



Article Comparison of Fenton and Ozone Oxidation for Pretreatment of Petrochemical Wastewater: COD Removal and Biodegradability Improvement Mechanism

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Abstract: Cost-effective pretreatment of highly concentrated and bio-refractory petrochemical wastewater to improve biodegradability is of significant importance, but remains challenging. This study compared the pretreatment of petrochemical wastewater by two commonly used chemical advanced oxidation technologies (Fenton and ozone oxidation), and the mechanisms of biodegradability improvement of pretreated wastewater were explored. The obtained results showed that in the Fenton oxidation system, the COD removal of petrochemical wastewater was 89.8%, BOD₅ decreased from 303.66 mg/L to 155.49 mg/L, and BOD₅/COD (B/C) increased from 0.052 to 0.62 after 60 min under the condition of 120 mg/L Fe²⁺ and 500 mg/L H₂O₂, with a treatment cost of about 1.78 $\frac{1}{8}$ kg_{COD}. In the ozone oxidation system, the COD removal of petrochemical wastewater was 59.4%, BOD₅ increased from 127.86 mg/L to 409.28 mg/L, and B/C increased from 0.052 to 0.41 after 60 min at an ozone flow rate of 80 mL/min with a treatment cost of approximately 1.96 \$/kg_{COD}. The petrochemical wastewater treated by both processes meets biodegradable standards. The GC-MS analysis suggested that some refractory pollutants could be effectively removed by ozone oxidation, but these pollutants could be effectively degraded by hydroxyl radicals (•OH) produced by the Fenton reaction. In summary, compared with ozone oxidation, petrochemical wastewater pretreated with Fenton oxidation had high COD removal efficiency and biodegradability, and the treatment cost of Fenton oxidation was also lower than that of ozone oxidation.

Keywords: Fenton oxidation; ozone oxidation; petrochemical wastewater; biodegradability; GC–MS analysis

1. Introduction

The global demand for and consumption of energy has increased rapidly in recent years. As a result, the petrochemical industry, which is an important industrial pillar of modern energy and plays an important role in the economic development of any country, has shown a continuous and steady growth trend, [1]. A large amount of highly toxic and biodegradable wastewater and waste residue will be produced in the industrial production process of petrochemical products, mainly composed of oily wastewater, phenol-containing wastewater, and high-salt wastewater, containing volatile phenol, benzene, organic acids, and other organic pollutants, which cannot be directly treated by traditional biological methods, and cause serious pollution to the natural water environment [2]. Therefore, it is necessary to pretreat petrochemical wastewater to improve its biodegradability and facilitate subsequent advanced treatment [3].



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Advanced oxidation technologies (AOPs) [4] with the potential to degrade various organic pollutants mainly include the Fenton/photo-Fenton method, the photocatalytic oxidation method, the ozone oxidation method, the ultrasonic oxidation treatment method, etc. [5,6], and have been proved to be an effective wastewater treatment technology which can generate hydroxyl radicals ($^{\bullet}$ OH) (E₀ = 2.80 V) and other radicals with strong oxidizing properties, which can effectively improve the biodegradability of effluent by high treatment efficiency and strong operability in the pretreatment of petrochemical wastewater [7,8]. Under certain pH conditions, the reaction of Fe^{2+} and H_2O_2 occurs to generate $^{\bullet}OH$ in a very simple and cost-effective way via Fenton oxidation [9], an advanced oxidation technology for effectively treating refractory organic wastewater, in which molecular organic pollutants are degraded to small molecular organic pollutants or mineralized to CO_2 and H_2O [10]. Marzie Dehboudeh et al. [11] used electro-Fenton technology to pretreat petrochemical wastewater, and then carried out advanced treatment using the activated sludge method, showing that under the conditions of pH = 3, current of 160 mA, and a H_2O_2 concentration of 65 mM, the COD removal rate was improved to 79%, while the B/C value increased from 0.44 to 0.776 after 30 min, which proved that the biodegradability of wastewater was greatly improved. Similarly, solar Fenton technology was used by Omid Pourehie et al. [12] to pretreat refinery wastewater, and showed that after 180 min of reaction at 694.7 mg/L H₂O₂, 67.3 mg/L Fe²⁺, and pH = 12, COD and TOC decreased to 79.6 % and 73.2 %, respectively, while the B/C values reached 0.36 to 0.62, also proving that the biochemical properties of the pretreated petrochemical wastewater were improved. Ozone is regarded as a strong oxidant with a strong oxidizing ability [13], rapid reaction, as well as being green and high efficiency, which can not only directly oxidize pollutants, but also produce •OH to effectively mineralize organic pollutants, successfully realizing water purification without secondary pollution [14]. Chi-Kang Lin et al. [15] and Huangfan Ye et al. [16] treated petrochemical wastewater by combining ozone oxidation pretreatment with advanced biological activated carbon treatment, and coagulation–ozonation (ICO) integration, respectively, and effectively improved biodegradability.

Fenton oxidation and ozone oxidation degrade organic pollutants by different mechanisms. Ozone oxidation mainly reacts directly with the unsaturated bonds of organic pollutants through its own oxidizing properties, and has certain limitations that only a part of organic pollutants' oxidation was promoted because of its selective oxidizing properties [17]. In contrast, the strong oxidizing •OH, which can degrade organic pollutants non-selectively, was generated in Fenton oxidation [18]. Although the pretreatment of petrochemical wastewater by Fenton and ozone oxidation have been studied, the comparison of Fenton and ozone oxidation on the COD removal of petrochemical wastewater and biodegradability improvement mechanism is still lacking.

In this work, the petrochemical wastewater was pretreated by Fenton and ozone oxidation, and the variations in COD, BOD₅, and B/C in the two systems were systematically compared. According to the GC–MS analysis, the mechanism of the improved biodegradability of the treated wastewater was explored. Additionally, the treatment costs of the two systems were compared. This study provided a technical reference for the pretreatment of bio-refractory petrochemical wastewater.

2. Materials and Methods

2.1. Materials and Real Wastewater

All chemicals used in this study were analytically pure without further purification. Main reagents include high purity oxygen (\geq 99.99%), ferrous sulphate heptahydrate (FeSO₄·7H₂O), hydrogen peroxide (H₂O₂) (30% w/v), concentrated sulphuric acid (98%), and sodium hydroxide (for pH adjustment), as well as dichloromethane. The primary instrumentation was a OzoniaLab 2B ozone generator, a pH meter, a Hach spectrophotometer DR2800, a magnetic stirrer, and gas chromatography-mass spectrometry (GC–MS).

High concentration production wastewater from a petrochemical wastewater treatment plant in Tianjin was used in this experiment. The wastewater samples were stored in the laboratory at 4 °C after sampling, with the initial pH of 6.26, the high COD of 2458.75 mg/L, and the B/C of 0.052, as shown in Table 1. The wastewater was used directly for the experiment without other treatment conditions.

Table 1. Petrochemical wastewater quality indicators.

Wastewater	pН	COD (mg/L)	BOD ₅ (mg/L)	B/C
Petrochemical wastewater	6.26	2458.75	127.86	0.052

2.2. Experimental Procedures

A 250 mL water sample of petrochemical wastewater was added to a 500 mL beaker with a certain amount of ferrous sulphate, and stirred using a magnetic stirrer at pH of 3.0, which was adjusted using H_2SO_4 and NaOH. A quantity of H_2O_2 was dropped into the solution when the ferrous sulphate was dissolved to carried out a Fenton oxidation experiment at an ambient temperature of 25 °C.

The supernatant was taken at regular intervals after a certain reaction time and analysed to determine its COD and BOD₅ values, respectively, in order to observe the changes in B/C values before and after treatment. The mixture of oxygen and ozone (1 g/L) from the ozone generator was passed into the 250 mL petrochemical wastewater water sample [19]. Different intake air flows were used to oxidize petrochemical wastewater for a certain period of time in an environment of 25 °C. The COD and BOD₅ values were measured by taking samples regularly.

2.3. Analysis Methods

The COD was determined using the potassium dichromate oxidation method (Hach spectrophotometer DR2800, USA) [20], and BOD₅ was determined according to the State Environmental Protection Administration (SEPA) of China standard method (SEPA, 2002). Three replicate tests were performed for each sample and the results are reported as mean values with an error of less than 5%. Gas chromatography–mass spectrometry (GC–MS) [21] was used to analyze the degradation products of petrochemical wastewater. The water samples were extracted with dichloromethane and pretreated with Welchrom[®] PS/DVB solid phase extraction columns to enrich for organic contaminants. The samples were separated and concentrated on a column equipped with an HP-5 (30 m \times 0.25 mm \times 0.25 μ m). The ramp-up procedure was 60 °C for 1 min, 20 °C/min to 220 °C for 1 min, and 5 °C/min to 280 °C for 4 min, and the detection spectra were retrieved qualitatively from the NIST-05 mass spectrometry database.

3. Results and Discussion

3.1. Pretreatment of Petrochemical Wastewater by Fenton Oxidation

3.1.1. Effect of Fe²⁺ Concentration

Figure 1 shows the effect of Fe^{2+} concentration on COD removal (Figure 1a), B/C values (Figure 1b), and BOD₅ variation (Figure 1c) during Fenton oxidation. When the wastewater is acidified to pH = 3 that is suitable for Fenton reaction, the COD is significantly reduced, but the B/C value is 0.26, which is still less than 0.3, indicating that the biochemical properties are still low and needs to be pretreated by Fenton oxidation. The COD decreased significantly from 560.60 mg/L to 376.19 mg/L when the Fe²⁺ concentration increased from 20 mg/L to 120 mg/L at 300 mg/L H₂O₂ after 60 min. This was due to the reaction between Fe²⁺ and H₂O₂ in the wastewater to produce the strongly oxidizing •OH (Equation (1)) [22], which can mineralize most organic pollutants. However, the COD increased to 504.04 mg/L when excess Fe²⁺ increased to 200 mg/L, because of the consumption of the generated •OH (Equation (2)) (Figure 1a) [23]. The B/C value reached 0.495 when Fe²⁺ was 120 mg/L, greater than 0.3, and higher than other experimental groups (Figure 1b), which also has the lowest BOD₅ of 186.21 mg/L (Figure 1c). It indicates that the pretreatment



effect was achieved under the selected condition of
$$120 \text{ mg/L Fe}^{2+}$$
 with higher biochemical properties.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$$
(1)

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-}$$
(2)

Figure 1. Effect of Fe²⁺ concentration on (**a**) COD removal; (**b**) B/C values; (**c**) BOD₅ variation during Fenton oxidation. Conditions are as follows: H_2O_2 concentration 300 mg/L; 250 mL wastewater; pH = 3.0.

3.1.2. Effect of H₂O₂ Concentration

Figure 2 shows the effect of H_2O_2 concentration on COD removal (Figure 2a), B/C (Figure 2b), and BOD₅ (Figure 2c) during Fenton oxidation. At 120 mg/L Fe²⁺ and a reaction time of 60 min, the H_2O_2 concentration increased from 100 mg/L to 500 mg/L, and COD decreased significantly from 978.58 mg/L to 250.79 mg/L, mainly due to the oxidation of Fe²⁺ by H_2O_2 in the wastewater to produce •OH (Equation (1)) [24]. However, when H_2O_2 was increased to 1000 mg/L, COD increased to 356.52 mg/L (Figure 2a), which was due to the consumption of the generated •OH by the excess H_2O_2 (Equation (3)) [25]. At 500 mg/L of H_2O_2 , the B/C value was 0.62, which was greater than 0.3 and higher than the B/C values of the other experimental groups (Figure 2b), and the BOD₅ of the reacted wastewater was the



smallest at 155.49 mg/L (Figure 2c). Therefore, 500 mg/L
$$H_2O_2$$
 was selected as the condition for the treatment of petrochemical wastewater by Fenton oxidation.

$$H_2O_2 + {}^{\bullet}OH \to H_2O + {}^{\bullet}O_2H \tag{3}$$

Figure 2. Effect of H_2O_2 concentration on (a) COD removal; (b) B/C values; (c) BOD₅ variation during Fenton oxidation. Conditions are as follows: Fe²⁺ concentration 120 mg/L; 250 mL wastewater; pH = 3.0.

3.2. Pretreatment of Petrochemical Wastewater by Ozone Oxidation

Figure 3 shows the effect of ozone flow rate on COD removal (Figure 3a), B/C values (Figure 3b), and BOD₅ variation (Figure 3c) during ozone oxidation. The COD decreased from 1991.10 mg/L to 998.25 mg/L as the ozone flow rate was increased from 10 mL/min to 80 mL/min (Figure 3a) at an ozone concentration of 1 g/L after 60 min. More ozone reacting with the organic pollutants in the increasing ozone flow rate results in the decline of COD. However, since ozone is a selective oxidant and reacts slowly with organics without electron-rich parts, the COD removal effect is more obvious in the first 5 min but not high in the following time, as show in data [26]. The B/C value was 0.41 (\geq 0.3), with a BOD₅ of 409.28 mg/L under 80 mL/min ozone flow rate (Figure 3c), indicating that high biodegradability was achieved for pretreated wastewater at this time.

3.3. Mechanisms of B/C Improvement

3.3.1. GC–MS Analysis of Wastewater

Table 2 lists the GC–MS composition analysis of wastewater, Fenton, and ozone oxidation. The wastewater composition is relatively complex and contains a variety of large

organic pollutants, such as tripropylene glycol methyl ether, Di-tert-butylphenol, and large organic acids. The relative abundance of organic pollutants in the wastewater samples is shown in Figure 4a. It can be seen that the relative abundance of Di-tert-butylphenol, 2-Amino-4,5,6-methylbenzoic acid and 2-Methyl-2-Pentanol are higher, at 25.31%, 33.45%, and 15.50% respectively. This result suggests that the main microscopic composition of their organic load is large-molecule organic pollutants, from which it can be inferred the COD composition of wastewater may be large polar organic pollutants that are difficult to biodegrade, organic acids, phenols, and other organic substances [27]. Because of the high content of macromolecular organic pollution in wastewater, it is difficult or not biodegradable.



Figure 3. Effect of ozone flow rate on (**a**) COD removal; (**b**) B/C values; (**c**) BOD₅ variation during Fenton oxidation. Conditions are as follows: ozone concentration 1 g/L; 250 mL wastewater; pH = 6.26.

Table 2. GC-MS analysis of petrochemical wastewater.

No.	Compound	Molecular Structure	Elemental Composition	t _R (min)	[M + H] + m/z	Wastewater	Fenton Oxidation	Ozone Oxidation
А	Ethanethioamide,N,N- dimethyl-	s N	C ₄ H ₉ NS	4.173	103.19	\checkmark		\checkmark
В	Acetamide,N- (aminocarbony)-	NH2 H	$C_3H_6N_2O_2$	4.485	102.09			\checkmark

No.	Compound	Molecular Structure	Elemental Composition	t _R (min)	[M + H] + m/z	Wastewater	Fenton Oxidation	Ozone Oxidation
С	Acetic acid glacial	ОН	$C_2H_4O_2$	4.666	60.05		\checkmark	\checkmark
D	Ammonium acetate	NH4 ⁺	C ₂ H ₇ NO ₂	4.804	77.08		\checkmark	
Е	2-Amino-4,5,6- methylbenzoic acid	$H_{3}N$ H_{0} H_{0} H_{0} H_{0} H_{1} H_{1} H_{1} H_{1} H_{1} H_{1} H_{1} H_{1} H_{1}	C ₈ H ₉ NO ₂	5.378	151.16	\checkmark	\checkmark	\checkmark
F	Guanidine,N,N'- dimethyl-	NH N H H	$C_3H_9N_3$	6.532	87.12	\checkmark		
G	Stearic acid	Лон	$C_{18}H_{36}O_2$	9.213	284.48	\checkmark	\checkmark	\checkmark
Н	Palmitic acid	он	$C_{16}H_{32}O_2$	14.13	256.42	\checkmark	\checkmark	\checkmark
I	tripropyleneglycol methyl ether	OH of of	C ₁₀ H ₂₂ O ₄	17.70	206.28	\checkmark		
J	Stearic acid, 2-(2-hydroxyethoxy) ethyl ester	~~~~ ⁰ ~~ ₀ ~~ ₀ н	C ₂₂ H ₄₄ O ₄	18.30	372.58	\checkmark	\checkmark	\checkmark
К	Hexanamide	O NH ₂	C ₆ H ₁₃ NO	19.92	115.17		\checkmark	\checkmark
L	Di-tert- butylphenol	OH	C ₁₄ H ₂₂ O	20.63	206.32	\checkmark	\checkmark	\checkmark
М	3,3-Dimethyl-1- (2- carboxyphenyl)triaze	ne contraction of the second s	$C_9H_{11}N_3O_2$	21.12	193.2025	\checkmark	\checkmark	\checkmark
N	2-Methyl-2- Pentanol	OH	C ₆ H ₁₄ O	21.91	102.17	\checkmark	\checkmark	\checkmark
0	Myristic-1-13C Acid	^O ^{BC} OH	C ₁₃ (13C)H ₂₈ O ₂	25.85	229.36			
Р	2-Acetyl-2- thiazoline	a a	C ₅ H ₇ NOS	25.85	129.18	\checkmark		\checkmark

Table 2. Cont.

 \surd indicates the presence of the pollutant in the water sample.

3.3.2. Biodegradability Improvement Analysis

The relative abundance of organic pollutants in the petrochemical water after the Fenton oxidation treatment for 60 min is shown in Figure 4b, and the quality of the petrochemical water was significantly improved. Some of the large molecule organic pollutants were completely removed, such as Myristic-1-13C Acid, 2-Acetyl-2-thiazoline, Guanidine, N,N'-dimethyl-. Small organic molecules, such as acetic acid and ammonium acetate were produced, and the relative abundance values of acetic acid and ammonium

acetate were 30.5% and 28.14%, respectively. It can be inferred that the organic species were reduced by the Fenton oxidation treatment, and the large molecules were oxidized to small molecules by the **°OH** generated from the Fenton reaction [28,29].



Figure 4. Types and relative abundance of pollutants in different water samples: (**a**) Wastewater; (**b**) Fenton oxidation; (**c**) Ozone oxidation.

The result of ozone oxidation treatment is shown in Figure 4c. The effluent organics were mainly aromatic hydrocarbons and small molecule organics, among which the relative abundance of Di-tert-butylphenol, 2-Amino-4,5,6-methylbenzoic acid were still high, at 19.53% and 22.53%, respectively. However, it can be found that there are still many small molecules of organic matter generated in the water samples oxidized by ozone, such as the relative abundance of acetic acid at 15.34%, from which it can be inferred that ozone molecules directly attack the chemical bonds of organic matter to break them, breaking the unsaturated bonds of organic matter and changing the benzene ring into an oxygen-containing heterocyclic ring. Other methods to form small molecules of organic matter also take place.

Macromolecular organic matters are difficult to biodegrade because they are too large and, thus, cannot be injected into microorganisms, preventing their effective biodegradation. Oxidation reactions break down these large molecules into short-chain intermediates, such as small organic acids, which can enter the cell and become readily biodegradable [30].

In summary, both Fenton and ozone oxidation could effectively improve the biodegradability of pretreated petrochemical wastewater, and Fenton oxidation had a more obvious improvement effect. The above difference was mainly caused by the different process mechanisms of Fenton and ozone oxidation. •OH, which generates from the Fenton reaction, mainly degrades organic pollutants through attacking double bonds in order to form carbocation, or by combining with carbocation intermediate to form additional product, capturing H⁺ by the C-H bond fracture of organic pollutants (Equation (4)) and degrading organic pollutants by electron transfer [31]. By contrast, O₃ degrades organic pollutants through reacting with organic compounds containing unsaturated bonds or receiving electrons to replace some functional groups of organic pollutants [32]. Compared with ozone oxidation, a much higher amount of small molecular organic acids was generated in the Fenton oxidation process according to the GC–MS results, which could be attributed to the fact that O₃ was a highly selective oxidant, which made it difficult to degrade organic pollutants without electron-rich fraction [33,34]. On the other hand, the generated •OH can attack macromolecular organic pollutants non-selectively. Therefore, Fenton oxidation is more suitable for the pretreatment of petrochemical wastewater.

$$R-H + {}^{\bullet}OH \to H_2O + R^{\bullet}$$
(4)

3.4. Treatment Costs

Economic efficiency is an important indicator of the feasibility of a technology [35]. In this study, we compared the COD removal, biochemical properties (B/C), and cost analysis of the two oxidation methods after treatment.

After Fenton and ozone oxidation treatment, the COD in wastewater was significantly reduced and the B/C value reached above 0.3, indicating significant improvement in biochemical properties. It is worth nothing that the COD removal effect and biochemical properties of the Fenton oxidation treated wastewater were better than ozone oxidation (Figure 5).



Figure 5. Comparison of COD, B/C values, and treatment costs in different Fenton and ozone oxidation systems.

The economic value of two methods was compared in terms of cost. For Fenton oxidation, the optimal dosing amounts of H_2O_2 and Fe^{2+} were 500 mg/L and 120 mg/L, respectively, while the cost of Fenton oxidation was approximately 1.77 kg_{COD} (30% H_2O_2 :6.71 kg; ferrous sulphate heptahydrate: 4.74 kg); For ozone oxidation, the ozone rate of 80 mL/min is the optimal condition, and the cost is about 1.96 kg_{COD} (liquid oxygen: 149.1 tg). However, the ozone oxidation method is limited by the high operating cost of the ozone generator and treatment cost, so the cost of ozone oxidation is relatively higher than the Fenton method. In summary, in terms of the overall COD removal and biochemical analysis, the Fenton method has better economic value of than the ozone oxidation method.

4. Conclusions

In this study, Fenton and ozone oxidation were used to pretreat petrochemical wastewater, and COD removal, B/C and intermediates in above two systems were compared. Under the conditions of pH = 3, 300 mg/L H₂O₂, and 120 mg/L Fe²⁺, the COD removal of the wastewater in Fenton oxidation system reached 89.8%, the B/C value reached 0.62, and the cost was about 1.78 kg_{COD} . In the ozone oxidation system, the COD removal of petrochemical wastewater reached 59.4% and the B/C value increased to 0.41 with a treatment cost of approximately 1.96 kg_{COD} at an ozone concentration of 1 g/L and a flow rate of 80 mL/min. The GC–MS results suggested that Fenton oxidation, including the acidification process, can efficiently degrade the refractory substances in the wastewater and generate more biodegradable small molecular organic acids, which is more conducive to the improvement of biodegradability. Furthermore, the treatment cost of Fenton oxidation is also lower than that of ozone oxidation. In conclusion, Fenton oxidation is more suitable for the pretreatment of petrochemical wastewater.

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