

Transformation characteristics of organic pollutants in Fered-Fenton process for dry-spun acrylic fiber wastewater treatment

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ABSTRACT

The Fered-Fenton process using Ti sheet as cathode and RuO₂/Ti as anode was employed for the pretreatment of dry-spun acrylic fiber manufacturing wastewater. The effects of feeding mode and concentration of H₂O₂ on chemical oxygen demand (COD) removal efficiency as well as the biodegradability variation during the Fered-Fenton process were investigated. The feeding mode of H₂O₂ had significant influence on COD removal efficiency: the removal efficiency was 44.8% if all the 60.0 mM H₂O₂ was fed at once, while it could reach 54.1% if the total H₂O₂ was divided into six portions and fed six times. The biochemical oxygen demand/COD ratio increased from 0.29 to above 0.68 after 180 min treatment. The transformation characteristics of organic pollutants during the Fered-Fenton process were evaluated by using gas chromatography–mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR) and fluorescence excitation–emission matrix (EEM) spectroscopy. Most of the refractory organic pollutants with aromatic structure or large molecular weight were decomposed during the Fered-Fenton process.

Key words | dry-spun acrylic fiber wastewater, EEM, Fered-Fenton, FTIR, GC-MS

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INTRODUCTION

In China, most of the acrylic fiber manufacturing plants use the dry-spun or wet-spun production method to produce various types of acrylic fiber. Of these two production methods, the dry-spun acrylic fiber (DAF) is the preferred product for its high quality and versatility. However, in the dry-spun production method, acrylonitrile (AN), dimethyl-formamide (DMF) and dozens of auxiliary agents are needed in the entire production process, which leads to refractory and complicated DAF wastewater containing toxic compounds (An *et al.* 2013). A conventional biological process is not efficient for the removal of refractory pollutants in DAF wastewater, especially for low polymers, and microbial activity would be inhibited by toxic compounds and high concentration of inorganic salts (Li *et al.* 2011a).

The Fered-Fenton process is a novel electrochemical advanced oxidation technology based on the conventional Fenton reaction and electrochemical process. In the Fered-Fenton process, Fenton reagent (H₂O₂/Fe²⁺) is externally added to the electrolytic cell (Zhang *et al.* 2012) and hydroxyl radicals (•OH) are generated in the solution by the Fenton's reaction between Fe²⁺ and H₂O₂ (Equation (1)). This species has high standard reduction potential that can react non-selectively with most organic pollutants and realize total mineralization. In the meantime, Fe²⁺ can be continuously regenerated at the cathode (Equation (2)) and consequently minimize the sludge production. The Fered-Fenton process not only improves ferrous regeneration and consequently the efficiency of Fenton chain reactions but also decreases

the cost of Fenton reagent and sludge treatment (Huang *et al.* 2008)



In our previous work, the performance of the Fered-Fenton method for the pretreatment of DAF wastewater was preliminarily investigated but the transformation characteristic of organic pollutants was not studied in detail. In this paper, we first investigated the influence of feeding mode of H_2O_2 on chemical oxygen demand (COD) removal efficiency as well as the biodegradability variation during the Fered-Fenton process. Based on these results, the transformation characteristics and organic pollutants during the Fered-Fenton process were analyzed fully by gas chromatography–mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR) and fluorescence excitation–emission matrix (EEM) spectroscopy.

MATERIALS AND METHODS

Raw wastewater and materials

The wastewater was obtained from a DAF manufacturing factory in Liaoning Province, northeast China. The wastewater processes COD of 1,126 mg/L, biochemical oxygen demand (BOD₅) of 326 mg/L, total organic carbon of 426 mg/L, $\text{NH}_4^+\text{-N}$ of 22 mg/L and pH 6.56.

Hydrogen peroxide (30%, w/w), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2SO_4 , Na_2SO_4 and NaOH used in this study were of analytical grade.

Experimental apparatus

Experiments were carried out in a 500 mL undivided cylindrical glass reactor located on a hot plate with variable magnetic stirring and a temperature control device (Figure S1, available online at <http://www.iwaponline.com/wst/070/441.pdf>). A RuO_2/Ti and Ti sheet with an exposed geometric dimension of 60×100 mm were used as the anode and cathode, respectively. In a typical experiment, 400 mL wastewater plus a weighed amount of solid $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were added to the reactor with mechanical stirring for continuous mixing of the reaction system and 0.05 M Na_2SO_4 was added as the supporting electrolyte. Following the addition of a volume of H_2O_2 , the DC power source was turned on and the Fered-

Fenton reaction was initiated. Prior to the Fered-Fenton reaction, the initial pH value of solutions was set at 3.0 with the addition of H_2SO_4 (3.0 M) and the reaction temperature was set at 25 °C. Samples were taken from the reactor at the determined reaction time for analysis.

Analytical methods

COD and BOD₅ were measured according to standard methods (SEPA 2002) and pH value was measured by the OHAUS Starter 3C pH meter. GC-MS, FTIR and EEM analyses were carried out according to the literature (Lai *et al.* 2012a; Wei *et al.* 2013).

RESULTS AND DISCUSSION

COD removal by Fered-Fenton process

In the Fered-Fenton process, H_2O_2 is the most important parameter because it is the source of $\bullet\text{OH}$ and the main cost for scale-up application. Recently, much attention has been focused on the effect of H_2O_2 feeding mode on the treatment efficiency. At the optimal operating conditions identified on the basis of preliminary tests (initial pH value of 3.0, Fe^{2+} dosage of 5.0 mM and current intensity of 0.2 A), the effects of feeding mode and concentration of H_2O_2 on COD removal in the Fered-Fenton process were investigated and the result is shown in Figure 1. The COD removal efficiency increased from 24.5 to 44.9% when the H_2O_2 dosage increased from 20.0 to 60.0 mM in a single injection mode. The feeding mode has significant influence on the COD removal efficiency: when the H_2O_2 was fed

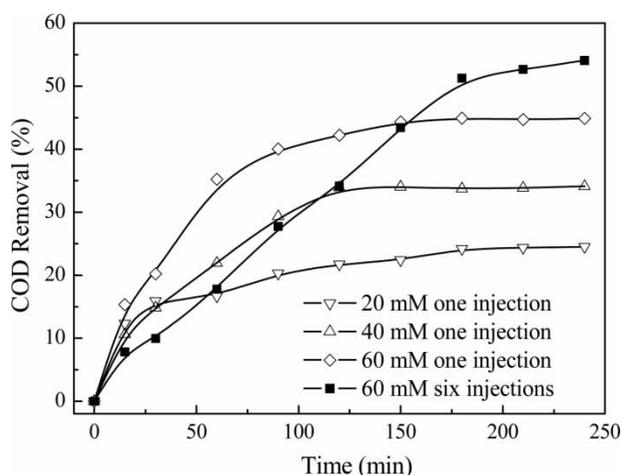


Figure 1 | Effect of H_2O_2 dosage and injection mode on COD removal efficiency.

once to reach 60.0 mM, the final COD removal efficiency only reached 44.9%; when the same amount of H_2O_2 was equally divided into six parts and one part was fed every 30 min, the final COD removal efficiency was increased to 54.1%.

In the single dosing mode, the high H_2O_2 concentration at initial reaction stage caused negative effect on both Fe^{2+} catalysis and COD removal of DAF wastewater. On one hand, catalytic Fe^{2+} was oxidized to Fe^{3+} by excess H_2O_2 and the oxidation capability of the Fenton system decreased (Pignatello 1992). On the other hand, superfluous H_2O_2 acted as a scavenger of the highly potent $\cdot\text{OH}$ to produce less reactive species such as $\text{HO}_2\cdot$, which reduced the probability of attack of organic molecules by $\cdot\text{OH}$, and caused the reduction of COD removal efficiency (Lee & Shoda 2008). Consequently, the multi-feeding mode of H_2O_2 could reduce these side reactions and improve the treatment efficiency of the Fered-Fenton system.

Biodegradability enhancement

Ordinarily, the wastewater is considered to be biodegradable when the BOD_5/COD (B/C) ratio is higher than 0.4 (Kallel et al. 2009). With a B/C ratio of 0.29, the raw DAF wastewater was clearly bio-refractory and difficult to be biodegraded by the activated sludge process. To analyze the potential use of combined chemical-biological treatments, the biodegradability of treated DAF wastewater was monitored by measuring the B/C ratio.

Figure 2 shows the COD, BOD_5 and B/C ratio variation of the DAF wastewater in the Fered-Fenton process under the optimum reaction conditions obtained in our previous work. As observed, a quick degradation was detected, with COD falling from 1,126 to 506 mg/L after 4.0 h reaction,

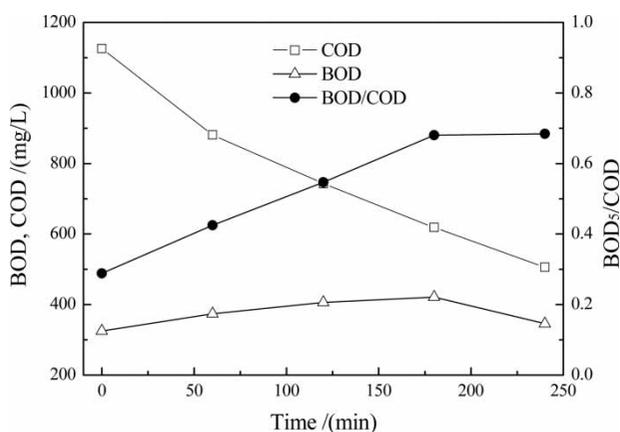


Figure 2 | The variation of biodegradability in the Fered-Fenton process.

corresponding to about 54.1% COD reduction. With the COD reduction, the BOD_5 slightly increased from 325 to 421 mg/L while the B/C ratio significantly increased from 0.29 to above 0.68 after 3.0 h of Fenton reaction. The B/C value did not increase further with the increased reaction time. The improved B/C value meant that the treated wastewater was readily biodegradable.

The improved biodegradability of DAF wastewater can be explained by the transformation of refractory organic pollutants in the Fered-Fenton process. GC-MS analysis (Figure 3) shows that dozens of organic pollutants were successfully identified in raw DAF wastewater, including aromatic compounds (72.42%), straight-chain paraffin (9.84%), alcohols (6.97%) and some other typical pollutants such as DMF (1.97%). Among these organic pollutants, mequinol (67.88%) might be mainly responsible for the low biodegradability and toxicity of the DAF wastewater. After the Fered-Fenton pretreatment, most peak intensities significantly decreased and some organics (such as DMF, octanol and mequinol) were not detected. However, some new organics (such as dimethyl-amine acrylonitrile) were detected after the Fered-Fenton pretreatment. The DAF wastewater contained high molecular weight organics and polymers, which were difficult to be detected by GC-MS. After Fered-Fenton oxidation, these high molecular weight pollutants would be oxidized to small organics, which were more readily detected by GC-MS (Lei et al. 2007). Furthermore, these small organic pollutants are more easily degraded compared to those high molecular weight pollutants with complex structure (Oller et al. 2011).

Regarding these results, the Fered-Fenton process was an effective method for transforming bio-refractory organic pollutants and can be considered as a promising process for the pretreatment of DAF wastewater prior to biological treatment.

FTIR adsorption spectra analysis

For the complexity of DAF wastewater, some macromolecular organics and high polymers of AN are difficult to be accurately detected by GC-MS analysis. In order to gain a better insight into the transformation characteristics of organic pollutants during the Fered-Fenton process, FTIR was applied to analyze the transformation of general functional groups. The absorbance bands are interpreted by information from previously published reports (Gnanasambam & Protor 2000; Ji et al. 2007; Sen et al. 2011; Lai et al. 2012a).

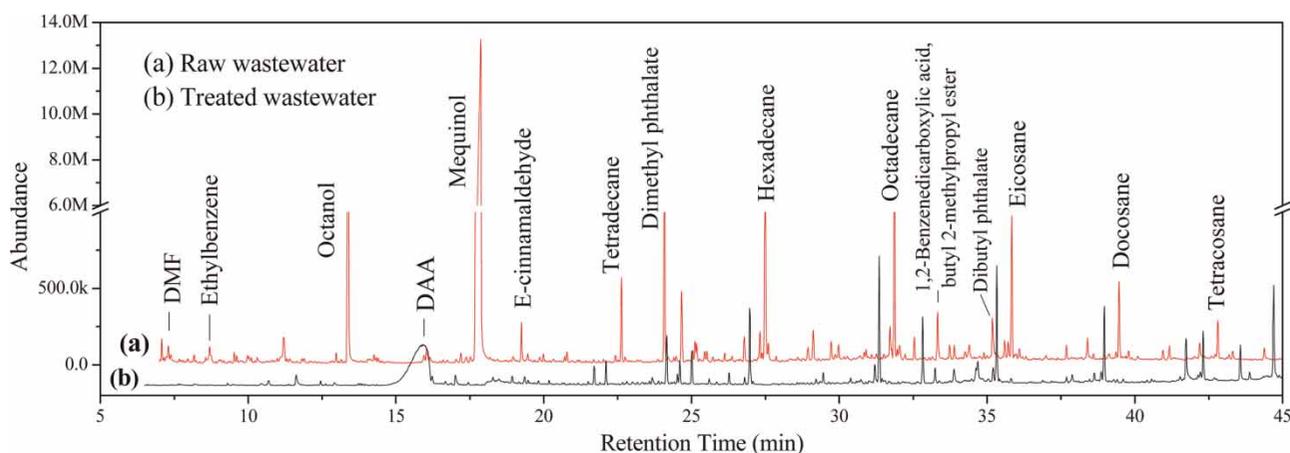


Figure 3 | GC-MS chromatogram of raw and treated DAF wastewater by the Fered-Fenton process.

The progressive changes observed in FTIR adsorption spectra of raw and treated DAF wastewater at different reaction time were obtained. As shown in [Figure 4\(a\)](#), the raw wastewater showed peaks at 3,447, 2,942, 2,245, 1,734, 1,637, 1,456, 1,203 cm^{-1} , etc. Of these peaks, the broad peak at around 3,447 cm^{-1} may be attributed to the overlap of N—H stretching, O—H stretching and hydrogen-bonded OH of carboxylic acids in the inter- and intra-molecular hydrogen bonding of polymeric compounds, such as alcohols, phenols and carboxylic acids ([Gnanasambandam & Protor 2000](#); [Lai et al. 2012a](#)); the band at 2,942 cm^{-1} is attributed to the stretching of CH_2 group; the band at 2,245 cm^{-1} is attributed to the stretching of $\text{C} \equiv \text{N}$ in fatty nitriles ([Lai et al. 2012b](#)); the band at 1,734 cm^{-1} is indicative of the $\text{C}=\text{O}$ stretching vibration due to non-ionic carboxyl

groups ($-\text{COOH}$, $-\text{COOCH}_3$) and may be attributed to hydrogen bonding between carboxylic or their esters ([Ji et al. 2007](#)); the band at 1,637 cm^{-1} is assigned to the N—H bending vibration and/or $\text{C}=\text{O}$ stretching ([Sen et al. 2011](#)); the band at 1,456 cm^{-1} may be attributed to the $\text{C}-\text{N}$ stretching of amine; the bands at 1,203 and 1,074 cm^{-1} are attributed to the stretching of $\text{C}-\text{O}$. It implies that the main organic pollutants in the DAF wastewater are aromatic compounds, phenolic and/or alcohol compounds and some nitrogenous compounds.

[Figure 4\(b\)](#) is the FTIR adsorption spectrum of the wastewater after 120 min reaction. This spectrum shows that the peak intensity at around 2,942, 2,245, 1,734 and 1,456 cm^{-1} sharply decreased after 120 min reaction. This may be attributed to the decomposition of aromatic compounds and nitrile compounds (e.g. polymers of AN). In addition, some new peaks at 615 cm^{-1} (N—H, O—N=O), 1,046 and 1,194 cm^{-1} ($\text{C}-\text{O}$ stretching vibration) appeared after 120 min of the Fered-Fenton process. It is clear that some by-products (e.g. carboxylic acid, amine and amide) are generated after the decomposition of the aromatic compounds and organic nitriles in DAF wastewater. [Figure 4\(c\)](#) shows that all the peak intensities of the treated DAF wastewater were weakened obviously after 240 min reaction. Some main peaks (e.g. peaks at 2,942, 2,245, 1,734 and 1,456 cm^{-1}) disappeared. The results indicate that the main pollutants in DAF wastewater could be removed efficiently by the Fered-Fenton process.

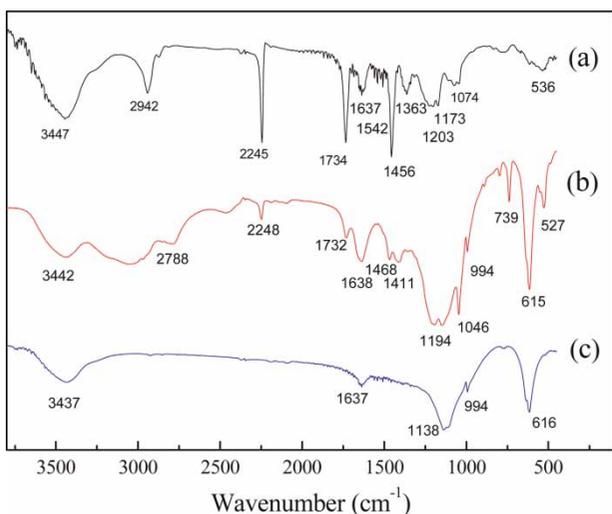


Figure 4 | FTIR spectra of wastewater at different reaction time: (a) raw wastewater, (b) after 120 min reaction, (c) after 240 min reaction.

EEM analysis

EEM spectra could help to assess chemical modification of organic components in water or wastewater. The progressive

changes observed in EEMs of DAF wastewater during the Fered-Fenton process are presented in Figure 5. Excitation and emission boundaries were operationally divided into five regions in order to better discriminate the fluorescence substances in wastewater (Chen *et al.* 2003). As shown in Figure 5(a), five fluorescence peaks (B_1 , B_2 , B_3 , T_1 and T_2) were observed for the raw DAF wastewater. Peak B_1 located at the E_x/E_m wavelengths of 220/295 nm in Region I was related to monocyclic aromatics, such as aniline, benzene, phenol and toluene (Bosco *et al.* 2006). Peak B_2 was centered at the E_x/E_m of 225/330 nm in Region II and peak B_3 was detected at the E_x/E_m of 285/320 nm in Region IV. These two intensive peaks were probably related to bicyclic aromatic compounds, including naphthalene, ethylbenzene and xylene (He *et al.* 2009). In addition, a shoulder peak (T_1) was detected at the E_x/E_m of 230/410 nm in Region III and another peak (T_2) was found at the E_x/E_m of 325/400 nm in Region V. These two peaks were likely due to fulvic-like

compounds which contained three to five aromatic rings, such as pyrene, benzopyrene, phenanthrene and furan (Bosco *et al.* 2006). After 60 min Fered-Fenton reaction, the three peaks (B_1 , B_2 and B_3) nearly disappeared and the fluorescence signals in Regions I, II and IV were greatly weakened (Figure 5(b)), which indicated that monocyclic and bicyclic aromatic compounds were fully decomposed by the Fered-Fenton reaction. The fluorescence intensity of peaks T_1 and T_2 significantly decreased in the first 60 min, which thereafter decreased slowly in the following 180 min (Figures 5(c) and 5(d)). After 240 min Fered-Fenton reaction, the peaks B_1 , B_2 and B_3 disappeared and the peak intensity of T_1 and T_2 were significantly decreased. These results indicated that most of the fluorescence compounds with simple structure were broken and oxidized after 60 min of Fered-Fenton reaction and the fluorescence compounds with complex structure could also be decomposed and transformed during the process, although it needed more reaction time. Furthermore,

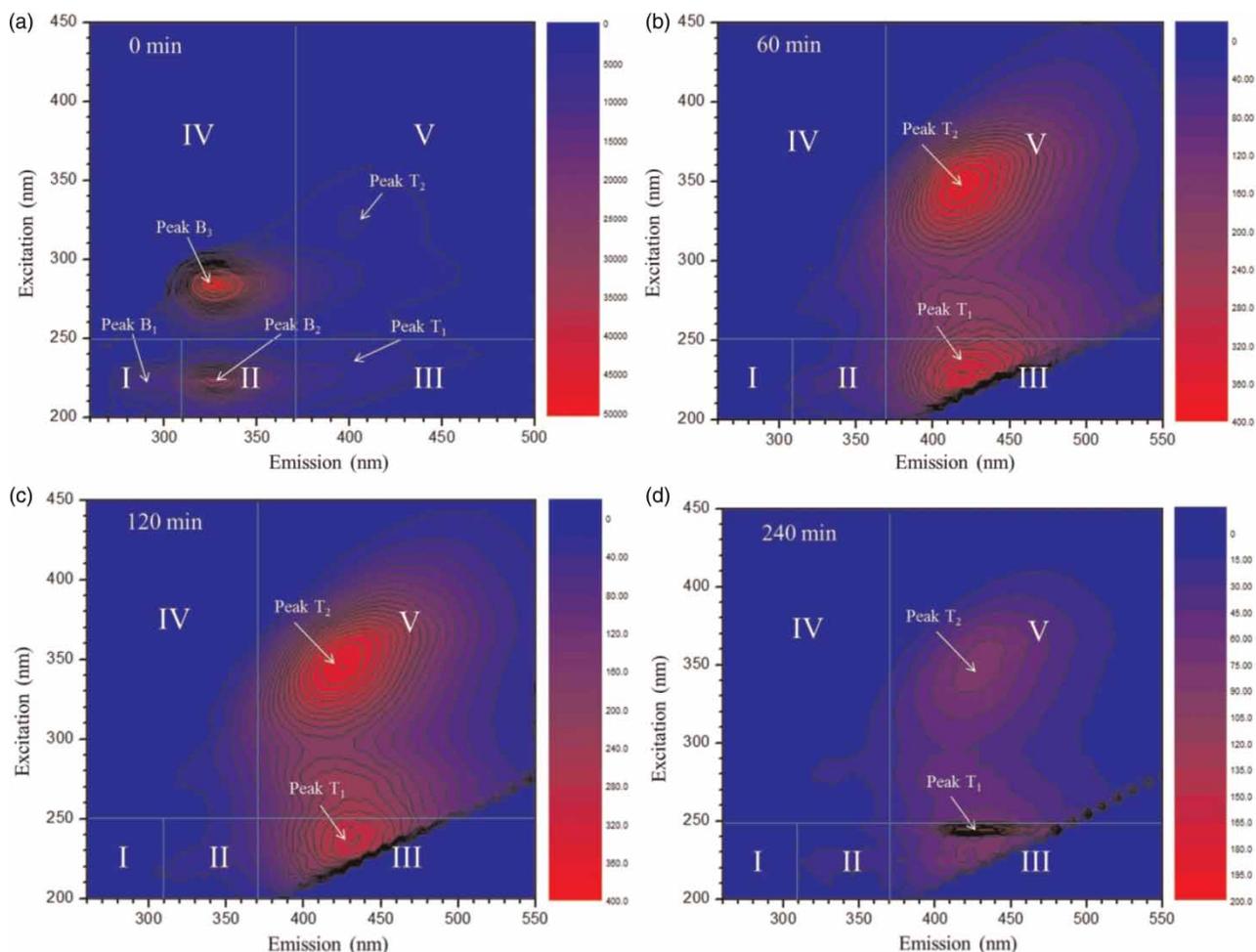


Figure 5 | EEM spectra of wastewater at (a) 0 min, (b) 60 min, (c) 120 min, and (d) 240 min in the Fered-Fenton process.

the peak T_1 and T_2 were red-shifted in both excitation and emission wavelengths after 60 min reaction. This result suggested that the carbonyl and carboxyl groups were generated in the aromatic structure after the complicated compounds were oxidized by the $\cdot\text{OH}$ (Chen *et al.* 2003).

Compared to the result of our previous research using the classic Fenton process (Wei *et al.* 2013), the Fered-Fenton process showed higher removal efficiency on fluorescence organics with complex structure. It should be noted that both Fenton and Fered-Fenton systems include oxidation and coagulation processes (Wu *et al.* 2010), and how to distinguish the contribution of different processes on pollutant removal needs further investigation.

CONCLUSIONS

The Fered-Fenton process is an effective method for the removal of organic pollutants from DAF wastewater. The feeding mode of H_2O_2 had significant influence on COD removal: the removal efficiency was 44.8% if all the 60.0 mM H_2O_2 was fed at once, while it would reach 54.1% if the total H_2O_2 was divided into six portions and fed six times. This advanced oxidation process significantly increased the biodegradation of DAF wastewater. After a reaction time of 3.0 h, the B/C ratio increased from 0.29 to 0.68, which was conducive for further biological degradation. GC-MS, FTIR and EEM analysis showed that most of the refractory and toxic organic pollutants with aromatic and complicated structure were efficiently destroyed during the Fered-Fenton process.

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