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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 H_2O_2 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 H_2O_2 . The decomposition rate was found in a sequence of: $UV/H_2O_2/Fe(III) > UV/H_2O_2 > Fe(II)/H_2O_2$. Two H_2O_2 injection methods, single and multiple points, were evaluated. The multiple-point H_2O_2 injection was more efficient to decompose the citric acid. The decomposition of the synthetic citric acid and the real derusting citric acid wastewater was also compared. The 93% COD reduction of the derusting wastewater was achieved using the UV/H_2O_2/Fe(III) treatment.

Key words: naval derusting wastewater; citric acid; UV photooxidation; Fenton-like **DOI**: 10.1016/S1001-0742(09)60209-6

Introduction

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 and 4% TEA (volume ratio of citric 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,

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the difficult rust deposites 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 H_2O_2 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 (H_2O_2) 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 V) (Legrini et al., 1993). Also, the Fenton oxidation process utilizing the activation of H₂O₂ 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 H₂O₂ 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/H2O2 and Fe(III), which benefits from iron metals already exiting in the derusting wastewater. This process is so-called Fenton-like oxidation. The irons 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/H₂O₂/Fenton reaction/Fenton-like reaction, was performed to see the optimum combinational method in the decomposition of the citric acid and the naval dersuting wastewater as a practice. Since this study is dependent on H_2O_2 , the difference between the single point and multiple-point injections of H₂O₂ 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

Table 1	Derusting wastewater characterization

Characteristics	Sample A	Sample B	Sample C	Sample D
Citric acid (%)	7.06	1.48	0.90	1.00
TEA (%)	4.25	1.57	0.03	0.00
PH	2.5	4.26	2.64	5.53
Alkalinity	0	0	0	600
(as CaCO ₃ mg/L)				
COD (mg/L)	140,000	60,000	46,700	51,200
Arsenic (mg/L)	1.00	0.00	0.00	0.00
Beryllium (mg/L)	0.00	0.00	0.00	0.00
Cadmium (mg/L)	1.40	0.10	0.06	1.47
Chromium (mg/L)	8.00	4.10	4.00	8.19
Copper (mg/L)	0.00	5.80	5.72	23.1
Iron (mg/L)	710	1052	1042	1456
Lead (mg/L)	24.0	2.30	2.24	8.32
Mercury (mg/L)	0.05	0.00	0.00	0.00
Nickel (mg/L)	0.10	10.1	10.4	13.3
Selenium (mg/L)	0.10	0.30	0.25	0.36
Silver (mg/L)	0.50	0.00	0.00	0.00
Zinc (mg/L)	0.00	77.3	76.9	200

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 Pfiger (USA) and 30% strength of H₂O₂ 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 H₂O₂ solution was made in different molarity concentrations. The ratio of citric acid to H₂O₂ was set as 1:6 (molarity ratio) for the comparison experiments. The acid solution was introduced to the reactor after UV lamp warming up, avoiding the early instability of lamp. The temperature was maintained at $40 \pm 3^{\circ}$ C in a water cooling system. Samples were withdrawn intermittently during photolysis and subject to IC analysis immediately. IC was used to quantify the citric acid. The IC system (2000i, Dionex Co., USA) was equipped with an ion chromatography exclusion (ICE) column in conjunction with a HPICE-ISC separator column and a HPICE-ISC suppressor (Rich et al., 1980; Keppel, 1981; Lebel and Yen, 1984; Nadkarni and Brewer, 1987). The eluent was 0.0005 mol/L HCl with a flow rate of 0.8 mL/min. Fresh samples were injected to the IC without dilution. UV-Vis

spectrophotometer (UV-25, Becakman, 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 Mallinckrodt (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 H_2O_2 injection, 300 mL of 30% strength of H_2O_2 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% H_2O_2 were added at 20, 50, and 80 min of UV times. The H_2O_2 consumption, COD reduction, and citric acid decomposition were evaluated. In the experiment of the real naval desusting wastewater, the multiple H_2O_2 injections were also carried out. Every two hours for the entire UV irradiation time (18 hr), 35 mL of 30% H_2O_2 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

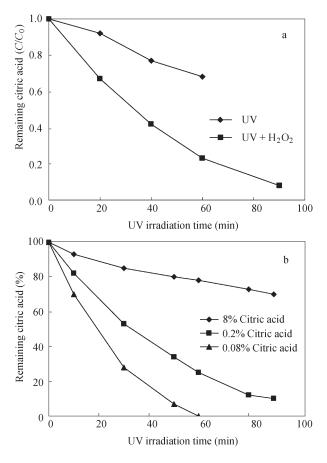


Fig. 1 Comparison of citric acid decomposition of UV only and UV + H_2O_2 (0.2% citric acid and 30% H_2O_2) (a) and various citric acid decompositions under the UV photooxidation with H_2O_2 (b).

decomposed (Fig. 1a). On the other hand, when H_2O_2 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/ H_2O_2 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 H_2O_2 .

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 photooxiation, 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 reacting site of the Fe(III)-citrate complex.

The OH radical is naturally electrophilic (Walling, 1975; Ikemizu 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 indiscreetly. 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 H_2O_2 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, Fe^{2+} and H_2O_2 must be added continuously to keep the reaction proceed (Chiou et al., 2006). This may cause another big precipitation problem to further produces

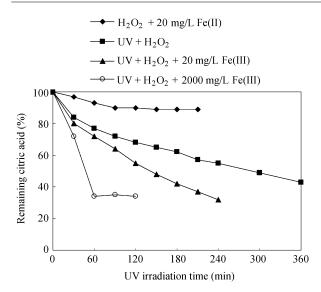


Fig. 2 Comparison of citric acid decomposition under different oxidation methods (30% H₂O₂ solution).

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:

$$Fe(OH)^{2+} + hv \to Fe^{2+} + OH$$
(1)

$$Fe(OH)_6^{3+} + hv \rightarrow Fe^{2+} + OH + H^+$$
(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_2O_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 Fe³⁺ to Fe²⁺ 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 Fe³⁺ was added. More than 65% of citric acid was decomposed in the method of UV/H₂O₂/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 H₂O₂ 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/H₂O₂ 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_2O_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.

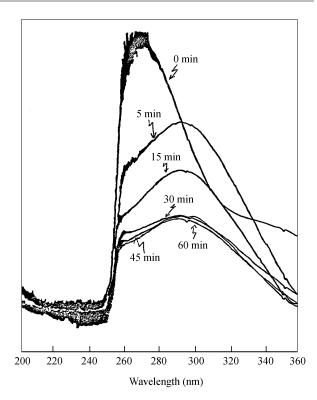


Fig. 3 $\,$ UV spectra of photodegradation of Fe(III)-citrate complex in the process of UV/H_2O_2.

Apparently 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_2O_2 as significantly as Fe(II) could. However, Fe(II) surpasses Fe(III) as to consume H_2O_2 (Kusic et al., 2006; Chiou et al., 2006).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH + OH^-$$

$$k_1 = 76 \text{ (mol/L)}^{-1} \text{sec}^{-1}$$
(3)

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2 \cdot + H^+$$

$$k_2 = 0.02 \text{ (mol/L)}^{-1} \text{sec}^{-1}$$
(4)

After the decomposition of the Fe(III)-citrate complex, the reoxidized Fe(III) cannot form a complex with the citric acid under UV and therefore can freely react with H_2O_2 to help form OH radicals. This can be supported by the results of H₂O₂ consumption, as seen in Fig. 4a. Large amounts of the OH radical and strong Fe(III) oxidizer result in a sizable reduction of the citric acid concentration in the process of UV/H₂O₂ and 2000 mg/L of Fe(III) (Fig. 2). When a high concentration of Fe(III) was applied, Fe(III) likely functions to catalyze H_2O_2 as a charge transfer oxidant as well as to strongly decompose the acid compound. Therefore, reactions above are important in decomposing the acid complex by producing the strong oxidant, Fe(III), which is generated from the chain reaction of Reactions (3) and (4). This Fe(III) can destroy the organic complex. Thus, overall destruction mechanism can

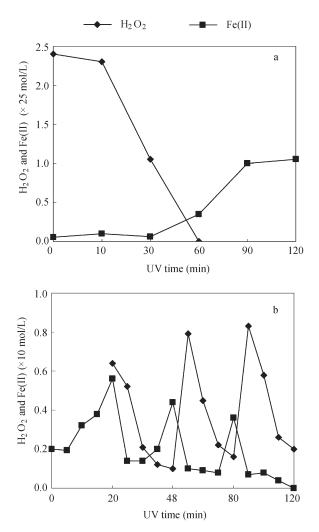


Fig. 4 H_2O_2 consumption and Fe(II) change of single point H_2O_2 injection (a) and multiple-point H_2O_2 injections (b).

be explained as follows.

 $H_2O_2 + hv \to 2OH \cdot$ (5)

 $RH (Fe^{3+} - Citrate) + hv \longrightarrow RH + Fe^{3+}$ (6)

$$\longrightarrow \mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \longrightarrow \mathrm{Fe}^{3+} + \mathrm{OH}_{\bullet} + \mathrm{OH}_{\bullet}$$
(7)

$$OH \cdot + RH \longrightarrow RH \cdot + H_2O \tag{8}$$

$$OH \cdot + H_2 O_2 \to HO_2 \cdot + H_2 O \tag{9}$$

$$OH \cdot + Fe^{2+} \longrightarrow Fe^{3+} + OH^{-}$$
(10)

$$Fe^{3+} + RH \longrightarrow RH + Fe^{2+}$$
 (11)

$$Fe^{3+} + RH \cdot \longrightarrow RH^{+} + Fe^{2+}$$
(12)

$$\operatorname{Fe}^{3+} + \operatorname{H}_2\operatorname{O}_2 \longrightarrow \operatorname{Fe}^{2+} + \operatorname{HO}_2 \cdot + \operatorname{H}^+$$
 (13)

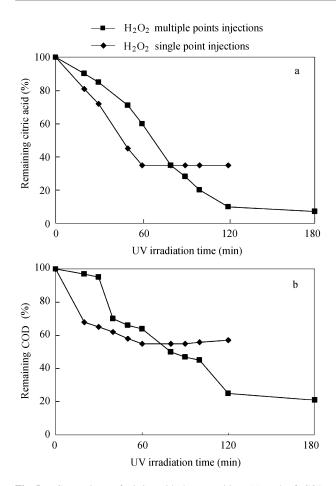
Destruction mechanisms occurred in the derusting wastewater include the UV induced destruction, OH radical induced destruction, and ferric ion induced destruction. For the UV induced mechanism, as seen in Reactions (6) and (7), the energy from UV can be directly used for the destruction of organic complex. For the OH radical induced destruction, the OH radicals are generated from H_2O_2 dissociation by the direct irradiation of UV (Reaction (5)) or from the reaction with Fe²⁺ (Reaction (7)).

For the destruction induced by Fe^{3+} (Reactions (11) and (12)), Fe^{3+} can attack the organic target since Fe^{3+} is quite strong oxidant (Neyens and Baeyens, 2003). The role of Fe^{3+} is important, because Fe^{3+} helps to oxidize the target organic compound and to produce the OH radical through the Fe^{2+} formation as in Reactions (6) and (7). Therefore, the presence of iron salts can reduce the scavenging effect of OH radical from H_2O_2 . The peroxide combination with metal salts or UV is more effective than the single use of H_2O_2 , as seen in the kinetic values.

2.3 Single H_2O_2 injection and step-feeding (multiple) H_2O_2 injection in the synthetic citric acid solution

The two sets of experiments with single point and multiple points of the H_2O_2 injection, were designed to evaluate the effectiveness of the H2O2 injection and its concentration distribution in terms of the citric acid oxidation. Both experiments used equal quantities of H_2O_2 to treat the 8% citric acid solutions with 2000 mg/L of Fe(III). As shown in Fig. 4a, the addition of H₂O₂ was made initially before the UV irradiation for the one-time injection. The amount of H₂O₂ 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 H₂O₂ was used to decompose the Fe(III)-organic complex to Fe³⁺ 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 H₂O₂ after the decomposition of the Fe(III)-organic complex was also utilized to transform this increased amount of Fe^{2+} (Reaction (7)) to the strong oxidizer, 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 H_2O_2 , Fe(II), and RH. Reaction (9) is undesirably happening because OH radical is wasted to react with H₂O₂ newly added to the system, which is socalled 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/H₂O₂ and Fe(III) is dependent upon the amount of H_2O_2 .

For the staged injection, one third of H_2O_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 H_2O_2 . It is speculated that the staged H_2O_2 addition may efficiently avoid the shock loading of H_2O_2 , thus maintaining the optimum concentration of H_2O_2 during the entire reaction. The staged H_2O_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 H_2O_2 injection. In Fig. 5a, the rapid reduction of citric acid was made within 60 min of UV time. However,



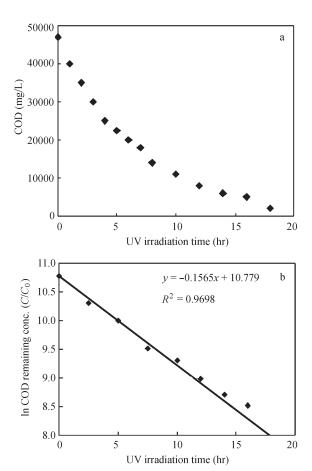


Fig. 5 Comparison of citric acid decomposition (a) and of COD reduction (b) between single point H_2O_2 injection and multiple points H_2O_2 injections.

somewhat steady reduction was noticed for the staged injection of H_2O_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 H_2O_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 H_2O_2 are more effective than the one-time addition, because the rapid consumption of H_2O_2 can be prevented in the staged addition of H_2O_2 .

2.4 Staged H_2O_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 H_2O_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/H₂O₂/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

Fig. 6 COD reduction of the naval derusting wastewater during the UV photooxidation in the presence of H_2O_2 and Fe(III) (a) and kinetic reaction of COD reduction and UV radiation time (b).

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/H2O2/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_2O_4 were identified. The destruction of the citric acid basically results in a precipitation of Fe(OH)3, which may interfere with the UV/H₂O₂ 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 H_2O_2 amount (Fig. 5a). As the Fe(II)/ H_2O_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 H_2O_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/H₂O₂ 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: $UV/H_2O_2/Fe(III) > UV/H_2O_2 > Fe(II)/H_2O_2$. 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 H_2O_2 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 H_2O_2 , the photooxidation is dependent upon the frequency of addition as well as the amount of H_2O_2 . One-time addition of H_2O_2 caused the scavenging of H_2O_2 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 H_2O_2 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

- Antonov B N, Pchelintsev V M, 1974. Inhibition of solutions of compositions with complexations in high concentrations. *Teploenergetika*, 9: 83–88.
- Arthur D L, 1995. Field tests of UV/H₂O₂ system to treat citric acid/triethanolamine wastewater. Final report, Acorn Park, Cambridge, MA, USA.
- Catalkaya E C, Kargi F, 2007. Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: A comparative study. *Journal of Hazardous Materials*, 139: 244–253.

- Chiou C S, Chen Y H, Chang C T, Chang C Y, Shie J L, Li Y S, 2006. Photochemical mineralization of di-*n*-butyl phthalate with H₂O₂/Fe³⁺. *Journal of Hazardous Materials*, B135: 344–349.
- Ikemizu K, Orita M, Sagiike M, Morooka S, Kato Y, 1987. Ozonation of organic refractory compounds in water in combination with UV radiation. *Canadian Journal of Chemistry*, 55: 369.
- Koppel I R, 1981. Analytical Chemistry and Applied Spectroscopy. John Wiley and Sons, Inc., New York. 241.
- Kusic H, Koprivanac N, Bozic A L, Selanec I, 2006. Photoassisted Fenton type processes for the degradation of phenol: A kinetic study. *Journal of Hazardous Materials*, B136: 632–644.
- Lebel A, Yen T F, 1984. Ion chromatography for determination of metabolic patterns of sulfate-reducing bacteria. *Analytical Chemistry*, 56: 807–808.
- Lee J M, Kim J H, Chang Y Y, Chang Y S, 2009. Steel dust catalysis for Fenton-like oxidation of polychlorinated dibenzo-p-dioxins. Journal of Hazardous Materials, 163: 222–230.
- Legrini O, Oliveros E, Braun A M, 1993. Photochemical processes for water treatment. *Chemical Reviews*, 93: 671–698.
- Nadkarni R A, Brewer J M, 1987. Application of IC in environmental analysis. American Laboratory. 50.
- Neyens E, Baeyens J, 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, B98: 33–50.
- Pan B Y K, Chen J R, Yen T F, Alexandria V, 1990. Initial feasibility report on ultraviolet light and hydrogen peroxide method to treat citric acid wastewater, Technical Memorandum TM-90-5.
- Perrin D D, 1970. Masking and Demasking of Chemical Reactions. Wiley-Interscience, New York, USA.
- Primo O, Rivero M J, Ortiz I, 2008. Photo-Fenton process as an efficient alternative to the treatment of landfill leachates. *Journal of Hazardous Materials*, 153: 834–842.
- Rich W, Johnson E, Lois L, Kabra P, Stafford B, Marton L, 1980. Determination of organic acids in biological fluids by ion chromatography: Plasma lactate and pyruvate and urinary vanillylmandelic acid. *Clinical Chemistry*, 26: 1492–1498.
- Saritha P, Aparna C, Himabindu V, 2007. Comparison of various advanced oxidation processes for the degradation of 4chloro-2 nitrophenol. *Journal of Hazardous Materials*, 149: 609–614.
- Twort A C, Hoather R C, Law F M, 1974. Water Supply (2nd ed). Cox & Wyman, London, England.
- Walling C, 1975. Fenton's reagent revisited. Accounts of Chemical Research, 8: 125–131.

