

# Degradation of DMSO by ozone-based advanced oxidation processes

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## Abstract

The present study investigates the oxidation of dimethyl sulfoxide (DMSO) by conventional ozonation and the advanced oxidation processes (AOPs). The major degradation products identified were methanesulfinate, methanesulfonate, formaldehyde, and formic acid in ozonation process. The subsequent degradation of intermediates shows that methanesulfonate is more resistance to ozonation, which reduces the mineralization rate of DMSO. The effect of *t*-butanol addition and ozone gas flow dosage on the degradation rate was evaluated. The rate constant of the reaction of ozone ( $k_D$ ) with DMSO was found to be  $0.4162 \text{ M}^{-1} \text{ S}^{-1}$ . In the second part of this study, DMSO degradation and TOC mineralization were investigated using  $\text{O}_3/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2$  and  $\text{UV}/\text{H}_2\text{O}_2$  processes. In all these processes the degradation of target organics is more pronounced than TOC removal. The efficiencies of these processes were evaluated and discussed. The formation of sulfate ion in all AOPs have been identified and compared with other processes. Overall it can be concluded that ozonation and ozone-based AOPs are promising processes for an efficient removal of DMSO in wastewater.

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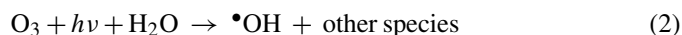
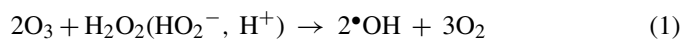
**Keywords:** DMSO; Ozone; AOPs; TOC; Wastewater; Mineralization

## 1. Introduction

New developments in the variety of fields to meet the ever-increasing requirements of human beings have also led to the presence of new compounds in the effluent streams of processing plants, which are not readily degraded by the conventional effluent treatment systems. The destruction of persistent organic pollutants has acquired novel technologies because of inadequate conventional biological, physical and chemical treatment methods. Therefore, new studies have been carried out to promote new technologies in the last two decades. Ozone is widely used as an oxidant in pollution abatement in aqueous media. It has the advantage of being an eco-friendly oxidant as its use is residue-free. One of the main problems of ozonation in the treatment of wastewater is the appearance and accumulation of refractory compounds that interfere with mineralization of the organic matter present in water. Some substances are even refractory to those single oxidation processes, and new alternatives have been developed for the elimination of these contaminants, such as advanced oxidation processes (AOPs),

which consist of the combination of single oxidants. These AOPs employ high oxidation-potential sources to produce the primary oxidant species, hydroxyl radical, which react with most organic compounds with rate constants within the range of  $10^7$ – $10^{10} \text{ l mol}^{-1} \text{ S}^{-1}$  [1].

Procedures based upon the use of different oxidants like ozone and hydrogen peroxide with UV radiation, etc., have demonstrated a significant efficiency on wastewater treatment. Several studies performed with  $\text{O}_3/\text{UV}$  [2–4],  $\text{O}_3/\text{H}_2\text{O}_2$  [5–7] and  $\text{UV}/\text{H}_2\text{O}_2$  [8–10] provided promising treatment options. The decomposition of aqueous ozone in pure water is initiated by its reaction with hydroxide ion (Eq. (1)), and this reaction leads to the production of free radicals that propagate the decomposition process by chain of radical reactions and produce hydroxyl radical. The purpose of introducing ultraviolet (UV) radiation in the ozonation process is to enhance the ozone decomposition, yielding more free radicals for reaching a higher oxidation rate (Eq. (2)):



DMSO is being introduced into semiconductor manufacturing processes to replace the solvents containing phenol with

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high toxicity. Moreover, due to its solvent property and water miscibility, DMSO has become more attractive in industrial use. Although DMSO itself has low toxicity, the biological treatment of wastewater containing DMSO is known to be somehow difficult because aerobic biological processes cannot achieve an effective level of DMSO decomposition, and anaerobic biological processes can produce volatile and noxious compounds, such as dimethyl and hydrogen sulfides, which makes it difficult to control the treatment process. Lee et al. investigated DMSO degradation and its degradation intermediates and mineralization using UV/H<sub>2</sub>O<sub>2</sub> process [11]. Koito et al. also found that DMSO could be efficiently decomposed into methanesulfonic acid without producing any reduced and harmful sulfur-containing byproducts using the same process [12].

The aim of the research presented here is to assess the potential of ozonation and AOPs for the oxidation of DMSO, its degradation intermediates and to compare O<sub>3</sub>, UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> processes efficiency. Thus, it is important to select proper treatment technique to improve the overall efficiency of the wastewater treatment unit. In this work, the oxidation techniques mentioned above have been substantially investigated.

## 2. Experiments

### 2.1. Chemicals

Hydrogen peroxide (30%, w/w), DMSO, CH<sub>3</sub>SO<sub>3</sub>H, HCO<sub>2</sub>H, CH<sub>2</sub>O and CH<sub>3</sub>SO<sub>2</sub>Na (Aldrich), obtained from Merck Chemical Co., Taiwan, were of analytical grade and used without further purification. For all experimental work, deionized water Milli q-Plus, resistance = 18.2 MΩ was used. The solution pH was adjusted by using 0.1N H<sub>2</sub>SO<sub>4</sub> and or NaOH.

### 2.2. Ozone and AOPs experiments in lab scale experiments

Ozone was generated from dried pure oxygen by corona discharge using an ozone generator (Ozonair RXO-5), which can produce 6% ozone concentration (w/w) in the oxygen enriched gas stream. To better maintain the performance and efficiency of the ozone system, the oxygen was dried using a molecular sieve before being entered into the ozone generator. A 0.5-l semi-batch reactor, which was made of pyrex glass with the dimensions of 7.5 cm diameter and 11.5 cm tall, was used to facilitate the operation of all ozone-based oxidation processes (Fig. 1). Ozone was introduced through a porous fritted diffuser that can produce fairly fine bubbles with diameter less than 1 mm, which had been determined using a camera with close-up lens and image analysis software Matrox Inspector 2.0 [13]. The gas flow rate was regulated by a mass flow controller (Brooks 5850E). The gaseous ozone concentrations in the inlet and outlet stream were determined spectrophotometrically by the absorbance of ozone measured in a 2-mm flow-through quartz cuvette at the wavelength 254 nm. An extinction coefficient of 3000 M<sup>-1</sup> cm<sup>-1</sup> was used to convert absorbances into concentration units [14]. Ozone applied dosage is defined as the product of gas flow rate, ozone

concentration, and ozonation period, divided by the reactor volume. All experiments were operated at 25 °C using a water jacket around the reactor. In UV light based process, a low-pressure UV lamp (UV pen ray lamp) with an output intensity of 5.5 mW cm<sup>-2</sup> was placed at the center of the reactor and shielded by a vertically immersed quartz jacket which was circulated with coldwater to avoid heat accumulation. A black box placed outside the reactor was employed to minimize any penetration of UV light when a UV-enhanced facility was operated. UV/H<sub>2</sub>O<sub>2</sub> process was also carried out using the same apparatus and similar conditions.

### 2.3. Analytical methods

Samples were drawn out from the reactor at desired time intervals in the course of the experiments. The residual dissolved ozone in the samples was removed immediately by stripping with nitrogen gas (99.99%). DMSO and H<sub>2</sub>O<sub>2</sub> were analyzed by HPLC (LC-10 AT Shimadzu) equipped with an ultra aqua C<sub>18</sub> column (5 μm, 250 mm × 4.6 mm) employing UV detection at wavelength of 214 nm. The mobile phase consisted of water containing acetonitrile with a ratio of 60:40 and the flow rate was 1.0 ml/min. The retention time of H<sub>2</sub>O<sub>2</sub> and DMSO are 2.5 and 3.1 min, respectively, and the standard deviation of these retention times was lower than 0.1 min. The ionic intermediates of DMSO were identified by using an ion chromatograph (IC, Dionex, DX-120) with a conductivity detector. Methanesulfonate, methanesulfinate and formate were analyzed using an IonPac AS 9-HC anionic column (4 mm × 250 mm) with 90 mM Na<sub>2</sub>CO<sub>3</sub> as the eluent solution (flushing rate = 1.0 ml min<sup>-1</sup>). The intermediates were identified by comparison of their retention times with those of the authentic compounds. The following retention times for each intermediate were obtained in ion chromatography analysis and the standard deviation of all retention times was less than 0.1 min: methanesulfonate (4.8 min), methanesulfinate (4.0 min), formate (4.4 min). The solution pH was measured with a Crison GLP-22 pH-meter.

## 3. Results and discussion

### 3.1. DMSO decomposition in the presence of radical scavenger

The first part of this work is mainly evaluating the oxidizing ability of ozone towards DMSO under various experimental conditions. In order to eliminate the greatest possible degree of hydroxyl radical in solution, the reaction was carried out with a pH of 3, and in the presence of *t*-butanol, a compound that reacts very slowly with ozone ( $k_D = 0.03 \text{ M}^{-1} \text{ S}^{-1}$ ) [15], although its ability to react with hydroxyl radicals ( $k_{OH} = 5 \times 10^{-8} \text{ M}^{-1} \text{ S}^{-1}$ ) is widely known [16]. Therefore, the presence of *t*-butanol in the ozonation process has substantially avoided the reactivity of free radicals towards our target organics. Fig. 2 depicts DMSO (1 g/l) degradation at different initial concentrations of *t*-butanol at pH 3. It can be noted that the DMSO degradation is slightly retarded in the presence of *t*-butanol, which shows that DMSO is at least partially oxi-

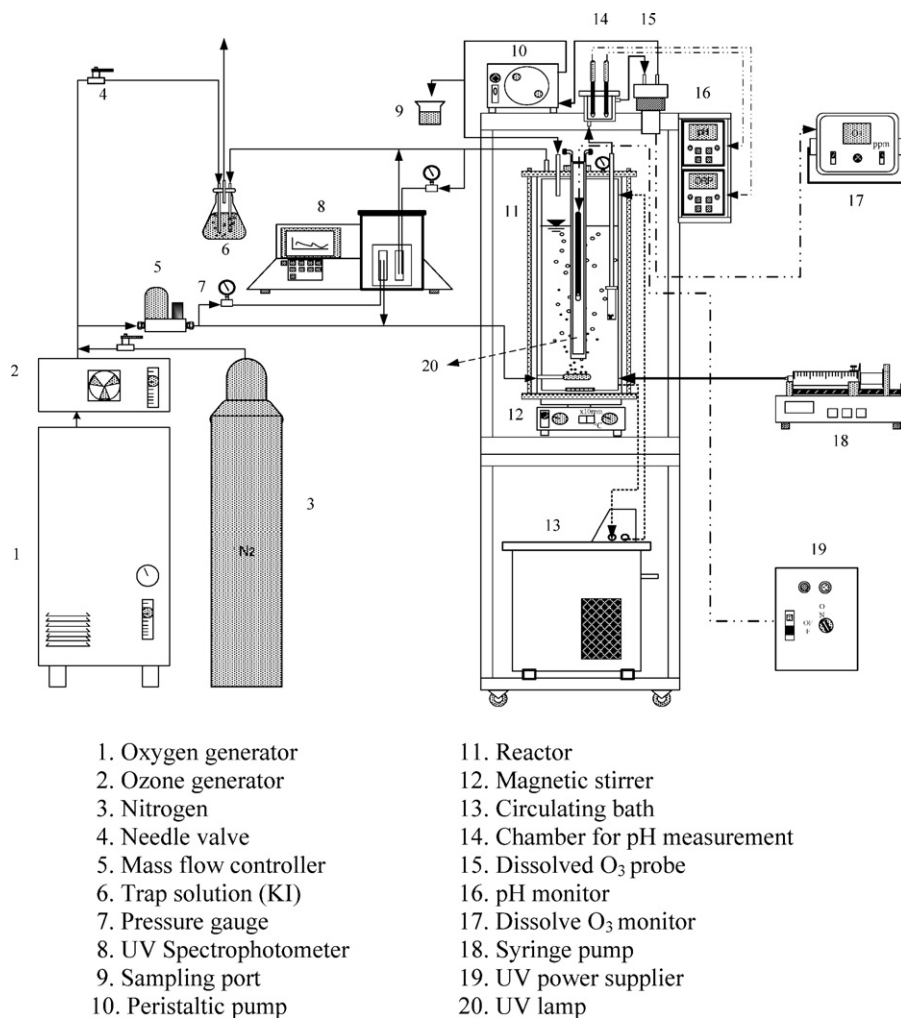


Fig. 1. System set-up for ozone-based advanced oxidation processes.

dized by hydroxyl radical even at pH 3. Although the removal rate is slightly inhibited in initial reaction periods, the overall removal rates at 60 min are almost same in all reactions and this shows that 0.05 M of *t*-butanol concentration is enough to inhibit the radical pathways completely. Similar observations were also observed by Polo et al. in the degradation of

1,3,6-naphthalenetrifluoronic acid by ozonation [17]. This radical reaction could be attributed to the decomposition of ozone, which eventually leads to a hydroxyl radical or to the formation of radicals from the direct attack of ozone. In conclusion, there is no obvious inhibition effect is observed in the presence of *t*-butanol.

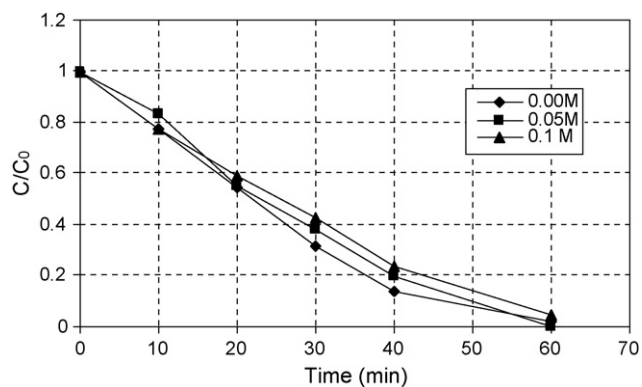


Fig. 2. Effect of *t*-BuOH on the degradation of DMSO by ozonation. [DMSO]=1000 mg/l; pH 3.0 ± 0.1; applied ozone dosage = 18.4 mg/l min<sup>-1</sup>; temperature = 52 °C.

### 3.2. Analysis of DMSO degradation product by ozonation process

In order to avoid any DMSO degradation induced by free radicals, the reaction has been carried out under the presence of 0.05 M *t*-butanol. Hence the degradation intermediate observed in this process is totally due to the reaction between molecular ozone and DMSO. Ion chromatography analysis shows that methanesulfinate (CH<sub>3</sub>SO<sub>2</sub><sup>-</sup>) and methanesulfonate (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>) were identified as major sulfur-containing intermediates, whereas formic acid (HCOOH) was identified as a non-sulfur intermediate. The formation of formaldehyde (HCHO) was also identified as a reaction intermediate. However, due to analytical limitation, we could not estimate its concentration quantitatively and accurately. Lee et al. also observed

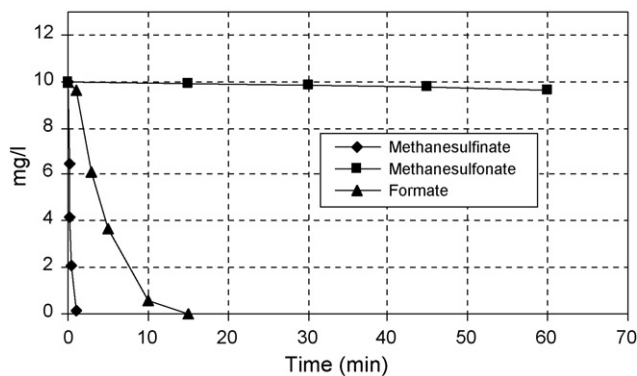


Fig. 3. Degradation of DMSO intermediates as a function of time by ozonation. [Intermediates]=10 mg/l; pH  $3.0 \pm 0.1$ ; applied ozone dosage =  $18.4 \text{ mg/l min}^{-1}$ ; temperature =  $25^\circ\text{C}$ .

all the above-said intermediates during UV/H<sub>2</sub>O<sub>2</sub> treatment of DMSO [11]. In order to understand the fate of these intermediates, the decomposition of these compounds have been studied at 10 mg/l of initial concentration at pH 3 under the identical conditions used for DMSO degradation and the results are shown in Fig. 3. The figure clearly shows that methanesulfinate and formate are more easily degraded than methanesulfonates. The complete degradation of methanesulfinate and formate were observed within a minute and 15 min, respectively. However, the suphonate degradation is quite different from the former two; about 3.7% of methanesulfonate degradation was observed after 60 min. The higher removal rate of methanesulfinate and formate are due to their fast reaction with ozone. The first-order rate constants of these reactions were found to be  $2.2596$  and  $0.3191 \text{ min}^{-1}$ , respectively, which shows higher reactivity towards ozone. However, the opposite effect was noted in methanesulfonate, of which the rate constant was found to be  $0.0005 \text{ min}^{-1}$ . Thus, a low removal rate was observed in the degradation of methanesulfonate.

### 3.3. Determination of direct reaction constant ( $k_D$ )

The direct reaction constant ( $k_D$ ) of DMSO is performed at pH 3. Second-order rate constant for DMSO was determined under conditions where the organic pollutant was excess. Due to the analytical limitation for low concentration measurements of DMSO, the ozone decreases was monitored instead of the disappearance of the DMSO compound [18,19]. The indigo method was applied to monitor the ozone disappearance. As we discussed above, DMSO degradation was slightly inhibited in the presence of *t*-butanol, however, we did not observe any inhibition effect in the direct rate constant measurement experiments. So direct rate constant experiments were studied in the absence of *t*-butanol. In this experiment, the reactor was filled with 500 ml of  $1.79 \times 10^{-4} \text{ M}$  aqueous ozone solution and DMSO solution (0.1278 M) was then injected and the study was commenced. The reaction rate is expressed as first-order with respect to dissolved ozone concentration [ $\text{O}_3$ ] and first-order with respect to the organic compound [DMSO]. Thus, in Fig. 4 it can be seen that when  $-\ln(C_{(\text{O}_3)_t}/C_{(\text{O}_3)_0})$  is plotted against time, the data could fit with a straight line, having a regression coefficient of

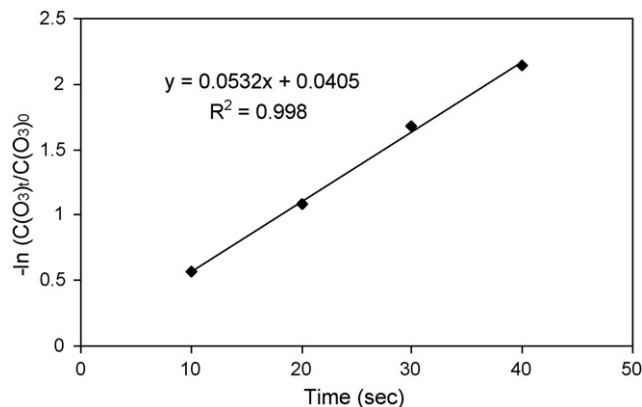


Fig. 4. Determination of direct reaction constant between ozone and DMSO. [DMSO]=0.1278 M; pH  $3.0 \pm 0.1$ ; [ $\text{O}_3$ ]<sub>0</sub> =  $1.79 \times 10^{-4} \text{ M}$ ; temperature =  $25^\circ\text{C}$ .

0.998. From Fig. 4 it can be deduced that the value of  $k_{\text{obs}}$  is  $0.0532 \text{ s}^{-1}$ , and therefore, the value of  $k_D$  is  $0.4162 \text{ M}^{-1} \text{ S}^{-1}$ . This reaction rate constant implies that ozone is not a potential oxidizing agent for the degradation of DMSO.

### 3.4. Effect of influent ozone dosages

Experiments of DMSO degradation by ozone have been studied by modifying the influent applied ozone doses from  $9.2$  to  $36.8 \text{ mg/l min}^{-1}$  and the results are presented in Fig. 5. It is apparent that the degradation rate of DMSO is enhanced with the increase of the applied ozone dosage. The figure clearly shows that increase of the influent applied ozone dosage from  $9.2$  to  $27.6 \text{ mg/l min}^{-1}$  would result in the decomposition of DMSO from  $427$  to  $801 \text{ mg/l}$  at the 30 min period. Based on the data in Fig. 5, it can be calculated that averagely  $1.5 \text{ mg}$  of inflow ozone was consumed by per mg of DMSO removal. However, higher ozone dosage did not increase the degradation rate appreciably. Similar results were also reported by Benitez et al. in the degradation of 4-chloro-2-methylphenoxyacetic acid [20] and Stowell and Jensen in the chlorendic acid degradation [21]. The dissolved ozone concentration in aqueous solution was found to be increased linearly with gaseous ozone concentration based upon Henry's law. Moreover, a high-applied ozone dosage

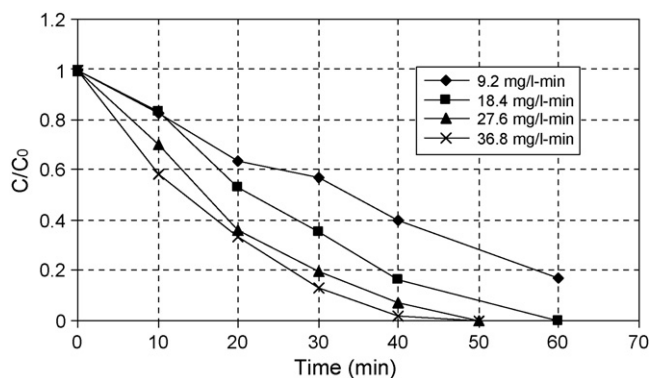


Fig. 5. Effect of ozone gas flow dosage on the degradation of DMSO by ozonation. [DMSO]=1000 mg/l; pH  $3.0 \pm 0.1$ ; temperature =  $25^\circ\text{C}$ .



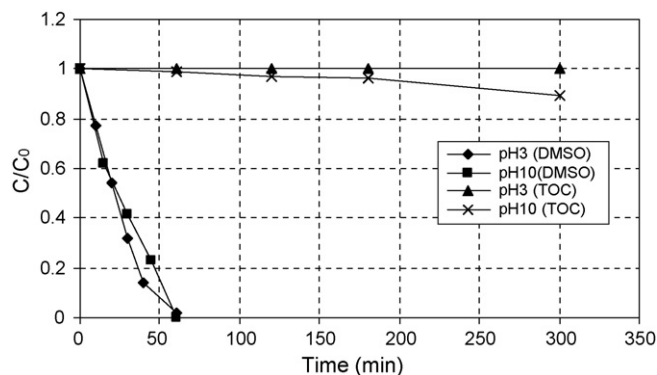


Fig. 6. Effect pH on the DMSO degradation and TOC removal by ozonation process. [DMSO] = 1000 mg/l; applied ozone dosage = 18.4 mg/l min<sup>-1</sup>; temperature = 25 °C.

(36.8 mg/l min<sup>-1</sup>) could not further increase the dissolved ozone concentration in the system, thus resulting in a limited improvement of DMSO degradation. It is concluded that the DMSO oxidation is more favorable in solutions containing higher dissolved ozone concentrations within the experimental range of this research.

### 3.5. Advanced oxidation processes

Since ozonation process alone is not effective in DMSO mineralization, the reaction has been tested by the combination of different oxidants such as O<sub>3</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, and UV/H<sub>2</sub>O<sub>2</sub>. All processes at pH 10 have been studied by the addition of 1 g/l of boric acid buffer (H<sub>3</sub>BO<sub>4</sub>/NaOH) solution. However, at pH 3, the solution pH was merely adjusted by using H<sub>2</sub>SO<sub>4</sub>. All reactions have been carried out at initial DMSO concentration 1 g/l at 25 °C. UV/H<sub>2</sub>O<sub>2</sub> process was also carried out under similar conditions of other AOP processes without purging ozone.

#### 3.5.1. Degradation of DMSO by ozonation process

In general, direct molecular ozone is predominant in an acidic medium, whereas radical chain reaction is predominant in a basic medium [22]. In order to assess the efficiency of both reaction pathways towards DMSO degradation, the reaction has been studied at pH 3 and 10, respectively. Fig. 6 depicts DMSO degradation by ozonation process as a function of reaction time. Apparently, a huge difference in DMSO degradation and its TOC removal rate is noted. After 30 min of ozonation, 68.2%, 58.5% of DMSO degradation, and 0%, 10.9% of TOC removal at 300 min was observed at pH 3 and 10, respectively. DMSO decomposition efficiencies seems to be close at pH 3 and 10 and this observation indicated that DMSO removal could be simply achieved via both reaction pathways, whereas TOC removal could be more pronounced by the radical mechanism. This low TOC removal at pH 10 suggests that the concentration of the oxidizing agent is not enough to completely degrade the intermediates produced by DMSO. Since hydroxyl radical is a more powerful oxidizing agent than ozone, the overall removal efficiency of DMSO in an alkaline medium is more efficient than an acidic medium.

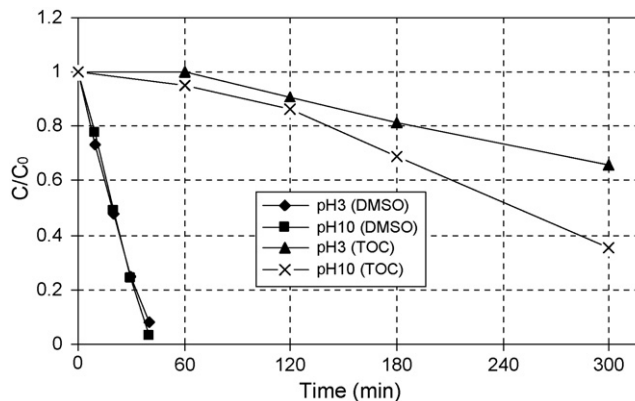
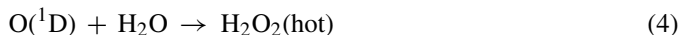
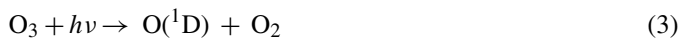


Fig. 7. Effect pH on the DMSO degradation and TOC removal by O<sub>3</sub>/UV process. [DMSO] = 1000 mg/l; applied ozone dosage = 18.4 mg/l min<sup>-1</sup>; UV light intensity = 5.5 mW cm<sup>-2</sup>; temperature = 25 °C.

#### 3.5.2. Ozonation in the presence of UV light

Generally, ozone in the presence of an initiator (H<sub>2</sub>O<sub>2</sub> or UV) can produce more hydroxyl radicals and is expected to enhance the decomposition rate of pollutants present in wastewater. In order to achieve more TOC removal, DMSO degradation has been investigated in the presence of UV light. Fig. 7 depicts DMSO decomposition and its TOC removal as a function of reaction time. In the blank tests (data not shown), the photolysis of DMSO by 254 nm irradiation alone was found to be trivial. It indicates that direct attack by UV irradiation on DMSO is negligible. About 75.2%, 76% of DMSO decomposition in 30 min and 34.2%, 64.6% of TOC removal at 300 min was observed at pH 3 and 10, respectively. Moreover, higher removal efficiencies were observed in UV/O<sub>3</sub> process over ozonation process at both pHs, which indicates that UV light irradiation enhances the removal efficiency. Nevertheless, the TOC removal efficiency is more pronounced than DMSO decomposition at both pHs. Like the ozonation process, alkaline pH is more favorable for the degradation of all these compounds. This enhancement of the removal rate in the presence of UV light is due to generation of hydroxyl radicals from ozonation. Eqs. (1), (3)–(7) [23]:



#### 3.5.3. Ozonation in the presence of H<sub>2</sub>O<sub>2</sub>

Ozonation in the presence of hydrogen peroxide (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) was also carried out to test DMSO decomposition and its TOC removal efficiency. The effect of hydrogen peroxide (1 g/l) addition to the ozonation process at two different pHs on DMSO degradation is shown in Fig. 8. The addition of hydrogen peroxide causes 72.9% and 59.2% of DMSO degradation after 30 min at pH 3 and 10, respectively. Thus, an acidic medium is favorable for efficient DMSO degradation. However, TOC removal was not observed in acid medium, whereas only 4% of TOC removal

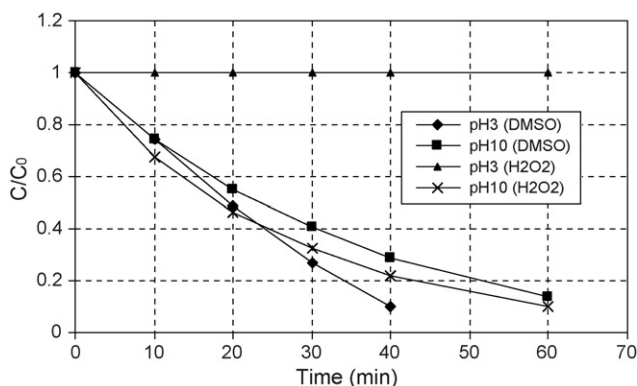
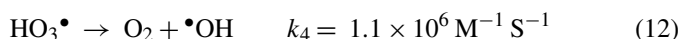
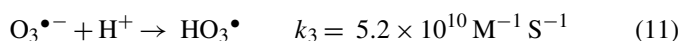
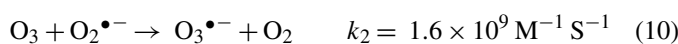
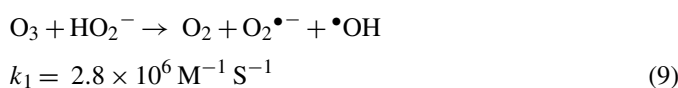
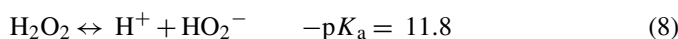


Fig. 8. Effect pH on the DMSO degradation and TOC removal by O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process. [DMSO] = 1000 mg/l; [H<sub>2</sub>O<sub>2</sub>] = 1000 mg/l; applied ozone dosage = 18.4 mg/l min<sup>-1</sup>; temperature = 25 °C.

was observed in a basic medium at 60 min of reaction time (the TOC data is not presented in Fig. 8). Apparently, DMSO decomposition results are very close to the ozonation process. Addition of H<sub>2</sub>O<sub>2</sub> enhances the decomposition rate slightly at pH 3 and 10 and this result shows that addition of hydrogen peroxide did not improve the degradation rate appreciably. In order to understand this outcome clearly, the hydrogen peroxide decomposition was also measured during the ozonation process and the results are shown in Fig. 8. In an acidic medium (pH 3), H<sub>2</sub>O<sub>2</sub> was not decomposed, whereas in a basic medium almost 99% of the added H<sub>2</sub>O<sub>2</sub> was consumed at 60 min. These results suggested that H<sub>2</sub>O<sub>2</sub> did not react with ozone in an acid medium and the DMSO degradation is mainly facilitated by ozone. However, the H<sub>2</sub>O<sub>2</sub> decomposition at pH 10 is due to the reaction between ozone and the conjugate base of hydrogen peroxide as shown by Eqs. (8)–(12) [24]:



It was reported that the conjugate base of H<sub>2</sub>O<sub>2</sub> at millimolar concentrations could initiate the decomposition of ozone much more rapidly into hydroxyl radical than with the hydroxide ion [25]. In conclusion, addition of H<sub>2</sub>O<sub>2</sub> to the ozonation process did not enhance the removal rate appreciably.

### 3.5.4. UV/H<sub>2</sub>O<sub>2</sub> process

Other commercially attracted AOPs are hydrogen peroxide photolysis. In order to compare the efficiency of this process with other AOPs, the reaction has been carried out under identical conditions of ozone-based processes previously mentioned. Fig. 9 depicts DMSO and H<sub>2</sub>O<sub>2</sub> decomposition as a function of reaction time at two different pHs. Almost complete

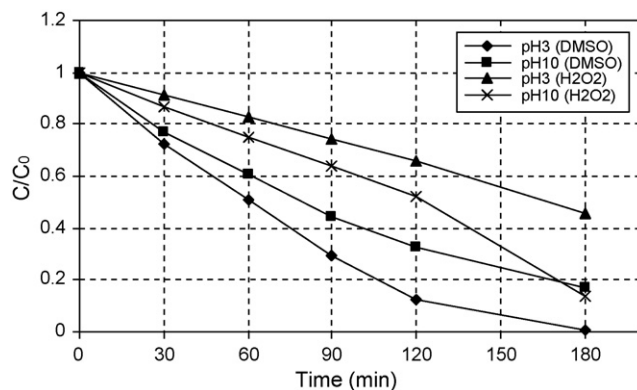


Fig. 9. Effect pH on the DMSO degradation and by UV/H<sub>2</sub>O<sub>2</sub> process. [DMSO] = 1000 mg/l; [H<sub>2</sub>O<sub>2</sub>] = 1000 mg/l; UV light intensity = 5.5 mW cm<sup>-2</sup>; temperature = 25 °C.

degradation of DMSO was observed at 180 min of reaction time at pH 3, whereas at the same time 83% of decomposition was observed at pH 10. Moreover, no TOC removal was observed at both pH after 180 min (data not given in Fig. 9). The decomposition is likely to be the generation of hydroxyl radicals by UV photolysis of H<sub>2</sub>O<sub>2</sub>. It seems that DMSO degradation in an acidic medium is more favorable than in an alkaline medium. However, hydrogen peroxide decomposition results are opposite to the target pollutant decomposition results. Since at constant light intensity (5.5 mW cm<sup>-2</sup>) the photolysis rate of H<sub>2</sub>O<sub>2</sub> might be the same at these two pHs, the larger decrease in concentration of H<sub>2</sub>O<sub>2</sub> in a basic medium may be due to the existence of its conjugate form. The abundant existence of residual H<sub>2</sub>O<sub>2</sub> concentration in alkaline pH solution would scavenge the hydroxyl radicals to lower the efficiency of DMSO degradation. Therefore, it can be concluded that acidic medium is efficient for DMSO decomposition under the experimental conditions.

### 3.6. Comparison of AOPs

DMSO decomposition (1 g/l) and its TOC (60 min) removal efficiency and sulfate ion formation, has been taken for comparison under optimum conditions of each process. All three ozone-based AOP processes are efficient at basic medium. Thus, we used basic medium removal efficiency for comparisons, whereas UV/H<sub>2</sub>O<sub>2</sub> process is efficient at acidic medium, hence we used acidic medium removal efficiency for comparisons. First-order rate constants (*k*) and the percentage of TOC conversion after 60 min of reaction time (*φ*<sub>60</sub>) of these AOPs were calculated from the degradation curves and presented in Table 1. As we discussed before, a remarkable difference between the DMSO degradation and TOC removal were noted in all these processes. Degradation was almost complete within an hour in ozonation and UV-enhanced ozonation processes. At the same time, 86.4% and 17.2% of degradation were noted in O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> processes. At the same time, about 1%, 4.8%, 3.8% and 0% of TOC removal was observed in O<sub>3</sub>, UV/O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> processes, respectively. Further quan-

Table 1  
Comparison of various AOP processes of DMSO degradation rate constant of TOC

Processes	$k$ min <sup>-1</sup>	$t_{1/2}$ (min)	$R^2$	$\varphi_{60}$ (%)
O <sub>3</sub>	0.0193	35.90	0.9675	1.0
O <sub>3</sub> /UV	0.0248	27.94	0.9976	4.8
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	0.0148	46.82	0.9435	3.8
UV/H <sub>2</sub> O <sub>2</sub>	0.0073	94.93	0.9928	0.0

[DMSO] = 1000 mg/l; [H<sub>2</sub>O<sub>2</sub>] = 1 g/l; reaction time = 60 min; applied ozone dosage = 18.4 mg/l min<sup>-1</sup>; UV light intensity = 5.5 mW cm<sup>-2</sup>; temperature = 25 °C.

titative interpretation of the results requires a kinetic model. The degradation kinetics of the DMSO by these AOPs used may be expressed by first-order kinetics. Although all AOP processes obey first-order kinetics, a slight deviation is observed in ozonation and hydrogen peroxide enhanced ozonation process. From Table 1, the rate constant of each process is compared and the efficiencies of UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> processes are 3.39-, 1.69- and 1.28-fold lower than UV/O<sub>3</sub> process. From these results we can conclude easily that the UV/O<sub>3</sub> process is most efficient and UV/H<sub>2</sub>O<sub>2</sub> process is least efficient. Although O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process is less efficient than ozonation process in DMSO degradation, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process is more efficient in TOC removal. The low TOC removal in all these processes is mainly due to the resistance of methanesulfonate to oxidation during the DMSO degradation. As we discussed earlier, methanesulfonate has strong resistance to ozonation and also has a comparatively low reactivity towards hydroxyl radical ( $0.8 \times 10^6$  M<sup>-1</sup> S<sup>-1</sup>). In conclusion, UV light-enhanced ozonation process is more efficient in DMSO decomposition and TOC removal than other AOPs.

Mineralization is the ultimate goal of the oxidation processes and this is usually determined by the measurements of (TOC) and inorganic anions. DMSO contains one sulfur heteroatom and hence the mineralization of DMSO would produce sulfur-containing inorganic ions, such as sulfate ion (SO<sub>4</sub><sup>2-</sup>), as a mineralization product. Many authors observed sulfate ion as a mineralization end product in sulfur-containing organic pollutants in degradation studies [26–28]. The formation of sulfate ion is quantitatively estimated by using ion chromatography. Since at high initial DMSO concentration (1 g/l), the mineralization is too slow and hence the formation of sulfate ion is studied at low initial concentration of DMSO (0.01 g/l). Fig. 10 depicts sulfate ion formation as a function of reaction time in all these AOPs processes under similar experimental conditions. After 150 min, about 4.91, 3.86, 1.22 and 0.76 mg/l of sulfate ions were observed in O<sub>3</sub>, UV/O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> processes, respectively. The order of efficiencies of these processes is different from TOC removal efficiencies. Since the substrate and its intermediates concentration are low, the excess of hydroxyl radical may be scavenged by ozone (Eq. (13)) and thus lower efficiencies was observed in UV/O<sub>3</sub> process.

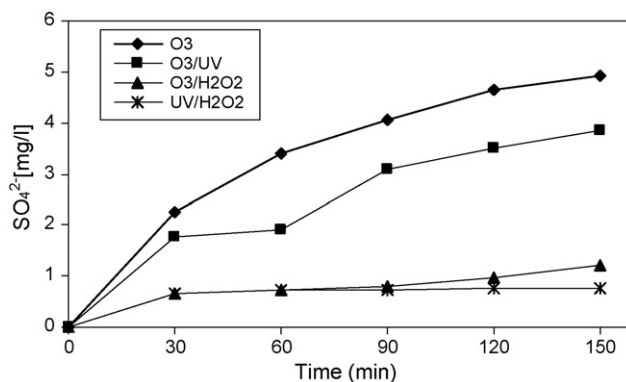


Fig. 10. Effect of sulfate ion formation on various AOPs. O<sub>3</sub> process: [DMSO] = 10 mg/l, pH 10.0; applied ozone dosage = 18.4 mg/l min<sup>-1</sup>; temperature = 25 °C. UV/O<sub>3</sub> process: [DMSO] = 10 mg/l; pH 10.0; applied ozone dosage = 18.4 mg/l min<sup>-1</sup>; UV light intensity = 5.5 mW cm<sup>-2</sup>; temperature = 25 °C. O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process: [DMSO] = 10 mg/l; [H<sub>2</sub>O<sub>2</sub>] = 1000 mg/l; pH 10.0; applied ozone dosage = 18.4 mg/l min<sup>-1</sup>; temperature = 25 °C. UV/H<sub>2</sub>O<sub>2</sub> process: [DMSO] = 10 mg/l; [H<sub>2</sub>O<sub>2</sub>] = 1000 mg/l; pH 10.0; UV light intensity = 5.5 mW cm<sup>-2</sup>; temperature = 25 °C.

#### 4. Conclusions

The direct rate constant ( $k_D$ ) values showed that ozone itself is not an effective oxidizing agent for the degradation of DMSO containing wastewater. 1 g/l of DMSO is completely removed in 60 min of reaction time. The DMSO removal rate increases from 59.8 to 98%, when the ozone gas applied dosage increases from 9.2 to 36.8 mg/l min<sup>-1</sup>. The first-order rate constants of DMSO degradation intermediates, such as formate, methanesulfinate, and methanesulfonate are found to be 2.2596, 0.3191 and 0.0005 min<sup>-1</sup>, respectively. DMSO degradation is more efficient in alkaline medium in all ozone-based AOPs, whereas UV/H<sub>2</sub>O<sub>2</sub> process is efficient in acidic medium. However, all ozone-based AOP processes are more efficient than UV/H<sub>2</sub>O<sub>2</sub> process. DMSO decomposition and its TOC mineralization efficiencies were in the following order O<sub>3</sub>/UV ≈ O<sub>3</sub> > O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> > UV/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>/UV > O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> > O<sub>3</sub> > UV/H<sub>2</sub>O<sub>2</sub>, respectively. The formation of sulfate ions at low initial DMSO concentration were in the following order O<sub>3</sub> > UV/O<sub>3</sub> > O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> > UV/H<sub>2</sub>O<sub>2</sub>. Finally, it is concluded that UV light-enhanced ozonation is the potential candidate for DMSO abatement in wastewater.

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