Degradation of di-2-ethylhexyl phthalate in aqueous solution by advanced oxidation process

Maryam Zarean, Bijan Bina[1], Afshin Ebrahimi[1], Hamidreza Pourzamani[1], Fatemeh Esteki

Department of Environmental Health Engineering, Student Research Center, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran, [1]Environment Research Center, Research Institute for Primordial Prevention of Non-communicable Disease, Isfahan University of Medical Sciences, Isfahan, Iran

Address for correspondence:
Prof. Bijan Bina,
Department of Environment Health Engineering, School of Health, Isfahan University of Medical Sciences, Hezar Jerib Ave., Isfahan, Iran.
E-mail: bina@hlth.mui.ac.ir

ABSTRACT

Aims: This study was conducted to compare the effectiveness of conventional technologies, UV irradiation and ozonation process, and UV/O_3 as advanced oxidation processes to remove phthalate from aqueous solutions.

Materials and Methods: The initial concentration of di-2-ethylhexyl phthalate (DEHP) was 5 mg/L. The photolysis, ozonation, and UV/O_3 processes were conducted separately at different contact times (5-30 min). Then, the DEHP residuals in the solutions were analyzed by gas chromatography mass spectrometry. The effect of ozone dosage was also evaluated in the range of 50-400 mg/h on DEHP degradation. Kinetic and the rate constants were determined.

Results: The results indicated that using UV and ozonation alone, the maximum DEHP removal efficiency were 43% and 50%, respectively. The UV/O_3 process considerably improved the degradation of DEHP up to 80%. The synergistic effect observed in the combined processes mainly due to the effects of UV in enhancing the ozone decomposition, led to higher degradation for 30 min treatment. A kinetic study showed the degradation in UV/O_3 followed the first-order model. In addition, the maximum DEHP removal rate was 74% with 200 mg/h ozone dosage by ozonation alone process, but it was 93% at same condition by UV/O_3 process.

Conclusion: It could be found that the UV/O_3 process is a method for DEHP degradation in aqueous solution and may be recommended as a supplement with other processes for treatment of solutions containing low DEHP concentrations.

Key words: Advanced oxidation processes, di-2-ethylhexyl phthalate, kinetics, ozonation, ozone dosage

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INTRODUCTION

Phthalate esters (PAEs) are a kind of plasticizer and the most important industrial chemicals, which is used to improve the flexibility of polyvinyl chloride plastics and known as endocrine disruptors.[1-3] Phthalates are chemically colorless, odorless, flavorless, and stable liquids over a wide temperature range and barely soluble in water.[4] They have been detected in surface and groundwater in ng/L and

even in mg/L. In addition, they are known to be hazardous chemicals to human health since they have been associated to organ damage, birth defects, infertility, as well as testicular cancer.[5,6] Di-(2-ethylhexyl)-phthalate (DEHP) that is one of the most commonly used phthalate diesters is a ubiquitous environmental pollutant with respect to its production, use and occurrence in the environment.[7,8] Exposure of the general population to DEHP can occur due to the use of medical devices (medical tubing and blood bags), cosmetics, lubricants, insect repellents, paints, and intake from food and the environment (air, soil, and water).[2,6,9,10] Over time, DEHP will leach out from these abundantly products and accumulate in the environment.[7]

The biotransformation of phthalates under both aerobic and anaerobic conditions has been studied, but it is not suitable for applying in drinking water treatment due to the requirement of long hydraulic retention time and less biomass existing in waterworks.[5,11] Adsorption is only a way to shift the contaminations, and it is an efficient method to remove PAEs due to its higher n-octanol/water partition coefficients (K_{ow}), but not to minimize them.[12] Advanced oxidation processes (AOPs) would be the most powerful method for PAEs minimization and degradation.[5] This method involves the generation of free radicals such as hydroxyl OH° radicals that enhance the degradation process.[13] Among the numerous AOPs developed so far, some of the main innovations readily applicable in the full scale are the AOPs involving UV/H_2O_2, O_3/H_2O_2, UV/O_3, Fe^{2+}/H_2O_2, $UV/O_3/H_2O_2$, and catalytic ozonation.[14] Because of high ozonation oxidant capacity, it has been investigated as an alternative way to decompose organic micropollutants in water solutions.[4] In ozonation process, the phthalates are attacked through two different reaction mechanisms:

1. Radical oxidation by highly oxidative free radicals such as hydroxyl OH° radicals, which are generated from the decomposition of ozone in an aqueous solution and
2. Direct ozonation by the ozone molecules, especially by specific functional groups (nucleophilic positions, double bonds).[14,15]

The aim of introducing the UV radiation into the ozonation treatment was to enhance ozone decomposition and yielding more OH° radicals, which are responsible for greater oxidation. Chen *et al.*, Study results indicated that hydrolysis,

anaerobic transformation, and UV/O_3 processes could destroy some PAEs.[16]

The main objective of this study was to compare the effectiveness of conventional technologies, UV irradiation and ozonation processes, and the simultaneously using of two advanced treatment processes, UV/O_3, to remove DEHP from aqueous solutions. In addition, determination of the reaction constants was done, alone, and in combined processes. The synergistic effect due to the application of UV on the ozonation of DEHP was also investigated.

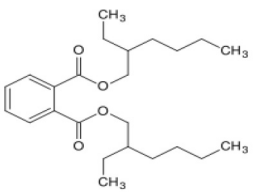## MATERIALS AND METHODS

Chemicals
All chemical substances used were analytical grade. Chemicals used in this study include: Analytical grade DEHP (Sigma-Aldrich Chemicals, analytical standard, Fluka), HPLC grade methanol (Merck Co., Germany, 99.9% purity), methyl-tert-butyl ether, MTBE, (Merck Co., Germany). The pH was adjusted to desired values with 1 N sulfuric acid and 1 N sodium hydroxide (Merck Co., Germany) and was measured by a pH-meter (Metrohm HerisauE520). Deionized water used was purified by a Millipore Milli-Q water purification system. DEHP stock solution dissolved in a mixture of methanol and deionized water (1:100) was established at a concentration of 100 mg/L, and were kept at a temperature of 4°C, then diluted to 5 mg/L before use, which this value was equal to 835 mg/L chemical oxygen demand (COD). Table 1 presents the physicochemical characteristics of DEHP.

Experimental set-up
In the present study, UV irradiation and ozonation processes separately, and combination UV and ozonation (UV/O_3) were used for DEHP degradation.

The experimental setup consisted of an ozone reactor, an ozone generator, an ozone off-gas destruction system, a Pyrex cylindrical reactor, and a UV lamp. The ozone reactor was a closed Pyrex cylindrical, with a height of 16 cm and an inner diameter of 10 cm. Ozone was generated using a laboratory generator (O and W, China) with a dosing capacity of 1 g O_3/h at the oxygen feed and was distributed into the reactor through a diffuser placed at the bottom. The ozone in the

Table 1: Properties of di-(2 ethylhexyl) phthalate						
Compound	Structure	Formula	Molecular Weight (g/mol)	Log (K_{ow})	Solubility in water at 25°C g/L	CAS number
DEHP		$C_{24}H_{38}O_4$	390.56	8.71	<0.001	117-81-7

off-gas stream of the reactor was quenched and destructed in a 2% KI solution. A stirrer (Labinco-90-402) was used during the process to provide adequate mixing. The ozonation processes were conducted at varying contact times (i.e., 5, 10, 15, 20, and 30 min), using ozone flow rate of 100 mg/h.

The UV processes were carried out with a 150 W high-pressure mercury-vapor lamp (λ = 254 nm; incident radiation intensity = 7.1 w/m^2). During the tests, the lamp was fixed at the center of the reactor. Due to increase in temperature during the UV process, the temperature of all the experiments was kept at 25 ± 3°C by cooling water under a batch reaction. The initial concentration of the DEHP aqueous solution was 5 mg/L, and UV photolysis processes were conducted at varying contact times (i.e., 5, 10, 15, 20, and 30 min).

In the following series of experiments was performed using UV/O$_3$ treatment combination. The experimental setup is shown in Figure 1. The combined UV/O$_3$ treatment was also carried out at varying contact times (i.e., 5, 10, 15, 20, and 30 min), using an ozone flow rate (100 mg/h) and 500 ml of DEHP solution (5 mg/L). In all tested conditions, an aqueous solution (500 ml) of DEHP was used.

Analytical methods

After the application of each process, the samples were analyzed immediately to avoid a further reaction. The DEHP extraction from the water solutions was carried out by solid phase extraction cartridges (Cartridge, SPE, CHROMABOND® C_{18}ec-3 mL/500 mg, German). A C_{18} column was washed with 5 ml methanol and 10 ml of ultrapure water. Then, the sample of 300 ml was passed through the C_{18} column with a flow rate of 5 ml/min under vacuum. The adsorbed compounds in the C_{18} column were eluted with 2 ml of methanol. The extraction solution was dried under a nitrogen gas flow, and the extracts were diluted with 100 µL of MTBE in 2-mL vials for gas chromatography mass spectrometry (GC/MS) analysis. The injection volume of the analytical solution was 3 µL, and the detection limit of DEHP concentration was 0.1 µg/L.[17]

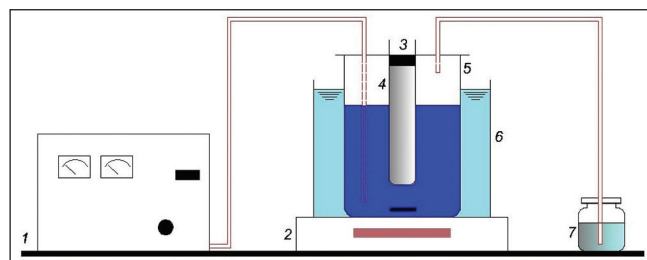Gas chromatography mass spectrometry analysis was performed using an Agilent technology 7890A gas chromatograph equipped with a 5975C quadrupole mass selective detector. A Phenomenex HP5 column 30 m long with a 0.32 mm i.d. and 0.25 µm film thickness was used for the GC separation using the following oven temperature program: 100°C hold for 1 min with heating to 210°C at the 10°C/min and heating to 250°C at 5°C/min and heating to 280°C at 30°C/min (6 min hold). The interface temperature and injector temperature were 250°C. All injection volumes were 3 µL in the splitless mode. Helium (99.99% purity) was used as the carrier gas at a flow rate of 1 ml/min. Compounds eluting from the GC column were identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a database.

Chemical oxygen demand was estimated by the method described in the Standard Methods for the Examination of Water and Wastewater (5220 D. Closed Reflux, Colorimetric Method).

RESULTS

Di-2-ethylhexyl phthalate removal efficiency of UV, ozonation, and UV/O$_3$ processes

This experiment was conducted with different reaction times between 5 and 30 min on the fixed condition of other parameters. Figure 2 compares the efficiency of DEHP removal by UV, ozonation, and UV/O$_3$ processes. Results showed that the increase in reaction time could raise the removal efficiency of DEHP. The UV alone process resulted in 43% DEHP removal at 30 min, indicating that UV irradiation had a weak effect on DEHP degradation. Compared with the UV photolysis, the ozonation process alone, and UV/O$_3$ processes showed much higher DEHP removal efficiencies. Removal percent of DEHP in ozonation and UV/O$_3$ processes after 30 min of treatment were 50% and 80%, respectively. As shown in Figure 2, (UV/O$_3$ curve), the removal percent of DEHP increased from 26% to 80% after 5-30 min of treatment, respectively. At the same contact times, the ozonation process also showed removal efficiency, increasing from 12% to 50%.

Figure 1: Experimental set-up: (1) Ozone generator; (2) magnetic stirrer; (3) high-pressure UV lamp; (4) Quartz tube; (5) reactor; (6) temperature-controlled bath; (7) KI solution
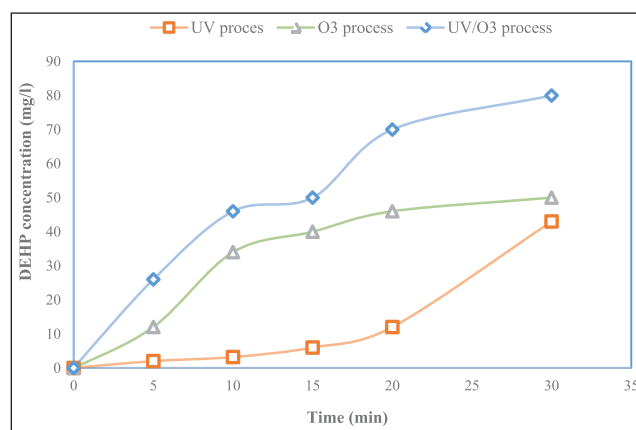

Figure 2: Efficiency of UV, ozonation, and combined UV/O$_3$ processes in di-2-ethylhexyl phthalate (DEHP) removal. Experimental conditions: DEHP concentration: 5 mg/L, ozone dose: 100 mg/h, pH: 7, temperature: 25°C

The results of the residual concentration of DEHP during UV, ozonation, and UV/O$_3$ processes are shown in Table 2. This stage of experiments was conducted with DEHP concentration of 5 mg/L, 100 mg/h ozone dose, pH 7, and 30 min reaction time at a temperature of 25°C. As shown in this table, the residual concentration of DEHP in UV and ozonation process was 2.8 and 2.5 mg/L, respectively that were equal to 43 and 50% removal [Figure 2]. However, the DEHP residual concentration in UV/O$_3$ was observed to be lower than both ozonation and UV processes. The residual concentration of DEHP was 1 mg/L by UV/O$_3$ process after a reaction time of 30 min. These results showed that UV/O$_3$

process has positively influenced DEHP degradation. The two chromatograms of treated and untreated solutions of DEHP are represented in Figure 3a and b.

The efficacy of a given water solution treatment should be based not only on the contaminant degradation yield, but also COD removal is an important parameter. It noted that theoretical COD content of initial concentration of the DEHP aqueous solution (5 mg/L) was about 13 mg/L, but its COD content was 835 mg/L due to methanol was added to the stock solution. Figure 4 compares the removal of COD during the UV, ozonation, and UV/O$_3$ processes.

In the ozonation process, after a run time of 30 min with 100 mg/h ozone dose, 49% of COD remained (409 mg/L). Furthermore, COD concentration in UV photolysis was 420 mg/L. The UV/O$_3$ process showed a much higher removal efficiency of COD eliminating than the UV and ozonation processes. In the UV/O$_3$ process, even at the same mentioned conditions, 43% of COD (360 mg/L) still remained while the DEHP concentration was 1 mg/L (equal to 80% removal of DEHP).

Table 2: Summary of DEHP residual concentrations (as mg/l)			
Time (min)	DEHP residual concentration		
	UV	O$_3$	UV/O$_3$
0	5	5	5
5	4.9	4.4	3.7
10	4.84	3.3	2.7
15	4.7	3	2.5
20	4.4	2.7	1.5
30	2.8	2.5	1

Effect of ozone dosage on di-2-ethylhexyl phthalate degradation in ozonation and UV/O$_3$ processes

To determine the effect of the ozone dosage on DEHP removal efficiency in ozonation and UV/O$_3$ processes, a series of experiments were carried out by varying ozone dosage from 50 to 400 mg/h. To detect the effect of ozone dose on the degradation of DEHP, the ozone dose was varied. Other variables were kept constant. Figure 5 shows the results of the ozone dosage effect on the degradation of DEHP by ozonation and UV/O$_3$ processes. As can be seen in this figure, the degradation rate of DEHP increases rapidly with ozone concentration in ozonation and UV/O$_3$ processes. In this case, the DEHP removal rate was improved from 21.2% to 94% as the ozone concentration increased from 50 to 400 mg/h at 30 min. However, the DEHP degradation rate in UV/O$_3$ process was much faster than the ozonation
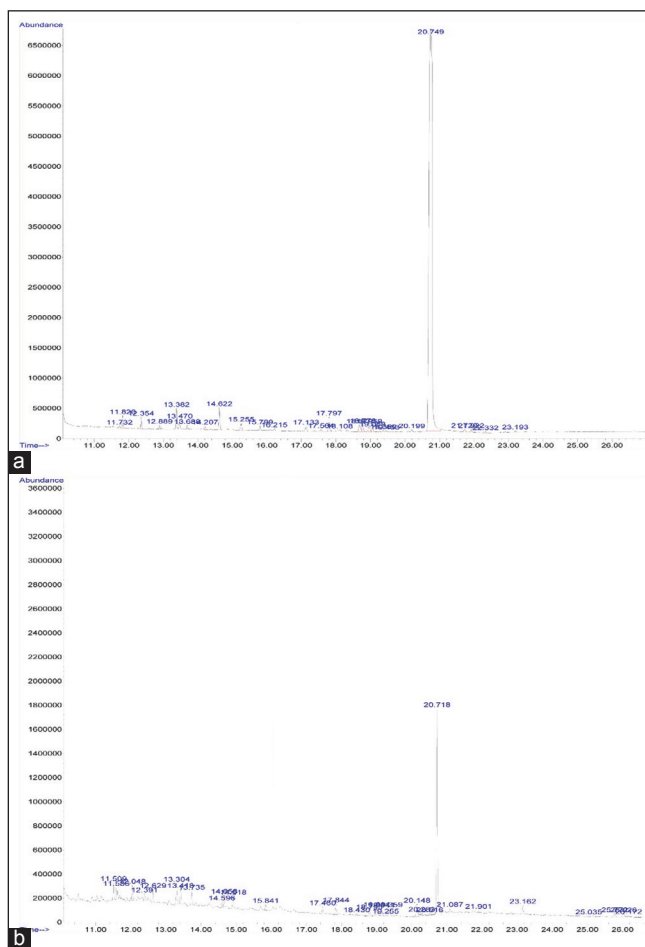

Figure 3: Gas chromatography mass spectrometry chromatograms on a di-2-ethylhexyl phthalate extract from (a) untreated solution and (b) treated solutions by UV/O$_3$ process
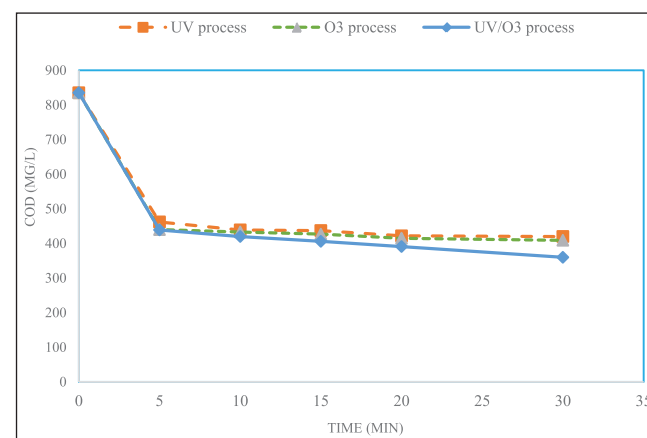

Figure 4: Variation of chemical oxygen demand removal percentage. Experimental conditions: Di-2-ethylhexyl phthalate concentration: 5 mg/L, ozone dose: 100 mg/h, pH: 7, temperature: 25°C

process [Figure 5]. At 200 mg/h ozone dosage, DEHP can be almost eliminated 93% by UV/O$_3$ process while the DEHP removal rate by ozonation was only 74%. Thus, the maximum DEHP removal rate was 94% with 400 mg/h ozone dosage by ozonation alone process, but it was 93% with 200 mg/h ozone dosage by UV/O$_3$ process.

Kinetics of di-2-ethylhexyl phthalate degradation

Di-2-ethylhexyl phthalate degradation rates were measured in the presence of UV alone, as well as in ozonation and the UV/O$_3$ processes. The reactions and their rates can be compared if all of them can be fitted in the same order. Analytical data obtained during half hour treatment by UV, ozonation, and UV/O$_3$ were used to determine the reaction orders of the experiments. The linear regression was applied for the estimation of the several integral orders of reactions (zero, first, and second). Kinetics of DEHP degradation are shown in Table 3.

According to the results reported in the previous sections, the UV/O$_3$ process was an efficient method for DEHP degradation. As shown in Table 3, the high regression coefficient (R^2 = 0.982) indicates the UV/O$_3$ process follow first-order reaction model and also a value of k = 0.0533 l/min was found. The following equation was used to evaluate the synergistic effect on the rate of DEHP degradation in the UV/O$_3$ process.

$$\text{Synergistic effect}^{[17]} = \frac{k_{UV+o_3}}{(k_{UV}+k_{O_3})} = 1.29 \qquad (1)$$

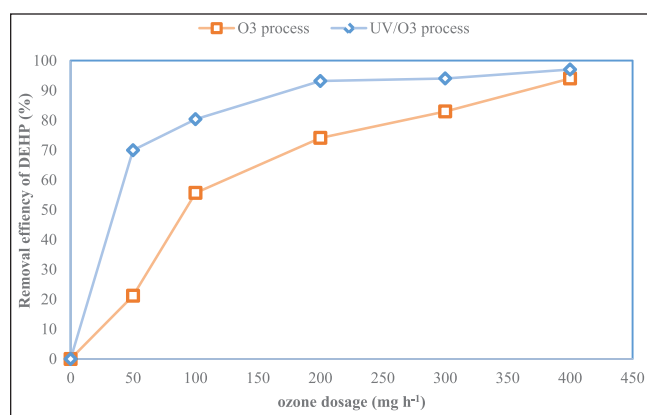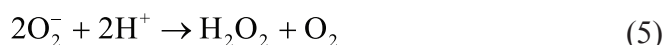The synergistic effect of UV and ozonation may be quantified as the normalized difference between the rate

Figure 5: The effect of ozone dosage on degradation of di-2-ethylhexyl phthalate (DEHP) by ozonation and UV/O$_3$ processes. Experimental conditions: DEHP concentration: 5 mg/L, pH: 7, contact time: 30 min, temperature: 25°C

constants obtained from UV/O$_3$ and the sum of the separate photolysis and ozonation rate constants. The rate constant of the combined process of UV and ozonation was twice (0.0533/0.0413) that of the sum of the individual processes.

DISCUSSION

In this study, DEHP degradation was performed by UV photolysis, ozonation, and combination of UV and ozonation processes [Figure 2]. Approximately 43% of the initial concentration of DEHP was degraded using UV photolysis. Thus, UV process had a low reactivity to degrade DEHP. UV process may be described by the following reactions:[17]

$$\text{DEHP} \xrightarrow{\;hv\;} \text{DEHP*} \qquad (2)$$

$$\text{DEHP*} + \text{O}_2 \xrightarrow{\;hv\;} \text{DEHP}^+ + \text{O}_2^- \qquad (3)$$

$$\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ \qquad (4)$$

$$2\text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \qquad (5)$$

$$\text{H}_2\text{O}_2 \xrightarrow{\;hv\;} 2°\text{OH} \qquad (6)$$

$$2°\text{OH} + \text{DEHP} \rightarrow \text{Intermediate DEHP} \qquad (7)$$

Oh *et al.*, also reported that the removal percentage of diethyl phthalate (DEP) was 17% by UV photolysis.[18] However, in the present study, the removal percentage of DEHP in ozonation process was 50% [Figure 2]. Ozonation process also may be described by the following reactions:[17]

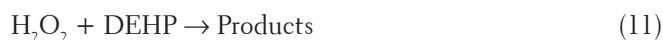$$\text{DEHP} + \text{O}_3 \rightarrow \text{Intermediate products} \qquad (8)$$

Oh *et al.*, reported that removal percentage of DEP was 72% by the ozonation process alone.[18] This agrees with the results of Medellin-Castillo *et al.* who also reported that the DEP removal percentage was 62% in the ozonation process with 60 min reaction time.[1]

Our results demonstrated that the UV/O$_3$ process had a positive effect on DEHP removal in aqueous solution [Figure 2]. In this study, an obvious difference between ozonation and UV/O$_3$ processes was that the combination of UV by ozone had a synergistic effect in degradation of DEHP. The UV irradiation could accelerate the decomposition of ozone, and reduced the selective oxidation of DEHP. In the consequence, the ozone molecules that absorb some of the

Table 3: DEHP degradation reaction constants and synergistic effect of UV/O$_3$

Process	Zero order		First order		Second order		Synergistic effect
	k, min^{-1}	R^2	k, min^{-1}	R^2	k, min^{-1}	R^2	
UV	0.0046	0.716	0.0172	0.753	1.0134	0.793	−
Ozonation	0.0071	0.933	0.0241	0.894	0.017	0.847	−
UV/O$_3$	0.0262	0.941	0.0533	0.982	0.0259	0.921	1.29

incoming photons, leads to its degradation to atomic O(1D) form.[19] It then reacts with water forming H_2O_2 and the new reactive species are formed from H_2O_2. This enhances the degradation of the organic substrate as below equations:[20]

$$O_3 \xrightarrow{h\nu} O(^1D) + O_2 \qquad (9)$$

$$O(^1D) + H_2O \rightarrow H_2O_2 \qquad (10)$$

$$H_2O_2 + DEHP \rightarrow Products \qquad (11)$$

$$H_2O_2 \rightarrow 2^\circ OH \qquad (12)$$

The same study reported that ozone/UV process was shown to have the highest efficiency (96%) for the elimination of DEP and its by-products.[18] Therefore the high-to-low order of removal efficiency of DEHP was UV/O_3 >ozonation >UV, respectively. Furthermore, the results of the residual concentration of DEHP during UV photolysis, ozonation, and UV/O_3 processes showed that UV/O_3 process has positively influenced DEHP degradation [Table 2]. The residual concentrations of DEHP were 2.8, 2.5, and 1 mg/L in UV, ozonation, and UV/O_3 processes at same conditions, respectively. Ozone decomposition into °OH radicals can be accelerated by UV irradiation. A significant enhancement of the DEHP degradation rate ($k_{UV + O_2} = 5.33 \times 10^{-2}$ 1/min) was observed during the application of the UV/O_3 combined process. Oh *et al.* reported a significantly increased degradation rate of DEP when using a combined UV and ozonation process.[18] Results from Jing *et al.* also showed that dimethyl phthalate (DMP) removal rate by UV/O_3 process was 90.3% at 60 min oxidation reaction. It is due to the °OH radicals generated in the UV/O_3 process.[21] The °OH is believed to be the key reactive species that can effectively eliminate the DEHP via the UV/O_3 process, which can produce a high concentration of °OH.

To quantify the decomposition of DEHP, COD content in the DEHP solution was monitored [Figure 4]. COD concentration in UV photolysis and ozonation processes were 420 and 409 mg/L after 30 min contact times. However, the UV/O_3 process showed 56% of COD removal efficiency (360 mg/L COD). Results in Figure 4 are indicating that the by-products obtained with UV/O_3 system present a similar toxicity with that of DEHP; however, the DEHP concentration was reduced to 1 mg/L.

Our results also showed that the increase of ozone dosage from 50 to 400 mg/h had a positive effect on ozonation and UV/O_3 processes. It is reported that, ozone can participate in the reaction process of °OH generation, therefore, more ozone was added, and the more ozone radicals would be formed.[19] As can be seen in Figure 5, DEHP degradation rate was enhanced when the ozone dose increased. Since ozone would not consume the generated °OH, thus, the more ozone introduced in the reaction solutions, the more °OH radicals would be generated, resulting in higher degradation of DEHP. In addition, the increased ozone concentration in the air

bubbles, which carried the ozone molecules, enhanced the driving force for the transfer of ozone from the gas phase into the phthalate solution. This, in turn, resulted in more ozone dissolving in the solution and a higher rate of mass transfer.[22] Jing *et al.* reported that DMP removal rate improved from 58.3% to 97.1% as the ozone concentration increased from 20 mg/h to 100 mg/h at 30 min run time. Their results showed that both DMP and TOC removal rates in UV/O_3 process increased compared to the ozonation process alone.[21]

In the present study, DEHP decomposition constants were exhibited zero, first and second-order reaction kinetics in both the individual and the combined processes [Table 3]. As respects to the UV/O_3 process had the highest efficiency in the DEHP decomposition, our results showed DEHP removal kinetics in UV/O_3 process follow the first order reaction.

CONCLUSION

The results of the present study have clearly delineated that UV irradiation combined with ozonation provides a promising technique for the degradation of DEHP, and this is attributed to the enhanced ozone decomposition in collapsing yielding additional free radicals. Furthermore, a combination of UV photolysis and ozonation processes resulted in inducing a synergistic effect. Besides, ozone dosage is one of the most parameters that could be used in DEHP degradation from aqueous solution. Therefore, it could be introduced for DEHP removal in high concentration. DEHP removal in UV/O_3 process can be described by the first-order reaction.

It is also recommended to use chromatography techniques to investigate by-products formed due to using UV/O_3 process.

ACKNOWLEDGMENTS

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