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Degradation of H-acid by combined photocatalysis and ozonation processes

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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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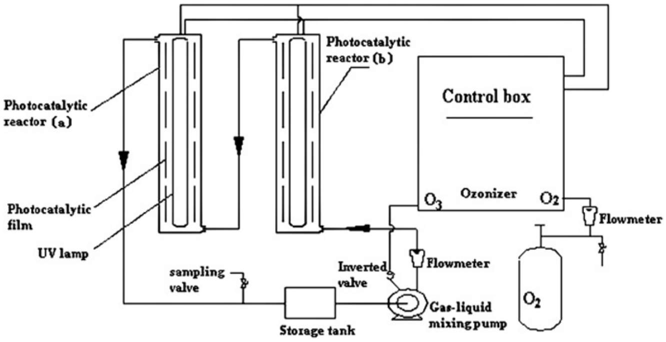

Fig. 1. Schematic drawing of the combination of photocatalysis and ozonation used for the degradation of H-acid.

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

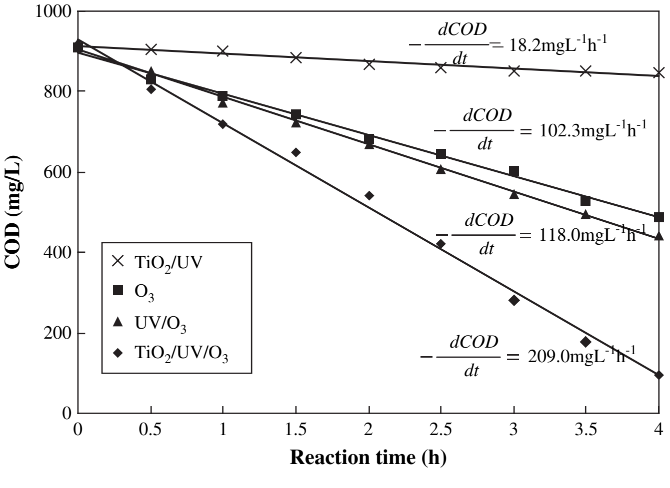

Fig. 2. Time courses of COD removal in different processes. [H-acid] = 1000 mg/L, O_3 dosage = 12.6 mg/min.