Applying fenton process in acrylic fiber wastewater treatment and practice teaching

Chunhui Zhang¹ and Shan Jiang
China University of Mining & Technology (Beijing), Beijing 100083, P.R. China
¹truemanjung@163.com

Abstract. Acrylic fiber manufacturing wastewater, containing a wider range of pollutants, high concentration of refractory organics, poisonous and harmful matters, was significant to treat from the effluents of wastewater treatment plants (WWTPs). In this work, a Fenton reactor was employed for advanced treatment of the WWTP effluents. An orthogonal test and a parametric study were carried out to determine the effect of the main operating conditions and the Fenton process attain excellent performance on the degradation of pollutants under an optimal condition of ferrous dosage was 6.25 mM, hydrogen peroxide was 75 mM and initial pH value was 3.0 in 90 min reaction time. The removal efficiency of COD, TOC, NH₄⁺-N and TN reached from 45% to 69%. Lastly, as a teaching advice, the Fenton reactor was used in practicing teaching nicely.

1. Introduction

The acrylic fiber, usually called artificial wool, which was made of acrylonitrile and various complex materials by the function of polymerization and drawing. Over the past decades, the acrylic fiber industry has rapidly progressed in many developing countries [1]. At present, the production capacity of acrylic fiber is 920,000 tons per year in China [2]. A large amount of wastewater was discharged inevitably during the production process of acrylic fiber. Most of pollutants in acrylic fiber wastewater are characterized by toxic, and bio-refractory [3].

Currently, the biological treatment processes such as Anoxic-Oxic (A/O) and Anaerobic-Anoxic-Oxic (A²O) technic have been used for the degradation of acrylic fiber wastewater. However, highly toxic compounds are refractory to be biodegraded, what is more, some compounds can poison microorganisms to reduces the efficiency of anaerobic digestion [4]. The suspended matter and oligomer can house on the surface of microorganisms, influencing the effective contact between the microorganisms and the contaminants in wastewater [5]. As a result, the ordinary biological technologies are insufficient to achieve acceptable pollution remediation. Especially, the chemical oxygen demand (COD) concentrations in acrylic fiber wastewater effluent treated by biological processes are difficult to meet the emission standards of China [6]. Therefore, a range of advanced treatment methods, such as membrane process, chemical oxidation and photo-catalysis, have been integrated into the conventional bio-physical processes [7-12]. However, these technologies are either inefficient or high cost [13]. Therefore, an efficient and reliable advanced treatment method for acrylic fiber wastewater is still needed.

Advanced oxidation processes (AOPs) based on the generation of hydroxyl radicals (•OH) are widely used in the treatment of bio-refractory industrial wastewater. A promising technique among the AOPs for the removal of recalcitrant organics is Fenton process which usually consists of Fe²⁺ and
H$_2$O$_2$[14]. Fenton process is attractive because of its simplicity and high removal efficiency [15]. The typical Fenton reagent includes ferrous ions (Fe$^{2+}$) and hydrogen peroxide (H$_2$O$_2$). In acidic condition, hydroxyl radicals were generated from the decomposition of H$_2$O$_2$ which was catalyzed by Fe$^{2+}$. According to different forms of catalysts, Fenton technologies are divided into homogeneous and heterogeneous phase Fenton technology, the former using Fe$^{2+}$ as catalyst while the latter using iron powder, iron and manganese oxide minerals instead of Fe$^{2+}$. The reaction mechanism of Fenton can be described by the simplified Eqs as follow [16].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH$$  \hspace{1cm} (1)
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^- + H^+$$  \hspace{1cm} (2)
$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$$  \hspace{1cm} (3)
$$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + O_2 + H^+$$  \hspace{1cm} (4)
$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2^-$$  \hspace{1cm} (5)
$$Fe^{2+} + HO_2^- \rightarrow Fe^{3+} + HO_2^-$$  \hspace{1cm} (6)
$$RH + \cdot OH \rightarrow R^- + H_2O$$  \hspace{1cm} (7)
$$R^- + Fe^{3+} \rightarrow R^- + Fe^{2+}$$  \hspace{1cm} (8)
$$R^- + H_2O_2 \rightarrow OH + ROH$$  \hspace{1cm} (9)

In this study, the acrylic fiber wastewater effluent, which was treated after A/O biological method, would be advanced treated by the Fenton process to meet the strict discharge standard in China as a teaching experiment. The method of orthogonal test was educated and designed. The effects of four key operational parameters, including Fe$^{2+}$ dosage, H$_2$O$_2$ dosage, pH and reaction time were investigated according to the removal efficiency of COD concentrations in wastewater. Under the optimal operational parameters, the removal efficiencies of COD, TOC, NH$_3$-N, TN and 16 types of organic pollutants were investigated to study the operation of methods and instruments for the pollutants detection.

2. Materials and methods

2.1. Water sample

The acrylic fiber manufacturing wastewater sample used in this study was collected from wastewater treatment plant (WWTP) effluents in Jilin QiFeng Chemical Fiber Co. Ltd. which was treated by A/O process. The wastewater samples were collected 3 times within 24 h and were well mixed with equal volume for the relatively constant emission of secondary effluents. The above samples were stored at 4 ºC under a refrigerator until sample pretreatment, which occurred within 12 h of the sample collection. The main water quality parameters are presented in table 1.

| Parameter | Unit | Value |
|-----------|------|-------|
| COD       | mg O$_2$/L | 249-270 |
| TOC       | mg/L | 90-100 |
| NH$_3$-N  | mg/L | 60-66 |
| TN        | mg/L | 78-95 |

* The quantity of samples analyzed: 4.

2.2. Chemical and materials

The analytical reagents NaOH (5.0 M) and H$_2$SO$_4$ (3.0 M) were purchased from Beijing Chemical Reagent Co., Ltd, China. The ferrous sulfate (FeSO$_4$ • 7H$_2$O) and hydrogen peroxide (H$_2$O$_2$, 30%) were purchased from Beijing Lanyi Chemical Co., Ltd, China. All chemicals were at least of analytical grade and were used as received without any further purification treatments.
2.3. Experimental process

Fenton oxidation experiments were conducted in 500 mL batch reactors at 25 °C with mechanical stirring for continuous mixing of the reaction system. The pH was adjusted with 3.0 M H₂SO₄ solution and 5.0 M NaOH solution. In a typical experiment, a weighed amount of FeSO₄ • 7H₂O was dissolved in 300 mL of wastewater sample with stirring (120 rpm). Fenton oxidation was then initiated by the addition of H₂O₂ solution (30%, w/w). Samples were withdrawn from the reactor at predetermined intervals, and the reaction was terminated by adjusting the pH to 10.0, which instantaneously consumed the remaining H₂O₂. Finally, stirring was stopped and the solution was left undisturbed for 30 min to settle out the flocs. The supernatant was withdrawn and filtered for analyses. Also, previous preliminary experiment indicated the Fenton process could achieve the best treatment effect while the reaction time was more than 75 min. Thus, in order to attain a higher process efficiency as well as lower time and cost conditions, 90 min was selected for following reactions.

2.4. Analytical methods

GC-MS was used for organic compound analysis. Prior to GC-MS measurement, 200 mL of water sample was extracted by HLB (500 mg/6 mL, Waters Inc, USA) and C-18 (500mg/6 mL, Supelco Inc., USA) solid-phase extraction columns after the filtration of 0.45 μm glass fiber membrane. First of all, the HLB and C-18 columns were sequentially activated with 5 mL of CH₂Cl₂ (Waters Inc., USA), CH₃OH and ultrapure water with the flow rate of 6 mL/min. The HLB column was then eluted with 10 mL mixing solution of CH₂Cl₂ and CH₃OH (9/1, v/v) for three times, and the C-18 column was eluted with 10 mL mixture solution of hexane and CH₂Cl₂ (7/3, v/v) for three times. The eluent was mixed, dehydrated with anhydrous sodium sulfate, and concentrated to 0.5 mL with the aid of nitrogen flow. 1μL of concentrated liquor was injected to the 7890/5975 GC-MS system (Agilent, USA) equipped with an HP-5 capillary column with an inner diameter of 0.25 mm and a length of 30.0 m. The GC column was operated in a temperature programmed mode at 40 ℃ for 2 min, and then raised at 5 ℃/min to 290 ℃(held for 4 min). Other analytical techniques such as pH, COD, H₂O₂, TN, NH₄⁺-N and TP were carried out in our laboratory according to the standard methods of China [17].

3. Results and discussion

3.1. Orthogonal experiment

In the Fenton process, three main influencing factors, including Fe²⁺, H₂O₂ and the initial pH, are the most important parameters [18]. Since the above parameters potentially affect the removal efficiency in the Fenton process, the orthogonal test L₉(3)³ table was designed to detect the optimal conditions (table 2), and the results are shown in table 3.

| Table 2. Factors and levels of orthogonal test. |
|-----------------------------------------------|
| Variable                                      |
|                                               |
| Level 1 | 2     | 3    |
| A (H₂O₂ initial concentration) (mM)           | 37.5 | 56.25 | 75  |
| B (Fe²⁺ dosage) (mM)                          | 1.56 | 3.13  | 6.25 |
| C (Initial pH)                                | 3.0  | 5.0   | 7.0  |

According to table 3, K₁, K₂, K₃ represent the sum of COD removal efficiency for each factor which is corresponding by level 1, 2 and 3. And k₁, k₂, k₃ represent their mean value. The order of significant effect on COD removal efficiency was Fe²⁺ dosage (B) > H₂O₂ initial concentration (A) > Initial pH (C). It can be concluded that the optimal running condition of Fe²⁺, H₂O₂, and pH was 6.25mM, 56.25mM and 3.0, respectively in the Fenton process.
Table 3. The results of orthogonal experiment.

| No. | A: H₂O₂(mM) | B: Fe²⁺(mM) | C: pH | COD removal efficiency (%) | Rank |
|-----|-------------|-------------|-------|----------------------------|-------|
| 1   | 37.5        | 1.56        | 3     | 43.52                      | 8     |
| 2   | 37.5        | 3.13        | 5     | 49.74                      | 6     |
| 3   | 37.5        | 6.25        | 7     | 58.41                      | 2     |
| 4   | 56.25       | 1.56        | 5     | 46.95                      | 7     |
| 5   | 56.25       | 3.13        | 7     | 41.51                      | 9     |
| 6   | 56.25       | 6.25        | 3     | 60.76                      | 1     |
| 7   | 75          | 1.56        | 7     | 52.79                      | 5     |
| 8   | 75          | 3.13        | 3     | 53.51                      | 4     |
| 9   | 75          | 6.25        | 5     | 57.57                      | 3     |

K₁ 151.671 143.259 157.79 1
K₂ 149.22 144.759 154.26
K₃ 163.869 176.739 152.70 9
k₁ 50.557 47.753 52.597
k₂ 49.740 48.253 51.420
k₃ 54.623 58.913 50.903
Range 4.883 11.160 1.694

3.2. Removal efficiency under the optimal experimental condition

In the above optimal reaction parameters of orthogonal experiment, Fe²⁺ dosage was fixed at 6.25 mM and initial pH was fixed at 3.0. The removal efficiencies of the Fenton process in acrylic fiber wastewater effluent are summarized in table 4.

Table 4. The removal efficiencies of Fenton process in acrylic fiber wastewater effluent*.

| Parameter | Unit | Influent | Effluent | Discharge limit for acrylic fiber wastewater in China |
|-----------|------|----------|----------|-----------------------------------------------------|
| COD       | mg O₂/L | 258.6 | 88.4 | 160 |
| TOC       | mg/L | 92.3 | 28.2 | 30 |
| NH₄⁺-N   | mg/L | 63.5 | 26.4 | 25 |
| TN        | mg/L | 83.8 | 34.5 | 50 |

* The quantity of samples analyzed: 4.

In order to evaluate the degradation effect of toxic refractory organic pollutants containing in acrylic fiber wastewater effluent, a gas chromatography-mass spectrometry (GC-MS) was used to detect the concentration of the toxic and hazardous substances. The relative contents of the pollutants before and after the treatment of Fenton process are shown in table 5.

From table 5, it can be seen that the influents and effluents of wastewater contain 16 types of major organic pollutants. Most of the organic pollutants are aromatic hydrocarbons. After advanced treatment by the Fenton process, 11 types of organic pollutants can be completely removed, implying the Fenton system used in this study can effectively destruction the organic pollutants present in the wastewater. At the same time, there are 5 types of organic pollutants include undecane (C₁₁H₂₄), dibutyl phthalate and Diisobutyl phthalate (C₁₆H₃₂O₄) were still detected, a probably reason could be that the undecane was the final degraded product from long chain alkane. For the C₁₆H₃₂O₄, it might be...
hard to degrade since low molecular weight organic matter would be firstly oxidized in Fenton process and the C_{16}H_{22}O_{4} had a high initial concentration. Generally, the Fenton process can remove most of the organic pollutants in acrylic fiber wastewater effectively.

| Organic pollutants | Retention time (min) | Similarity (%) | Detected by GC-MS |
|--------------------|----------------------|----------------|-------------------|
|                    |                      |                | Untreated | Treated |
| C_{11}H_{24}       | 14.532               | 94             | √         | √       |
| C_{13}H_{14}       | 24.509               | 62             | √         | nd*     |
| C_{15}H_{22}O      | 25.643               | 96             | √         | nd      |
| C_{14}H_{22}O      | 25.732               | 94             | √         | nd      |
| C_{16}H_{26}O_{4}  | 27.657               | 59             | √         | nd      |
| C_{18}H_{38}       | 32.404               | 99             | √         | nd      |
| C_{16}H_{22}O_{4}  | 33.656               | 90             | √         | √       |
| C_{16}H_{22}O_{4}  | 35.535               | 94             | √         | √       |
| C_{17}H_{19}N      | 40.446               | 97             | √         | nd      |
| C_{24}H_{10}       | 43.488               | 98             | √         | nd      |
| C_{18}H_{13}N      | 44.882               | 50             | √         | nd      |
| C_{21}H_{44}       | 45.073               | 93             | √         | nd      |
| C_{18}H_{22}O_{4}  | 45.51                | 90             | √         | nd      |
|                    | 46.617; 48.1         |                | √         | nd      |
| C_{26}H_{54}       | 49.528                | 98             | √         | nd      |
|                    | 52.244               |                | √         | nd      |
| C_{28}H_{58}       | 50.907; 53.703       | 98             | √         | √       |
| C_{30}H_{42}       | 52.24                | 98             | √         | √       |

* nd: Not detected

3.3. Discussion and application in practice teaching

It has been verified in the previous orthogonal test that the optimum technological parameters of Fe^{2+}, H_{2}O_{2}, and pH was 6.25mM, 56.25mM and 3.0 in the Experiment. Under the conditions, excellent removal efficiencies of COD, TOC and TN was attained which was 66, 69.4 and 59% severally. In the Fenton process, H_{2}O_{2} is the most important factor as it is the source of ·OH and the main cost for scale-up application [19]. However, the experimental result shows that the COD removal efficiency decreased when added more H_{2}O_{2}. The occurrence of this phenomenon may be attributed to the following reasons. Under an appropriate value of H_{2}O_{2} dosage between 56.25 and 75 mM, the ·OH quantity rapidly increased with the increase of H_{2}O_{2} concentration. Thus, the oxidation capability of the Fenton system was enhanced to attain a higher COD removal efficiency. By contraries, catalytic Fe^{2+} was oxidized to Fe^{3+} and the oxidation capability of the Fenton system decreased while added excess H_{2}O_{2}. Superfluous H_{2}O_{2} acted as a scavenger of the highly potent ·OH to produce the hydroperoxyl radical, which had a much lower oxidation ability than ·OH [19-21]. So the COD removal efficiency was not further increase when surpassed the optimum dosage of H_{2}O_{2} in the system.

What is more, as a teaching advice, the Fenton reactor had been used in the experimental teaching in undergraduates’ water treatment courses. Through hands-on Fenton experiment in the laboratory, the students made a further understanding of the Fenton device and achieved a combination of theory and practice.
4. Conclusions
Based on former studies and discussion on the COD removal from acrylic fiber manufacturing wastewater, the Fenton process holds excellent performance on the degradation of pollutants under an optimal condition of ferrous dosage was 6.25 mM, hydrogen peroxide was 75 mM and initial pH value was 3.0 in 90 min reaction time. The removal efficiency of COD, TOC, NH$_4$$^+$-N and TN reached from 45% to 69%. Meanwhile, most organic pollutants could also be removed completely that suggested the Fenton process was an effective way to treat acrylic fiber wastewater.

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