

# Pretreatment of furfural industrial wastewater by Fenton, electro-Fenton and Fe(II)-activated peroxydisulfate processes: a comparative study

C. W. Yang, D. Wang and Q. Tang

## ABSTRACT

The Fenton, electro-Fenton and Fe(II)-activated peroxydisulfate (PDS) processes have been applied for the treatment of actual furfural industrial wastewater in this paper. Through the comparative study of the three processes, a suitable pretreatment technology for actual furfural wastewater treatment was obtained, and the mechanism and dynamics process of this technology is discussed. The experimental results show that Fenton technology has a good and stable effect without adjusting pH of furfural wastewater. At optimal conditions, which were 40 mmol/L H<sub>2</sub>O<sub>2</sub> initial concentration and 10 mmol/L Fe<sup>2+</sup> initial concentration, the chemical oxygen demand (COD) removal rate can reach 81.2% after 90 min reaction at 80 °C temperature. The PDS process also has a good performance. The COD removal rate could attain 80.3% when Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> initial concentration was 4.2 mmol/L, Fe<sup>2+</sup> initial concentration was 0.1 mol/L, the temperature remained at 70 °C, and pH value remained at 2.0. The electro-Fenton process was not competent to deal with the high-temperature furfural industrial wastewater and only 10.2% COD was degraded at 80 °C temperature in the optimal conditions (2.25 mA/cm<sup>2</sup> current density, 4 mg/L Na<sub>2</sub>SO<sub>4</sub>, 0.3 m<sup>3</sup>/h aeration rate). For the Fenton, electro-Fenton and PDS processes in pretreatment of furfural wastewater, their kinetic processes follow the pseudo first order kinetics law. The pretreatment pathways of furfural wastewater degradation are also investigated in this study. The results show that furfural and furan formic acid in furfural wastewater were preferentially degraded by Fenton technology. Furfural can be degraded into low-toxicity or nontoxic compounds by Fenton pretreatment technology, which could make furfural wastewater harmless and even reusable.

**Key words** | electro-Fenton, Fe(II)-activated peroxydisulfate, Fenton, furfural wastewater

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## INTRODUCTION

Furfural is an important chemical in the petrochemical industry and chemical industry (Singh *et al.* 1986; Zeitsch 2001). The furfural production industry is one of the pillar industries of northeastern China. But furfural wastewater could cause serious environmental pollution if it was discharged without treatment. The wastewater has the characteristics of low pH value, high temperature and extremely high chemical oxygen demand (COD) concentration (Gairola & Smirnova 2012; Avci *et al.* 2013). Furfural and furan formic acid in furfural wastewater have biological toxicity and the high concentration of organic acid also could destroy the anaerobic sludge system. There fore, most traditional treatment technologies failed to decompose furfural wastewater (Wirtz & Dague 1993; Borghai

& Hosseini 2008). Recently, the application of the Fenton, electro-Fenton and sulfate radical processes to treat organic wastewater has been studied (Liu *et al.* 2013; Yuan *et al.* 2013; Tugba & Idil 2013). The Fenton process, which uses ferrous ion as a homogeneous catalyst and hydrogen peroxide as oxidizing reagent, is frequently applied in pretreatment of high-concentration organic wastewater (Chamarro *et al.* 2001; Fontecha-Cámara *et al.* 2011). Electro-Fenton processes also offer many advantages such as minimal operational cost and high degree of mineralization of pollutants compared to other known chemical and photochemical processes (Lei *et al.* 2013). In addition, sulfate radicals, which are generated through peroxydisulfate disintegration in the presence of

$\text{Fe}^{2+}$ , have very high oxidation potential (Ahmed *et al.* 2012). They can quickly destroy most of the organic compounds. Nonetheless, the feasibility of these three technologies applied in the treatment of furfural wastewater is concerned. In our opinion, it is critical to find an applicable technology for practical applications in furfural industrial wastewater treatment.

In this comparative study the pretreatment of furfural industrial wastewater by Fenton, electro-Fenton and sulfate radical methods has been carried out. A suitable pretreatment technology for actual furfural wastewater treatment was obtained, and the mechanism and dynamics process of this technology are discussed.

## EXPERIMENTAL PROCEDURE

### Chemicals

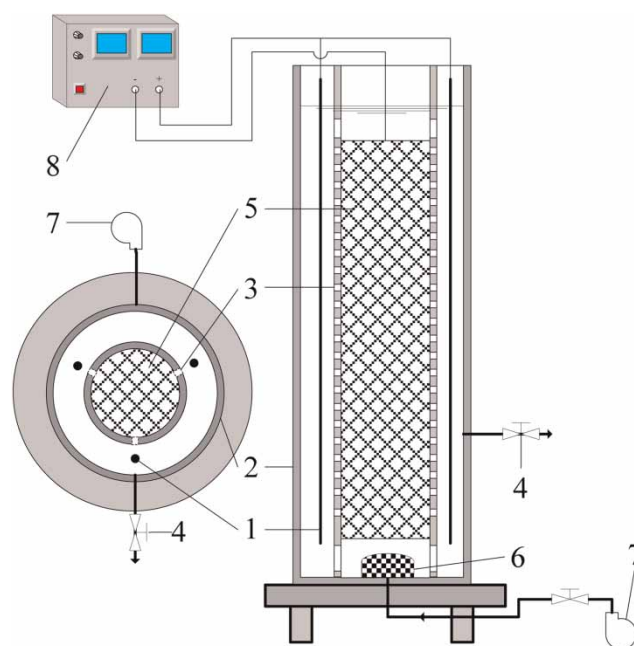
Furfural wastewater was obtained from a furfural production factory in Jilin province in northeast China, and it had the characteristic of  $\text{pH} = 3.0 \pm 0.1$ ,  $\text{COD} = 13,110 \text{ mg/L}$  and temperature =  $95^\circ\text{C}$ . Sodium sulfate (anhydrous, 99%), sulfuric acid (analytical reagent grade, 98%),  $\text{MnO}_2$  (analytical reagent grade, 99%), and sodium hydroxide (analytical reagent grade, 99%) were purchased from Shenyang chemical reagent factory (China). All sample solutions were prepared with deionized water from an ion exchange system.

### Procedures and equipment

Fenton and peroxydisulfate (PDS) experiments were performed in a 500 mL beaker with water bath. The parameters are also set at certain values in the experiments.

The electro-Fenton process was performed in an internal circulation batch reactor (ICBR) with 1 L working volume, which was connected to a direct current power supply (Figure 1). The scrap iron of metal processing (average diameter of particles is 10 mm) as the cathode was placed in the interior container above the aerator. The scrap iron was bathed by 10% w/w  $\text{H}_2\text{SO}_4$  for 20 min and then washed with deionized water until  $\text{pH} = 7.0$ . The wall of the interior container had holes for enhancing the current efficiency. The anodes were steel sticks (4 mm diameter, 55 cm long) between the outside and interior wall of the container. A constant potential difference (15 V) was applied with a power supply (ATTEN APR-6402 Shenzhen China).

In the electro-Fenton process, continuous saturation of air was bubbled under the cathode with  $0.1 \text{ m}^3/\text{min}$  air



**Figure 1** | Schematic diagram of electro-Fenton internal circulation batch reactor experimental set-up. 1. anode, 2. outside wall of container, 3. wall of interior container with holes, 4. sample outlets, 5. scrap iron cathode, 6. aeration header, 7. air compressor, 8. power supply.

velocity. Steel anodes provided ferrous ions during the reaction. Concentration of sodium sulfate and  $\text{pH}$  were adjusted to working value.  $\text{COD}$  and  $\text{pH}$  of furfural wastewater were recorded to contrast the feasibility of different processes.

### Analysis procedures

Samples were taken at specified reaction time to measure the  $\text{COD}$  of furfural wastewater. To avoid the error of  $\text{COD}$  values for existing  $\text{H}_2\text{O}_2$  in the solution, the samples firstly were adjusted to  $\text{pH} 10$ , then filtered with a filter membrane ( $0.22 \mu\text{m}$ ),  $\text{MnO}_2$  ( $0.1 \text{ mmol/L}$ ) was added, and then the samples were placed for 24 hours at room temperature ( $18^\circ\text{C}$ ). The  $\text{COD}$  of the samples was measured by a  $\text{COD}$  analyzer ( $\text{COD-571}$ , Shanghai China).

The  $\text{COD}$  removal rate was defined as the following expression:

$$\eta = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100\% \quad (1)$$

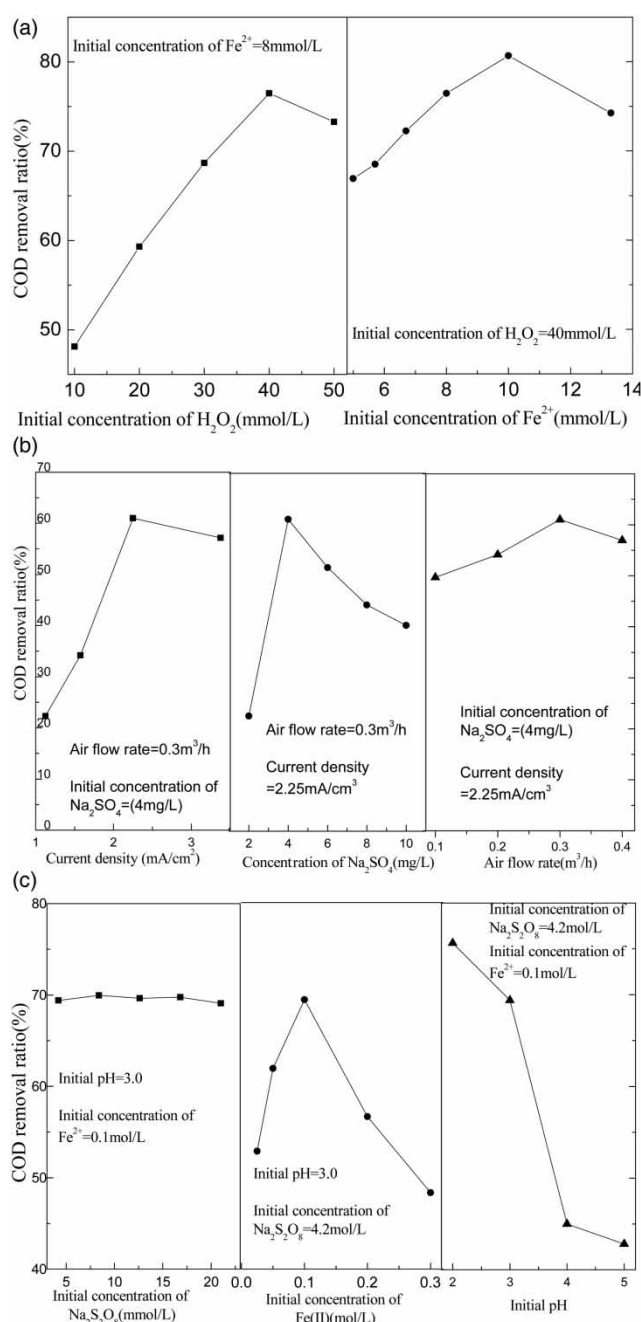
where  $\eta$  is the  $\text{COD}$  removal rate,  $\text{COD}_0$  is the  $\text{COD}$  of furfural wastewater before reaction and  $\text{COD}_t$  is the  $\text{COD}$  of furfural wastewater after reaction.

The intermediate products were analyzed by high-performance liquid chromatography (HPLC) (Shimadzu LC-6A Kyoto, Japan) and an ultraviolet detector (230 nm wavelength). In the HPLC analysis, Agilent Zorbax-C8 (5  $\mu\text{m}$ ) columns (1.0 mm  $\times$  150 mm) and a mobile phase of acetonitrile/water (7:3, v/v) at a steady flow rate of 1 mL/min were used. The injection volume was 20  $\mu\text{L}$  and column temperature was maintained at 30  $^{\circ}\text{C}$ .

## RESULTS AND DISCUSSION

### Fenton process pretreatment of furfural wastewater

The optimum conditions of Fenton process in treatment of furfural wastewater were studied in this experiment. The temperature of the wastewater was kept at room temperature (20  $\pm$  5  $^{\circ}\text{C}$ ), and initial pH of the wastewater was 3.0  $\pm$  0.1. Numerous studies (Dutta *et al.* 2009; Boye *et al.* 2002; Yang & Wang 2009) have shown that the acid pH value was suitable for Fenton process. So the pH value of the wastewater was not adjusted in the experiment. The  $\text{H}_2\text{O}_2$  and  $\text{FeSO}_4$  concentration was researched as a single factor. The initial  $\text{FeSO}_4$  concentration was kept at 8 mmol/L, and the initial  $\text{H}_2\text{O}_2$  concentration was set at 10, 20, 30, 40 and 50 mmol/L. The influence of different initial  $\text{H}_2\text{O}_2$  concentration on the COD removal rate in furfural wastewater was investigated, and the experimental results are shown in Figure 2(a). We found that the COD removal rate in the wastewater was increasing rapidly with the increase of  $\text{H}_2\text{O}_2$  initial concentration. When the  $\text{H}_2\text{O}_2$  initial concentration increased from 10 mmol/L to 40 mmol/L, the COD removal rate accordingly increased from 48.12 to 76.47%. When the initial concentration was greater 40 mmol/L, the COD removal rate began to fall. It can be seen that an optimal  $\text{H}_2\text{O}_2$  concentration range exists under the condition of the same concentration of  $\text{FeSO}_4$ . This is because when the  $\text{H}_2\text{O}_2$  concentration is low, the  $\text{H}_2\text{O}_2$  is the main factor in the reaction process to generate  $\bullet\text{OH}$ , and the higher the concentration, the higher the reaction efficiency with the more  $\bullet\text{OH}$ . So the COD removal rate increased with the increase of  $\text{H}_2\text{O}_2$  initial concentration. But with the  $\text{H}_2\text{O}_2$  concentration continuing to increase, excess  $\text{H}_2\text{O}_2$  will participate in an adverse reaction, shown in Equation (2), which leads to the decrease of the COD removal rate.



**Figure 2** | The optimal reaction conditions of three process treatments of the furfural wastewater in the condition of original pH (3.0  $\pm$  0.1). (a) Fenton process (temperature = 20  $^{\circ}\text{C}$ ); (b) electro-Fenton process (temperature = 20  $^{\circ}\text{C}$ ); (c) sulfate radical process (temperature = 70  $^{\circ}\text{C}$ ).



However, during the 90 min of reaction,  $\text{Fe}^{2+}$  initial concentration increased from 5 mmol/L to 10 mmol/L; accordingly, furfural wastewater COD removal rate

increased from 66.89 to 80.67%. When the  $\text{Fe}^{2+}$  concentration further increased, the COD removal rate descended. For instance, when the  $\text{Fe}^{2+}$  initial concentration was 13 mmol/L, the COD removal rate was reduced to 74.26%. This is because the annihilation reaction of  $\text{Fe}^{2+}$  and  $\bullet\text{OH}$  may happen under the condition of high  $\text{Fe}^{2+}$  concentration (Equation (3)).

### The electro-Fenton process pretreatment of furfural wastewater

The principal technological parameters of the electro-Fenton reaction include aeration gas velocity, current density, and concentration of electrolyte (Ting *et al.* 2009). The optimum reaction parameters of the electro-Fenton process were identified in this study.

First of all the optimal current density was obtained in the conditions of 0.3 m<sup>3</sup>/h aeration rate, 4 mg/L  $\text{Na}_2\text{SO}_4$  initial concentration, and 90 min reaction time. As shown in Figure 2(b), the COD removal rate increases with the increase of current density when the current density is less than 2.25 mA/cm<sup>2</sup>. For current density of 1.125, 1.575, 2.25 and 3.375 mA/cm<sup>2</sup>, the furfural wastewater COD removal rates are 22.3, 34.19, 61 and 57.17%, respectively. This is mainly because the electric oxidation and the reduction rate of the cathode and anode will increase with the increasing of current density under small current density. At the same time, the formation rate of  $\text{H}_2\text{O}_2$  on the cathodic surface also increases, which will promote generation of  $\bullet\text{OH}$ . However, furfural wastewater COD removal rate will decline when the current density is higher than 2.25 mA/cm<sup>2</sup>. This is because the high current density will improve the electrolysis voltage of the reactor under the same conditions. Extreme voltage can lead to side reactions and pH deviation from optimal value, which will result in reduced concentration of  $\text{H}_2\text{O}_2$ . Then the furfural wastewater COD removal rate decreased with the increase of current density when the current density above 2.25 mA/cm<sup>2</sup>.

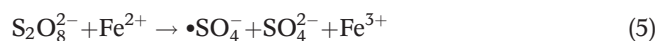
Keeping the current density of 2.25 mA/cm<sup>2</sup>, cathode aeration volume of 0.3 m<sup>3</sup>/h, and changing different electrolyte  $\text{Na}_2\text{SO}_4$  concentration, the influence of different electrolyte concentration on furfural wastewater COD removal rate was investigated. When the concentration of  $\text{Na}_2\text{SO}_4$  was 2.0, 4.0, 6.0, 8.0 and 10.0 mg/L, the COD removal rate accordingly reached 22.51, 61, 51.55, 44.26 and 57.17%. It can be seen that the COD removal rate firstly increased with the increase of concentration of the  $\text{Na}_2\text{SO}_4$  electrolyte. When the electrolyte

concentration increased to more than 4 mg/L, the removal rate declined with the increase of the concentration. Thus when the  $\text{Na}_2\text{SO}_4$  electrolyte concentration is 4 mg/L, the COD removal rate is the most effective and can reach 61%.

The influence of different cathode aeration gas velocity on furfural wastewater COD removal rate also was investigated. When the aeration gas velocity was 0.1, 0.2 and 0.3 m<sup>3</sup>/h, accordingly the COD removal rates were 49.68%, 54.17% and 61%, respectively. This is because the dissolved oxygen in the aqueous phase is increased with the increase of aeration gas velocity, in which the efficiency of the cathode generating  $\text{H}_2\text{O}_2$  also is raised. At the same time, the mass transfer efficiency of the solution phase is also improved by the increasing air, which will efficiently promote Fenton reaction. In addition aeration has the effect of air stripping, which means aeration can remove parts of the volatile organic compounds. However, when the air is increased to 0.4 m<sup>3</sup>/h, a large number of bubbles were produced on the top of the ICBR and COD removal rate reduced to 56.94%. For the ICBR in this study, optimal aeration rate for degradation of furfural wastewater is 0.3 m<sup>3</sup>/h.

### The PDS process pretreatment of furfural wastewater

Sulfate radicals ( $\bullet\text{SO}_4^-$ ) can be generated by  $\text{Fe}^{2+}$  and thermal oxidizing auxiliary conditions in PDS technology. The reaction process is given by the following equations:



The influence of different  $\text{Na}_2\text{S}_2\text{O}_8$  initial concentration on the COD removal rate is firstly investigated in the experiment. The initial experimental conditions were as follows: pH was 3.0,  $\text{Fe}^{2+}$  initial concentration was 0.1 mol/L and the temperature was kept at 70 °C. We examined the experiment for 90 min and the experimental results are shown in Figure 2(c). The experimental results show that the furfural wastewater COD removal rate remained constant with the increase of the initial concentration of the  $\text{Na}_2\text{S}_2\text{O}_8$ . For example, when  $\text{Na}_2\text{S}_2\text{O}_8$  initial concentration was 4.2 mmol/L, COD removal rate was 69.4%, and when the initial concentration was 21.0 mmol/L, COD removal rate reached 69.1%. Thus the impact of the  $\text{Na}_2\text{S}_2\text{O}_8$  initial concentration on the COD removal rate was not significant



within the concentration range of this study. So we chose  $\text{Na}_2\text{S}_2\text{O}_8$  concentration of 4.2 mmol/L in the follow-up experiments.

$\text{Fe}^{2+}$  plays a catalytic role in the reaction process and the effect of its initial concentration is also shown in Figure 2(c). The initial experimental conditions were as follows: pH was 3.0,  $\text{Na}_2\text{S}_2\text{O}_8$  initial concentration was 4.2 mmol/L and the temperature was kept at 70 °C. During the experiment for 90 min,  $\text{Fe}^{2+}$  concentrations were 0.025, 0.05, 0.1, 0.2 and 0.3 mol/L; accordingly the COD removal rates were 52.9, 61.9, 69.0, 56.6 and 48.34%. The results show that the lower and higher  $\text{Fe}^{2+}$  concentrations will have a negative effect on the COD removal rate.

The pH value is one of the critical parameters of the reaction conditions in PDS technology, and we have carried on the experimental study about it. Under the above experimental conditions, we changed the pH value. As the pH value increased from 2.0 to 5.0, furfural wastewater COD removal rate collapsed rapidly from 75.6 to 42.8%. It can be seen that the furfural wastewater treatment in PDS technology was better under acidic condition. This is mainly because  $\text{Fe}^{2+}$  exists in aqueous solution in ionic form under acid condition, and it has good catalytic activity. At the same time, the furfural in wastewater and some intermediates such as furan formic acid appear with ionic form in aqueous solution, which makes it easier for the sulfate radical to degrade these organic pollutants in water by electron transfer.

The above experimental results show that the optimal conditions for degrading furfural wastewater in the PDS technology are as follows:  $\text{Na}_2\text{S}_2\text{O}_8$  initial concentration is 4.2 mmol/L,  $\text{Fe}^{2+}$  initial concentration is 0.1 mol/L, the temperature is 70 °C, pH value is 2.0, which allows the COD removal rate to reach 75.6%.

### The influence of different temperature on furfural wastewater COD removal rate

Furfural wastewater has the characteristic of high temperature (its average temperature is higher than 90 °C). It is necessary to study temperature influence on the degradation, so as to provide assistance for the practical application. Optimum reaction parameters of Fenton, the cathode electric Fenton and PDS technology were chosen from the above results. Experimental processes for the three kinds of technologies were investigated for 90 min, and we obtained three distinct reaction effects caused by temperature changes.

The influence of the reaction temperature on the degradation of furfural wastewater in the Fenton, electro-Fenton and PDS process is shown in Figure 3(a). For the Fenton

process, the COD removal rate showed a trend of slight rise when the temperature is increased from 20 to 90 °C. The COD removal rate increased from 79.2% at 20 °C to 81.2% at 90 °C. The temperature impact on COD removal rate is not obvious in treating furfural wastewater by the Fenton process.

But for the electro-Fenton technology, the temperature effects on COD removal rate are higher. The high temperature is not conducive to improving the electro-Fenton reaction efficiency. For example, when the reaction temperature is 20 °C, furfural wastewater COD removal rate can reach 61%, but when the temperature rose to 60 °C, the COD removal rate is quickly dropped to 21.2%, and when the temperature is 90 °C, the COD removal rate was only 5.9%. This is mainly because, under the condition of high temperature, dissolved oxygen in water solution decreases, and the efficiency of  $\text{H}_2\text{O}_2$  generation by the cathode reduces. At the same time  $\text{H}_2\text{O}_2$  more easily decomposes without  $\bullet\text{OH}$  generation at high temperature. So the condition of low temperature is better for the production of  $\text{H}_2\text{O}_2$  in the cathode electro-Fenton system, and more advantageous for degradation of organic pollutants in water.

Temperature also has a great influence for degrading furfural wastewater in PDS process. The COD removal rate increases rapidly with the temperature increase when the temperature is below 60 °C. For example, the COD removal rate was 55.3% at 40 °C, and the removal rate increased to 86.9% at 60 °C. But when the temperature reached 70, 80 and 90 °C, the COD removal rates were 75.6, 80.3 and 73.1%. This is mainly because when the temperature increased from 40 to 60 °C,  $\text{Na}_2\text{S}_2\text{O}_8$  activation effect rises with temperature increase (Equation (4)), which would produce more  $\bullet\text{SO}_4^-$  with oxidation activity. In addition, high temperature leads to increased activity of the organic matter in water solution. The probability of  $\bullet\text{SO}_4^-$  contact with organic matter clearly improved. So the COD removal rate rises rapidly with the increase of temperature. But when the temperature is above 60 °C,  $\bullet\text{SO}_4^-$  could be consumed by reaction with additional ion such as  $\text{Cl}^-$  (Tsao & Wilmarth 1959). So a higher temperature is disadvantageous to furfural wastewater degradation by PDS process.

### The pH variation of furfural wastewater in these three processes

Based on the above experimental results, we found the optimum reaction temperature is 80 °C in Fenton process, 20 °C in electro-Fenton process and 60 °C in PDS process. The pH value changes were investigated in the three processes under

the above optimum experimental conditions, and the results are shown in Figure 3(b). For the Fenton process, the pH value decreased from 3.0 to 2.3 in the first place, and then gradually increased to 2.7. The pH value in electric Fenton process is much higher than the traditional Fenton process, and it increased from 3.0 to 5.2 for 90 min reactions. For PDS process, the pH value quickly fell from 2.0 to 1.0 in degrading furfural wastewater and stabilized in the value.

In the Fenton process, the pH values change mainly because  $\bullet\text{OH}$  reacts with organic matter in furfural wastewater to form organic acids, which caused the pH value of the solution to increase. Then the organic acids are oxidized by hydroxyl free radical into  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ; so the increase of the pH value is not obvious. The degradation pathways of the Fenton process are the same for the electro-Fenton process. Organic acids are also oxidized and mineralized in furfural wastewater. But at the same time, the reduction

reaction will happen in the cathode surface (Equation (6)). So the pH value in the solution bulk phase will gradually rise



In the degradation of furfural wastewater by PDS process, the hydrogen extraction reaction also happened in addition to the electron transfer. So the  $\text{H}^+$  concentration in solution phase increased, which caused the pH value to maintain a low level.

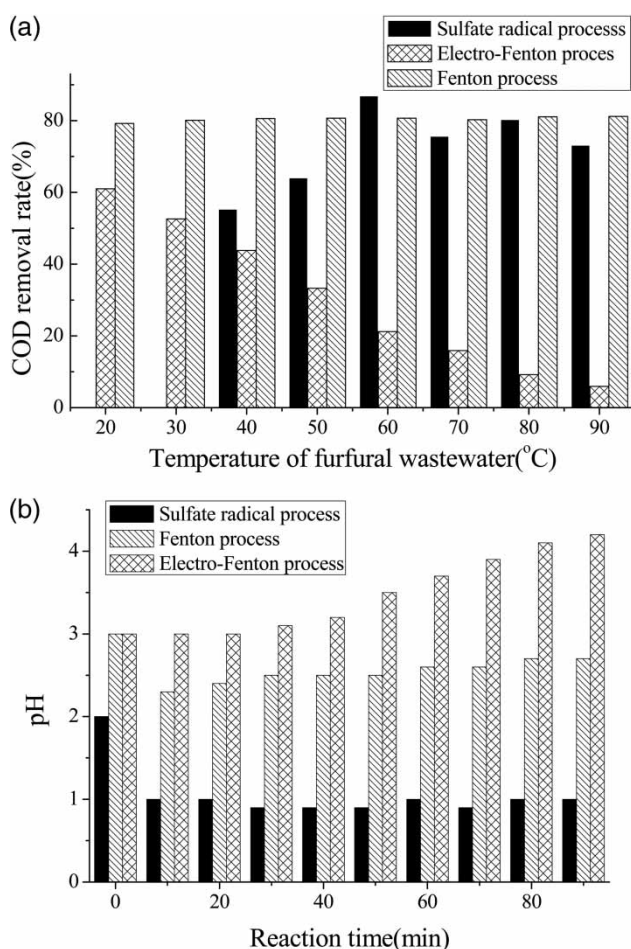
### Kinetics study of furfural wastewater degradation by these three processes

Under the respective optimal conditions of Fenton, electro-Fenton and PDS processes, the furfural wastewater was treated for 120 min. The reaction kinetics characteristics of the three processes were investigated under different temperatures. We fitted the calculation with the results of the experiment. The results show that the relationship between the COD and time accord with the first order kinetic process as shown in Equation (7)

$$\ln(\text{COD}_0/\text{COD}_t) = kt \quad (7)$$

where  $k$  ( $\text{min}^{-1}$ ) is the reaction rate constant, and  $t$  (min) is the reaction time.  $\text{COD}_0$  (mg/L) is the initial COD value of furfural wastewater, and  $\text{COD}_t$  (mg/L) is the value at time  $t$ .

The fitting results are shown in Table 1. The reaction rate constants of Fenton, electro-Fenton and PDS processes respectively are 0.01404, 0.0084 and 0.01655  $\text{min}^{-1}$ . The reaction rate constant of electro-Fenton process is far less than that of Fenton, which suggests that Fenton process has better oxidation efficiency and speed under the optimum reaction condition. Electro-Fenton process is not suitable for furfural wastewater treatment because of lower reaction rate constants and inapplicability under the condition of high



**Figure 3** | The influence of temperatures on the COD removal rates (a) and pH variation (b) of the Fenton, electro-Fenton and sulfate radical processes in treatment of furfural wastewater in the optimal reaction conditions.

**Table 1** | First order equation parameters of furfural wastewater COD by Fenton, electro-Fenton and sulfate radical processes in the optimal conditions

Different process	$k$	$R^{2a}$	$n^b$	$p^c$
Electro-Fenton process	0.0084	0.9948	9	< 0.0001
Fenton process	0.01404	0.9955	9	< 0.0001
Sulfate radical process	0.01655	0.9960	9	< 0.0001

<sup>a</sup>Determination coefficient.

<sup>b</sup>The number of selected points in the kinetics calculation.

<sup>c</sup>The possibility deviation.

temperature. Compared with the technology of Fenton, PDS process has a higher reaction rate constant. But there are also disadvantages in practical application of PDS because its low pH value is not easy to adjust after processing and the process is unfavorable for degradation of furfural wastewater under high temperature condition.

### The reaction mechanism study of furfural wastewater degradation by Fenton process

Using HPLC, we also analyzed the degradation process of furfural wastewater by Fenton process under the optimum conditions. The possible intermediate products were determined by retention times of absorption peaks, which are furan formic acid, oxalic acid and acetic acid, respectively.

This degradation reaction is very complex due to furfural, furan formic acid, oxalic acid and acetic acid compounds existing in furfural wastewater. On the HPLC analysis, furfural and furan formic acid concentrations were reduced when the reaction was 10 min, while acetic acid and oxalic acid concentrations increased slightly. This is because the electrophilic effect of the furfural aldehyde group and oxygen in the furan ring causes the  $\bullet\text{OH}$  adjacent to the carbon atoms in the aldehyde group to become nucleophilic. Although carbonyl acids also have electrophilic effect, hydroxyl steric hindrance makes difficult the  $\bullet\text{OH}$  reaction with carbonyl acids. After reaction for 30 min, the concentrations of several compounds were dropped. Because the furfural and furan formic acid concentrations were low, the probability of  $\bullet\text{OH}$  attacking acid compounds increased.

By the study, furfural and furan formic acid in furfural wastewater was preferentially degraded by Fenton process. The furfural and its derivatives have biological toxicity, so it is not appropriate to treat furfural wastewater directly using biological treatment. Furfural can be degraded into low-toxicity or nontoxic compounds by Fenton pretreatment technology, which could make furfural wastewater harmless and even reusable.

### CONCLUSIONS

Fenton, electro-Fenton and PDS processes were utilized for the pretreatment of furfural wastewater. The experimental results show that Fenton technology has a good and stable effect without adjusting pH. Under the optimum experimental conditions, namely  $\text{H}_2\text{O}_2$  initial concentration is 40 mmol/L,  $\text{Fe}^{2+}$  concentration is 10 mmol/L,

reaction temperature is 80 °C and the reaction time is 90 min, furfural wastewater COD removal rate can reach 81.2%.

Electro-Fenton also showed a good pretreatment effect at room temperature. Nonetheless, the ability to degrade furfural wastewater by electro-Fenton process drops with the temperature increase from 30 to 90 °C. Because the high temperature can reduce  $\text{H}_2\text{O}_2$  generation and increase decomposition rate of the  $\text{H}_2\text{O}_2$ , electro-Fenton technology has no advantage in furfural wastewater pretreatment. PDS process also has a good effect under the optimum condition. However, the pH value drops rapidly in the reaction and more sodium sulfate is decomposed without reaction with organic pollutants and intermediate products under the high temperature, which leads to the decrease of the COD removal rate. So PDS process is not suitable for treatment of the actual furfural wastewater. Utilizing Fenton, electro-Fenton and PDS processes in pretreatment of furfural wastewater, their kinetic processes follow the pseudo first order kinetics law.

The pretreatment pathways of furfural wastewater degradation are also investigated in this study. The results show that the generated hydroxyl radicals by the Fenton process mainly attack furfural and furan formic acid, which leads to rapid oxidation of furfural and furan formic acid into small organic molecules.

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