

Degradation of *p*-nitrotoluene in aqueous solution by ozonation combined with sonolysis

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Abstract

p-Nitrotoluene (PNT) is a nitroaromatic compound that is hazardous to humans and is a suspected hormone disrupter. The degradation of PNT in aqueous solution by ozonation (O₃) combined with sonolysis (US) was investigated in laboratory-scale experiments in which pH, initial concentration of PNT, O₃ dose and temperature were varied. The degradation of PNT followed pseudo-first-order kinetics, and degradation products were monitored during the process. The maximum degradation was observed at pH 10.0. As the initial concentration of PNT decreased, the degradation rate increased. Both temperature and ozone dose had a positive effect on the degradation of PNT. Of the total organic carbon (TOC) reduction, 8, 68, and 85% were observed with US, O₃, and a combination of US and O₃ after reaction for 90 min, respectively, proving that ozonation combined with sonolysis for removal of TOC is more efficient than ozonation alone or ultrasonic irradiation alone. Major by-products, including *p*-cresol, 4-hydroxybenzaldehyde, 4-hydroxybenzoic acid, 4-(oxomethylene) cyclohexa-2,5-dien-1-one, but-2-enedioic acid, and acetic acid were detected by gas chromatography coupled with mass spectrometry.
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Keywords: *p*-Nitrotoluene; Sonolysis; Ozonation; Degradation pathway

1. Introduction

Nitroaromatic compounds are used in many industrial processes, including the preparation of pesticides, explosives, textiles and paper. Therefore, these compounds are often detected as water pollutants as a result of their release in industrial effluents [1,2]. If these effluents are discharged into water without proper treatment, they are hazardous to humans and the environment. Among these nitroaromatic compounds, *p*-nitrotoluene (PNT) is a common pollutant. It is an intermediate formed during the production of trinitrotoluene (TNT), and studies have demonstrated that it is a suspected hormone disrupter [3,4].

The combination of ozonation and sonolysis (US/O₃) is an advanced oxidation process. Compared with ozonation or sonolysis alone, it appears to be more effective and uses less energy, and it has the advantages of being non-selective, leading to no

secondary pollution, and being particularly effective in removing persistent and biorefractory pollutants from water [5]. Thus, US/O₃ oxidation has become a focus of intense investigation. Ozone is decomposed to generate very reactive free radicals, such as the hydroxyl radical (•OH), which is important in the degradation of PNT. In the US/O₃ process, the mass transfer and decomposition of O₃ can be enhanced by ultrasound to increase the production of free radicals for better degradation [6,7]. The role of ozonation with US and the related oxidation process with several aromatic compounds have been examined by different authors [5,6,8–10].

The degradation of PNT has been studied by many researchers, including photocatalytic degradation [11], bio-transformation [12], and UV-catalyzed Fenton oxidation [13]. However, most of these studies paid little attention to the degradation of PNT by US/O₃. In this study, we performed experiments in which we varied conditions, including pH, initial concentration of PNT, O₃ dose and temperature, to examine the influence of these factors on the extent and rate of degradation, and the mechanism of PNT degradation by US/O₃ is proposed.

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2. Experimental

2.1. Reagents

p-Nitrotoluene (crystalline form, molecular mass 137.14 g/mol) as obtained from Jiangsu Huaihe Chemicals Co. Ltd. is over 99.5% pure and was used without further purification.

2.2. Apparatus

As shown earlier [14], the experimental apparatus consisted of a cylindrical Pyrex glass reactor (diameter 80 mm, height 120 mm) coupled with an ultrasonic processor (YIY-UL04-B, Shanghai Yiyuan Ultrasonic Equipment Co. Ltd.), an O₃ supply system (CHYF-3A, Hangzhou Rongxin Electronic Equipment Co. Ltd.) and an exhaust treatment system. The ultrasonic processor (400 W output, variable power control) was equipped with a 20-kHz converter (diameter 106 mm, height 225 mm) and a pure titanium probe (tip diameter 16 mm, height 164 mm), with a processing capability of 100–1000 mL. The glass cylinder was plugged with a polyethylene cap during operation. The probe was partially immersed in the liquid fixed at the center of the polyethylene cap. The oxygen flow-rate to the generator was monitored with a rotameter incorporated into the ozone generator. In this experiment, the ozone doses in the feed were kept at 1.8–3.8 g/h. Surplus ozone was passed into gas absorption bottles containing 2% (w/v) KI solution. The experiments were carried out in a temperature-controlled bath.

An aqueous solution (500 mL) of PNT at different concentrations was used. PNT was degraded with the chosen O₃ dose and/or US energy density. Samples were taken with a glass syringe at various time-points and passed through a membrane filter (0.45 μm pore size) and analyzed for solutes.

2.3. Analytical methods

The analysis of PNT was performed by high-pressure liquid chromatography (HPLC) using an Agilent instrument (1100 series, Agilent, USA) by comparison with the retention time of the standard compound. Aliquots of 25 μL were injected to determine the concentration of PNT, running with a mobile phase of ammonium formate (the pH was adjusted to 3.8 with formic acid)/isopropyl alcohol (60:40, v/v). The separation was performed using an Agilent ZORBAX Eclipse XDB-Phenyl column (250 mm × 4.6 mm i.d.) at a flow-rate of 0.8 mL/min and a column temperature of 40 °C. A UV detector was used with the wavelength set at 280 nm.

Intermediate products were detected by gas chromatography coupled with mass spectrometry (GC/MS) (GC, Varian cp3800 system; MS, Varian Saturn 2000 mass spectrometer). The gas chromatograph was equipped with a WCOT fused silica series column (30 m × 0.25 mm i.d., film thickness 0.25 μm) and interfaced directly to the mass spectrometer. The GC column was operated at a temperature of 80 °C for 2 min and then increased to 250 °C at the rate of 15 °C/min. The other experimental conditions were: EI impact ionization 70 eV; helium as

the carrier gas; injection temperature 280 °C; source temperature 80 °C.

Total organic carbon (TOC) was determined with a TOC-V_{CPH} total organic carbon analyzer. The pH value was measured with a PHS-25 instrument (Rex Analytical Instrument Co. Ltd., Shanghai, China). The US power dissipated into the reactor was adjusted and estimated by calorimetry in order to ensure comparable US conditions [15]. The O₃ concentrations were determined by an iodimetric method [16].

2.4. Procedures

Phosphate buffers were prepared in deionized water by the reaction of calculated amounts of sodium hydroxide solution and phosphoric acid solution, to yield an ionic strength of 0.0667 M. A 100 mg/L aqueous stock solution was prepared by dissolving 100 mg of PNT in 1000 mL of phosphate buffer, and stored at 4 °C. Dye solutions of various strengths were made from the stock by the appropriate dilution with phosphate buffer.

For the preparation of GC/MS samples, 100 mg of PNT was dissolved in 1000 mL of phosphate buffer (pH 10.0). Samples of 10 mL were removed from the reactor at 5, 15, 30, and 45 min. After the pH value of the samples was adjusted to 2.0 with HCl, intermediate products were detected by GC/MS without degassing the samples.

3. Results and discussion

3.1. Effect of pH

The degradation experiment of the effect of pH was repeated over the range of 4.0–12.0. As shown in Fig. 1a, the PNT degradation kinetics obtained during US/O₃ fitted a first-order curve. Pseudo-first-order rate constants at various pH values are given in Table 1. The rate constants were 0.094, 0.11, 0.15, 0.19, 0.20 and 0.090 min⁻¹ when pH values were 4.0, 5.8, 7.0, 8.0, 10.0 and 12.0, respectively. The degradation rate increased as the pH increased from 4.0 to 10.0, and then decreased at pH values higher than 10.0.

In general, the O₃ molecule itself was one of the main reactive species under acidic conditions, so the degradation of PNT exhibited low efficiency [17]. As the solution became more basic, the rate of O₃ decomposition to secondary oxidants, such as hydroxyl radicals, increased [18]. However, the rate of degradation decreased at pH values higher than 10.0, which might be attributed to two factors. First, a high pH creates more free radical scavengers (i.e. CO₃²⁻, HCO₃⁻, etc.), resulting in a decrease in the concentration of •OH [19,20]. Second, the rate of reaction of •OH with the various phosphate species added to the solution as pH buffers in our experiments would be expected to be slowest in the pH range 2.8–4.5 [21]. The optimal pH during these experiments was 10.0.

3.2. Effect of initial concentration of PNT

The effect of the initial concentration on degradation of PNT was studied for various initial concentrations and the results are

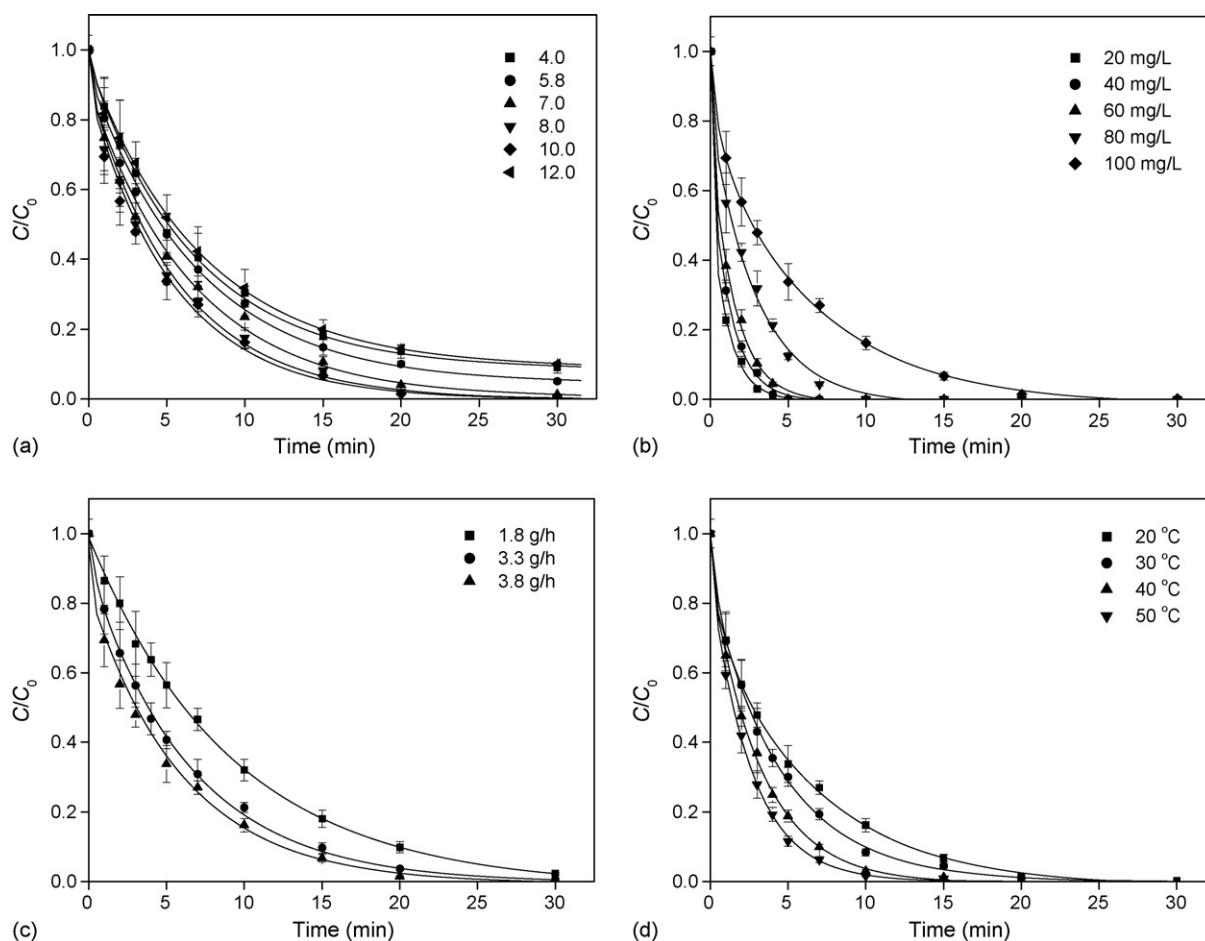


Fig. 1. Effect of process variables on the degradation of PNT. (a) Effect of initial pH: C_0 100 mg/L; O_3 dose 3.8 g/h; US energy density 0.3 W/mL; temperature 20 °C. (b) Effect of initial concentration: pH 10.0; O_3 dose 3.8 g/h; US energy density 0.3 W/mL; temperature 20 °C. (c) Effect of O_3 dose: C_0 100 mg/L; pH 10.0; US energy density 0.3 W/mL; temperature 20 °C. (d) Effect of temperature: C_0 100 mg/L; pH 10.0; O_3 dose 3.8 g/h; US energy density 0.3 W/mL.

shown in Fig. 1b and Table 1. As can be seen, a higher initial concentration led to a slower degradation rate, i.e. 1.2, 0.98, 0.77, 0.43 and 0.20 min^{-1} pseudo-first-order rate constants when the initial concentration of PNT was 20, 40, 60, 80 and 100 mg/L,

respectively. The overall degradation rate of PNT depends on the number of hydroxyl radicals generated and on the rate of release of hydroxyl radicals into the surrounding medium [22]. Our experiments were performed under the same operating condi-

Table 1
Pseudo-first-order rate coefficients of various operation parameters during degradation

| Operation parameters | | | | Pseudo-first-order (k) (min^{-1}) |
|----------------------|-------------------------------------|------------------|------------------|--|
| pH | Initial concentration, C_0 (mg/L) | Ozone dose (g/h) | Temperature (°C) | |
| 4.0 | 100 | 3.8 | 20 | $9.4 \times 10^{-2} \pm 1.1 \times 10^{-2}$ |
| 5.8 | 100 | 3.8 | 20 | $1.1 \times 10^{-1} \pm 7.2 \times 10^{-3}$ |
| 7.0 | 100 | 3.8 | 20 | $1.5 \times 10^{-1} \pm 2.2 \times 10^{-2}$ |
| 8.0 | 100 | 3.8 | 20 | $1.9 \times 10^{-1} \pm 2.6 \times 10^{-2}$ |
| 10.0 | 100 | 3.8 | 20 | $2.0 \times 10^{-1} \pm 2.2 \times 10^{-2}$ |
| 12.0 | 100 | 3.8 | 20 | $9.0 \times 10^{-2} \pm 1.3 \times 10^{-2}$ |
| 10.0 | 80 | 3.8 | 20 | $4.3 \times 10^{-1} \pm 5.2 \times 10^{-2}$ |
| 10.0 | 60 | 3.8 | 20 | $7.7 \times 10^{-1} \pm 9.8 \times 10^{-2}$ |
| 10.0 | 40 | 3.8 | 20 | $9.8 \times 10^{-1} \pm 1.4 \times 10^{-1}$ |
| 10.0 | 20 | 3.8 | 20 | $1.2 \pm 1.1 \times 10^{-1}$ |
| 10.0 | 100 | 3.3 | 20 | $1.7 \times 10^{-1} \pm 1.6 \times 10^{-2}$ |
| 10.0 | 100 | 1.8 | 20 | $1.2 \times 10^{-1} \pm 1.9 \times 10^{-2}$ |
| 10.0 | 100 | 3.8 | 30 | $2.3 \times 10^{-1} \pm 2.5 \times 10^{-2}$ |
| 10.0 | 100 | 3.8 | 40 | $3.2 \times 10^{-1} \pm 2.4 \times 10^{-2}$ |
| 10.0 | 100 | 3.8 | 50 | $3.6 \times 10^{-1} \pm 3.1 \times 10^{-2}$ |

tions, which indicated that the rate of release of hydroxyl radicals was almost constant. Therefore, the cavities and $\bullet\text{OH}$ radicals in the solution approached a steady state. Additionally, the competition between the intermediate products and PNT for $\bullet\text{OH}$ became intense owing to the non-selective reactivity of $\bullet\text{OH}$. These two factors lead to a decreasing rate of degradation with an increase of initial concentration. The effect of the initial concentration has been investigated by other researchers [23,24], who have reported results that agree with ours.

3.3. Effect of O_3 dose

In order to evaluate the effect of O_3 dose on the degradation of PNT with US/ O_3 , increasing O_3 dose was applied at pH 10.0 as shown in Fig. 1c and Table 1. The pseudo-first-order rate constant increased from 0.12 min^{-1} with an O_3 dose of 1.8 g/h to 0.20 min^{-1} with an O_3 dose of 3.8 g/h. The results indicated that O_3 had a positive effect on the degradation rate of US/ O_3 .

As the ozone dose increased, the area of the gas–liquid interface increased, which resulted in an increase of ozone concentrations in the solution and an increase of the formation of the free radicals with a consequent increase in the rate of PNT degradation. However, as the concentration of ozone in the liquid phase approached its maximum value, the process became increasingly controlled by the rate of chemical reaction. Any further improvement in ozone mass transfer would have a diminished effect on the observed reaction rate [25]. Therefore, optimization of O_3 dose is necessary to minimize energy consumption and the amount of exhaust O_3 gas.

The actual optimum dose of O_3 can be determined by the O_3/PNT ratio required for complete degradation, which is related to the concentration of PNT and the consumption of PNT by degradation, which can be obtained by further experiments for individual treatment systems.

3.4. Effect of temperature

Effect of temperature on the degradation of PNT by US/ O_3 was examined in the range 20–50 °C. Fig. 1d and Table 1 show that the degradation rate of PNT increased gradually as the temperature increased (rate constants of 0.20, 0.23, 0.32 and 0.36 min^{-1} were obtained at temperatures of 20, 30, 40 and 50 °C, respectively). The same results were obtained by Weavers and Hoffmann [7]. Due to its reduced solubility as the temperature increased, the concentration of O_3 in aqueous solution decreased. On the other hand, during US, the increase of the temperature caused greater decomposition of ozone, so the rate of mass transfer during ozone dissolution was enhanced [26]. As a result, ozone decomposes faster to give reactive intermediates at higher temperatures despite the lower solubility of ozone at higher temperatures.

3.5. Enhanced mineralization

The destruction of TOC is the ultimate goal of advanced oxidation processes [27]. As shown in Fig. 2, the total mineralization at 90 min in the US, O_3 and US/ O_3 schemes was

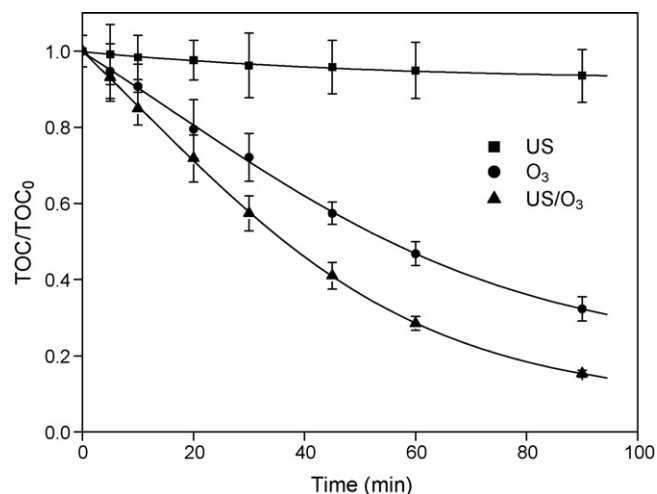


Fig. 2. Comparison of US, O_3 and US/ O_3 for TOC removal: C_0 100 mg/L; pH 10.0; O_3 dose 3.8 g/h; US energy density 0.3 W/mL; temperature 20 °C.

8, 68, and 85%, respectively. Ozonation alone was more effective than US for the removal of TOC, and the combination of the two resulted in a synergetic increase in the overall rate of degradation. It is likely that the following theories are responsible for the increase of degradation efficiency. When used alone, ozone transfers first from the gas phase into the liquid phase, and then undergoes bulk solution reactions of the substrate with ozone or radicals from O_3 autodecomposition that occur in the absence of sonolysis. As for individual sonolysis of the substrate, reactions include both direct pyrolysis of the substrate and pyrolysis of H_2O in a cavitation bubble producing $\bullet\text{OH}$ [8]. However, in the combined system, a myriad of tiny air bubbles are produced, due to the cavitation effect of ultrasound, to enable most O_3 to enter the liquid phase or react on the gas–liquid interface. The increase of mass transfer and decomposition processes of O_3 coupled with transient local high temperature and ultra-high pressure upon the collapse of cavities enhance the production of free radicals $\bullet\text{OH}$ for further oxidation of organic pollutants, resulting in a higher reaction rate [10,24].

Hence, ozonation combined with sonolysis for the removal of TOC is more efficient than using ozonation alone or ultrasonic irradiation alone.

3.6. Intermediates and a possible reaction mechanism

On the basis of the intermediates (Table 2) detected in this experiment by GC/MS, a possible reaction pathway for the decomposition of PNT in the US/ O_3 process is proposed in Fig. 3. In general, $\bullet\text{OH}$ radicals are the primary oxidizing species in the US/ O_3 process. The initial $\bullet\text{OH}$ attack can occur at the C–N bond of PNT, yielding *p*-cresol (D_1) with release of NO_3^- . Parallel with this degradation, the nitro group is lost from the benzene ring by vapor phase pyrolysis due to the high temperatures that are achieved during bubble collapse conditions, and the *p*-methylphenyl radical would be formed (S_1), which would be transformed easily into D_1 by $\bullet\text{OH}$. Further oxidation of D_1 led to 4-(oxomethylene) cyclohexa-2,5-dien-1-one (D_4). Then

Table 2
Intermediate compounds identified by GC/MS

| Symbol | Compounds | Structural formula | Sample time (min) | | | |
|----------------|---|----------------------|-------------------|----|----|----|
| | | | 5 | 15 | 30 | 45 |
| D ₁ | <i>p</i> -Cresol | | ✓ | | | |
| D ₂ | 4-Hydroxybenzaldehyde | | ✓ | ✓ | ✓ | |
| D ₃ | 4-Hydroxybenzoic acid | | ✓ | ✓ | ✓ | |
| D ₄ | 4-(Oxomethylene) cyclohexa-2,5-dien-1-one | | | ✓ | ✓ | |
| D ₅ | But-2-enedioic acid | | | ✓ | ✓ | ✓ |
| D ₆ | Acetic acid | CH ₃ COOH | | ✓ | ✓ | ✓ |

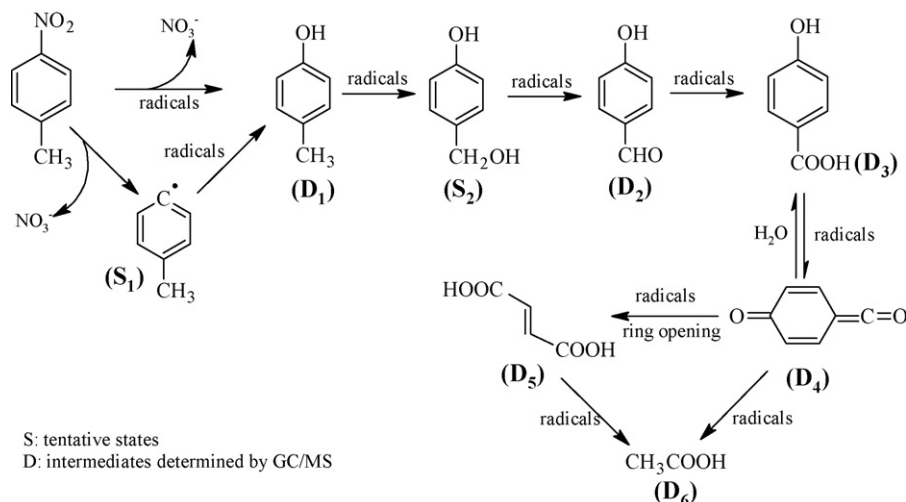


Fig. 3. The probable degradation pathway of PNT.

the aromatic ring of **D₄** may open to give carboxylic acids such as but-2-enedioic acid (**D₅**) and acetic acid (**D₆**).

It should be emphasized that the existence and reaction of compound **D₄** need to be classified further. The compound **D₄** could be detected by GC/MS, which may be attributed to the presence of residual ozone (without degassing the samples). Although Tomazela et al. also reported the existence of compound **D₄** [28], the physicochemical property was still unclear. Therefore, further experiments need to be done to ascertain whether compound **D₄** could add water to an aqueous solution to yield compound **D₃**. In other words, there might be a mutual transformation between compounds **D₃** and **D₄**.

4. Conclusions

We determined PNT degradation in aqueous solution by US combined with O₃. The experimental results indicate that the rate of degradation is influenced by the initial concentration of PNT,

temperature, O₃ dose and pH. The efficiency of ozone treatment was enhanced by the mechanical effects of US. The joint action of US and O₃ induced a synergetic effect on removal of TOC. Total mineralization after 90 min with US, O₃ and US/O₃ was 8, 68, and 85%, respectively. Intermediate products, including *p*-cresol, 4-hydroxybenzaldehyde, 4-hydroxybenzoic acid, 4-(oxomethylene) cyclohexa-2,5-dien-1-one, but-2-enedioic acid, and acetic acid were detected by GC/MS.

The results obtained by experiment confirm that US/O₃ oxidation is an effective technology for the removal of nitroaromatics, despite their high level of stability. The US/O₃ oxidation process may be applied as a new methodology for reducing the levels of other endocrine-disrupting chemicals in aqueous solution. More work is needed to determine the precise mechanisms for the sonolytic ozonation reported here, but the clear synergy achieved by the use of combined techniques are worthy of further study and may form the basis of important techniques for environmental treatment.

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