11) \\
\text{Fe}^{3+} + \text{RH}^- & \rightarrow \text{RH}^+ + \text{Fe}^{2+} \quad (12) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad (13)
\end{align*}
\]

Destruction mechanisms occurred in the derusting wastewater include the UV induced destruction, OH radical induced destruction, and ferric ion induced destruction. For the UV induced mechanism, as seen in Reactions (6) and (7), the energy from UV can be directly used for the destruction of organic complex. For the OH radical induced destruction, the OH radicals are generated from \text{H}_2\text{O}_2 dissociation by the direct irradiation of UV (Reaction (5)) or from the reaction with \text{Fe}^{2+} (Reaction (7)).

For the destruction induced by \text{Fe}^{3+} (Reactions (11) and (12)), \text{Fe}^{3+} can attack the organic target since \text{Fe}^{3+} is quite strong oxidant (Neyens and Baeyens, 2003). The role of \text{Fe}^{3+} is important, because \text{Fe}^{3+} helps to oxidize the target organic compound and to produce the OH radical through the \text{Fe}^{2+} formation as in Reactions (6) and (7). Therefore, the presence of iron salts can reduce the scavenging effect of OH radical from \text{H}_2\text{O}_2. The peroxide combination with metal salts or UV is more effective than the single use of \text{H}_2\text{O}_2, as seen in the kinetic values.

### 2.3 Single \text{H}_2\text{O}_2 injection and step-feeding (multiple)

**\text{H}_2\text{O}_2 injection in the synthetic citric acid solution**

The two sets of experiments with single point and multiple points of the \text{H}_2\text{O}_2 injection, were designed to evaluate the effectiveness of the \text{H}_2\text{O}_2 injection and its concentration distribution in terms of the citric acid oxidation. Both experiments used equal quantities of \text{H}_2\text{O}_2 to treat the 8% citric acid solutions with 2000 mg/L of Fe(III). As shown in Fig. 4a, the addition of \text{H}_2\text{O}_2 was made initially before the UV irradiation for the one-time injection. The amount of \text{H}_2\text{O}_2 added at the beginning of the UV time, became consumed at a relatively fast rate. At the same time, the concentration of Fe(II) increased in a mild rate. A majority portion of \text{H}_2\text{O}_2 was used to decompose the Fe(III)-organic complex to \text{Fe}^{3+} and the partially oxidized form of organic, as shown in Reaction (6). As seen in Fig. 4a, the increased amount of Fe(II) after 60 min was found. In the chain reaction system, a remaining amount of \text{H}_2\text{O}_2 after the decomposition of the Fe(III)-organic complex was also utilized to transform this increased amount of Fe(II) into strong oxidizer, \text{Fe}^{3+}, which would be later used to completely mineralize the partially oxidized organic. The OH radical is consumed through Reactions (8), (9), and (10) with similar rates. Therefore, the availability of the OH radical depends upon the concentrations of \text{H}_2\text{O}_2, \text{Fe}(II), and RH. Reaction (9) is undesirably happening because OH radical is wasted to react with \text{H}_2\text{O}_2 newly added to the system, which is so-called scavenging of OH radical. Therefore, there was little reduction of the citric acid after 60 min as shown in Figs. 5a and 5b, even though the UV irradiation was applied all along the process. This phenomenon reveals that the citric acid oxidation with the help of UV/\text{H}_2\text{O}_2 and Fe(III) is dependent upon the amount of \text{H}_2\text{O}_2.

For the staged injection, one third of \text{H}_2\text{O}_2 amount was added at three different points of time in Fig. 4b, whenever a rapid increase of Fe(II) was observed. The increase of Fe(II) indicates for the shortage of OH radical to carry out Reaction (3), which is partially attributable to the depletion of \text{H}_2\text{O}_2. It is speculated that the staged \text{H}_2\text{O}_2 addition may efficiently avoid the shock loading of \text{H}_2\text{O}_2, thus maintaining the optimum concentration of \text{H}_2\text{O}_2 during the entire reaction. The staged \text{H}_2\text{O}_2 addition was found to be more effective than the one-time addition at the initial stage, as presented in Fig. 5. The citric acid oxidation and COD reduction were more obvious in the staged \text{H}_2\text{O}_2 injection. In Fig. 5a, the rapid reduction of citric acid was made within 60 min of UV time. However,
somewhat steady reduction was noticed for the staged injection of \( \text{H}_2\text{O}_2 \). After 3 hrs of the UV irradiation with chemical additives, more than 90% of citric acid was decomposed (Fig. 5a). For the COD reduction in Fig. 5b, most citric acid reduction in terms of COD was made at the initial stage of process for the single point injection of \( \text{H}_2\text{O}_2 \), while the COD reduction in the staged process was minimal before 30 min. However, 80% of COD was removed in the staged process. Therefore, the separate additions of \( \text{H}_2\text{O}_2 \) are more effective than the one-time addition, because the rapid consumption of \( \text{H}_2\text{O}_2 \) can be prevented in the staged addition of \( \text{H}_2\text{O}_2 \).

### 2.4 Staged \( \text{H}_2\text{O}_2 \) injection in the naval citric acid wastewater and kinetic reaction

The naval citric acid wastewater was treated with the UV/Fe(III) in the staged process of multiple \( \text{H}_2\text{O}_2 \) injections. The wastewater (sample D) contains iron 1456 mg/L, as the amount used for the Fenton-like reaction. The COD reduction of the derusting wastewater (sample D) was monitored for 18 hr, as presented in Fig. 6a. The initial COD concentration of the wastewater was around 50,000 mg/L and the final COD was 3500 mg/L after 18 hr of the UV/\( \text{H}_2\text{O}_2/\text{Fe(III)} \) treatment. Almost 93% of COD was removed. As presented in Fig. 6b, the relation of COD reduction and UV irradiation obeys the first-order kinetic reaction, because the plot of COD reduction and UV time shows the linear relation with \( R = 0.9698 \). The initial COD of sample C was also reduced to 300 mg/L after 18 hr of the UV/\( \text{H}_2\text{O}_2/\text{Fe(III)} \) treatment with 99% reduction (data not shown). As a drawback of this experiment, the metal precipitation was encountered during the photooxidation of the derusting wastewater. Two types of precipitates such as Fe(OH)\(_3\) and FeC\(_2\)O\(_4\) were identified. The destruction of the citric acid basically results in a precipitation of Fe(OH)\(_3\), which may interfere with the UV/\( \text{H}_2\text{O}_2 \) treatment. A number of precipitates may block the UV penetration. In addition, the UV irradiation is of great significance to allow the radical chain reaction to repeatedly happen, particularly, OH radical is induced by the UV irradiation (Reaction (5)). Due to this reason, the decomposition of the citric acid seems to highly depend on the \( \text{H}_2\text{O}_2 \) amount (Fig. 5a). As the Fe(II)/\( \text{H}_2\text{O}_2 \) process without the UV made only 10% of citric acid reduction (Fig. 2), the role of UV is important in allowing the Fe(III) and \( \text{H}_2\text{O}_2 \) to do as a strong oxidant through the chain reaction. The photooxidation of derusting wastewater in the presence of TEA, is slightly different from that of citric acid alone. TEA may elevate the pH of the wastewater, decreasing the precipitation of Fe(II) and Fe(III). It was however indicated that TEA is preferentially decomposed under the UV/\( \text{H}_2\text{O}_2 \) treatment (Arthur, 1995). This study...
emphasizes on the decomposition of the citric acid wastewater.

3 Conclusions

In terms of the removal efficiency of the derusting wastewater under different treatment methods, the order was found: UV/H₂O₂/Fe(III) > UV/H₂O₂ > Fe(II)/H₂O₂. The UV irradiation may be hindered by the metal precipitation in the derusting wastewater, but the UV photooxidation could proceed in the chain reaction with H₂O₂ and Fe(III), with less sludge production. Fenton-like oxidation may overcome the drawback of Fenton oxidation by reducing a large amount of sludge. The mutual dependence between UV/H₂O₂/Fe(III) was observed in order to completely decompose the target compound. In the presence of H₂O₂, the photooxidation is dependent upon the frequency of addition as well as the amount of H₂O₂. One-time addition of H₂O₂ caused the scavenging of H₂O₂ at the beginning of the process, which resulted in that the decomposition of the citric acid complex was made initially. The staged process of step-feeding H₂O₂ injections was more effective than the one-time addition, preventing the rapid consumption of H₂O₂ added. The naval derusting wastewater was successfully treated in the UV photo-Fenton-like oxidation with exiting iron metals in the wastewater. The high removal efficiency was observed, and the process showed the first order of kinetic reaction.

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References


