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Dyes and Pigments 76 (2008) 604–609

DYES and PIGMENTS

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Degradation of H-acid by combined photocatalysis and ozonation processes

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Received 12 September 2006; received in revised form 23 November 2006; accepted 23 November 2006
Available online 4 January 2007

Abstract

The combination of TiO_2-assisted photocatalysis and ozonation (TiO_2/UV/O_3) to degrade H-acid (1-amino-8-naphthol-3,6-disulfonic acid) was investigated. It was observed that a synergistic effect occurs in this process. The effects of O_3 dosage, initial solution pH and initial concentration of H-acid on the efficiency of the process were also studied. The results showed that COD (chemical oxygen demand) removal rate increased with increasing O_3 dosage whereas initial solution pH had little effect. An H-acid solution of 500–2000 mg/L could be efficiently degraded using TiO_2/UV/O_3. The intermediates formed in the early phase of degradation were studied using UV–vis absorption spectra, IC, HPLC–MS and IR; four possible intermediates, 1-amino-5,7,8-trihydroxynaphthalene-3,6-disulfonic acid, 1-amino-2,4,5,8-tetrahydroxynaphthalene-3,6-disulfonic acid, 8-hydroxy-1,2-naphthoquinone-3,6-disulfonic acid and 8-hydroxy-1,4-naphthoquinone-3,6-disulfonic acid, were proposed.

Keywords: H-acid; Degradation; Photocatalysis; Ozonation; Synergistic effect; Intermediates

1. Introduction

H-acid (1-amino-8-naphthol-3,6-disulfonic acid) is an important intermediate of synthetic dyes, such as direct and reactive dyes. Since the wastewater from the manufacturing process exhibits high COD and colour as well as low pH and BOD/COD (BOD, biochemical oxygen demand), H-acid wastewater offers many problems.

Of several advanced oxidation technologies (AOTs), photocatalysis has great potential for the removal of relatively recalcitrant organic pollutants from wastewaters. However, it was suggested [1,2] that only low concentration of H-acid could be efficiently degraded by photocatalysis and ozonation was found to be more efficient for high concentration recalcitrant organics [3,4]. Thus the combination of photocatalysis and ozonation (TiO_2/UV/O_3) offers the potential to efficiently remove these organics in a wide range of concentrations [5–7]. In recent work, although some intermediates from the degradation of H-acid produced by the photocatalytic oxidation process or ozonation were identified [2,8,9], the degradation pathway of the naphthalene ring remains unclear.

In this paper, the combined effect of TiO_2/UV/O_3 on the degradation of H-acid was studied and the effect of varying experimental parameters, such as ozone dosage, pH and H-acid concentration, on the efficiency of COD removal was also investigated. The initial oxidation pathway of H-acid in the process was elucidated, and the major intermediates were carefully investigated using UV–vis absorption spectra, HPLC–MS and IR.

2. Experimental

2.1. Reactor

The equipment for the photocatalytic oxidation and ozonation experiments comprised three parts namely the photocatalytic reactor (reactors a and b), the ozonizer system and the

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doi:10.1016/j.dyepig.2006.11.006

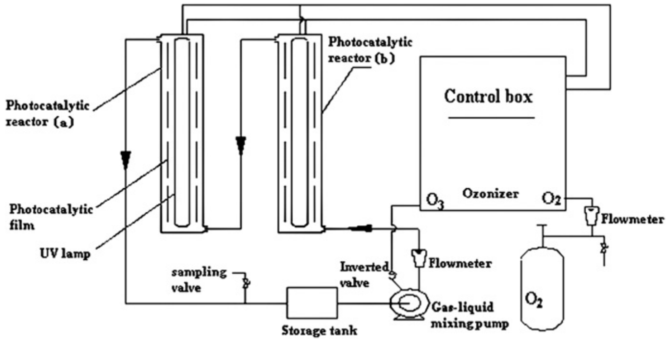

Fig. 1. Schematic drawing of the combination of photocatalysis and ozonation used for the degradation of H-acid.

aeration system, as shown in Fig. 1. Reactors a and b have the same size (800 mm long, 65 mm diameter, 2 L net volume) and structure; they were connected in series. Each photocatalytic reactor comprised a TiO_2 thin film supported on a glass surface and a coaxial UV source (a 39 W UV lamp with a characteristic wavelength of 254 nm) surrounded by a quartz thimble. For ozonation the TiO_2 thin film was removed and pure oxygen was used to generate ozone in the ozonizer. The ozone dose could be adjusted from 0 mg/min to 27.6 mg/min with an increase in O_2 flow rate from 0 mL/min to 600 mL/min. Ozone containing pure oxygen was continuously bubbled into the gas–liquid mixing pump which was used to circulate 5 L of H-acid solution and gas through the photocatalytic reactors and the storage tank.

2.2. Chemicals

Commercial grade H-acid was purified before use. Methanol, dibutylammonium and acetic acid used in HPLC analysis were purchased from Sigma (St. Louis, MO, USA). Water used in HPLC analysis was prepared using Milli-Q purification unit (Milli-Q Gradient A10, Millipore Inc. USA). Other chemicals used were of analytical grade.

2.3. Analytical methods

The amount of ozone generated was determined by iodometry. The pH value of the solution was measured using a PHS-25 (Shanghai REX Instrument Factory, China) pH meter. COD and BOD_5 were measured according to standard methods. TOC was measured using a total organic carbon analyzer (Shimadzu, Japan). The UV–vis spectra of the samples were recorded using a UV–vis spectrophotometer (V-560, JASCO, Japan) and the concentrations of sulfate ion, ammonium ion and nitrate ion were quantified by ion chromatography (IC, Shimadzu HIC-VP Super). The intermediates produced during the degradation of H-acid were monitored using HPLC–MS (Shimadzu HPLC-2010A system) equipped with a C-18 column. The mobile phase was composed of A (30% methanol + 70% water) and B (70% methanol + 30% water) containing 2.5 mmol/L dibutylammonium acetate, and the gradient elution consisted of 0%B–30%B over 10 min at a flow rate of 0.2 mL/min. MS was performed with electrospray ionization source (ESI), spray voltage 4.5 V and CID voltage 70 V, using scan mode.

3. Results and discussion

3.1. Synergistic effect of combined photocatalysis and ozonation

Oxidative degradation of H-acid solution was investigated using O_3, TiO_2/UV, UV/O_3, TiO_2/UV/O_3. As shown in Fig. 2, the removal rate of COD was lowest for the TiO_2/UV process without ozone, with only 7.37% COD removal after 4 h. For the other processes, in the presence of ozone, COD removal rate was $> 100\ \mathrm{mg\,L^{-1}\,h^{-1}}$. Moreover, when H-acid was decomposed using the combination of TiO_2/UV and O_3, COD removal rate was considerably higher than the sum of that using TiO_2/UV and O_3 alone, which implies a synergistic effect between photocatalysis and ozonation. The mechanism can be represented as follows.

$$O_3 + TiO_2 \rightarrow O_3(\mathrm{adsorb})TiO_2$$

$$TiO_2 + h\nu \rightarrow h^+ + e^-$$

$$O_3 + e^- \rightarrow O_3^-\bullet$$

$$H^+ + O_3^-\bullet \rightarrow HO_3\bullet$$

$$HO_3\bullet \rightarrow O_2 + \bullet OH$$

$$O_3 + h\nu(\lambda < 310\ \mathrm{nm}) \rightarrow \bullet O + O_2$$

$$\bullet O + H_2O \rightarrow 2OH$$

As a good electron acceptor, ozone can produce hydroxyl radicals, effectively preventing the recombination of electron/hole and prolong the lifetime of the hole. The hole generated by TiO_2/UV has the ability to oxidize many organic compounds by electron transfer. Ozone can be also directly

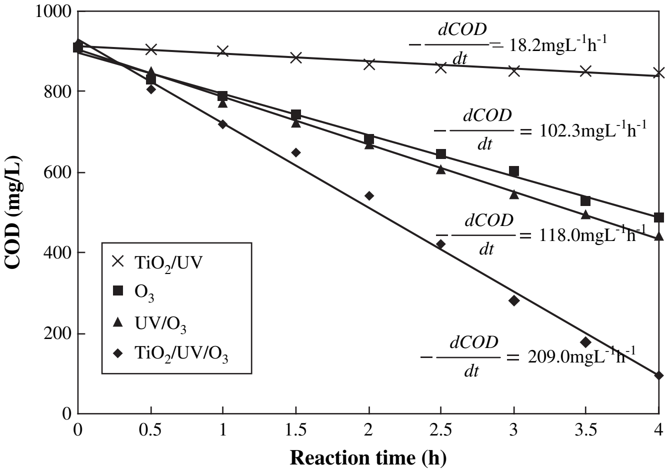

Fig. 2. Time courses of COD removal in different processes. [H-acid] = 1000 mg/L, O_3 dosage = 12.6 mg/min.

photoactivated using light at 254 nm and hydroxyl radicals generated. Thus the concentration of hydroxyl radicals increases. It is well known [7,10,11] that the hydroxyl radical is a powerful oxidant and can oxidize organic compounds completely. In conclusion, the TiO_2/UV/O_3 process is more efficient than the TiO_2/UV or O_3 process.

3.2. Effects of operating parameters

3.2.1. Effect of O_3 dosage

The data presented in Table 1 show that COD removal rate increased with increasing ozone dosage; however, the removal rate of COD increased slowly when the ozone dosage was increased from 21.2 mg/min to 27.6 mg/min.

3.2.2. Effect of initial pH

Since both the TiO_2/UV process and the O_3 process show pH dependence [1,2,9], it was important to examine the influence of pH on the degradation of H-acid in the combined TiO_2/UV/O_3 process. As presented in Table 2, the COD removal rate reached over 81.8% in the pH range of 3.4–11.7. Initial solution pH had little influence on the efficiency of the process, which was similar to the degradation process of 2,4-dichlorophenoxyacetic acid using TiO_2/UV/O_3 [5]. It was found that the pH value of the solution decreased at the beginning, then increased after 2–3 h, indicating that acidic compounds formed as a result of degradation and that some of these were further degraded.

3.2.3. Effect of initial concentration of H-acid

When the O_3 dosage was 12.6 mg/min, the COD removal rates at different initial concentrations of H-acid were similar, as shown in Table 3; finally, COD was reduced to below 100 mg/L. The results clearly indicate that H-acid at a concentration of 500–2000 mg/L can be efficiently degraded using TiO_2/UV/O_3.

3.3. Proposed degradation pathway

When H-acid was degraded using the combination of TiO_2/UV and O_3, the COD removal rate was higher than the sum of the two methods alone. This synergism could be due to the greater production of hydroxyl radicals by ozone over TiO_2. To further understand the initial oxidation process of H-acid, the intermediates were determined in the early phase of the degradation of H-acid.

Table 1
Effect of ozone dosage on the degradation of H-acid

Ozone dosage (mg/min)	7.0	9.3	12.6	21.2	27.6
Removal rate of COD (mg/L h)	144	160	208	274	282
R^2	0.9963	0.9998	0.9965	0.9973	0.9988

[H-acid] = 1000 mg/L, TiO_2/UV/O_3 process.

Table 2
Effect of initial pH on COD removal rate

Initial pH	pH values at the given reaction times (h)				COD removal at 4 h (%)
	1	2	3	4	
3.4	3.0	2.7	3.0	4.5	89.6
7.4	4.3	3.2	3.3	5.0	87.8
11.7	7.6	6.9	6.3	6.3	81.8

[H-acid] = 1000 mg/L, O_3 dosage = 12.6 mg/min, TiO_2/UV/O_3 process.

3.3.1. The changes of COD and TOC

The intermediate products were analyzed by the changes of COD and TOC over 60 min, as shown in Fig. 3. The removal rate of COD was faster than that of TOC. In particular, after 10 min of reaction, 9.6% COD was removed, but the TOC did not reduce, indicating that H-acid was only partially mineralized and its oxidation products accumulated at the initial stage of oxidation.

3.3.2. Sulfate and ammonium ions produced

There are two sulfonic groups, one amino group and one hydroxy group in the H-acid. During oxidation, $-SO_3^-$ is, theoretically, readily released from the naphthalene ring and oxidized to SO_4^{2-}. The $-NH_2$ group may be released from the naphthalene ring and oxidized to NH_4^+, NO_2^- or NO_3^-. Generally NO_2^- is unstable and easily oxidized to NO_3^-. In the TiO_2/UV/O_3 process, the concentration of NH_4^+ increased more quickly than that of SO_4^{2-} at the beginning of the reaction and then remained stable for 20 min, as shown in Fig. 4. Hence we concluded that some $-NH_2$ was removed from the naphthalene ring in the initial 10 min of reaction. Moreover, a number of compounds without $-NH_2$ were also observed in HPLC–MS. At the end of the process, the concentration of SO_4^{2-} was higher than that of NH_4^+, but some $-SO_3^-$ was not converted into SO_4^{2-} and was still connected to the naphthalene ring; NO_3^- ions were not detected during the reaction.

3.3.3. UV–vis spectra

It was found that the colour of the aqueous H-acid solution firstly deepened and then gradually became paler during the early stage of the reaction. The UV–vis spectra (Fig. 5) showed that the absorption peaks of H-acid at wavelengths 235 nm and 358 nm gradually declined. Meanwhile, a new peak at 520 nm appeared which gradually disappeared after 60 min. This indicated that some intermediate products formed and then were degraded.

Table 3
Effect of initial concentration of H-acid on COD removal rate

Initial concentration of H-acid (mg/L)	2000	1400	1000	800	500
Removal rate of COD (mg/L h)	193.9	208.6	209.0	199.9	190.7
R^2	0.9951	0.9970	0.9944	0.9921	0.9974

O_3 dosage = 12.6 mg/min, TiO_2/UV/O_3 process.

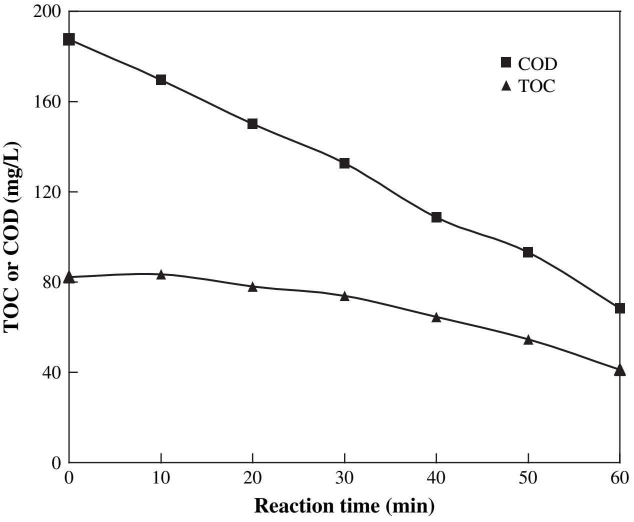

Fig. 3. COD and TOC removal in reaction process. [H-acid] = 200 mg/L, O_3 dosage = 12.6 mg/min, TiO_2/UV/O_3 process.

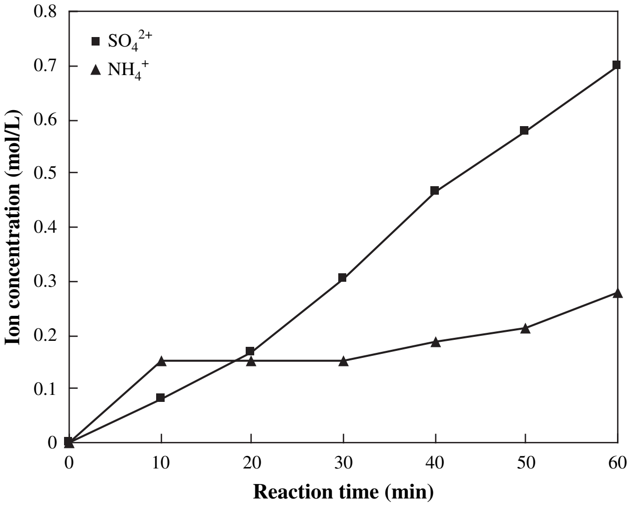

Fig. 4. Changes of ions concentration in reaction process. [H-acid] = 200 mg/L, O_3 dosage = 12.6 mg/min, TiO_2/UV/O_3 process.

3.3.4. IR spectra

From the above analysis, we could conclude that the concentration of the intermediates was greatest after 10 min. Therefore one sample was taken at that time, concentrated by evaporation and then analyzed using IR, as shown in Fig. 6(b). Comparing the IR spectra of H-acid (Fig. 6(a)) and its intermediates (Fig. 6(b)), it is evident that the characteristic C═O stretching vibration at 1646 cm^{-1} emerged in the spectrum of the intermediates, while the characteristic peaks for $-SO_3^-$ (1046 cm^{-1} and 1217 cm^{-1}), $-NH_2$ (3208 cm^{-1}) and −OH (3422 cm^{-1}) were still present. The characteristic peak for $-NO_2$ was not detected. This was different from the intermediate produced in the degradation process of H-acid using ferrous-hydrogen peroxide, although the colour of its solution was also initially deeper and then gradually became lighter [12]. The intermediates containing $-NH_2$, −OH, $-SO_3^-$ and C═O were proposed in TiO_2/UV/O_3 process.

3.3.5. HPLC−MS

The sample taken at 10 min was further identified using HPLC−MS, as shown in Table 4. Two oxidation products with *m*/*z* 350 and *m*/*z* 366 corresponded to the peak at 3.044 min in HPLC (data not shown), owing to incomplete separation. Collision-induced dissociation was used to further analyze the structure of the two compounds. Two fragmented ions, *m*/*z* 332 and *m*/*z* 268, were observed. It is reasonable to assume that the fragment ion *m*/*z* 332 generated from *m*/*z* 350 ($[M-H_2O-H]^-$) and *m*/*z* 366 ($[M-2OH-H]^-$), and the fragment ion *m*/*z* 268 generated from *m*/*z* 366 ($[M-SO_3H-OH-H]^-$).

It was reported that autoxidation of *o*-hydroxyaminonaphthalenes and *p*-hydroxyaminonaphthalenes would occur if they were exposed to air [13]. Thus, the hydroxy group in the structure of the intermediate with *m*/*z* 350 should not lie in the *o*-position or *p*-position of the amino group. Finally we could conclude that hydroxy groups substituted the hydrogen atoms in the naphthalene ring during the reaction and the intermediate with *m*/*z* 350 was 1-amino-5,7,8-trihydroxynaphthalene-3,6-disulfonic acid, whose characteristic UV−vis peak was 520 nm. The other intermediate with *m*/*z* 366 was the unstable 1-amino-2,4,5,8-tetrahydroxynaphthalene-3,6-disulfonic acid.

Table 4
Result of HPLC−MS

Compound (molecular weight)	Molecular formula	RT[a] (min)	λ_{max} (nm)	MS	
				m/*z*	Fragment ions
H-acid (319)	$C_{10}H_9O_7NS_2$	3.100	235	318	$[M-H]^-$
			358		
1-Amino-5,7,8-tri-hydroxynaphthalene-3,6-disulfonic acid (351)	$C_{10}H_9O_9NS_2$	3.044	520	350	$[M-H]^-$
			302	332	$[M-H_2O-H]^-$[b]
1-Amino-2,4,5,8-tetrahydroxynaphthalene-3,6-disulfonic acid (367)	$C_{10}H_9O_{10}NS_2$	3.044	520	366	$[M-H]^-$
			302	332	$[M-2OH-H]^-$[b]
				268	$[M-SO_3H-OH-H]^-$[b]
8-Hydroxy-1,2-naphthoquinone-3,6-disulfonic acid (334)	$C_{10}H_6O_9S_2$	3.513	435	333	$[M-H]^-$
8-Hydroxy-1,4-naphthoquinone-3,6-disulfonic acid (334)	$C_{10}H_6O_9S_2$	4.076	420	333	$[M-H]^-$

[a] RT − retention time in HPLC.

[b] Fragmentor voltage is 70 V, the others were 0 V.

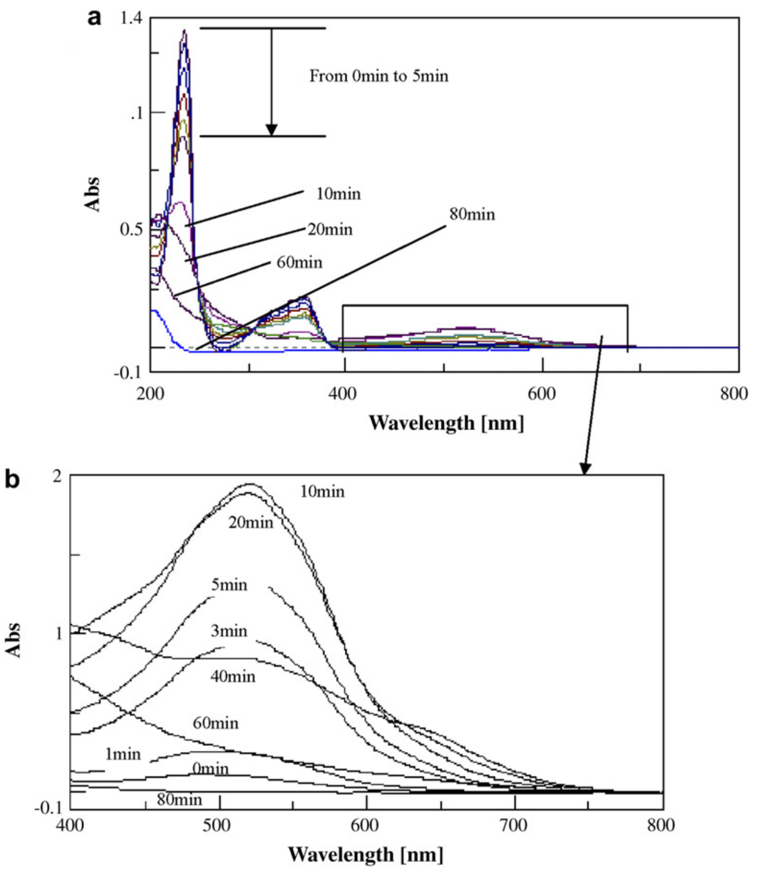

Fig. 5. UV–vis spectra of H-acid degradation in $TiO_2/UV/O_3$ process. (a) Samples taken at different times were diluted to 1/20 using water before measuring, (b) samples were directly measured without diluting. [H-acid] = 200 mg/L, O_3 dosage = 12.6 mg/min.

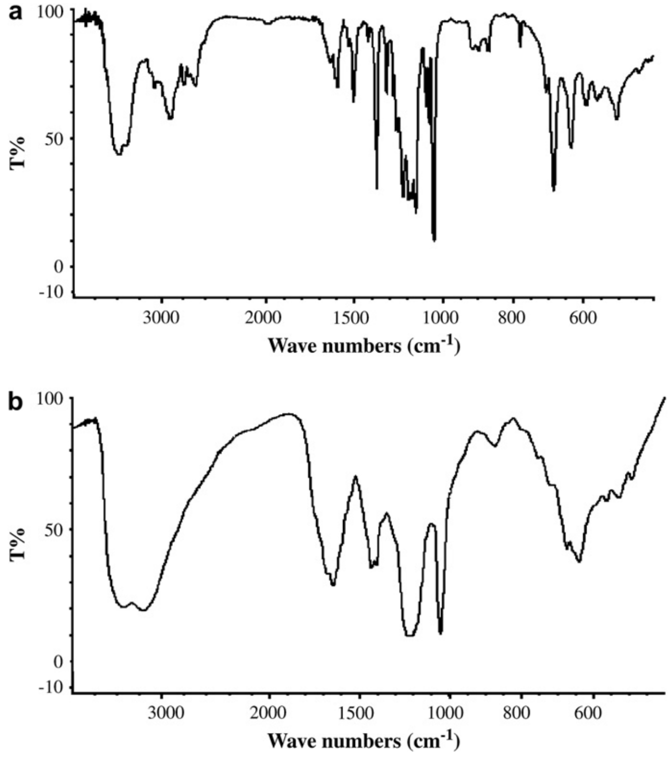

Fig. 6. Infrared spectra of pure H-acid (a) and its oxidation products (b).

The peaks of 3.513 min and 4.076 min in HPLC spectrum corresponded to the same *m*/*z* 333 in mass spectra (see Table 3). It was concluded that these two intermediates were two isomers, 8-hydroxy-1,2-naphthoquinone-3,6-disulfonic acid and 8-hydroxy-1,4-naphthoquinone-3,6-disulfonic acid.

When the colour of the solution became paler during the degradation of H-acid, another sample was taken and analyzed using HPLC–MS. As the compounds with *m*/*z* 195 corresponded to the two peaks (RT 3.223 min and RT 4.676 min) in the HPLC spectrum (data not shown), it is proposed that the compounds were isomers, whose structures need to be further identified.

4. Conclusions

The present study demonstrated that COD removal rate increased by 73% when H-acid was degraded using a combination of TiO_2/UV and O_3, showing that a synergistic effect existed in this process. Moreover, H-acid at a concentration of 500–2000 mg/L could be decomposed rapidly using $TiO_2/UV/O_3$. COD removal rate clearly increased with the increase of ozone dosage, but the pH value had less effect on it in this process.

By identifying the degradation intermediates of H-acid, we concluded that some hydroxyl radicals firstly substitute a hydrogen atom or an amino group on the naphthalene ring during degradation with $TiO_2/UV/O_3$. Thus some intermediates containing three or four hydroxy groups were formed and these were further oxidized to naphthoquinone. Among them, the four major compounds identified were 1-amino-5,7,8-trihydroxynaphthalene-3,6-disulfonic acid, 1-amino-2,4,5,8-tetrahydroxynaphthalene-3,6-disulfonic acid, 8-hydroxy-1,2-naphthoquinone-3,6-disulfonic acid and 8-hydroxy-1,4-naphthoquinone-3,6-disulfonic acid. Accordingly, the oxidation process of H-acid by hydroxyl radicals in the early phase of the $TiO_2/UV/O_3$ process was elucidated in detail. We conclude that the ring structure with hydroxyl in H-acid was initially destroyed and then benzene rings were degraded to organic acids, CO_2 and H_2O.

Further work is needed to separate the four possible intermediates and the compounds with *m*/*z* 195.

Appendix A. Supplementary information

Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.dyepig.2006.11.006.

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