Decomposition of dimethyl phthalate in an aqueous solution by ozonation with high silica zeolites and UV radiation

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Abstract

This study investigates the enhanced ozonation of dimethyl phthalate (DMP), which is a pollutant of concern in water environments, with high silica zeolites and ultraviolet (UV) radiation. Semibatch ozonation experiments are performed under various reaction conditions to examine the effects of inlet gas ozone concentration, high silica zeolite dosage, and UV radiation intensity on the decomposition of DMP. The complete removal of DMP can be efficiently achieved via both O_3 and O_3/UV treatments. Note that the presence of high silica zeolites accelerates the decomposition rate of DMP in the O_3 process. On the other hand, the removal efficiencies of both chemical oxygen demand (COD) and total organic carbons (TOC) are significantly enhanced by employing the ozonation combined with UV radiation. The O_3/UV process is also advantageous for the utilization efficiency of fed ozone especially in the late ozonation period. Furthermore, the correlation between the COD removal percentage (%) and the mole ratio of ozone consumed to the DMP treated ($mol\,mol^{-1}$) is obtained. The clear-cut removal relationship of the TOC with COD during the ozonation of DMP has also been presented. Consequently, the results evaluate the flexibility of ozonation system associated with high silica zeolites and UV radiation for the removal of DMP and provide the useful information in engineering application.
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Keywords: Ozone; Ozonation; High silica zeolites; UV radiation; Dimethyl phthalate

1. Introduction

Many environmental hormones such as phthalic acid esters have been found in the wastewater that comes from urban sewage and factories due to the fast economic development in the recent years [1]. The large amounts of phthalic acid esters are often leached from the plastics dumped at municipal landfills. These pollutants are refractory to the environmental microorganism and accumulate in the natural water bodies that causes the wide distribution within the aqueous system like rivers, lakes, and groundwater as well as the noticeable influence on the ecological environment [2]. That could damage the endocrine system of the human body while the phthalic acid esters are overdosed through the eating or inspiration.

Dimethyl phthalate (DMP) is one of the most common phthalic acid esters. The chemical structure of DMP is composed of a benzene ring with methyl ester groups attached in the para position. DMP has been used as a plasticizer in tools, automotive parts, toothbrushes, food packaging, cosmetics, insecticide, etc. Accordingly, DMP has been frequently detected in wastewater effluents and river water because of its high mobility in the aquatic system [3]. DMP has endocrine disrupting effects on aquatic species by altering the action of endogenous steroid hormones. Therefore, DMP is an aqueous pollutant of concern in water and wastewater systems. The common method for DMP removal in the wastewater is biological treatment, which is based on the metabolic degradation of DMP by microorganism under aerobic or anaerobic conditions. However, several studies have found that phthalates with long alkyl-chains are poorly degraded and some of them are considered refractory to biological treatment. Bauer et al. [2] studied the hydrolysis, anaerobic transformation, and O_3/ultraviolet (UV) processes to destroy some phthalic acid

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Nomenclature

A_q	outer area of quartz tubes submerged in solution (cm^2)
C_{AGi0}	concentration of inlet gas ozone (mg/L or M)
C_{AGe}	concentration of off-gas ozone (mg/L or M)
C_{ALb}	concentration of dissolved ozone (mg/L or M)
C_{BLb}	concentration of DMP in liquid (mg/L)
C_{BLb0}	initial concentration of DMP in liquid (mg/L or M)
C_{COD}	concentration of COD in liquid (mg/L)
C_{COD0}	initial concentration of COD in liquid (mg/L)
C_{TOC}	concentration of TOC in liquid (mg/L)
C_{TOC0}	initial concentration of TOC in liquid (mg/L)
COD	chemical oxidation demand
DMP	dimethyl phthalate
F_s	fraction of emitting light absorbed by the solution
$[I]$	UV radiation intensity (W/L)
$[I_{uv}]$	light intensity measured on outer surface of quartz tubes housing UV lamps (W/cm^2)
k_B	pseudo-first order reaction rate constant of DMP (min^{-1})
K_{ow}	octanol–water partition coefficient
m_{O3A}	mass of ozone applied (mol)
m_{O3R}	mass of ozone consumed (mol)
Q_G	gas flow rate (L/min)
r^2	correlation coefficient
t	time (min)
$t_{f,DMP}$	time for concentration reduction of DMP greater than 98% (min)
T	temperature (°C)
TOC	total organic carbons
UV	ultraviolet
V_F	volume of free space (L)
V_L	volume of bulk liquid (L)
W_{cat}	high silica zeolite dosage (g/L)

Greek letters

η_{COD}	removal efficiency of COD (%)
η_{TOC}	removal efficiency of TOC (%)

esters and concluded that only the O$_3$/UV process is able to efficiently decompose di-(2-ethylhexyl) phthalate and benzyl butyl phthalate.

Ozonation is an effective process to remove organic pollutants. The compounds are attacked through two different reaction mechanisms: (1) direct ozonation by the ozone molecules and (2) radical oxidation by highly oxidative free radicals such as hydroxyl free radicals, which are formed by the decomposition of ozone in the aqueous solution [4]. The radical oxidation is considered nonselective and vigorous. The purpose of introducing UV radiation in the ozonation process is to enhance the ozone decomposition, yielding more free radicals for a higher oxidation performance. In addition, heterogeneous catalytic ozonation is a novel type of advan-

tage oxidation that combines ozone with the adsorptive and oxidative properties of solid phase metal oxide catalysts to accelerate the ozonation rate. High silica zeolites have been introduced as the hydrophobic adsorbent in the ozonation processes to increase the removal efficiency of target pollutant [5–7]. The high silica zeolites have an excellent adsorption affinity toward ozone molecules and hydrophobic pollutants, as the dissolved ozone can be concentrated inside the pores of the high silica zeolites. Fujita et al. [6] and Sagehashi et al. [7] found that the decomposition rates of trichloroethene and 2-methylisoborneol during ozonation increase in the presence of high silica zeolites, respectively. These phenomena are attributed to the concentrated dissolved ozone on the high silica zeolites.

The chemical oxygen demand (COD) and total organic carbons (TOC) are often used to indicate the treatment performance of the targeted solution [8]. The COD value can represent a variety of organic compounds in various oxidation states. When some chemical species are oxidized with ozonation time, the decrease of COD is employed to characterize the change of these fractions. TOC is a convenient and direct expression of total organic content as an index of mineralization. If a relationship has been established between the COD and TOC, then the TOC can be used as an estimate of COD for the specific solution. However, one may note that since the TOC value is independent of the oxidation state of organic compounds and does not vary proportional to the COD value. The information regarding the practicability of DMP removal via ozonation treatments is limited and desirable. Recently, the heterogeneous Ruthenium (Ru)/Al$_2$O$_3$ catalyzed ozonation of DMP was performed to study the TOC removal [9]. The results indicated that the mineralization of DMP during ozonation could be promoted by the use of the Ru/Al$_2$O$_3$ catalysts, showing a maximum TOC removal of approximately 80%. Nevertheless, the degradation rate of DMP decreased with the addition of Ru/Al$_2$O$_3$ catalysts due to the hindrance to gas diffusion. In addition, the preparation of the Ru/Al$_2$O$_3$ catalysts is relatively complicated and expensive.

The present work focuses on the enhanced ozonation combined with high silica zeolites and UV radiation for the removal of DMP as the model compound of phthalic acid esters. Semibatch ozonation experiments are performed in the completely stirred tank reactor under the conditions of various inlet gas ozone concentrations, high silica zeolite dosages, and UV radiation intensities. The concentration variations of DMP, COD, and TOC of the solution are analyzed at specified time intervals to study the decomposition of DMP. The clear-cut relationships between the COD removal and the ozone consumption as well as the TOC removal have been obtained. The synergistic effect of UV radiation on the ozonation of DMP with or without the high silica zeolites is also studied. These parameters are crucial for the performance evaluation of DMP ozonation and still need to be investigated. Therefore, the results of this study can provide the referable information about the proper application of ozonation with high silica zeolites and UV radiation for the removal of DMP.
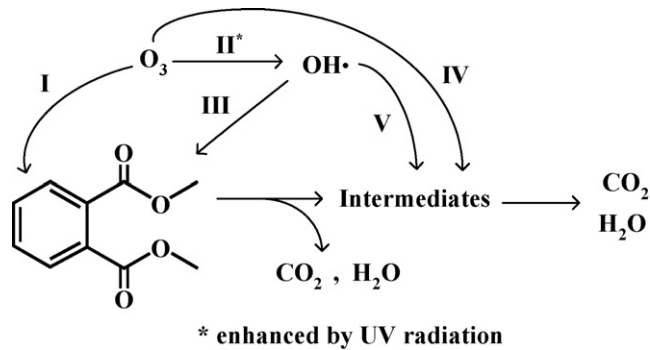
Fig. 1. The molecular structure and simplified scheme of the decomposition pathways of the ozonation of DMP with UV radiation.

2. Materials and methods

2.1. Chemicals

DMP, with a chemical formula of $C_{10}H_{10}O_4$ purchased from Merck (Darmstadt, Germany), has a molecular weight of 194.19 Da, a boiling point of 282 °C, and a CAS registry number of 84-66-2. The molecular structure of DMP is shown in Fig. 1. All experimental solutions were prepared with deionized water without other buffers. The initial concentration of DMP (C_{BLb0}) in the aqueous solution consisting of DMP as the only target was 0.4 mM (77.7 mg/L). The initial COD (C_{COD0}) and TOC (C_{TOC0}) values of the prepared solution were measured about 134 and 45 mg/L, respectively. The initial pH value of the solution was 5.60. The high silica zeolites, ZSM-5 (SiO_2/Al_2O_3 ratio = 1000), were obtained from Acoros (Geel, Belgium).

2.2. Instrumentation

The airtight reactor of 17.2 cm inside diameter was made of Pyrex glass with an effective volume of 5.5 L and equipped with a water jacket to maintain a constant solution temperature at 25 °C in all experiments. The design of the reactor was based on the criteria of the shape factors of a standard six-blade turbine [10]. The gas diffuser in a cylindrical shape with a pore size of 10 μm was located at the bottom of the reactor. Two quartz tubes having an outside diameter of 3.8 cm symmetrically installed inside the reactor were used to house the UV lamps. The low-pressure mercury lamps (model PL-S, Philips, Taiwan) provided UV radiation emitting principally at 254 nm. The radiation intensity was measured by a digital radiometer (Ultra-Violet Products (UVP), Upland, CA, USA) with a model UVP-25 radiation sensor. The generation of ozone from pure oxygen was controlled by an ozone generator (model LAB2B, Ozonia, Dübendorf, Switzerland) with a gas flow rate (Q_G) of 1.94 L/min. The fed (C_{AGi0}) and discharged (C_{AGe}) concentrations of the gaseous ozone were determined by a UV photometric analyzer (model SOZ-6004, Seki, Tokyo, Japan), which was calibrated with the KI titration method [11]. The UV photometric analyzer equipped with a quartz cell measured the UV absorbance of the ozone-containing gas, which was proportional to the value of C_{AGi0} or C_{AGe}. The indigo method was used to

analyze the dissolved ozone concentration (C_{ALb}) in the aqueous solution [12].

The concentration of DMP (C_{BLb}) was analyzed using a high-performance liquid chromatography (HPLC) system, with a 250 mm × 4.6 mm column (model ODS-2, GL Sciences Inc., Tokyo, Japan) and a diode array detector (model L-2455, Hitachi, Tokyo, Japan) at 230 nm. The HPLC solvent with a flow rate of 1.0 mL/min had a composition of methanol/water of 50:50. The injection volume of the analytical solution was 40 μL, and the detection limit of DMP analysis was 0.01 mg/L. The COD value (C_{COD}) was measured by the COD analyzer (model PhotoLab S12, Wissenschaftlich-Technische Werkstatten GmbH & Co. KG (WTW), Weilheim, Germany) using the reagent (model C1/25, WTW, Weilheim, Germany) with the measure range of 15–160 mg/L. The repeatability of the C_{COD} measurement was performed with the relative standard deviation of 1–3%. The concentration of TOC (C_{TOC}) was analyzed by the TOC analyzer (model 1010, OI Corporation, College Station, Texas, USA). The TOC instrument applies the UV-persulfate technique to convert the organic carbons for the subsequent analysis by an infrared carbon dioxide analyzer calibrated with the potassium hydrogen phthalate standard. A pH meter (model 300T, Suntex, Taipei, Taiwan) with the sensor was used to measure the pH value of solution. All fittings, tubings, and bottles were made of stainless steel, Teflon, or glass. The experimental apparatus sketch employed in this work is shown in Fig. 2.

2.3. Experimental procedures

The semibatch experiments under the conditions of different C_{AGi0}, high silica zeolite dosages (W_{cat}), and UV radiation intensities ([I]) for the ozonation of DMP were performed in duplicate to confirm the observation. 3.705 L of solution (V_L) were used in each experiment, while the total sampling volume was within 5% of the solution. The stirring speed was 800 rpm to ensure the
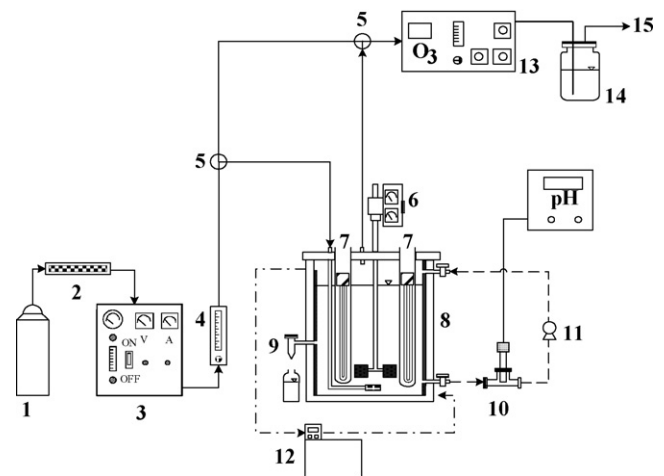

Fig. 2. The experimental apparatus sketch. —, – –, — · — : ozone gas stream, experimental solution, isothermal water. Components: (1) oxygen cylinder, (2) drying tube, (3) ozone generator, (4) flow meter, (5) three-way valves, (6) stirrer, (7) ultra-violet (UV) lamps, (8) reactor, (9) sample port, (10) pH sensor, (11) circulation pump, (12) thermostat, (13) gas ozone detector, (14) KI solution, and (15) vent to hood.

Table 1
Comparison of ozonation results at time for concentration reduction of DMP greater than 98% ($t_{f,DMP}$) under various experimental conditions

Cases	C_{AGi0} (mg/L)	W_{cat} (g/L)	$[I]$ (W/L)	$t_{f,DMP}$ (min)	η_{COD} (%)	η_{TOC} (%)	pH	k_B (min^{-1})
	8	1	0	60	NM[a]	NM[a]	3.23	0.0899
	14	0	0	30	39.7	NM[a]	3.33	0.131
O$_3$	14	0.1	0	30	NM[a]	NM[a]	3.25	0.144
	14	1	0	30	41.9	29.7	3.51	0.153
	14	4	0	30	37.7	26.1	3.34	0.167
	29	1	0	15	NM[a]	NM[a]	3.29	0.271
	14	0	0.332	30	38.7	37.6	2.50	0.177
O$_3$/UV	14	1	0.332	30	NM[a]	NM[a]	2.67	0.186
	14	0	0.648	30	44.8	32.6	3.26	0.177
	14	1	0.648	30	57.9	36.7	3.18	0.203

Initial values of pH, C_{BLb0} are 5.60, 0.4 mM.

[a] NM: not measured.

complete mixing of liquid and gas phases according to the previous study [13]. The effect of W_{cat} on the ozonation processes was evaluated with three different dosages of 0.1, 1, and 4 g/L. Two $[I]$ values of 0.332 and 0.648 W/L were adopted to test the contribution of UV radiation. The employed light intensity $[I]$ with the unit of W/L was defined as the average applied power of UV radiation per unit volume of the well-mixed system, which was proportional to the number of photons absorbed by the solution per unit volume and time. The $[I]$ value was calculated from the product of $[I_{uv}](A_q/V_L)F_s$, where $[I_{uv}]$ is the light intensity measured on the outer surface of the quartz tubes housing the UV lamps with the unit of W/cm^2, A_q is the outer area (cm^2) of the quartz tubes submerged in the solution, and F_s is the fraction of the emitting UV light absorbed by the solution. The value of F_s was detected close to the unit in all the experiments by measuring the transmittance of the UV radiation through the solution.

Before the ozonation experiments were started, the ozone-containing gas with C_{AGi0} of 8, 14, or 29 mg/L was bypassed to the photometric analyzer to ensure the ozone concentration and stability. A portion of the gas stream at the preset flow rate was directed into the reactor when the ozonation system was ready to initiate. Samples were drawn out from the reactor at desired time intervals in the course of ozonation. The residual dissolved ozone in the samples was removed immediately by stripping with oxygen. A circulation pump was used to transport the liquid from the reactor to the pH sensor and reflow it with a flow rate of 0.18 L/min during ozonation.

3. Results and discussion

3.1. Decomposition of DMP during ozonation

The variations of C_{BLb}, C_{COD}, C_{TOC}, and C_{AGe} with ozonation time (t) under the experimental conditions of sole O$_3$ and O$_3$/UV ($W_{cat}=0$ g/L) are shown in Fig. 3. The results indicate that the C_{BLb}, C_{COD}, and C_{TOC} decrease while the C_{AGe} increases with ozonation time. Note that the DMP can be effectively removed via both O$_3$ and O$_3$/UV processes. In contrast,
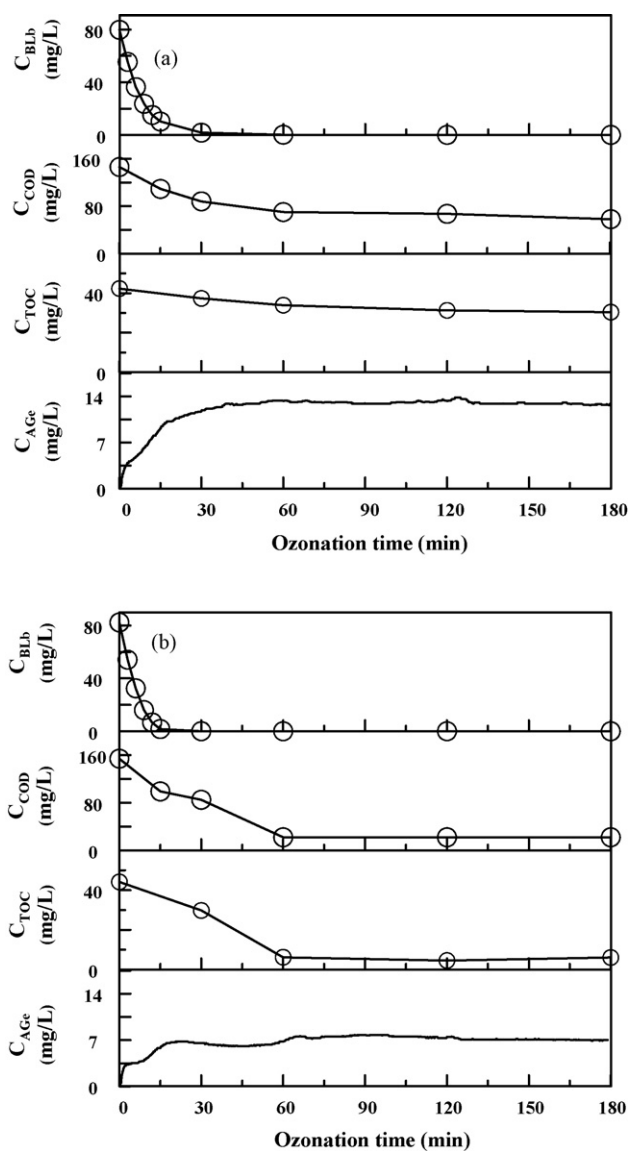

Fig. 3. Variations of C_{BLb}, C_{COD}, C_{TOC} and C_{AGe} with time for the ozonation of DMP in the semibatch system. $C_{BLb0}=0.4$ mM, $Q_G=1.95$ L/min, $V_L=3.705$ L, $T=25$ °C. (a) $C_{AGi0}=14$ mg/L; (b) $C_{AGi0}=14$ mg/L, $[I]=0.648$ W/L.

the variations of C_{COD}, C_{TOC}, and C_{AGe} show a significant difference between the O_3 and O_3/UV processes. The eliminations of C_{COD} and C_{TOC} in the O_3/UV treatment are more remarkable especially in the late ozonation period. According to the variation of C_{AGe}, the O_3 treatment apparently has a low utilization efficiency of fed ozone as the C_{AGe} value approaches to C_{AGi0} in a short time.

The time required for the concentration reduction of DMP greater than 98% is marked as a characteristic time ($t_{f,DMP}$) during the ozonation of DMP. The comparison of ozonation results at $t_{f,DMP}$ under various experimental conditions is summarized in Table 1. The $\eta_{COD} = (C_{COD0} - C_{COD})/C_{COD0}$ and $\eta_{TOC} = (C_{TOC0} - C_{TOC})/C_{TOC0}$ denote the removal percentages of COD and TOC, respectively. The results show that the decomposition of DMP accompanies with the noteworthy diminutions of COD and TOC. Nevertheless, the intermediates generated from the decomposition of DMP still contribute over 42 and 62% of the initial COD and TOC, respectively. Furthermore, the η_{COD} and η_{TOC} at $t_{f,DMP}$ in the O_3/UV cases generally have higher values compared with those in the O_3 cases, implying a difference in oxidation mechanisms. In addition, the pH value of the solution remarkably decreases from 5.60 to 2.50–3.51 in the early ozonation period ($t < t_{f,DMP}$), suggesting the generation of the acidic groups such as organic acids from the decomposition of DMP by ozonation [14].

The effects of the C_{AGi0}, W_{cat}, and $[I]$ on the destruction of DMP are shown in Fig. 4. The adsorption of DMP on the high silica zeolites is negligible due to its low octanol–water partition coefficient value (log $K_{ow} = 1.53$) [15]. Additionally, the volatility of DMP with the Henry's Law constant of 0.0011 L atm mol^{-1} at 25 °C is insignificant in the aqueous solution verified by the gas stripping test (Fig. 4a). The direct photolysis of DMP is found to be relatively slow with or without the presence of the high silica zeolites (Fig. 4b). The pseudo-first order reaction rate constant of DMP (k_B) in the expression of $C_{BLb}/C_{BLb0} = e^{-k_B t}$, which is applied to describe the elimination of DMP by ozonation, is obtained from the experimental data as shown in Table 1. Comparing the k_B values of the ozonation cases, it is worth addressing that the C_{AGi0} is the most important factor for the decomposition rate of DMP. The value of $t_{f,DMP}$ with $C_{AGi0} = 29$ mg/L is about half and one-fourth of those with $C_{AGi0} = 14$ and 8 mg/L, respectively. The correlation for the k_B in the O_3 cases can be derived proportional to C_{AGi0} as k_B (min^{-1}) $= 0.010\ C_{AGi0}$ (where C_{AGi0} in mg/L) with $r^2 = 0.921$. The k_B value of 0.177 min^{-1} in the O_3/UV cases at $C_{AGi0} = 14$ mg/L and $W_{cat} = 0$ g/L would increase 35% compared with that in the O_3 case (0.131 min^{-1}). On the other hand, the addition of W_{cat} shows the remarkable and moderate enhancements on the k_B value for the O_3 and O_3/UV cases, respectively.

In order to illustrate the possible roles of ozone and UV radiation on attacking the DMP and its intermediates, a simplified scheme of the decomposition pathways of DMP via the ozonation with UV radiation is proposed in Fig. 1. One may notice that the methyl carboxylate groups are electron withdrawing and deactivating meta-directing substituents for the electrophilic aromatic substitution [16]. The initial attack of
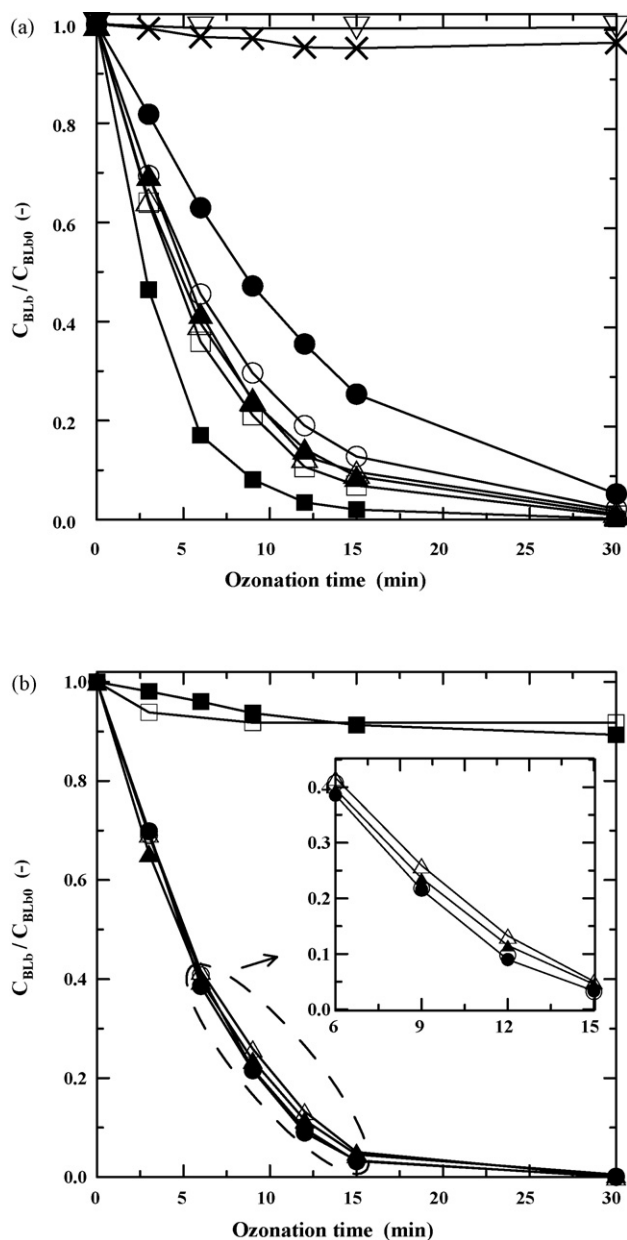

Fig. 4. Variations of C_{BLb}/C_{BLb0} with time for the ozonation of DMP in the semibatch system. $C_{BLb0} = 0.4$ mM, $Q_G = 1.95$ L/min, $V_L = 3.705$ L, $T = 25$ °C. (a) (○) $C_{AGi0} = 14$ mg/L; (△) $C_{AGi0} = 14$ mg/L, $W_{cat} = 0.1$ g/L; (□) $C_{AGi0} = 14$ mg/L, $W_{cat} = 4$ g/L; (●), (▲), and (■) $C_{AGi0} = 8$, 14, and 29 mg/L. $W_{cat} = 1$ g/L; (×) gas stripping only; (▽) adsorption on high silica zeolites, $W_{cat} = 1$ g/L. (b) (○) $C_{AGi0} = 14$ mg/L, $[I] = 0.648$ W/L; (●) $C_{AGi0} = 14$ mg/L, $W_{cat} = 1$ g/L, $[I] = 0.648$ W/L; (△) $C_{AGi0} = 14$ mg/L, $[I] = 0.332$ W/L; (▲) $C_{AGi0} = 14$ mg/L, $W_{cat} = 1$ g/L, $[I] = 0.332$ W/L; (□) UV only, $[I] = 0.648$ W/L; (■) $W_{cat} = 1$ g/L, $[I] = 0.648$ W/L.

ozone molecules on DMP via reaction I is primarily on the benzene ring. Fig. 5 is postulated simply to depict that ozone attacks the substituted benzene ring with the consideration of the occurrence of subsequent possible reactions at preferred positions around the ring. The initial attacks of ozone on DMP may be proceeded via (a) ozone dipolar cycloaddition on the 2, 3 bond or (b) an electrophilic substitution of ozone on carbon 2 or 3 [17,18]. The ozone dipolar cycloaddition is considered the major oxidation pathway since that the two methyl car-
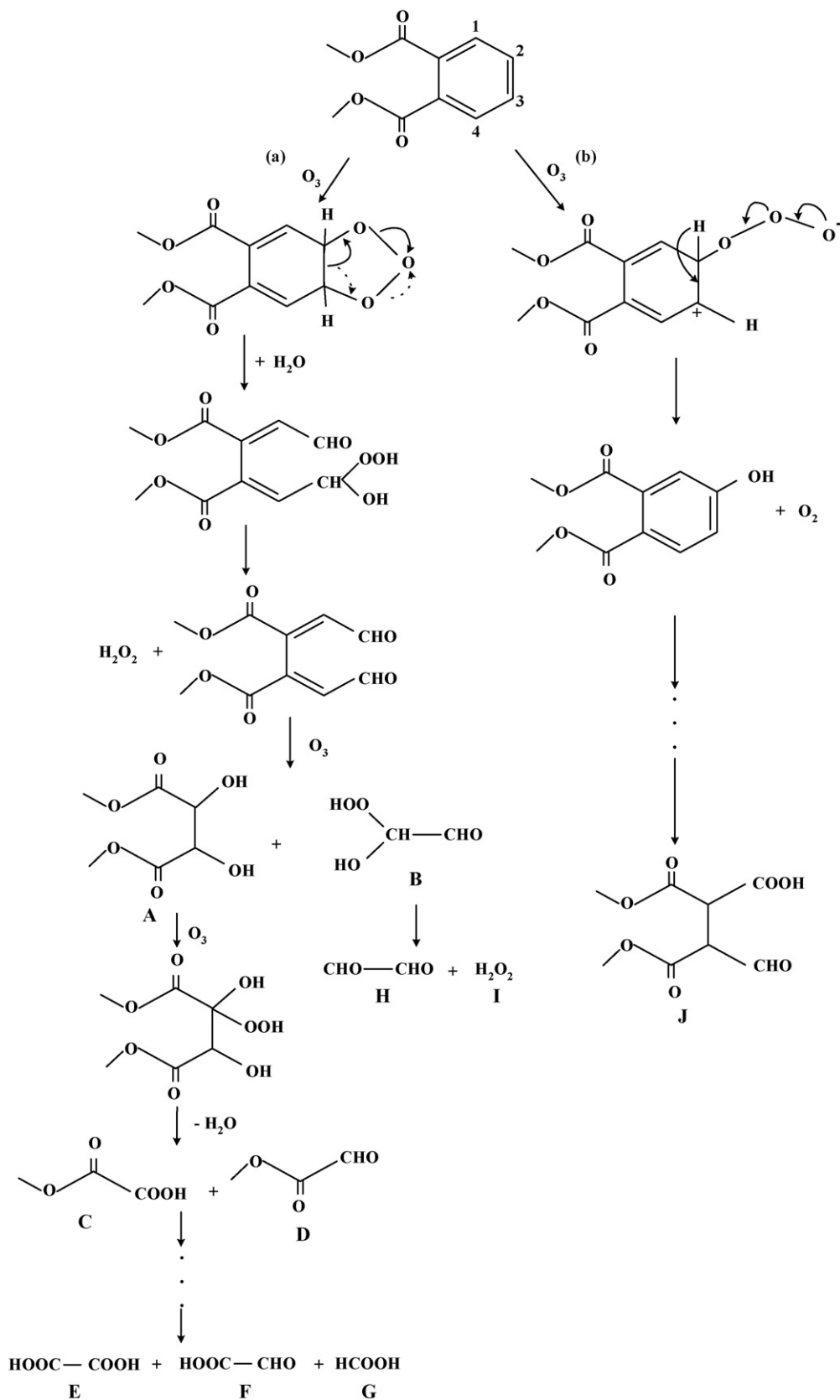
Fig. 5. Ozonation mechanism of DMP with ozone molecules. The cases of initial attack by (a) ozone dipolar cycloaddition on the 2, 3 bond, and (b) an electrophilic substitution of ozone on carbon 2.

boxylate groups are strongly electron withdrawing to deactivate the electrophilic substitution reaction. The intermediates may include dimethyl D-tartrate (denoted as A in Fig. 4), carboxyl methyl carboxylate (C), formaldehyde methyl carboxylate (D), oxalic acid (E), glyoxylic acid (F), formic acid (G), glyoxal (H) and 2,3-dimethyl-carboxylate-3-formyl-propanoic acid (J). Some peroxides such as hydroperoxy ethanal (B) and hydrogen peroxide (I) also appear during the ozonation. The generation of these byproducts as the competitors for oxidation may hinder the decomposition of DMP. With the presence of the high silica zeolites, the decomposition rate of DMP is enhanced by contacting the concentrated dissolved ozone on the zeolite surface [5,6]. The major contribution of UV radiation is to generate OH$^\bullet$ via reaction II. This promotes the radical oxidation of OH$^\bullet$ with DMP noted as reaction III, which is more vigorous than the direct ozonation of O_3 with DMP. In the O_3/UV cases, the pathway of reaction I via O_3 would become weaker concurrently due to the decrease of the dissolved ozone concentration. As a whole, the decomposition rates of DMP shown in Fig. 4b are the sum of the contributions of reactions I and III.

3.2. Removal of COD associated with ozone consumption and removal of TOC

Fig. 6 shows the variation of η_{COD} with ozonation time under different experimental conditions. The η_{COD} value continuously increases with the oxidation of successive products formed. The η_{COD} rapidly increases in the initial period and then gradually reaches a stable value. Note that the η_{COD} in the O_3 treatments has a limitation of about 60% (Fig. 6a), indicating that the intermediates generated during the ozonation are highly resistant to ozone molecules resulting in the deactivation of reaction IV. Moreover, the effect of W_{cat} on the removal rate of COD is insignificant because that the oxidation of these intermediates, which are commonly more hydrophilic than DMP, mainly occurs in the bulk solution rather than on the high silica zeolites. Instead, the removal rate of COD is remarkably promoted with the value of [I], which relates to the contribution extent of reaction V. The η_{COD} in the O_3/UV treatments can be enhanced greater than 86% in 120–180 min.

To further investigate the difference between the O_3 and O_3/UV cases, the variation of the ozone consumption per mol DMP treated, $m_{O3R}/(C_{BLb0}V_L)$, with the ozone applied per mole of DMP, $m_{O3A}/(C_{BLb0}V_L)$, in the semibatch reactor is depicted in Fig. 7. The masses of ozone applied (m_{O3A}) and consumption (m_{O3R}) are calculated by Eqs. (1) and (2), respectively, where V_F is the volume of free space in the reactor [19,20].

$$m_{O3A} = Q_G \times C_{AGi0} \times t \tag{1}$$

$$m_{O3R} = \int_0^t (C_{AGi0} - C_{AGe})dt - C_{ALb}V_L - C_{AGe}V_F \tag{2}$$

The slopes of the curves in Fig. 7 represent the utilization efficiencies of fed ozone. It is evident that Fig. 7 shows two distinct trends of $m_{O3R}/(C_{BLb0}V_L)$ with $m_{O3A}/(C_{BLb0}V_L)$ for the O_3 and O_3/UV cases individually. Obviously, the presence of UV radiation is advantageous for the utilization efficiency of ozone
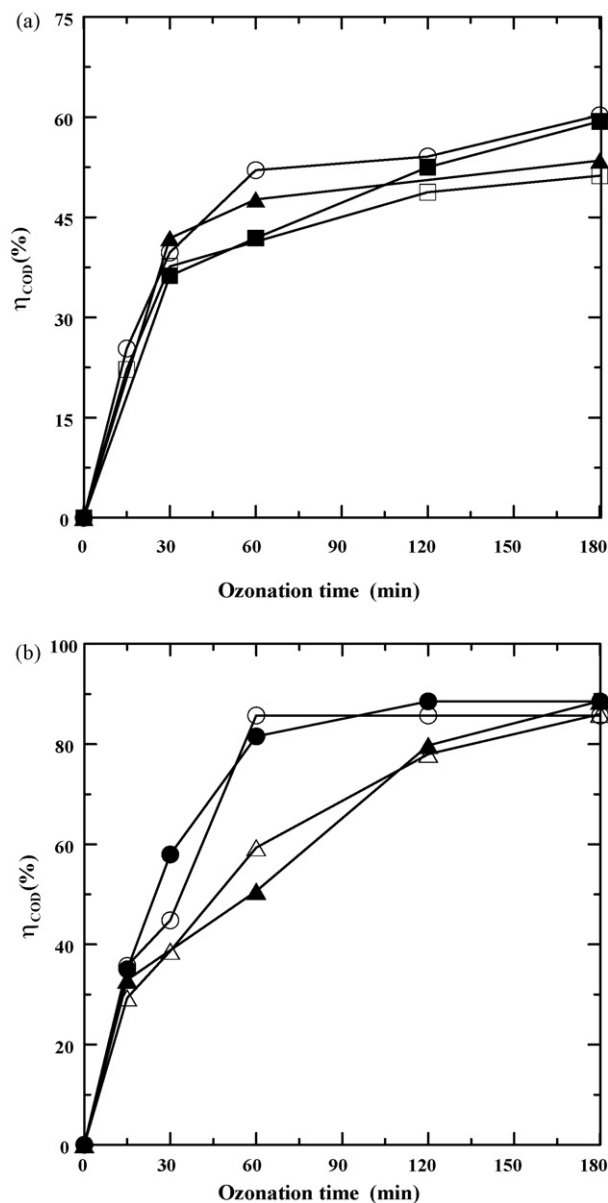

Fig. 6. Variations of η_{COD} with time for the ozonation of DMP in the semibatch system. Notations are the same as specified in Fig. 4.

especially when $m_{O3A}/(C_{BLb0}V_L) > 10$. For instance, the utilization efficiencies of ozone applied are close to 16% and 51% for the O_3 and O_3/UV cases, respectively, at $m_{O3A}/(C_{BLb0}V_L)$ of 68 mol mol^{-1} and almost independent of C_{AGi0} and W_{cat}. It should be mentioned that the dissolved ozone concentration in the O_3/UV treatments would remain low to attain the high gas–liquid mass transfer rate of ozone. Thus reaction II is principal for the consumption of dissolved ozone in the late ozonation stage of DMP.

The correlation between the η_{COD} and $m_{O3R}/(C_{BLb0}V_L)$ is illustrated in Fig. 8 by integrating the results in Figs. 6 and 7. It is worth noting that the variations of the η_{COD} with $m_{O3R}/(C_{BLb0}V_L)$ in the O_3 and O_3/UV treatments are similar when $\eta_{COD} < 60\%$. However, the η_{COD} in the O_3/UV cases would consistently increase with $m_{O3R}/(C_{BLb0}V_L)$ for the higher
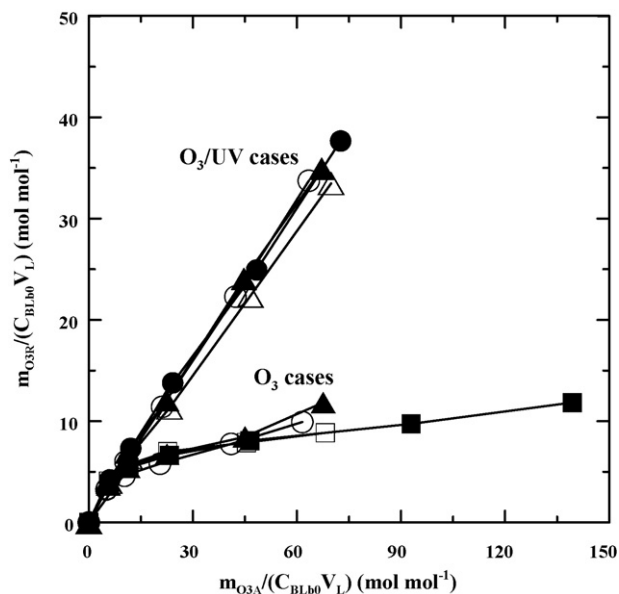
Fig. 7. $m_{O3R}/(C_{BLb0}V_L)$ vs. $m_{O3A}/(C_{BLb0}V_L)$ for the ozonation of DMP in the semibatch system. Notations are the same as specified in Fig. 4.

oxidation regime, while that in the O_3 cases comes to a standstill. Accordingly, the COD removal from the decomposition of DMP can be divided into two stages. For the regime of small η_{COD}, the elimination of COD primarily comes from the oxidation of the benzene ring of DMP resulting in the small difference between the O_3 and O_3/UV cases due to the high reactivity at the moment. The increase of η_{COD} in the stage of $\eta_{COD} \geq 60\%$ is characterized by the oxidation of the intermediates mostly composed of the methyl ester groups that only can be proceeded in the O_3/UV processes. Furthermore, the O_3/UV processes with the higher [I] has more vigorous activity for the further oxidation of the intermediates via reaction V.
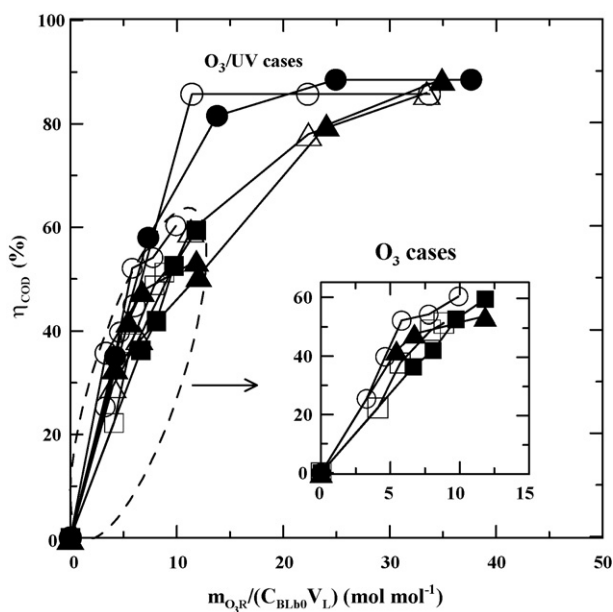

Fig. 8. η_{COD} vs. $m_{O3R}/(C_{BLb0}V_L)$ for the ozonation of DMP in the semibatch system. Notations are the same as specified in Fig. 4.
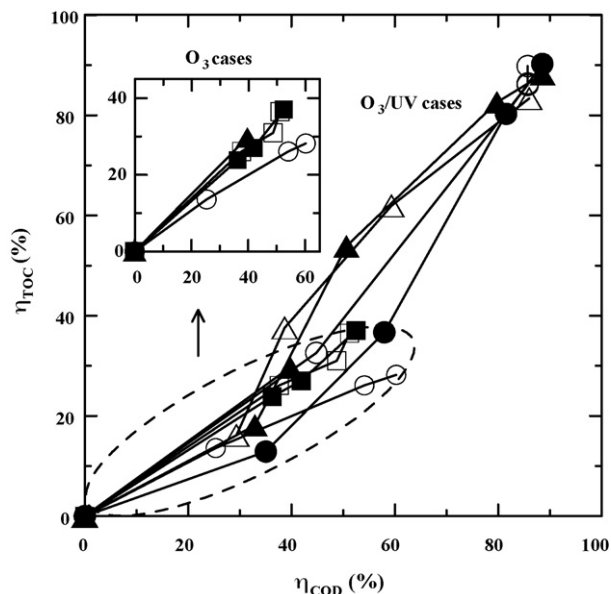

Fig. 9. η_{TOC} vs. η_{COD} for the ozonation of DMP in the semibatch system. Notations are the same as specified in Fig. 4.

The characteristic curve of η_{TOC} with η_{COD} in Fig. 9 is useful to illustrate the relationship between the mineralization and oxidation degrees during the ozonation of DMP. The η_{TOC} value is apparently lower compared with the η_{COD} value in the early stage of ozonation due to the fact that ozone is primarily consumed for the opening of the benzene ring, accompanying the low diminution of TOCs. It is apparent that the η_{TOC} also has a limitation of about 37% in the O_3 cases, while the η_{TOC}/η_{COD} ratio with the range of 0.47–0.71 confirms the existence of partially oxidized organics. The η_{TOC} in the O_3/UV cases progressively increases with the η_{COD} as the η_{TOC}/η_{COD} ratio is close to the unit that shows the nonselective and vigorous oxidation ability. In summary, the decomposition rate of DMP increases with the ozone concentration of feed gas and the high silica zeolite dosage. The combination of ozone with UV radiation gives significant contribution for the destruction of DMP and subsequent oxidation after the disappearance of DMP. Consequently, the O_3/UV process is recommended for treating the DMP-containing solution as far as the COD and TOC reduction is concerned, although the O_3 process may be sufficient for removing the DMP.

4. Conclusions

Ozonation is employed as an effective way for the removal of dimethyl phthalate in the aqueous solution. The destruction of DMP would accompany with the noteworthy diminutions of chemical oxidation demand (COD) and total organic carbons (TOC). Note that the results of the O_3 and O_3/UV cases show a remarkable difference in respect of both oxidation and mineralization performances. The nearly complete removal of DMP can be achieved within 15–60 min under the conditions of this study. The decomposition rate of DMP primarily increases with the ozone concentration of feed gas. Moreover, the presence of high silica zeolites and UV radiation is advantageous to the removal

of DMP. The removal percentages of COD (η_{COD}) and TOC (η_{TOC}) in the sole O_3 processes have the limitations of about 60 and 37%, respectively. The effect of high silica zeolites on the promotion of the η_{COD} and η_{TOC} in ozonation is insignificant. On the other hand, the further oxidation of the intermediates can be attained in the O_3/UV processes, which have the higher utilization efficiency of fed ozone during ozonation. Thus the radical oxidation is predominant in the late ozonation period of DMP and enhanced with the intensity of UV radiation. Furthermore, the ozone consumption per mole of DMP treated is presented as a useful and convenient index to assess the η_{COD} value. The distinct relationship between the η_{TOC} and η_{COD} for the ozonation of DMP has been obtained. Initially, the partially oxidized organics with low ratio of η_{TOC} to η_{COD} are mainly generated from the opening of the benzene ring of DMP. Afterward the nonselective and vigorous oxidation would appear in the O_3/UV processes with the higher ratio of η_{TOC}/η_{COD} close to the unit.

Acknowledgment

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