



Degradation process and kinetics study of actual urotropine wastewater by Fenton method

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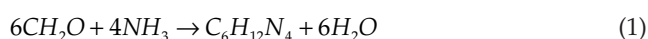
ABSTRACT

The degradation of actual urotropine wastewater was investigated by Fenton oxidation process. The effect of initial pH, dosages of Fe^{2+} and H_2O_2 , reaction time and temperature of reaction on chemical oxygen demand (COD) and total organic carbon (TOC) removal was analyzed. The optimal conditions for COD and TOC removal of urotropine wastewater were determined. When the pH = 7.0, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ dosage = 4, H_2O_2 dosage = 16.5784 g/L, reaction temperature = 45°C, reaction time = 3 h were given, the removal of COD and TOC was 93.53% and 81.27%, respectively. The experimental results indicated that the removal efficiency was strongly dependent on initial pH, the concentration of Fenton reagents, time and temperature of the reaction. Second-order reaction kinetic model provides the best correlation of the data. Primary substances were identified by gas chromatography-mass spectrometry (GC-MS), and the possible reaction pathway was proposed based on the analysis in Fenton oxidation process. This study may lead as provide guidance to related industries treating the urotropine production wastewater by Fenton oxidation process.

Keywords: Degradation; Kinetics; Urotropine; Wastewater; Fenton

1. Introduction

Urotropine, $(\text{CH}_2)_6\text{N}_4$, is widely used in pharmaceutical and chemical industries as a primary feed material and an intermediate material [1]. The production method of urotropine is the reaction of formaldehyde with ammonia or ammonium salts at industrial scale [2], as shown in Eq. (1). Therefore, the reaction residues, are the main chemical composition in the production wastewater [2].



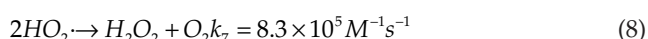
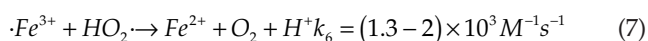
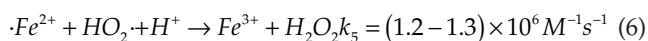
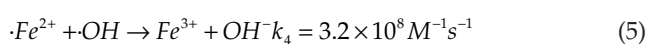
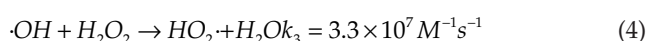
Urotropine is a very stable molecule with a cyclic symmetric structure like adamantane [3], which makes the molecule recalcitrant to oxidation via methylotrophic pathway reactions so that minimum soil microbes can

degrade it for utilization [4]. In addition, the urotropine is a commonly used insecticide and hexamine is resistant to biodegradation, even when sludge has been acclimated for a long period. Previous studies reported that *brevundimonas diminuta* and a *phyllobacterium* sp. could utilize urotropine as the only source of carbon, nitrogen and energy. The growth rate of these bacteria was lower on urotropine wastewater than the growth culture. Therefore, this technique could not be very advantageous for the degradation of urotropine. [5]. However, urotropine removal could reach 93.88% and COD removal could be 85.60% when cow-dung is used, in urotropine wastewater, as a co-substrate [6]. The physicochemical separation methods (like exchange resins and activated carbon absorption) have been investigated for the treatment of urotropine wastewater [7,8], however, these methods only transfer the pollutant from one phase to another. The chemical method is the most common treatment method. The COD removal attained to 94% after 5 h by a novel Electro-Fenton method, which applied H_2O_2 and

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electro generated ferrous ion for treating the high strength urotropine-containing wastewater [7]. The Fenton-based reaction, using H_2O_2 as an oxidant and transition metal ions (such as iron ions) as a catalyst, is being used for the remediation of soil and groundwater contamination with refractory synthesized or natural organic compounds [9]. The ferrous ions are commonly used for homogeneous catalysis, while the heterogeneous catalysis involves metal oxides and supported iron oxides [10].

The Fenton process, one of the advanced oxidation processes (AOPs), is widely used as an effective and useful remediation method for highly concentrated waste waters due to its effectiveness in the production of hydroxyl radicals ($\cdot OH$) [11]. Fenton's oxidation method is based on the use of mixture of hydrogen peroxide and iron salts (Fe^{2+}) at room temperature [12]. Once H_2O_2/Fe^{2+} was added to wastewater in proportion, the $\cdot OH$ generated rapidly, and they could undergo a variety of oxidation reactions, as shown in Eqs. (2)–(8) [13,14].



The generated $\cdot OH$ radical, a powerful oxidant that redox potential reach +2.8 V, could attack a wide range of organic pollutants [13].

At present, urotropine has important applications in our daily life, military, pharmaceutical, agricultural and also in food industries. However, there are few previous literatures on wastewater from such substances, and some literature is on simulated wastewater. This type of wastewater was directly collected from the manufacturer of urotropine and that is the actual industrial wastewater, the gap between actual and theoretical remains often different. The objectives of this research are to explore the actual wastewater treatment by Fenton oxidation reaction. This article will explore the optimal conditions of Fenton reaction in the process of treating actual urotropine wastewater, as well as the degradation process and kinetics.

2. Experimental

2.1. Materials

The raw wastewater used for this experiment collected from a factory located in Shenzhen (China). The chemicals

used in this experiment are hydrogen peroxide (30% w/w), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sulfuric acid and sodium hydroxide. All chemicals used were of analytical grade and were used as received without any further purification and were obtained from Chengdu Kelong chemical engineering (Chengdu, China). Throughout the experiment deionized water was used.

2.2. Experimental method

First of all, the pH of reaction mixture was adjusted by sulfuric acid and sodium hydroxide, and measured by a pH-meter (PHS-4C⁺, Century Ark). The experiment was run at a constant temperature in a water bath with magnetic stirring (SHA-C, Jiangsu Zhengji). The chemical oxygen demand (COD) is measured in a COD reactor (QDJCYQ16060877, Jingcheng, China) using a dichromate method TOC and TC were determined by (H51304500977AE, Shimadzu, Japan). NH_4-N , NO_3-N and NO_2-N were determined by autoanalyzer (3-AA3, seal, China). Before and after Fenton processes, substances which are already present in the urotropine wastewater was detected by GC-MS (QP2010puls, Shimadzu, Japan).

2.3. Procedures

The collected 50 mL urotropine raw wastewater poured into a 100 mL beaker with three replications, then diluted sulfuric acid with a ratio of 1:1 and 1:5 was added and 30% sodium hydroxide solution was added to adjust solution pH values and the addition of Fenton reagent ($FeSO_4 \cdot 7H_2O$ and H_2O_2) was followed. Then this solution was kept in a water bath with constant temperature. Finally, the solution pH was adjusted to 9 to settle down iron ions, and the supernatant was measured for its characteristics. The TOC and COD removal of urotropine wastewater was calculated according to the following equation:

$$X_{TOC}(\%) = \frac{TOC_0 - TOC_t}{TOC_0} * 100\% \quad (9)$$

$$X_{COD}(\%) = \frac{COD_0 - COD_t}{COD_0} * 100\% \quad (10)$$

where X_{TOC} and X_{COD} refer to TOC and COD removal ratio, TOC_0 and COD_0 are the initial concentration before the oxidative process, and TOC_t and COD_t are the concentration of different times in the oxidative process, respectively.

3. Results and discussion

3.1. Optimization of system parameters

3.1.1. Effect of H_2O_2 and Fe^{2+} dosage

The COD and TOC removal rate were increased followed by a decrease with the increase of H_2O_2/Fe^{2+} ratio, (Figs. 1a and 1b) and the highest peak value was found when the ratio was 4. When the H_2O_2/Fe^{2+} ratio was low, the $\cdot OH$ radicals were trapped by excess Fe^{2+} ions (reaction (4) in Introduction) [15]. Whereas the production of $\cdot OH$ radical was not enough to oxidize organic pollutants when the

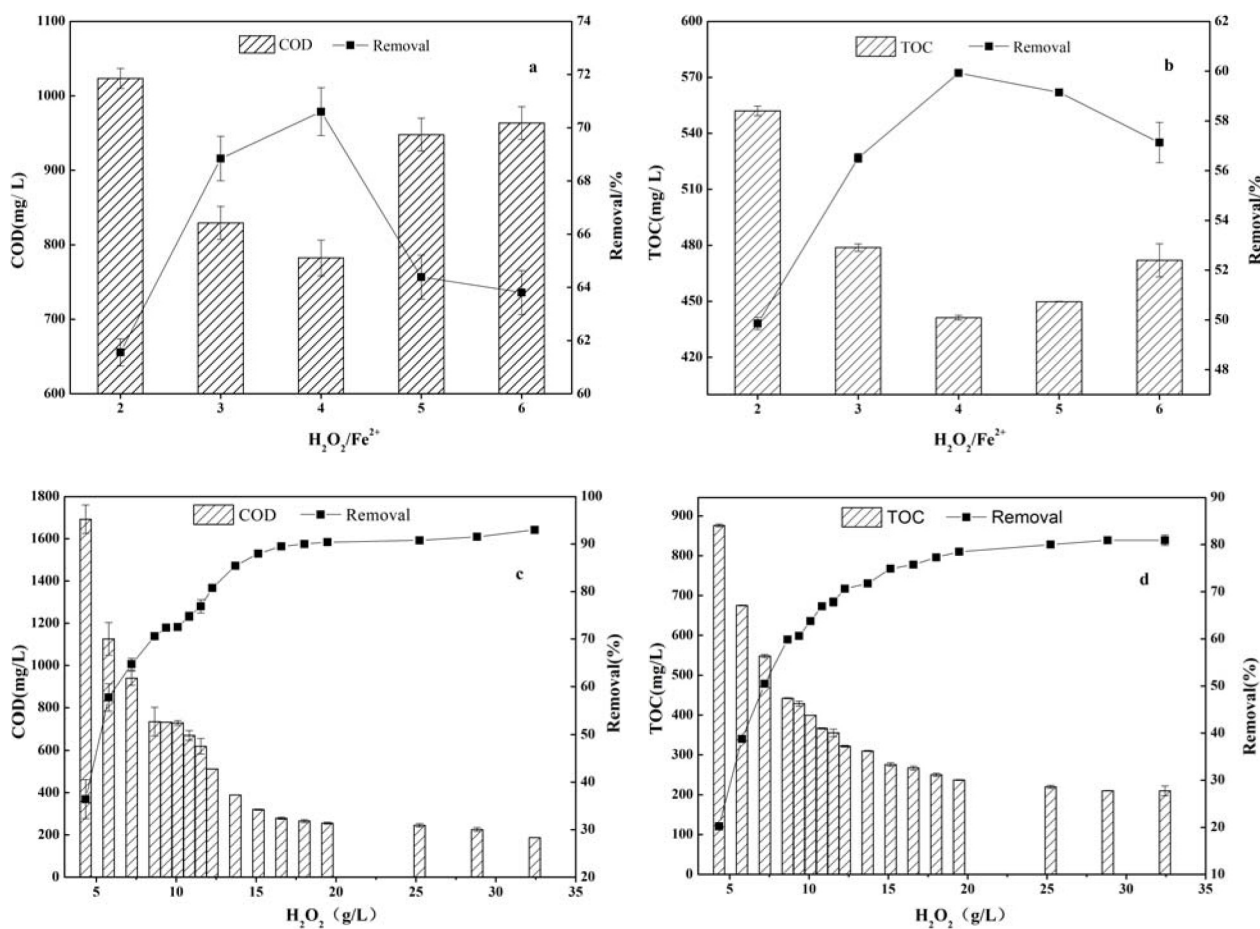


Fig. 1. Effect of H_2O_2/Fe^{2+} dosage and H_2O_2 dosage on COD and TOC removal in the Fenton process (pH was 3, temperature was 20°C, reaction time was 2 h; a and c is COD actual concentration and degradation rate under different conditions, b and d is TOC actual concentration and degradation rate under different conditions).

H_2O_2/Fe^{2+} ratio was high. Moreover, excessive H_2O_2 would interfere with the measurement of COD. The residual H_2O_2 in Fenton process could consume $K_2Cr_2O_7$, which led to the increase of measurement value of inorganic COD [16].

As we increased the dosage of H_2O_2 from 4.3 to 32.4 g/L, the removal rate of COD and TOC was removed from 1615 to 187 mg/L and 876 to 210 mg/L, respectively (Figs. 1c and 1d). The removal rate of COD and TOC was rapidly increased till 15.1 g/L of dosage, but as the dosage of hydrogen peroxide increased more than 15.1 g/L it shows a gentle increase. By the increasing H_2O_2 dosage the concentration of $\cdot OH$ was expected to increase (reaction (2)), and that was also lead to increased oxidation rates of organic compounds. Reaction (3) shows that when H_2O_2 dosage was too high, it led to the reduction of $\cdot OH$ radical. When the H_2O_2 dosages range from 8.6 to 10.1 g/L, the removal of COD was stopped to decrease further, while the removal of TOC was continued to decrease. That was probably due to the presence of intermediate (like amino detected) during the degradation.

3.1.2. Effect of solution pH

Although high degradation efficiencies have been reported at acidic condition for a variety of contaminants in

Fenton reaction [17], when the pH value ranges from 1.6–7 the removal rate of COD and TOC has been increased and reached 91.62% and 79.23% at pH 7, respectively in actual urotropine wastewater (Fig. 2). When the ferric and ferrous hydroxides (e.g. $Fe(OH)^{2+}$, $Fe(OH)_2^{2+}$ and $Fe(OH)_6^{3-}$) were generated in the reaction as pH starts to become near neutral from acidic environment. The organic contaminants in wastewater could be removed indirectly by co-precipitation and enmeshment of the ferrous and ferric hydroxide floc [18,19]. If the pH is increased from 7 to 8.5, the removal efficiency of COD and TOC was slow because the production of hydroxyl radical was inhibited. Therefore, the degradation of organic pollutant in water at alkaline pH is not beneficial, but more flocculation (ferric and ferrous hydroxides) can be produced.

3.1.3. Effect of reaction temperature

Reaction temperature had a positive effect on the degradation of urotropine wastewater (Fig. 3). The removal rate of COD and TOC was increased from 81% to 93.4% and 68.8% to 81.4% respectively, when the temperature was increased from 25 to 45°C. Fenton reaction could be accelerated by increasing the temperature of the solution [20]. According to the Arrhen-

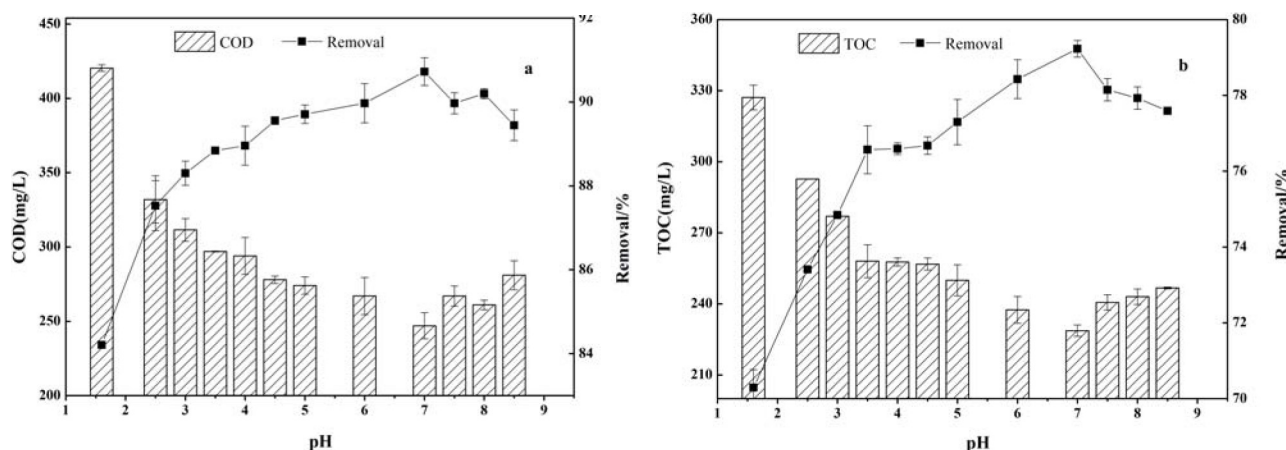


Fig. 2. Effect of pH on TOC and COD removal in the Fenton process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio was 4, H_2O_2 concentration was 8.6 g/L, temperature was 20°C, reaction time was 2 h).

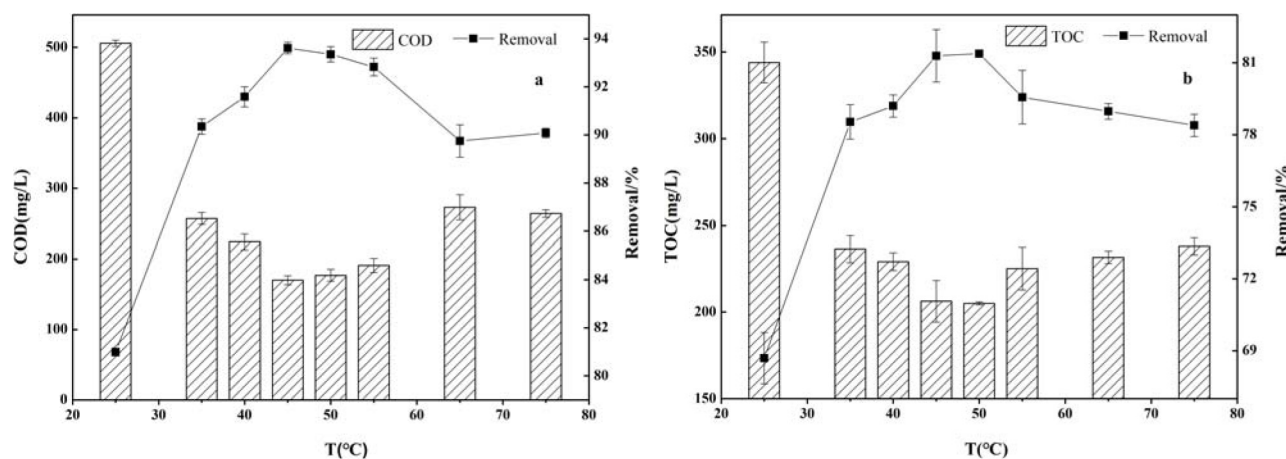


Fig. 3. Effect of reaction temperature on TOC and COD removal in the Fenton process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio was 4, H_2O_2 concentration was 8.6 g/L, pH was 7, reaction time was 2 h).

nius equation, if the temperature is higher, more energy is produced to overcome the reaction activation energy [21]. On the basis of the Arrhenius equation [Eq. (11)], the reaction rate constant of Reaction (4) will have a rapid increase compared with that of the side Reaction (5) when E_a is relatively low. Whenever E_a is relatively high, the experiment may show the opposite results. It means that the reaction rate constant of the side Reaction (4) will increase more quickly.

$$K = Ae^{-E_a/RT} \quad (11)$$

where k is reaction rate constant, R is molar gas constant, T is thermodynamic temperature, E_a is apparent activation energy and A is pre-exponential factor.

3.1.4. Effect of reaction time

A chain of experiments were conducted from 10 min, 20 min, 30 min, 40 min, 1 h to 5 h (Fig. 4). When the reaction time was between 10 min to 1 h the removal efficiency of TOC and COD was increased. In contrast, The TOC and COD removal rate remained at the slower speed till reac-

tion time increased from 2 h to 5 h. This phenomenon could be attributed to the reaction kinetics. The initial Fenton reaction was mainly catalyzed by Fe^{2+} , and the Fe^{2+} concentration decreased instantly due to the consumption in the initial reaction process. Subsequently, the system was dominated by Fenton-like reaction catalyzed by Fe^{3+} [22], and thus the reaction rate remained almost the same.

3.2. Degradation process

The characteristics of urotropine wastewater before and after Fenton reaction are collected in Table 1. The optimal conditions for COD and TOC removal of urotropine wastewater were determined, the removal rate of COD and TOC was 93.53% and 81.27%, respectively. When the pH = 7.0, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ dosage = 4, H_2O_2 dosage = 16.5784 g/L, reaction temperature = 45°C and reaction time were 3 h.

The Fenton reaction is not conducive to the degradation of Dimethyl phenol under neutral conditions. All the pollutants were degraded by Fenton processes except Dimethyl phenol as shown in Table 2. The alcoholic compounds were oxidized to form carboxylic acid compounds.

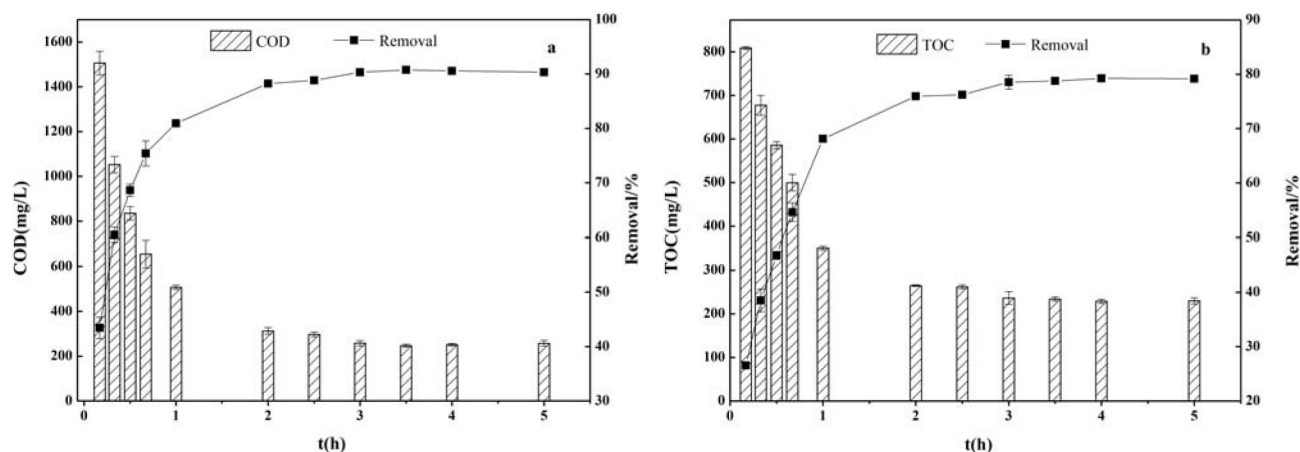


Fig. 4. Effect of reaction time on TOC and COD removal in the Fenton process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio was 4, H_2O_2 concentration was 8.6 g/L, pH was 7, temperature was 45°C).

Table 1
Representative characteristics of urotropine wastewater before and after Fenton reaction

Index	Raw value	After Fenton
TOC (mg/L)	1101 ± 61.2 ^a	236 ± 14.3
TC (mg/L)	1321 ± 31.4	243 ± 14.3
COD (mg/L)	2662 ± 72.7	257 ± 11.9
$\text{NH}_4\text{-N}$ (mg/L)	253.4	640.1
$\text{NO}_2\text{-N}$ (mg/L)	0.087	0.508
$\text{NO}_3\text{-N}$ (mg/L)	2.225	39.675
pH	8.5 ± 0.05	9 ± 0.05

^aData in the table are in the form of "Mean ± Standard deviation"

Table 2
Substance existed in urotropine wastewater before and after Fenton reaction

Before reaction		After reaction	
Substance	Concentration (mg/L)	Substance	Concentration (mg/L)
dimethylamine	232	ethyleneimine	34
2-Methyl-1-propanol	222		
isoamylalcohol	537	Dimethyl phenol	154
2-ethyl butanol	137		
hexamethylenetetramine	233	Dibutyl phthalate	22
Dimethyl phenol	150		

And then the esterification reaction occurred between alcoholic compounds and carboxylic acid compounds. Subsequently, most of the ester compounds was mineralized to CO_2 and H_2O . Finally, a small number of ester compounds could be found after the Fenton reaction.

The concentration of ammonia nitrogen and nitric nitrogen in urotropine wastewater increased with the increase

of the reaction time from 10 min to 2 h (Fig. 5). The carbon-nitrogen bond of the urotropine and dimethylamine was broken by the attack of hydroxyl radicals. Finally, most of the carbon-nitrogen compounds could be converted into ammonia nitrogen, and a less part of them was converted into nitric nitrogen and ethyleneimine. Oxidation-reduction reactions could further occur between nitric nitrogen and Fe^{2+} under acidic condition, which also could decrease the concentration of nitric nitrogen. In addition, due to the hydrolysis of ferrous and iron ions, the solution of pH was decreased, and urotropine could be also degraded back to formaldehyde and ammonium.

Continuous absorption spectrum in the range of UV-vis spectra were further monitored at different time period in Fenton process (Fig. 6). The spectral intensity was changed at 210 nm and 240–340 nm in ultraviolet region. The absorption peak located at 210 nm was found declining and then remained unchanged with the increase of reaction time. This could be attributed to the transition of dimethyl phenol. The absorption peak in the range of 240–340 nm displayed a sharp decrease with the increase of reaction time, and disappeared after the interval of 2 h. It means that alcohols and amines were destroyed more than benzene series because the energy values of the transitions are much lower than that of the transitions. This results have a good consistency with the tendency of Fig. 4 and Table 2.

3.3. Kinetic study

Zero-order, first-order and second-order reaction kinetics were used to research the urotropine wastewater degradation in Fenton oxidation process in the present study. The kinetic equations were presented as below [23]:

$$\text{Zero-order reaction kinetics: } \frac{dc}{dt} = -k_0 \quad (12)$$

$$\text{First-order reaction kinetics: } \frac{dc}{dt} = -k_1 C \quad (13)$$

$$\text{Second-order reaction kinetics: } \frac{dc}{dt} = -k_2 C^2 \quad (14)$$

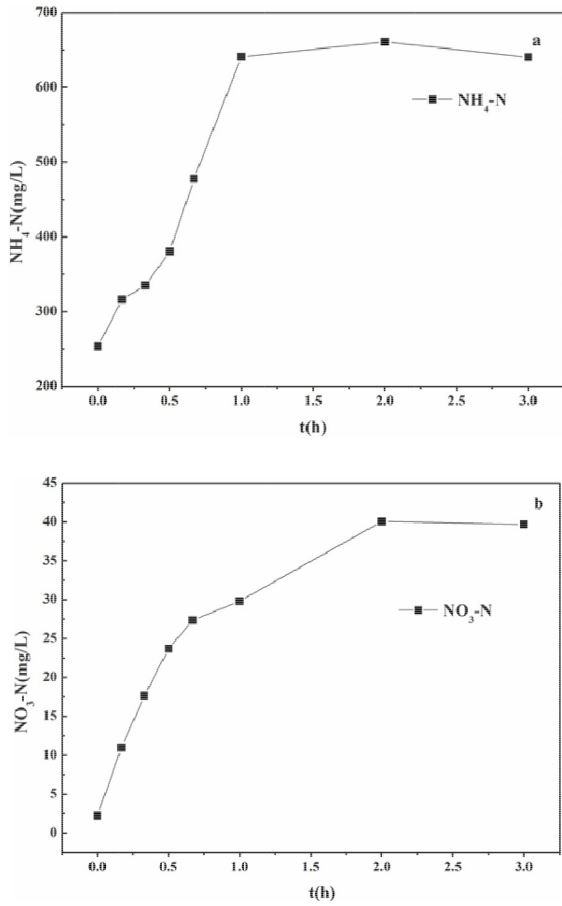


Fig. 5. Ammonia nitrogen and nitric nitrogen changes over time in the Fenton process.

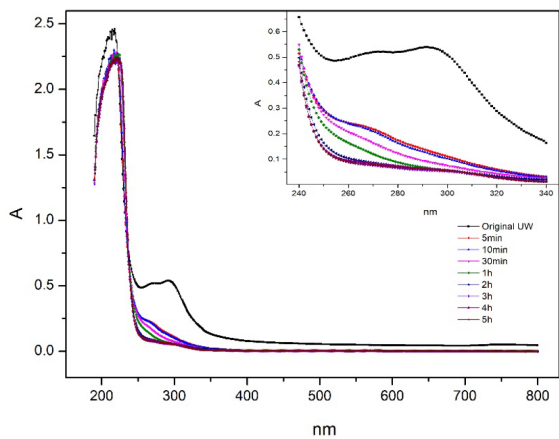


Fig. 6. Spectral changes in the UV-vis absorption spectra of urotropine wastewater in the Fenton process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio was 4, H_2O_2 concentration was 8.6 g/L, pH was 7, temperature was 45°C).

where C is the concentration of TOC; k_0 , k_1 and k_2 is the rate constants of zero-, first- and second-order reaction kinetics, respectively; t is the reaction time. The following equations could be obtained by integrating Eqs. (12)–(14) [23]:

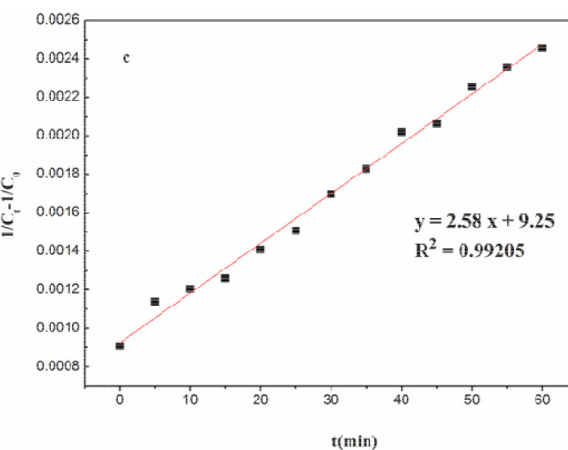
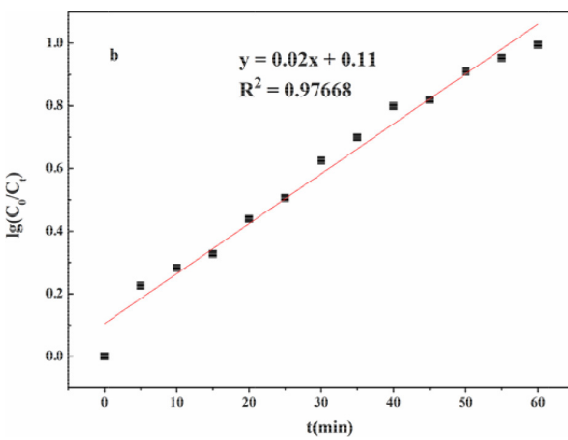
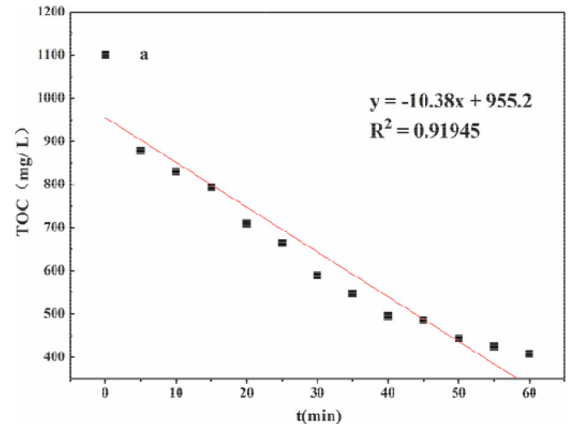


Fig. 7. Kinetics for the TOC removal of urotropine wastewater in the Fenton process (a is zero-order reaction kinetic model; b is first-order reaction kinetic model; c is second-order reaction kinetic model).

$$C_t = C_0 - k_0t \tag{15}$$

$$C_t = C_0 e^{-k_1t} \tag{16}$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2t \tag{17}$$

where C_t is the concentration of TOC at reaction time t .

Comparing the regression coefficients (R^2) obtained from Figs. 7a–c, it can be seen that the second-order reaction kinetic model could better explain the TOC removal in the Fenton oxidation process (Fig. 7c). It was better than the zero-order (Fig. 7a) and the first-order (Fig. 7b) reaction kinetics. The second-order reaction kinetics model reacted more to the relationship between the reactants. This may be attributed to due to the complex quality of the wastewater and various substances were formed during its degradation process. There is a definite connection between each substance, but not essentially a linear relationship only. The reaction kinetic for the COD removal of urotropine wastewater in Fenton oxidation was similar to that of the TOC removal.

4. Conclusions

The degradation of actual urotropine wastewater by Fenton oxidation was investigated. The experimental results showed that Fenton oxidation is suitable for the degradation of actual urotropine wastewater. The COD and TOC removal could be achieved 90.3% and 78.5% and accorded well with the second kinetic model. Current study provide an experimental and theoretical support for the treatment of actual urotropine wastewater.

Funding

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Conflicts of Interest

The authors declare no conflict of interest.

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Supporting information

1. Experimental data

Historical data of COD and TOC in *Optimization of system parameters* is given in the form of maximum, minimum and average values.

1.1. Effect of H_2O_2 and Fe^{2+} dosage

Table S1
The COD (mg/L) data of H_2O_2/Fe^{2+} dosage in effect of H_2O_2 and Fe^{2+} dosage

	2:1	3:1	4:1	5:1	6:1
Max	1032.9	845.1	829.4	963.5	979.0
Min	1013.7	813.8	735.5	932.4	947.9
Average	1023.3	829.4	782.5	947.9	963.5

Table S2
The TOC (mg/L) data of H_2O_2/Fe^{2+} dosage in effect of H_2O_2 and Fe^{2+} dosage

	2:1	3:1	4:1	5:1	6:1
Max	553.9	480.2	442.1	449.9	478.3
Min	550.2	477.4	440.4	449.7	465.7
Average	552.1	478.8	441.3	449.8	472.0

Table S3
The COD (mg/L) data of H_2O_2 dosage in effect of H_2O_2 and Fe^{2+} dosage

	4.3	5.8	7.2	8.6	9.4	10.1	10.8	11.5	12.3	13.7	15.1	16.8	18	19.5	25	28.8	32.4
Max	1740.2	1180.1	962.7	782.9	734.0	739.6	687.5	646.1	513.2	388.8	321.6	282.4	271.3	258.7	251.2	231.8	187.6
Min	1644.9	1071.4	916.1	689.1	734.0	723.8	654.5	593.9	512.8	388.8	318.5	275.6	260.7	253.3	240.3	220.2	186.0
Average	1692.5	1125.8	939.4	736.0	734.0	731.7	671.0	620.0	513.0	388.8	320.1	279.0	266.0	256.0	245.7	226.0	186.8

Table S4
The TOC (mg/L) data of H_2O_2 dosage in effect of H_2O_2 and Fe^{2+} dosage

	4.3	5.8	7.2	8.6	9.4	10.1	10.8	11.5	12.3	13.7	15.1	16.8	18	19.5	25	28.8	32.4
Max	878.4	675.7	550.9	442.9	433.3	399.6	367.5	362.0	323.6	310.8	279.3	270.6	252.8	237.9	222.8	210.6	218.6
Min	873.6	674.3	545.1	441.3	424.1	399.2	365.5	348.6	320.4	309.2	272.7	263.4	247.2	236.1	217.2	209.4	201.4
Average	876.0	675.0	548.0	442.1	428.7	399.4	366.5	355.3	322.0	310.0	276.0	267.0	250.0	237.0	220.0	210.0	210.0

1.2. Effect of solution pH

Table S5
The COD (mg/L) data in effect of solution pH

	1.6	2.5	3	3.5	4	4.5	5	6	7	7.5	8	8.5
Max	421.9	343.2	316.9	297.2	302.7	279.8	278.1	275.8	253.2	271.8	263.3	287.9
Min	418.9	320.8	306.1	296.8	285.3	276.2	269.9	258.2	240.8	262.2	258.7	274.1
Average	420.4	332.0	311.5	297.0	294.0	278.0	274.0	267.0	247.0	267.0	261.0	281.0

Table S6
The TOC (mg/L) data in effect of solution pH

	1.6	2.5	3	3.5	4	4.5	5	6	7	7.5	8	8.5
Max	330.8	292.8	277.7	262.9	258.9	258.6	254.6	241.5	230.4	242.9	245.3	247.0
Min	323.4	292.7	276.2	253.1	256.5	255.0	245.3	233.5	227.0	238.3	240.7	246.5
Average	327.1	292.8	277.0	258.0	257.7	256.8	250.0	237.5	228.7	240.6	243.0	246.8

1.2. Effect of solution pH

Table S7

The COD (mg/L) data in effect of reaction temperature

	25	35	40	45	50	55	65	75
Max	509.0	263.0	231.8	174.5	183.0	197.9	285.5	267.7
Min	502.8	251.0	216.2	165.5	171.0	183.9	260.2	260.2
Average	505.9	257.0	224.0	170.0	177.0	190.9	272.9	263.9

Table S8

The TOC (mg/L) data in effect of reaction temperature

	25	35	40	45	50	55	65	75
Max	352.3	241.9	232.6	214.7	205.6	233.7	234.0	241.5
Min	335.7	230.7	225.4	197.7	204.4	216.3	228.9	234.3
Average	344.0	236.3	229.0	206.2	205.0	225.0	231.5	237.9

1.3. Effect of reaction temperature

Table S9

The COD (mg/L) data in effect of reaction time

	0.17	0.33	0.5	0.67	1	2	2.5	3	3.5	4	5
Max	1543.1	1078.7	856.4	699.1	513.7	323.2	304.6	265.8	251.1	255.1	266.2
Min	1468.2	1026.2	814.0	611.8	500.8	302.1	290.0	249.1	242.0	246.9	248.4
Average	1505.6	1052.4	835.2	655.4	507.2	312.6	297.3	257.4	246.6	251.0	257.3

Table S10

The TOC (mg/L) data in effect of reaction time

	0.17	0.33	0.5	0.67	1	2	2.5	3	3.5	4	5
Max	811.0	693.5	591.5	513.0	354.2	266.1	265.3	246.5	237.3	232.1	234.7
Min	806.5	661.0	580.0	486.2	348.0	263.5	258.6	226.2	230.6	225.3	224.5
Average	808.8	677.3	585.8	499.6	351.1	264.8	261.9	236.3	233.9	228.7	229.6

1.4. Effect of reaction time

In order to ensure the purity of the sample, we calculated the amount of acid/alkaline used to regulate pH. Firstly, we calculated the dosage of 1+1 sulfuric acid when the pH was adjusted from 8.5 to 1.6.

Step 1, pH: 8.5–7

The hydrogen ion molar concentration of 1+1 sulfuric acid is 18.4 mg/L

$$\text{pH} = 8.5 \quad C(\text{H}^+) = 10^{-8.5} \text{ mg/L} \quad C(\text{OH}^-) = 10^{-5.5} \text{ mg/L}$$

Hydrogen ions supplied by 1+1 sulfuric acid are used to neutralize hydroxide ions in solution

$$\text{The equation is: } 18.4 * V_1 = 10^{-5.5} * 50 * 10^{-3}$$

Step 2, pH: 7–1.6

$$\text{pH} = 1.6 \quad C(\text{H}^+) = 10^{-1.6} \text{ mol/L}$$

Similarly, the hydrogen ions in the solution are provided by sulfuric acid.

$$\text{The equation is: } 10^{-1.6} * (V_2 + 50 * 10^{-3} + V_1) = 18.4 * V_2$$

$$V_{\text{H}_2\text{SO}_4} = 1000 * (V_1 + V_2) \approx 0.07 \text{ mL}$$

Then we calculated the dosage of 30% sodium hydroxide solution when the pH was adjusted from 1.6 to 9.

Step 1, pH: 1.6–7

$$\text{pH} = 1.6 \quad C(\text{H}^+) = 10^{-1.6} \text{ mol/L} \quad C(\text{OH}^-) = 10^{-12.4} \text{ mol/L}$$

The hydroxide ion molar concentration of 30% sodium hydroxide solution is 9.975 mol/L

Hydroxide ions supplied by 30% sodium hydroxide solution are used to neutralize hydrogen ions in solution

$$\text{The equation is: } 9.975 * V_1 = 10^{-1.6} * 50 * 10^{-3}$$

Step 2, pH: 7–9

$$\text{pH} = 9 \quad C(\text{H}^+) = 10^{-9} \text{ mol/L} \quad C(\text{OH}^-) = 10^{-5} \text{ mol/L}$$

Similarly, the hydroxide ions in the solution are provided by 30% sodium hydroxide solution

$$\text{The equation is: } 10^{-5} * (V_2 + 50 * 10^{-3} + V_1) = 9.975 * V_2$$

$$V_{\text{NaOH}} = 1000 * (V_1 + V_2) \approx 0.13 \text{ mL}$$

It is known from the calculation results, the amount of acid/alkaline used to regulate pH is negligible.

Table S11
Volume of hydrogen peroxide

Concentration of hydrogen peroxide (g/L)	Volume of hydrogen peroxide (mL)
4.3248	0.6
5.7664	0.8
7.208	1
8.6496	1.2
9.3704	1.3
10.0912	1.4
10.812	1.5
11.5328	1.6
12.2536	1.7
13.6952	1.9
15.1368	2.1
16.5784	2.3
18.02	2.5
19.4616	2.7
25.228	3.5
28.832	4
32.436	4.5

Even under the most extreme conditions (Volume of hydrogen peroxide is 4.5 mL), the additional of other chemicals is less than 10% of the actual volume of sample.

During the experiment, the volumes of Fenton reagent were recorded. In order to maintain the purity of sample, the Fenton reagent volume added have been counted on the issue of calculating processing efficiency. And the relationship between the concentration of hydrogen peroxide and the volume is given (See Table 11).

Even under the most extreme conditions (Volume of hydrogen peroxide is 4.5 mL), the additional of other chemicals is less than 10% of the actual volume of sample.