Title: Mechanism and kinetics of H-acid degradation in TiO2/O3/UV process

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Abstract: The mechanism and kinetics of synergetic effect in TiO2/O3/UV process on H-acid degradation were investigated. The experimental results showed that H-acid removal rate of TiO2/O3/UV process was the highest among TiO2/UV, O3/UV and TiO2/O3/UV processes. Investigation of reactions with suitable active species scavengers confirmed that H-acid was mainly oxidized by ozone and holes on TiO2 in the TiO2/O3/UV process. The recombination between holes and electrons in TiO2 reduced in the presence of ozone, as indicated by fluorescence emission spectra. Moreover, the intermediates generated during H-acid oxidation in various processes were analyzed by LC/MSD trap. It is proposed that H-acid was oxidized to polyhydroxy aromatics, benzene carboxylic acids and quinoids in the first step. Then, saturated aliphatics carboxylic acids formed and were mineralized to inorganic compounds through the Photo-Kolbe reaction. Finally, a kinetic study on TiO2/UV, O3/UV and TiO2/O3/UV processes was conducted and we confirmed that both ozonation and photocatalytic activity were improved in TiO2/O3/UV process because of the synergetic effect.
• The synergetic effect of TiO$_2$/O$_3$/UV process on H-acid destruction is confirmed.

• H-acid is mainly decomposed by ozone and holes in TiO$_2$/O$_3$/UV process.

• Ozone will restrain the recombination between holes and excited electrons in TiO$_2$.

• The reaction pathway of H-acid in TiO$_2$/O$_3$/UV process is proposed.

• The kinetics of H-acid degradation is investigated.
Mechanism and kinetics of H-acid degradation in TiO$_2$/O$_3$/UV process

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Abstract

The mechanism and kinetics of synergetic effect in TiO$_2$/O$_3$/UV process on H-acid degradation were investigated. The experimental results showed that H-acid removal rate of TiO$_2$/O$_3$/UV process was the highest among TiO$_2$/UV, O$_3$/UV and TiO$_2$/O$_3$/UV processes. Investigation of reactions with suitable active species scavengers confirmed that H-acid was mainly oxidized by ozone and holes on TiO$_2$ in the TiO$_2$/O$_3$/UV process. The recombination between holes and electrons in TiO$_2$ reduced in the presence of ozone, as indicated by fluorescence emission spectra. Moreover, the intermediates generated during H-acid oxidation in various processes were analyzed by LC/MSD trap. It is proposed that H-acid was oxidized to polyhydroxy aromatics, benzene carboxylic acids and quinoids in the first step. Then, saturated aliphatics carboxylic acids formed and were mineralized to inorganic compounds through the Photo-Kolbe reaction. Finally, a kinetic study on TiO$_2$/UV, O$_3$/UV and TiO$_2$/O$_3$/UV processes was conducted and we confirmed that both ozonation and photocatalytic activity were improved in TiO$_2$/O$_3$/UV process because of the synergetic effect.

Keywords: H-acid; TiO$_2$/O$_3$/UV Process; Degradation Mechanism; Kinetics
1. Introduction

Dyes have been widely used in kinds of areas, especially textile industry. The demand for dyes is continuously increasing with the development of synthetic fibers industry. As a result, ecological problems become more and more serious, threatening the living environment of human beings. H-acid (1-Amino-8-naphthol-3, 6-disulfonic acid) is a typical dye that causes the environmental problems. Wastewater containing H-acid from different manufacturing processes often presents color and low pH as well as high chemical oxygen demand (COD).

H-acid is highly soluble in water for the presence of sulfonic acid groups in the molecule. What’s more, the presence of a fused ring system in the H-acid molecule makes it difficult to be treated by any physiochemical method [1]. Also, it exhibits high COD and is toxic to microorganisms [2]. Therefore, conventional methods for removing pollutants such as biological, physical and chemical treatments are not effective to H-acid [3]. Currently, wastewater containing H-acid, as one of the most recalcitrant pollutants, is generally treated by evaporation-incineration technology [4]. Nevertheless, this technology is very unfavorable for the high cost and residues.

Advanced oxidation processes (AOPs), which provide the “in situ” production of hydroxyl radicals under mild experimental conditions, have attained great attention these years [5]. Among the AOPs, heterogeneous photocatalysis taking advantage of titanium dioxide (TiO$_2$) is a promising way to remove relatively recalcitrant organic pollutants from wastewaters [6]. The multi-faceted functional properties of TiO$_2$, such as its chemical, thermal stability and strong mechanical properties, have promoted its wide application in water treatment [7]. However, it is suggested that TiO$_2$ can only degrade pollutants at a low rate [8]. On the other hand, the elimination of pollutants in water by ozonation is also a well-known water treatment technique. Ozone, a strong oxidant, is efficient for
purifying contaminated wastewater, even though the concentration of pollutants is very high [9].

Nevertheless, the decrease in COD after ozonation is rather low. Therefore, combining photocatalysis with ozonation should be a promising way to treat recalcitrant organic compounds. In this case, a synergistic effect contributes to a rapid and thorough decomposition of organic compounds into carbon dioxide, water, or inorganic ions [10, 11]. In this process, different reactive species are generated abundantly in the following ways: direct photolysis of ozone, hydrogen peroxide (formed in the process) photolysis, positive holes oxidation and electron capturing ozonation. These reactive species lead to a high removal rate of organic pollutant [12, 13].

In a recent work, the synergetic effect in TiO$_2$/O$_3$/UV process on the degradation of H-acid was studied. The effect of experimental parameters, such as ozone dosage, pH and H-acid concentration, on the efficiency of COD removal was also investigated [6]. Parts of intermediates were analyzed by UV-vis absorption spectra, HPLC-MS and IR. However, the degradation pathway of H-acid and the mechanism of the reactions remain unclear. Therefore, this work aims to clarify the mechanism and reaction pathway of H-acid decomposition in TiO$_2$/UV/O$_3$ process. The intermediates and main oxidants in the process were also investigated. Additionally, the kinetics of the reaction was addressed.

2. Experimental

2.1 Chemicals

Analytical grade H-acid was obtained from Aladdin. A commercial TiO$_2$ Degussa P25, containing 70% anatase and 30% rutile, was used as catalyst. The average particle size of P25 is 30 nm and its BET surface area is 50±15 m$^2$ g$^{-1}$. High-performance liquid chromatography (HPLC) grade methanol, dibutylammonium and acid solvent was used for collecting HPLC data. Other chemicals used were of
analytical grade.

2.2 Experimental set-up for H-acid decomposition

Experiments were carried out in 0.5 L capacity tubular borosilicate glass photoreactor (100 mm long, 80 mm diameter). The reactor consists of necessary accessories (inlets for stirring, sampling, bubbling the gas field in the ozonation experiments from the bottom) for the development of different processes: O$_3$/UV, TiO$_2$/UV, and TiO$_2$/O$_3$/UV. The reactor walls are covered with aluminum foil to avoid release of radiation. About 0.4 L of H-acid solution with a concentration of 200 mg L$^{-1}$ was charged in the reactor for experiments. The ozone air stream (1.5 L/min) from the ozone generator (HY-002, Jiahuan Technology, China) was continually directed into the reactor with the production of 10 mg/L. The reactor was illuminated by a 20 W UV lamp with maximum light intensity output at 254 nm. The lamp was immersed into the solution. The amount of TiO$_2$ used in TiO$_2$/UV and TiO$_2$/O$_3$/UV processes was 1.0 g L$^{-1}$, individually.

Steadily, samples were withdrawn from the reactor for analysis of H-acid concentration, H$_2$O$_2$ concentration and intermediate products in different intervals, according to the requirements of experiments. Prior to the analysis, the solid was removed from samples by a filter (0.22 μm).

2.3 Analytical methods

H-acid was analyzed by high-performance liquid chromatography (Agilent 1100, American), equipped with Kromasil-C18 column. The intermediates produced during the degradation of H-acid were monitored using LC/MSD trap (LC-XTC-Trap-XCT) equipped with a Zorbax Eclipse XDB-C18 column. The mobile phase was composed of A (30% methanol+ 70% water) and B (70% methanol +
30% water) containing 2.0 mmol/L dibutylammonium acetate. The gradient elution consisted of 0%B-30%B over 10 min at a flow rate of 0.2 ml/min. From standard solutions, analyses were repeated to establish the precision of the method that resulted to be ±2% while accuracy was 1.5%. Mass spectrometry (MS) was performed with an electrospray ionization source (ESI), dry temperature 250 °C, APCI temperature n/a, HV capillary 3500 V, capillary exit -117.3 V, using scan mode from 50 m/z to 700 m/z. Fluorescence emission spectra were recorded on a Shimadzu RF-5301 type fluorescence spectrophotometer over a wavelength range of 280—500 nm. Hydrogen peroxide concentration was determined through the cobalt-bicarbonate method [14]. Detection limits and accuracy of this method were 0.5 μmol/L⁻¹ and 3%.

3. Results and discussion

3.1 Removal of H-acid

Degradation of H-acid was investigated in O₃/UV, TiO₂/UV, and TiO₂/O₃/UV processes. The evolution of H-acid concentration in different processes was compared, as shown in Fig. 1. The removal rate of H-acid in TiO₂/UV process was the lowest. After reacting for 15 min, only about 15% of H-acid was removed. At the end of the experiment, namely after reacting for 2 h, 20% of H-acid remained in the solution. Nevertheless, H-acid was degraded efficiently in both O₃/UV and TiO₂/O₃/UV processes and 98% of H-acid was removed in 20 min. It’s reported that unsaturated naphthalene nucleus with an electron-donating functional group—the amine group, react fairly fast with oxidative species [15]. Therefore, H-acid could be easily converted to other kinds of organics in O₃/UV process. Interestingly, this high reaction rate further increased when TiO₂/O₃/UV process was applied. The removal rate of H-acid was considerably higher than the sum of that using O₃/UV and
TiO$_2$/UV processes alone, which implies a synergistic effect between photocatalysis and ozonation. In a previous work [6], the synergistic effect is also confirmed in mineralizing the pollutants through COD analysis. Besides the reactions in O$_3$/UV and TiO$_2$/UV processes, the following reactions (Eq. (1)-(10)) should be also taken into consideration in TiO$_2$/O$_3$/UV process [16, 17]. In TiO$_2$/O$_3$/UV process, ozone is a stronger oxidant than oxygen and presents better potential to capture excited electrons from the conduction band of TiO$_2$ (Eq. (1)). Moreover, ozone can accept photogenerated electrons by reacting with superoxide radical anions to form ozonide radical anion (Eq. (2) and (3)). Then, the ozonide radical anion facilitates the hydroxyl radical generation in the next steps (Eq. (4)-(6)). The presence of reactive species, such as O$_2$ $^-$ and OH$, can degrade H-acid efficiently and therefore leads to a higher reaction rate than that in O$_3$/UV process.

\[ e^- + O_3 \rightarrow O_3^{**} \quad (1) \]

\[ e^- + O_2 \rightarrow O_2^{**} \quad (2) \]

\[ O_2^{**} + O_3 \rightarrow O_2 + O_3^{**} \quad (3) \]

\[ H^+ + O_3^{**} \rightarrow HO_3^{**} \quad (4) \]

\[ HO_3^{**} \rightarrow O_2 + OH^+ \quad (5) \]

\[ O_3^{**} + H_2O \rightarrow OH^+ + OH^- + O_2 \quad (6) \]

\[ TiO_2 + h\nu \rightarrow e^- + h^+ \quad (7) \]

\[ h^+ + OH^- \rightarrow OH^+ \quad (8) \]

\[ H_2O_2 + H^+ + O_2^{**} \rightarrow OH^+ + H_2O + O_2 \quad (9) \]

\[ H_2O_2 + e^- \rightarrow OH^+ + OH^- \quad (10) \]

Moreover, the photocatalytic activity of TiO$_2$ in ozone environment is improved. Since photogenerated electrons can be trapped by ozone efficiently or transferred to ozone through oxygen
indirectly, the recombination between holes and electrons is restrained. Therefore, degradation of H-acid is improved as more holes and hydroxyl are generated (Eq. (7) and (8)).

3.2 Evolution of H$_2$O$_2$ concentration

It is well-known that hydroxyl radical, which is a powerful and non-selective oxidant to organics, is a crucial species for mineralizing organic pollutants. Except for the reactions presented in Eq. (5) and (8), it is reported that hydrogen peroxide could raise the concentration of hydroxyl radical in aqueous solution through the Haber-Weiss mechanism (Eq. (9)) or photocatalytic reduction of H$_2$O$_2$ (Eq. (10)) [18]. Therefore, the concentration of H$_2$O$_2$ plays an important role in eliminating pollutants in aqueous solution. Here, the evolution of H$_2$O$_2$ concentration was investigated in order to clarify the mechanism of reactions.

The variation of H$_2$O$_2$ concentration over reaction time in O$_3$/UV, TiO$_2$/UV, and TiO$_2$/O$_3$/UV processes is shown in Fig. 2. The concentration of H$_2$O$_2$ increased at first and then decreased to a relative plateau value after reached a maximum value for all of the three processes. Referred to Fig. 1, it can be concluded that the H$_2$O$_2$ concentration decreased to its plateau value at the moment when H-acid has been just removed in both O$_3$/UV and TiO$_2$/O$_3$/UV processes. As H-acid could facilitate the generation of H$_2$O$_2$, high H-acid concentration is the main reason for the increment of H$_2$O$_2$ concentration in the first 5 min. Then, the H$_2$O$_2$ concentration began to decrease mainly because it was consumed by ozone and the intermediate products cannot form H$_2$O$_2$ as H-acid. In the ozone involved processes, H$_2$O$_2$ is generated in two ways: direct ozonation of unsaturated bonds through Criegee Mechanism (see the discussion in subsection 3.5) and free radical recombination. The latter one is unfavorable and minor [18]. In the absence of ozone, H$_2$O$_2$ is proposed to form in the reactions between hydroxyl radicals or holes and aromatic rings in organics [19]. In TiO$_2$/UV process, the H$_2$O$_2$
concentration took a longer time to reach a relative small maximum value compared with other process. What’s more, the difference between the maximum value and the plateau value was small. It should owe to the existence of H-acid in the solution as the source of H₂O₂ even after reacting for 120 min. In the previous work of FJ Beltran [12], the plateau value is only about 1.0 × 10⁻⁵ molL⁻¹ in the ozone involved processes. However, in our work, this value is four times larger, namely 4.0 × 10⁻⁵ molL⁻¹, indicating that ozonation is important in the whole TiO₂/O₃/UV process.

3.3 Effect of inhibitors on H-acid removal

As discussed in subsection 3.1 and the previous work reported by FJ Beltran [20], the following reactions on H-acid degradation should be considered in TiO₂/O₃/UV process:

Oxidation with positive holes:

H-acid + h⁺ → Products  (11)

Oxidation with hydroxyl radicals:

H-acid + OH⁻ → Products  (12)

Oxidation with the superoxide ion radical:

H-acid + O₂⁻ → Products  (13)

Ozone reaction:

H-acid + O₃ → Products  (14)

Direct photolysis:

H-acid → Products  (15)

The ozonation should exist in the process according to Fig. 1 and the discussion in subsection 3.2. The effect of photolysis can be neglected in this case because TiO₂ suspension with a concentration
over 0.3 gL\(^{-1}\) presents a high extinction coefficient [21]. However, the effect of other reactive species, such as hydroxyl radicals, holes on the surface of photocatalyst and superoxide, is still unclear. Therefore, iodide ion, t-butanol and benzoquinone which are usually used as inhibitors for holes, hydroxyl radicals and superoxide ion radical, respectively, were utilized to elucidate their role in the degradation of H-acid.

### 3.3.1 Effect of iodide ion

Iodide ion can react with the positive holes on valence band as reported by R. Palominos through the reactions shown below (Eq. (16)-(18)) [22]. Thus, if iodide ions are added to solution, the reactions in Eq. (8), (11) and (12) would be restrained. Figure 3 shows the concentration of H-acid over reaction time in the presence of iodide ions in TiO\(_2\)/UV process. After reaction for 120 min, only 15% of H-acid was degraded in the presence of iodide ions, while 82% of H-acid was removed in the case without adding this kind of ion. It can be deduced that the holes play an essential role in the oxidation of H-acid. However, it is still not clear whether the holes directly oxidized the H-acid through the reaction in Eq. (11) or indirectly oxidized it by the hydroxyl radicals generated through the reactions in Eq. (8) and (12). Therefore, the degradation of H-acid in TiO\(_2\)/O\(_3\)/UV process with hydroxyl radical scavenger should be investigated. It should be noticed that the effect of iodide ion was not confirmed in TiO\(_2\)/O\(_3\)/UV process, since iodide ions are not selective for holes when ozone presents.

\[
h^+ + I^- \rightarrow I^- \quad (16)
\]

\[
I^+ + I^- \rightarrow I_2^{*-} \quad (17)
\]

\[
h^+ + I_2^{*-} \rightarrow I_2 \quad (18)
\]
3.3.2 Effect of t-Butanol

The t-Butanol readily reacts with hydroxyl radical (\(k = 6 \times 10^9 \text{M}^{-1}\text{s}^{-1}\)), but it is practically inert against ozone (\(k = 1 \times 10^3 \text{M}^{-1}\text{s}^{-1}\)) [23]. Therefore, it is an appropriate hydroxyl radical scavenger in ozone involved systems. In our work, t-butanol was employed to investigate the effect of hydroxyl radicals on H-acid degradation in TiO₂/O₃/UV process. As shown in Fig. 4, the presence of t-butanol didn’t inhibit the removal rate of H-acid. Inversely, it slightly improved the reaction rate in the first 4 min and then the H-acid concentration reached a steady concentration in the later 6 min. There are two ways to explain the opposing effect of t-butanol. On one hand, the presence of t-butanol reduces both surface tension and viscosity of aqueous solutions and this effect increases the ozone mass transfer rate in gas-liquid [24]. On the other hand, this anomalous result confirms that the removal of H-acid is mainly due to the holes oxidation (Eq. (11)) and direct ozone reactions (Eq. (14)) but not the hydroxyl radical oxidation (Eq. (12)). However, when the hydroxyl radical was scavenged, the intermediates generated by holes oxidation and ozonation accumulated easily in the active sites on the surface of TiO₂, hindering the further reactions. That’s why the H-acid concentration was almost constant after reaction for 4 min.

3.3.3 Effect of benzoquinone

Benzoquinone is a substance usually employed as the scavenger of superoxide ion radical. It presents ability to trap superoxide anions by a simple electron transfer mechanism (Eq. (19)) [22]. Therefore, the existence of benzoquinone will affect the reactions in Eq. (3), (6) and (13). It is shown in Fig. 4 that the addition of Benzoquinone partially inhibited the H-acid degradation. Since the hydroxyl radical has little effect on the reaction rate of H-acid degradation, the reactions in Eq. (3) and (6) should have little
influence on the compressed rate. Therefore, the reaction in Eq. (13) contributed to the degradation of
H-acid, even though its influence was relatively small. This small contribution could attribute to the
fact that the superoxide radicals prefer to attack aromatic rings with a low electronic density [25], while
the naphthalene nucleus in H-acid is activated by amine group and hydroxyl groups. Also, it should be
noticed that the amount of superoxide ion radical was small in the reaction system because it is easy to
be consumed by the reaction in Eq. (3).

\[
\text{Benzoquinone} + \text{O}_2^{\cdot-} \rightarrow \text{Benzoquinone}^{\cdot-} + \text{O}_2 \quad (19)
\]

According to the preceding comments based on experimental results, H-acid should be mainly
degraded by the reactions in Eq. (11) and (14) in TiO$_2$/O$_3$/UV process.

3.4 Fluorescence emission spectra

According to literature [26], electron spin resonance (ESR) experiments in gas-solid regime has been
conducted on TiO$_2$ samples in the presence of O$_3$ at 77 K and the reaction in Eq. (1) was confirmed.
However, capturing electrons by ozone from the conduction band of TiO$_2$ under ultraviolet light in
aqueous solution has not been confirmed at present. In our work, the reaction in Eq. (1) was verified by
studying the fluorescence emission spectra of TiO$_2$ suspension.

Fluorescence emission spectrum is a practicable tool to give an insight into the optical and
photochemical properties of samples. In the presence of suitable light source, electrons and holes are
generated in the photocatalysts. Then, the recombination of electrons and holes releases energy in the
form of fluorescence emission [27].

Using an ultraviolet light with a 260 nm wavelength as the excitation source, the fluorescence
emission spectra of TiO$_2$ suspension in the presence of O$_3$ are achieved as shown in Fig. 5. It can be
seen that the samples presented a strong emission peak at about 370 nm. It is clear that the intensity of the emission spectrum from TiO₂ suspension without dissolving ozone was the strongest, which also indicates that the emission of 370 nm was caused by TiO₂ particles. When more ozone was absorbed by TiO₂ particles (as shown in Fig. 5: (3), (4), (5) and (6)), the intensity at 370 nm decreased. Moreover, after placing the sample in air for several hours to exclude the dissolved ozone, the intensity at 370 nm increased to almost the same value as that of the sample without dissolving ozone (as shown in Fig. 5: (2)).

In the photocatalytic reactions, the generation of electron-hole pairs would be generated after semiconductor is irradiated. In order to improve the photocatalytic activity, photoelectrons must be trapped for charge separation. When ozone is presented in solution, the ozone absorbed by TiO₂ particles is assumed to achieve this goal by the reaction in Eq. (1). As discussed above, the reaction in Eq. (1) is confirmed by the fluorescence emission spectra, which is important for the synergetic effect in TiO₂/O₃/UV process.

3.5 Intermediates detected by LC/MSD trap

Table 1 summarizes the intermediates and their relative abundance identified by LC-MS in TiO₂/UV, O₃/UV and TiO₂/O₃/UV processes. The detected samples were chosen based on their UV-vis spectra and the research in the previous work [6]. As shown in Table 1, small molecules, such as benzenesulfonic acid, phthalic acid and unidentified mediate B, were presented in TiO₂/UV and O₃/UV process after reacting for 20 min. However, none of these molecules was detected in TiO₂/O₃/UV process after a same reaction period. It is also noticed that the amount of intermediates which appeared in both TiO₂/O₃/UV and O₃/UV processes, was larger in the O₃/UV process. Thus, it could be induced
that a small quantity of smaller molecules were also produced in TiO$_2$/O$_3$/UV process, but they were soon mineralized by reactive radicals generated by the synergetic effect. The intermediates detected in TiO$_2$/O$_3$/UV process after reacting for 60 min supports this explanation. In this case, fewer types of intermediates were detected. What’s more, molecules that can form only after opening aromatic ring reaction, such as 2-Hydroxy-benzoic acid, appeared. It indicates that reactions mainly contributed to oxidize the organic without breaking the ring structure in the first 20 min. Nevertheless, after reaction for more than 20 min, reactions tended to destroy the original ring structure and then mineralized the products. During this period, a relatively large amount of intermediates were transformed into smaller molecules and they were detected after accumulating.

1-Amino-5,7,8-tri-hydroxynaphthalene-3,6-disulfonic acid was detected in both O$_3$/UV and TiO$_2$/O$_3$/UV processes but not in TiO$_2$/UV process, signifying that this product was produced through ozonation. Moreover, after reacting for 60 min in TiO$_2$/O$_3$/UV process, this intermediate still existed and was the only one which kept the naphthalene nucleus structure. It could be deduced that this intermediate is relatively stable under the current reaction environment. However, its amount was smaller in TiO$_2$/O$_3$/UV process than that in O$_3$/UV process, indicating that the former process was more capable of degrading it.

8-Hydroxy-1,2-naphthoquinone-3,6-sulfonic acid and 8-hydroxy-1,4-naphthoquinone-3,6-sulfonic acid formed in all of the processes. They should be the oxidation product of $o$-hydroxyaminonaphthalenes and $p$-hydroxyaminonaphthalenes. It was reported that these hydroxyaminonaphthalenes were easily oxidized to quinones [28]. After breaking the ring structure, these quinones were then converted to carboxylic acids [29].

The existence of 2-Amino-6-(2-carboxy-2-sulfo-vinyl)-4-sulfo-benzoic acid in TiO$_2$/O$_3$/UV process
should attribute to the Criegee Mechanism [30]. The process of this mechanism is shown in the Fig. 6. Interestingly, this intermediate was not detected in O$_3$/UV process, suggesting that photocatalysis facilitated the Criegee Mechanism in some way. However, this effect is not clear and further investigation is necessary.

Noticeably, even though H-acid still existed in TiO$_2$/UV process after reacting for 20 min, small molecules, benzenesulfonic acid and phthalic acid were detected. It should attribute to the strong mineralization ability of photocatalysis, as reported by previous literature [31].

According to the discussion above and the previous literature about the degradation of dyes [28-33], the pathways of H-acid destruction in TiO$_2$/O$_3$/UV process was proposed, presented in Fig. 7. It is seen that the reaction proceeds in two major steps pathways. In the first step, one ring in naphthalene nucleus was usually broken. Polyhydroxy aromatics, benzene carboxylic acids and quinoids were formed. The benzene carboxylic acids were mainly unsaturated. Therefore, the double bonds in branched chain were easily oxidized by ozone through Criegee Mechanism. In some cases, both rings in naphthalene nucleus were converted to quinone structure without breaking the ring structure, but their amount was relatively small and they would be transformed into carboxylic acids easily after further reactions. The second step led to the elimination of the total aromaticity. Many saturated aliphatics carboxylic acids were formed in the reactions. Since these carboxylic acids are not reactive to ozone [30], they are assumed to be eliminated by holes and hydroxyl radicals through Photo-Kolbe reaction (Eq. (20)-(24)) [34]. The details of reactions on aliphatics carboxylic acids have been presented in the previous work [30]. Finally, H-acid is totally mineralized to carbon dioxide and water.

\[
\text{RCO}_2^- + h\cdot \rightarrow R^* + CO_2 \quad (20)
\]
\[
\text{RCO}_2H + OH^* \rightarrow R^* + CO_2 + H_2O \quad (21)
\]
H\(^+\) + e\(^-\) \rightarrow H(a) \quad (22)

2R\(^*\) \rightarrow R_2 \quad (23)

R\(^*\) + H(a) \rightarrow RH \quad (24)

### 3.6 Kinetics study

In order to elucidate the reaction evolution in different processes, the kinetics of H-acid degradation in TiO\(_2\)/UV, O\(_3\)/UV and TiO\(_2\)/O\(_3\)/UV processes was investigated.

The rate-determining step of the TiO\(_2\)/UV is hypothesized to be the reaction between holes and adsorbed H-acid. The concentration of holes depends on the fractional sites coverage by oxygen, since oxygen works as an electron trap, hindering the electron-hole recombination as shown in Eq. (2). Thus, two types of sites, which adsorb the H-acid and oxygen, respectively, are supposed to exist on the surface of TiO\(_2\). Therefore, in our work, the reaction rate, \(r\), for second order surface oxidation of H-acid can be expressed in terms of Langmuir-Hinshelwood kinetics as Eq. (25):

\[
r = -\frac{dC}{dt} = k^*_{\text{oxygen}} \theta^*_{\text{oxygen}} \theta^*_{\text{H-acid}} \quad (25)
\]

In the equation, \(C\) is the H-acid concentration, \(t\) the time, \(k^*_{\text{oxygen}}\) the surface second order rate constant, and \(\theta^*_{\text{oxygen}}\) and \(\theta^*_{\text{H-acid}}\) are the fractional sites coverage by oxygen and H-acid, respectively. Owing to the fact that all the experiments were carried out in a batch reactor by continuously bubbling air to the liquid phase, it could be assumed that for all runs the \(\theta^*_{\text{oxygen}}\) is constant in TiO\(_2\)/UV process. Thus, the \(k^*_{\text{oxygen}}\) can be substituted by \(k'_{\text{oxygen}}\), a surface pseudo-first order rate constant.

The fractional sites coverage by H-acid is shown in Eq. (26):

\[
\theta^*_{\text{H-acid}} = \frac{K_{\text{irradiated}}C}{1 + K_{\text{irradiated}}C} \quad (26)
\]
In the equation, $K_{\text{irradiated}}$ is the equilibrium adsorption constant of H-acid on TiO$_2$ surface irradiated in the presence of oxygen. The limiting condition is that at the start of the reaction, $t = 0$, the initial H-acid concentration is the initial one, $C = C_0$. Through Eq. (25) and Eq. (26), the following integral relationship between $C$ and $t$ is obtained:

$$t = \frac{1}{k_{\text{oxygen}} K_{\text{irradiated}}} \ln \frac{C_0}{C} + \frac{1}{k_{\text{oxygen}}} (C_0 - C) \quad (27)$$

By utilizing a least-square best fitting procedure based on the data in Fig. 1 for TiO$_2$/UV process, the values of $k'_{\text{oxygen}}$ and $K_{\text{irradiated}}$ were determined, as shown in Table 2. The large value of $K_{\text{irradiated}}$, namely 83.1 ppm$^{-1}$ confirms the strong adsorption on the surface of TiO$_2$. As strong adsorption is essential to holes reaction [36], the discussion in subsection 3.3.2 is certified here. The Langumuir-Hinshelwood model adequately describes the kinetics of the process, since a good fit to the data was presented.

It is well known that ozonation is not only oxidation by ozone molecules but also by the hydroxyl radicals. However, according to the results and discussions shown in subsection 3.3, H-acid degradation is not affected by the existence of hydroxyl radicals. Therefore, hydroxyl radicals will not influence the kinetics of O$_3$/UV process for H-acid degradation. The degradation of H-acid in O$_3$/UV process is supposed to be first order with respect to the concentration of H-acid and ozone. However, when the amount of ozone is excessive or when the ozone concentration is assumed to reach a stationary at the interface, the oxidation rate follows a pseudo first order kinetics with respect to the H-acid concentration, as reported in previous literature [9]. Therefore, the rate equation is shown as follows:

$$-\frac{dC}{dt} = k_0 C \quad (28)$$

In the equation, $k_0$ is the pseudo first order rate constant. By applying a least-square best fitting
procedure based on the data of O$_3$/UV process in Fig. 1, the value of $k_0$ is obtained, shown in Table 2.

The limiting condition is that at the start of the reaction, $t = 0$, the initial H-acid concentration is the

initial one, $C = C_0$. The following integral relationship between $C$ and $t$ is obtained:

$$ t = -\frac{1}{k_0} \ln \frac{C}{C_0} $$ \hspace{1cm} (29)

By utilizing a least-square best fitting procedure based on the data in Fig. 1 for O$_3$/UV process, the

pseudo first order rate constant, $k_0$, was obtained, as shown in Table 2.

The H-acid oxidation process by TiO$_2$/O$_3$/UV process is the combination of homogeneous reaction

by ozone and heterogeneous reaction by holes on the surface of TiO$_2$. Therefore, the kinetic equation

for TiO$_2$/O$_3$/UV process could be obtained by integrating Eq. (25) and Eq. (26). The equation is as

follows:

$$ r = kC + k_{ozone}' \theta_{H-acid} $$ \hspace{1cm} (30)

In the equation, $k$ is the first order kinetic constant of homogeneous reaction occurring in the solution.

$\theta_{H-acid}$ is the fractional sites coverage of TiO$_2$ by H-acid. The $k_{ozone}'$ term is equal to the following sum:

$$ k_{ozone}' \theta_{ozone} + k_{oxygen} \theta_{oxygen} $$

in which $k_{ozone}$, $k_{oxygen}$ term are the second rate constants and $\theta_{ozone}$, $\theta_{oxygen}$ the fractional sites coverage

of TiO$_2$ surface by ozone and oxygen respectively. By considering that ozone and oxygen

concentrations were always constant, $k_{ozone}'$ is a pseudo-first order rate constant. According to the

Langmuir-Hinshelwood model, the $\theta_{H-acid}$ is given by:

$$ \theta_{H-acid} = \frac{KC}{1 + KC} $$ \hspace{1cm} (31)

In the equation, $K$ is the equilibrium adsorption constant of H-acid on the TiO$_2$ surface in the presence

of ozone. The limiting condition is that at the start of the reaction, $t = 0$, the initial H-acid concentration
is the initial one, \( C = C_0 \). Then, by substituting Eq. (31) into Eq. (30), the following equations are obtained:

\[
t = \frac{1}{k + k'_{\text{ozone}} K} \left[ -\ln C + \ln \left( \frac{k + k'_{\text{ozone}} K}{k K} + C \right) - \frac{1}{k} \ln (k + k'_{\text{ozone}} K + k K C) + C_c \right] (32)
\]

\[
C_c = \frac{1}{k + k'_{\text{ozone}} K} \left[ \ln C_0 - \ln \left( \frac{k + k'_{\text{ozone}} K}{k K} + C_0 \right) + \frac{1}{k} \ln (k + k'_{\text{ozone}} K + k K C_0) \right] (33)
\]

The values of \( k, k'_{\text{ozone}} \) and \( K \) were obtained, as shown in Table 2, after a least-square best fitting procedure using the data of TiO\(_2\)/O\(_3\)/UV process of reacting for 40 min in Fig. 1. However, this model presents a poor fitting to the data (\( R^2 = 0.823 \)). Then, the data of reaction for shorter period was used for several least-square best fitting procedures. Finally, a best fitting for the model was found to be the data of reaction in the first 3 minutes (\( R^2 = 0.998 \)), in which samples were taken every 30s and the values of \( k, k'_{\text{ozone}} \) and \( K \) are shown in Table 2. The results indicate that the kinetics of TiO\(_2\)/O\(_3\)/UV process followed the model presented in Eq. (32) at first. Nevertheless, with the reaction proceeding, some initially negligible factors became important and affected the kinetics of TiO\(_2\)/O\(_3\)/UV process. These factors should be related to the generation of intermediate products and their absorption on TiO\(_2\).

Here, the kinetic parameters of TiO\(_2\)/O\(_3\)/UV process in the first 3 minutes were employed to compare with those of the other two processes. According to the results, the highest reactivity of both heterogeneous and homogeneous reactions was reached in TiO\(_2\)/O\(_3\)/UV process. This result confirmed the synergetic effect between TiO\(_2\)/ UV and O\(_3\)/UV mentioned previously. Noticeably, the kinetic constant of heterogeneous reaction (oxidation by holes) in TiO\(_2\)/O\(_3\)/UV process was 7 times as large as that in TiO\(_2\)/UV process. The fact that the recombination between holes and electrons in TiO\(_2\) was strongly restrained by the reactions in Eq. (1)-(3) should be the main reason for this improvement. The equilibrium adsorption constant in TiO\(_2\)/O\(_3\)/UV process greatly decreased, compared to the TiO\(_2\)/ UV
This situation indicates that the active sites on the surface of TiO$_2$ were mainly occupied by O$_3$ in the former process. The kinetic constant of homogeneous reaction (oxidation by ozone) in the TiO$_2$/O$_3$/UV process was also larger than that in O$_3$/UV process. Here, the Eley-Rideal mechanism discussed by the previous work could present a good explanation [36]. Firstly, H-acid was adsorbed on the active sites of TiO$_2$ (Eq. (34)). Then, the reaction between ozone and adsorbed H-acid occurred on the active sites (Eq. (35)). In the reactions, S and H-acid-S represents the active sites on the surface of TiO$_2$ and its adsorbed species, respectively. The reactivity of ozonation through the reactions in Eq. (34) and (35) is higher than simple homogeneous ozonation.

\[
\text{H-acid} + S \rightarrow \text{H-acid-S} \quad (35)
\]

\[
\text{O}_3 + \text{H-acid-S} \rightarrow \text{Product} \quad (36)
\]

Ozone reaction in water is heterogeneous parallel-series gas liquid reactions in which ozone transfers from the gas phase (air, in our work) where it simultaneously reacts with pollutants while diffusing. If the reaction between pollutants and ozone is fast enough, the ozonation will take place near the gas-water interface. If not, the ozone will accumulate in the bulk water where the ozonation occurs [37]. Application of the film theory concept, Hatta number (Ha) allows an easy determination of the zone where the reaction between ozone and H-acid develops. Ha indicates the relative importance of chemical and physical absorption steps on a gas-liquid reaction. Its value for pseudo first-order reaction in our work can be determined as follows [38]:

\[
Ha = \frac{(k \cdot D_{\text{ozone}})^{0.5}}{k_L} \quad (37)
\]

In the equation, $k$, $k_L$ and $D_{\text{ozone}}$ are the first order rate constant, liquid phase mass transfer coefficient and H-acid diffusivity in water, respectively. The value of $k_L$ is taken as $2 \times 10^{-5}$ ms$^{-1}$, which is a typical value in gas-feeding systems constituted by diffuser plates [37]. The value of $D_{\text{ozone}}$ is taken as 1.3 ×
$10^{-9}$ m$^2$s$^{-1}$, as reported in the previous work [39].

Calculated with Eq. (37), the values of $H_a$, 0.13, was obtained. As reported by FJ Beltran [21], values of $H_a$ higher than 1 indicate that the reaction between ozone and organics is fast-moderate reaction. In this case, ozone dissolved in water mainly reacts with compounds in the water film layer. Therefore, the ozone reaches neither the bulk water nor the surface of TiO$_2$. On the other hand, a value of $H_a$ lower than 0.3 means that the ozone direct reaction locates in the low kinetic regime. At this circumstance, ozone could reach the surface of TiO$_2$ to capture electrons through the reactions in Eq. (1) and (3). In our case, the value of $H_a$ is lower than 0.3, indicating that part of ozone could reach the surface of TiO$_2$ and accomplish the reactions in Eq. (1)-(3). The synergetic effect in TiO$_2$/O$_3$/UV process is proved by this kinetic study.

4. Conclusion

H-acid was degraded efficiently in TiO$_2$/O$_3$/UV process because of the synergetic effect between ozonation and photocatalysis. By adding inhibitors in the solution, it was proved that H-acid was mainly degraded by ozone and holes on the surface of TiO$_2$. Fluorescence emission spectra results indicated that ozone was able to capture the electrons from the conduction band of TiO$_2$. This process made great contribution to the synergetic effect in TiO$_2$/O$_3$/UV process. Intermediates in different processes were detected by LC/MSD trap. H-acid was assumed to transform to polyhydroxy aromatics, benzene carboxylic acids and quinoids first. These intermediates were further oxidized to smaller molecules through Criegee Mechanism and Photo-Kolbe reaction. A kinetic model based on Langmuir-Hinshelwood equations described adequately the photoreactivity results and provided the values of kinetic constant of homogeneous reaction and kinetic and equilibrium adsorption constant of
heterogeneous reaction in TiO$_2$/O$_3$/UV process. The value of $H_a$ for TiO$_2$/O$_3$/UV process was calculated by using the kinetic parameters. Its value proves that ozone was able to reach water bulk and the synergetic effect discussed above in TiO$_2$/O$_3$/UV process existed.

**Acknowledges**

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**Reference**


Table 1: Intermediates and their abundance in different processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Intermediates</th>
<th>Relative abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂/O₃/UV reaction for 20min</td>
<td>1-Amino-5,7,8-tri-hydroxynaphthalene-3,6-disulfonic acid</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1,4,5,8-binaphthoquinone-3,6-disulfonic acid</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>8-Hydroxy-1,2-naphthoquinone-3,6-disulfonic acid</td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td>8-Hydroxy-1,4-naphthoquinone-3,6-disulfonic acid</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>1,2,5,8-Binaphthoquinone-3,6-disulfonic acid</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>2-Amino-6-(2-carboxy-2-sulfo-vinyl)-4-sulfo-benzoic acid</td>
<td>29.8</td>
</tr>
<tr>
<td></td>
<td>2-(2-Carboxy-vinyl)-6-hydroxy-4-sulfo-benzoic acid</td>
<td>31.9</td>
</tr>
<tr>
<td></td>
<td>2-Hydroxy-benzoic acid</td>
<td>9.6</td>
</tr>
<tr>
<td>TiO₂/O₃/UV reaction for 60min</td>
<td>1-Amino-5,7,8-tri-hydroxynaphthalene-3,6-disulfonic acid</td>
<td>56.3</td>
</tr>
<tr>
<td></td>
<td>2-Amino-6-(2-carboxy-2-sulfo-vinyl)-4-sulfo-benzoic acid</td>
<td>56.8</td>
</tr>
<tr>
<td></td>
<td>2-(2-Carboxy-vinyl)-6-hydroxy-4-sulfo-benzoic acid</td>
<td>17.5</td>
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<td></td>
<td>2-Carboxy-3-(3-carboxy-2-sulfo-vinyl)-1,4-benzoquinone-5-sulfonic acid</td>
<td>15.2</td>
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<tr>
<td></td>
<td>H-acid</td>
<td>175.1</td>
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<tr>
<td>TiO₂/UV reaction for 20min</td>
<td>Benzenesulfonic acid</td>
<td>47.2</td>
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<tr>
<td></td>
<td>8-Hydroxy-1,2-naphthoquinone-3,6-disulfonic acid</td>
<td>14.8</td>
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<tr>
<td></td>
<td>8-Hydroxy-1,4-naphthoquinone-3,6-disulfonic acid</td>
<td>30.9</td>
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<td></td>
<td>Phthalic acid</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>Unidentified Mediate A</td>
<td>15.3</td>
</tr>
</tbody>
</table>
The extracted ion chromatogram reveals the following compounds identified during the O$_3$/UV reaction for 20 min:

- 1-Amino-5,7,8-tri-hydroxynaphthalene-3,6-disulfonic acid: 117
- 2-(2-Carboxy-vinyl)-6-hydroxy-4-sulfo-benzoic acid: 42.1
- 8-Hydroxy-1,2-naphthoquinone-3,6-disulfonic acid: 43.8
- 8-Hydroxy-1,4-naphthoquinone-3,6-disulfonic acid: 22.0
- Unidentified Mediate A: 20.7
- Unidentified Mediate B: 3.1

※ This value is calculated through the Extracted Ion Chromatogram, approximately. Only the same mediate can be compared by this value.

※※ This mediate should be 1,4,5,8-binaphthoquinone-3,6-disulfonic acid or 1,2,5,8-Binaphthoquinone-3,6-disulfonic acid.

※※※ The specific structure of this mediate is not confirmed, but it should contain benzene ring and carboxyl.

Table 2 Values of kinetic constant and of adsorption equilibrium constant at different processes

<table>
<thead>
<tr>
<th></th>
<th>Kinetic constants</th>
<th>Equilibrium adsorption constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heterogeneous/ Homogeneous/</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppm·min$^{-1}$/min$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$/UV</td>
<td>2.404/—</td>
<td>83.11</td>
</tr>
<tr>
<td>O$_3$/UV</td>
<td>—/0.215</td>
<td>—</td>
</tr>
<tr>
<td>TiO$_2$/O$_3$/UV (reaction in 40 min)</td>
<td>0.451/0.246</td>
<td>11.223</td>
</tr>
<tr>
<td>TiO$_2$/O$_3$/UV (reaction in 3 min)</td>
<td>14.302/0.293</td>
<td>0.464</td>
</tr>
</tbody>
</table>
Figures Captions


Fig. 3: Time evolution of remaining concentration of H-acid during TiO$_2$/UV process. ■: in the absence of iodide ion; □: in the presence of iodide ion (C$_I$ = 3.0 × 10$^{-3}$ M).

Fig. 4: Time evolution of remaining concentration of H-acid. ■: TiO$_2$/O$_3$/UV; ○: in the presence of t-butanol (C$_{t-ButOH}$ = 5.0 × 10$^{-3}$ M); ◇: in the presence of benzoquinone (C$_{Benzoq}$ = 5.0 × 10$^{-5}$ M).

Fig. 5: Fluorescence emission spectra of TiO$_2$ suspension after inletting O$_3$ for different time: (1) 0 min; (2) 10 min, then placed in the air for long enough time; (3) 10 min; (4) 20 min; (5) 30 min; (6) 40 min. Samples were diluted to 1/100 using water before measuring.

Fig. 6: Process of Criegee Mechanism

Fig. 7: Proposed degradation pathways of H-acid
Fig. 1

Fig. 2
Fig. 3

Fig. 4
Fig. 5

![Graph showing intensity vs. wavelength]

(1) (2) (3) (4) (5) (6)

Wavelength (nm)

0 200 400 600 800 1000

Fig. 6

![Chemical reactions and structures]

O₂ → \[
\begin{array}{c}
\text{Structure 1} \\
\text{Structure 2} \\
\text{Structure 3}
\end{array}
\]

\[
\text{Structure 4} \xrightarrow{\text{O₂}} \text{Structure 5}
\]

\[
\text{Structure 6}
\]
continued