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Effects of nitrate on the advanced UV photolysis of di(2-ethylhexyl) phthalate degradation in aqueous solution

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ABSTRACT

One of the objectives of this study was to delineate the effect of nitrate on the oxidation of di (2-ethylhexyl) phthalate (DEHP) by conducting bench-scale UV/H_2O_2 operations under a variety of UV doses and initial concentrations of H_2O_2 and NO_3^-–N. Also, this study evaluated the two processes, UV alone and UV/H_2O_2, for DEHP oxidation. DEHP separation and quantification were performed using liquid chromatography–electrospray ionization tandem mass spectrometry system (LC-ESI-MS/MS). It was found that the UV photolysis of H_2O_2 is a more effective method of DEHP oxidation than the direct UV photolysis. It was observed that the DEHP oxidation efficiency of about 85.0% or higher could be achieved at a UV dose of 800 mJ/cm^2 with an initial H_2O_2 concentration of more than 30 mg/L in the absence of nitrate. Nitrate hindered the DEHP oxidation by acting as $^{\cdot}OH$ scavengers. The adverse effect by nitrate in the UV/H_2O_2 process was significantly greater than that in the UV oxidation-alone, and its oxidation was almost reduced to half by nitrate under some operating condition. However, it is noted that the DEHP oxidation efficiency of more than 70% could be expected at a UV dose of 600 mJ/cm^2 with an initial H_2O_2 concentration of 50 mg/L while considering the nitrate scavenging effect.

Keywords: DEHP; Hydroxyl radical; Nitrate; Scavenger; UV/H_2O_2

1. Introduction

Environmental contamination through anthropogenic activities is a wide spread and serious problem in many parts of the world. Great interest has been developed in recent years for the disposal of wastewaters generated by modern society. Phthalic acid esters (PAEs) are among the most commonly used industrial chemicals and are wide spread in the environmental matrices—and some of them are suspected mutagens and carcinogens. Phthalates have been detected in all environments due to global use of plastics, with the highest concentrations detected adjacent to phthalate production or plastic processing facilities. PAEs are also widely used industrial chemicals serving as additives in polyvinyl chloride, polyvinyl acetate, cellulosic, and polyurethane resins [1]. Studies focusing on the concentrations of PAEs in industrial wastewaters have found varying concentrations of PAEs, ranging from 10 to 300 μg/L in the wastewaters of chemical plants and nearby rivers [2] to 30 mg/L in wastewater near manufacturing plant producing plasticizers [3]. The most abundant PAEs in the environment is di(2-ethylhexyl) phthalate (DEHP) [4]. It is characterized by very low water solubility (0.6–400 μg/L at 20°C) and high octanol–water partition coefficient (log K_{ow}

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of 7.54) [5]. DEHP is not chemically bound to polymeric matrices and can mobilize from plastics. Owing to its stability and lipophilic nature, DEHP accumulates in fish tissues and tends to adsorb to suspended solids in surface and subsurface waters [6]. DEHP is characterized under the category of endocrine disrupting chemicals and it is regulated under the list of environmental priority pollutants [7]. Because it is suspected as carcinogens, it could damage liver, kidneys, and might damage the development of reproductive organs and interfere with development by acting as a mimic of the sex hormone estrogen [1].

However, this PAE has a low water solubility and long side chain, which makes it extremely stable and, consequently, difficult to biodegrade. Improved and more feasible treatment methods than those traditionally employed are required for such pollutants [8]. Advanced oxidation process (AOP) employing hydrogen peroxide with UV is an effective method in the degradation of organic pollutants. UV combined with hydrogen peroxide (UV/H_2O_2) is one of the AOP technologies for degradation of toxic organic pollutants. In UV/H_2O_2 process, the photolysis of H_2O_2 generates oxidizing species hydroxyl radical (·OH), which oxidize various organic compounds quickly [9]. Hydroxyl radicals, unlike other oxidants, are capable of oxidizing almost all the reduced materials in treated effluents, without any restriction to specific classes or groups of compounds [10]. The UV/H_2O_2 oxidation process generates hydroxyl radicals that can oxidize a broad range of organic pollutants quickly and nonselectively [11]. In addition, the UV/H_2O_2 oxidation process has been found to be very effective in the degradation of endocrine disruptors [12]. Typical concentrations of NO_3^-–N are known to range from 3 to 5 mg/L in biologically well-treated wastewater treatment plant effluents. However, the nitrate ion, NO_3^-, is a well-known strong absorber of UV light at a wavelength of below 250 nm [13]. NO_2^- from NO_3^- photolysis may interfere with the oxidation reactions of organic chemicals enhanced by hydroxyl radicals. Nitrate photolysis has three distinct mechanisms, which result in the formation of nitrite (NO_2^-), peroxynitrite (ONO_2^-), and ·NO_2. One of these mechanisms is the direct route to NO_2^- formation from NO_3^- photolysis, with a low quantum yield [13,14]. The considerable production of NO_2^- can be expected via the two other reactions, which produce the intermediates ONO_2^- and ·NO_2. These intermediates eventually undergo thermal reactions to NO_2^- form as a stable product [13,15]. The formation of hydroxyl radicals (·OH) can also be expected, together with one of the intermediates, ·NO_2, from nitrate photolysis. As NO_2^- accumulates, it can react with ·OH, and acts as an ·OH scavenger. The mechanisms involving H_2O_2 photolysis have been critically reviewed [13,16]. H_2O_2 also influences NO_2^- production. Since H_2O_2 photolysis is another source of hydroxyl radicals, it might be expected to decrease NO_2^- production. H_2O_2, however, appears to act in part as a scavenger of hydroxyl radicals. Peroxynitrite ions and their conjugate acid, peroxynitrous acid (ONO_2H) are strong oxidants. Hydroxyl radicals are also produced from the decomposition of peroxynitrous acid. Nitrite and oxygen can be formed from the reaction between peroxynitrous acid and hydrogen peroxide [16]. The literature review on the reactions related to the UV photolysis of hydrogen peroxide in the presence of nitrate revealed that both nitrate and hydrogen peroxide appear to act either as ·OH producers or, at some point of time, as ·OH scavengers, in an aqueous solution [17].

There are very limited numbers of studies, though, in which the effects of nitrate in an aqueous solution were systematically determined for the UV/H_2O_2 process [18–21]. In a previous study [18], the UV oxidation for Ethylenediaminetetraacetic acid degradation was studied at wavelengths of 222 and 254 nm in NO_3^- solutions, in the presence and absence of H_2O_2. The effects of the NO_3^- concentrations 0, 10, 20, 50, and 100 mg/L were investigated, where the NO_3^- concentration range in the present study differed from the earlier studies. In our previous studies [17,22,23], effects of nitrate on the UV photolysis were investigated for the degradation of Volatile Organic Compounds (VOCs), 2,4-dichlorophenol, and DEP in aqueous solutions. The oxidation of DEP was not severely hindered by nitrate ions (5.0 mg NO_3^-–N/L) with an initial H_2O_2 concentration of less than 10 mg/L at any reaction time. However, the scavenging effect was remarkable with an initial H_2O_2 concentration of 30 mg/L, when the reaction time ranged from 1.0 min to 2.0 min, and the effect was reduced with an initial H_2O_2 concentration of 50 mg/L at any reaction time. The scavenging effects on the oxidation depended on the concentration of the compounds dissolved in solutions, initial concentration of H_2O_2, and UV doses under the operating conditions described in those studies. No research has been conducted on the effect of nitrate on the UV oxidation of DEHP dissolved in aqueous solution. One of the objectives of this study was to delineate the effect of nitrate on the oxidation of DEHP by conducting bench-scale UV/H_2O_2 operations under different doses of UV light and initial concentrations of H_2O_2, and NO_3^-–N. Also, this study evaluated the two processes, UV alone and UV/H_2O_2 for DEHP oxidation. Therefore, the results of this study can provide a referable information about the

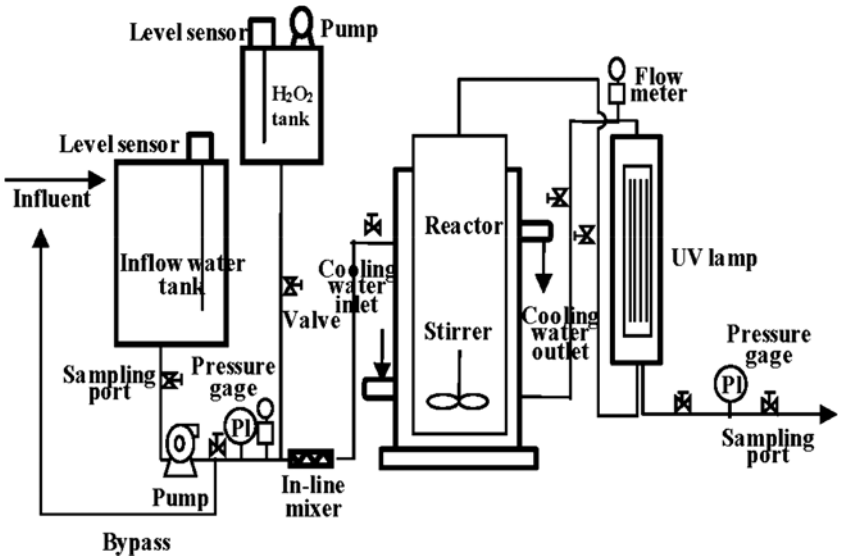

Fig. 1. Schematic diagram of the bench-scale UV/H_2O_2 AOP system.

proper application of UV irradiation with hydrogen peroxide for the oxidation of DEHP. The identification of the intermediates from the DEHP oxidation is not within the scope of this study.

2. Materials and method

2.1. Bench-scale UV/H_2O_2 AOP system

Experiments were carried out in a bench-scale UV/H_2O_2 AOP system, which consisted of a 30 L stirring reactor and a 20 L UV reaction chamber. The stirring reactor and UV chamber are made of a stainless steel. Also, they were interconnected with stainless steel pipes. The UV lamp in the chamber (Trojan Logic^{TM}LF18), with a nominal power of 50 W, emitted radiation at 254 nm (Fig. 1). All headspaces inside the reactors and pipes were completely eliminated during the experiments. All the experiments were performed in the batch mode at room temperature and the pH levels in the reactors were not controlled.

The aqueous solution (30 L) that was poured into the stirring reactor was prepared by dissolving 3 mL of the DEHP stock solution (1 mL DEHP/99 mL methanol) and 0.906 g of $NaNO_3$ in 30 L double distilled water. To completely mix the solution, the mixture was carefully stirred and was circulated in the UV reaction chamber with the use of the installed peristaltic pump for 3 min. Aliquots (857.1 μL) of H_2O_2 were injected before the aqueous solution was circulated to the UV reaction chamber, and the UV reaction chamber was filled with the aqueous solution to avoid headspace inside (DEHP concentration: 1 μg/mL, H_2O_2 concentration: 10 mg/L, NO_3^-–N concentration: 5 mg/L as an example). This aqueous solution was again completely mixed for a period of time, circulated in the UV chamber without UV irradiation. The UV lamp in the chamber was turned on to initiate the oxidation reaction. Samples (5 mL) were regularly collected according to the predetermined schedule. All the solvents and reagents used in this study, including DEHP (99.9%, Sigma-Aldrich, USA), hydrogen peroxide (35% w/w, Showa, Japan), and $NaNO_3$ (98%, Shinyo, Japan) were of analytical grade.

2.2. Analytical methods

DEHP separation and quantification were performed using liquid chromatography /electrospray ionization tandem mass spectrometry system (LC-ESI-MS/MS). A Series 1200 liquid chromatography from Agilent Technology (Waldbronn, Germany) was coupled to an Agilent 6490 Triple Quadrupole Mass spectrometer (Waldbronn, Germany). The HPLC system consisted of 1290 infinity (Agilent Technology) systems equipped with a binary pump, autosampler, thermostatted column compartment, and variable wavelength detector. A XDB C18 column (4.6 × 50 mm, 1.8 μm particle size) supplied by Agilent Technology was used for the separation of DEHP. 5 mM ammonium formate in distilled water and acetonitrile in the ratio of 1:9 were used as a binary mobile phase. The flow rate and the injection volume were 0.8 mL/min and 5 μL, respectively. Under these conditions the separation time was less than 7 min. These optimal conditions are shown in Table 1. The

Table 1
Operational conditions for LC-Ms/MS

HPLC (Agilent 1200)	
Column	Agilent XDB C18 (4.6 × 50 mm, 1.8 μm)
Column temperature	40℃
Mobile phase	5 mM ammonium formate in distilled water and acetonitrile
Flow rate	0.8 mL/min
Injection volume	5 μL
MS/MS (Agilent 6490)	
Ionization mode	ESI-positive
Gas temperature	350℃
Gas flow	10 L/min
Nebulizer pressure	40 psi
Capillary voltage	4,000 V

samples were injected directly into the chromatograph, without any previous sample preparation process.

3. Results and discussion

3.1. Effect of UV radiation dose on the UV/H_2O_2 process to degrade DEHP

This study was conducted for the profiles of oxidation efficiencies (%) of DEHP (1 μg/mL) as functions of the UV dose in the UV process, with four different initial H_2O_2 concentrations (0, 10, 30, and 50 mg/L), and with two different initial NO_3^-–N concentrations (0.0 and 5.0 mg/L) in an aqueous solution. In each case, the samples were collected after UV was radiated for 0, 0.5, 1.0, 1.5, and 2.0 minutes and the DEHP concentration was measured for each sample. It was noted that the UV exposures for 0.5, 1.0, 1.5, and 2.0 min accounted for UV doses of 200, 400, 600, and 800 mJ/cm^2, respectively, considering the reaction times and the UV intensities applied under the operating conditions.

Fig. 2(a) shows the profiles of oxidation efficiencies (%) of DEHP as functions of the UV dose in the UV process alone without any H_2O_2 addition. The profiles clearly indicate that DEHP was removed by the UV photolysis, and the oxidation efficiencies gradually increased as the UV dose increased in this bench-scale AOP operation. In the UV photolysis, the oxidation efficiencies at a UV dose of 800 mJ/cm^2 were about 43.6% with nitrate addition and about 50.2% without nitrate addition, respectively. No significant scavenging effects of nitrate on the DEHP oxidation were observed for the UV dose range of 200–800 mJ/cm^2.

Fig. 2(b) shows the DEHP was oxidized about 85.5% with an initial H_2O_2 concentration of 30 mg/L at a UV dose of 800 mJ/cm^2, in the absence of nitrate, in the UV/H_2O_2 process. The results indicated that the UV photolysis of H_2O_2 is a more effective method of DEHP oxidation than the direct UV photolysis. These results clearly show that H_2O_2 photolysis provides another source of hydroxyl radicals, as shown in the given chemical reaction [16].

$$H_2O_2 + hv \rightarrow 2{}^{\cdot}OH \tag{1}$$

However, the oxidation efficiency of the DEHP was about 50.7% with an initial H_2O_2 concentration of 30 mg/L and NO_3^-–N concentration of 5 mg/L at the 800 mJ/cm^2. The noticeable scavenging effect of nitrate on the UV oxidation of DEHP was also observed for its initially tested H_2O_2 concentration at 30 mg/L as shown in Fig. 2(b). This was because the photolysis of NO_3^- produced NO_2^- ions, which were accumulated during the reaction, as mentioned earlier [14,24]. The observed oxidation efficiencies consequently decreased due to the OH-radical scavenging of the photochemically generated NO_2^-, as shown in the following chemical reactions (see (2), (3)) [16]. NO_3^- was also reported to have caused a significant "inner filter" effect that could reduce the fraction of the incident UV absorbed by H_2O_2, which resulted in a significant reduction in the efficiency of the UV/H_2O_2 system [14].

$$NO_3^- + hv \rightarrow NO_2^- + O \tag{2}$$

$$NO_2^- + {}^{\cdot}OH \rightarrow {}^{\cdot}NO_2 + OH^- \tag{3}$$

The scavenging effect was remarkable with the initial H_2O_2 concentration of 30 mg/L at all the tested UV doses, and the largest difference in oxidation efficiency was about 38.1% at a UV dose of 400 mJ/

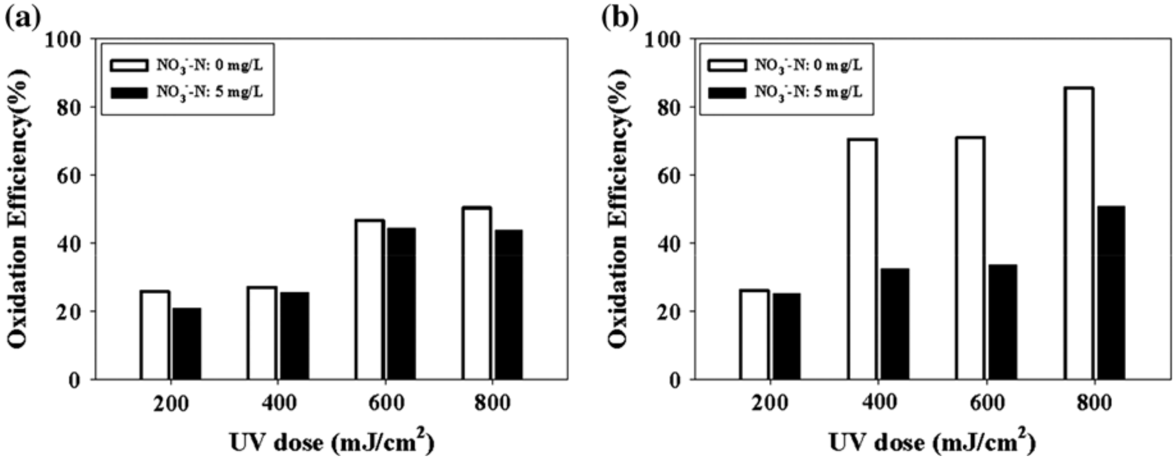

Fig. 2. Profiles of the oxidation efficiencies (%) of DEHP as a function of the UV dose with respect to different initial concentrations of NO_3^-–N for UV/H_2O_2 process; initial concentration of DEHP: 1 μg/mL; (a) UV irradiation alone without H_2O_2 addition and (b) UV irradiation with initial concentration 30 mg/L of H_2O_2.

cm^2. The impact of UV dose on the oxidation of DEHP has been investigated by varying the UV dose from 200 to 800 mJ/cm^2. The results clearly show that the oxidation efficiency increased with increasing UV dose with values ranging from 26.1 to 85.5%, with an initial H_2O_2 concentration of 30 mg/L without NO_3^-–N addition, however, from 25.3 to 50.7% at the same UV dose with NO_3^-–N addition of 5 mg/L. Also, it was observed that the DEHP oxidation efficiency of about 85.5% or higher could be achieved at a UV dose of 800 mJ/cm^2 with an initial H_2O_2 concentration of more than 30 mg/L without taking the nitrate scavenging effect into consideration. However, the DEHP oxidation efficiency of more than 50% could be, at best, expected at a UV dose 800 mJ/cm^2 with an initial H_2O_2 concentration of 30 mg/L while taking the nitrate scavenging effect into consideration.

3.2. *Effect of initial H_2O_2 concentration on the DEHP degradation*

Fig. 3 shows the effects of the initial H_2O_2 concentrations on the DEHP (1 μg/mL) oxidation investigated at two different UV doses (a) 400 and (b) 800 mJ/cm^2 with respect to two initial NO_3^-–N concentrations of 0 and 5 mg/L. About 26.9 and 27.2% of the DEHP were oxidized by UV irradiation without nitrate addition, at a UV dose of 400 mJ/cm^2, with initial H_2O_2 concentrations of 0 mg/L (i.e. by UV photolysis alone) and 10 mg/L, respectively (Fig. 3(a)). However, about 70.5 and 75.4% of the DEHP oxidation were achieved at the same UV dose, without nitrate addition, with initial H_2O_2 concentrations of 30 and 50 mg/L, respectively. These results clearly indicate that DEHP could be oxidized by UV irradiation alone, and the DEHP could be oxidized more than twice by adding H_2O_2. The enhancement of oxidation by addition of H_2O_2 is due to the increase in the hydroxyl radical concentration. At low concentration, H_2O_2 cannot generate enough hydroxyl radical and the oxidation rate is limited [11]. Also, it was reported that high concentration of H_2O_2 could restrain the reaction [25]. At the high H_2O_2 concentration, H_2O_2 can act as a free radical scavenger [26]. However, this phenomenon did not happen in the present experiment for the reason that the dosage might not reach the restrain point.

The DEHP oxidation efficiency by UV photolysis alone was 25.6% for the reactor with nitrate addition of 5 mg/L at the UV does of 400 mJ/cm^2. The oxidation rate of DEHP increases with increasing H_2O_2 concentration; the addition of 10–50 mg/L H_2O_2 increases the oxidation efficiency from 23.1 to 65.2% at the same nitrate addition and UV dose (Fig. 3(a)). The oxidation efficiencies of DEHP with nitrate addition were lower than those without nitrate. These nitrate scavenging effects on the DEHP oxidation were significant with those two different initial H_2O_2 concentrations tested in this study, but the nitrate scavenging effects were rather not noticeable in the UV irradiation alone and with initial H_2O_2 concentrations of 10 mg/L. The scavenging effect of nitrate on the DEHP oxidation was the largest when the H_2O_2 concentration was 30 mg/L at the UV dose of 400 mJ/cm^2 among conducted tests.

The effect of H_2O_2 addition (0–50 mg/L) on the photochemical degradation was investigated with and without nitrate at the UV dose of 800 mJ/cm^2. The oxidation efficiencies of DEHP with initial H_2O_2 con-

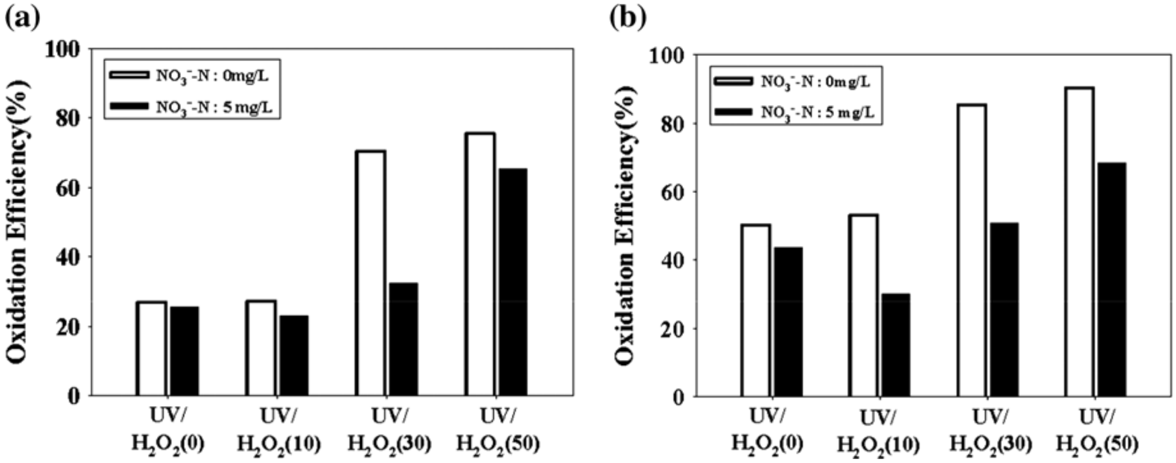

Fig. 3. Profiles of the oxidation efficiencies (%) of DEHP as a function of the initial concentration of H_2O_2 with respect to different initial concentrations of NO_3^-–N at the UV dose of (a) 400 mJ/cm^2 and (b) 800 mJ/cm^2; initial concentration of DEHP: 1 μg/mL. H_2O_2 concentration for each treatment is given in parentheses.

centrations of 0 and 10 mg/L, without nitrate addition, were about 50.2 and 53.2%, respectively. About 85.5 and 90.4% of the DEHP oxidation were achieved at the same UV dose with initial H_2O_2 concentrations of 30 and 50 mg/L, respectively (Fig. 3(b)). DEHP oxidations were increased by increasing the initial H_2O_2 concentrations. The highest DEHP oxidation, 90.4% was obtained with the initial H_2O_2 concentration of 50 mg/L at the UV dose of 800 mJ/cm^2. However, the oxidation efficiencies of DEHP by UV irradiation with nitrate, at the initial H_2O_2 concentrations of 0, 10, 30, and 50 mg/L, were 43.6, 30.2, 50.7, and 68.3%, respectively. In all the treatments without nitrate addition, obtained DEHP oxidation efficiencies were even higher than those obtained with nitrate addition (Fig. 3(b)). The scavenging effect of nitrate on the DEHP oxidation through the UV photolysis of H_2O_2 was clearly observed. The differences in their oxidation efficiency were about 34.8 and 22.1% at the H_2O_2 concentrations of 30 and 50 mg/L, respectively.

About 26.9 and 50.2% oxidation of the DEHP were achieved by UV irradiation alone, without H_2O_2 and nitrate addition, at the UV doses of 400 and 800 mJ/cm^2, respectively. The oxidation efficiency was almost doubled by increasing the UV dose from 400 to 800 mJ/cm^2, without addition of nitrate and H_2O_2. The nitrate scavenging effect on the DEHP oxidation was remarkable with those three different initial H_2O_2 concentrations tested in this study, except for only UV irradiation, at the UV dose of 800 mJ/cm^2. In the case of no nitrate existence, the practical H_2O_2 concentration and UV dose for more than 85% oxidation turned out to be 30 mg/L and 800 mJ/cm^2, respectively. However, in the presence of nitrate in the aqueous solution, the H_2O_2 concentration proved to be demanded over 50 mg/L at a UV dose of 800 mJ/cm^2 for more than 68% oxidation of DEHP (Fig. 3).

Experiment results from this study clearly describe that nitrate ions act as scavengers in the UV oxidation with the tested concentration ranges of H_2O_2. The scavenging effect of nitrate ions on the DEHP oxidation was greater with the UV photolysis of H_2O_2 than with the direct UV photolysis. The oxidation of DEHP was severely hindered by nitrate with an initial H_2O_2 concentration of more than 30 mg/L at tested UV doses.

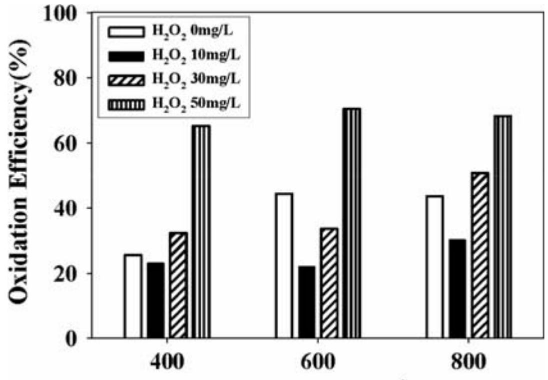

Fig. 4. Oxidation efficiencies (%) of DEHP as functions of UV doses (400, 600, and 800 mJ/cm^2) at the four different H_2O_2 concentrations (0, 10, 30, and 50 mg/L) in the bench-scale UV/H_2O_2 operation; initial concentration of DEHP: 1 μg/mL and NO_3^-–N concentration: 5.0 mg/L.

3.3. Oxidation efficiency of DEHP in the aqueous solution containing nitrate

Fig. 4 shows the profiles of oxidation efficiencies (%) of DEHP as functions of initial H_2O_2 concentrations (0, 10, 30, and 50 mg/L) at three different UV doses of 400, 600, and 800 mJ/cm^2 for the UV/H_2O_2 process. The DEHP concentration into the UV/H_2O_2 system was 1 μg/mL with an average NO_3^-–N concentration of 5.0 mg/L. The oxidation patterns of DEHP at the UV dose of 400 mJ/cm^2 were very similar to those at the UV dose of 600 and 800 mJ/cm^2. The lowest efficiency at the H_2O_2 concentrations of 10 mg/L and the highest efficiency at the H_2O_2 concentrations of 50 mg/L were shown at all tested UV doses. These show that the UV photolysis of H_2O_2 was most effective for DEHP oxidation with the H_2O_2 concentration of 50 mg/L at the UV dose of 600 mJ/cm^2 in the aqueous solution containing nitrate of 5 mg/L. It was noted that about 70.5% of the influent DEHP was oxidized under these operating conditions, even if the relatively high NO_3^-–N concentration of about 5.0 mg/L was observed in the influent.

4. Conclusions

Different variables (UV doses, H_2O_2 concentrations, presence or absence of nitrate) were tested on DEHP oxidation in order to select to investigate the optimal conditions in the two bench-scale AOP operation (UV alone and UV/H_2O_2). It was found that DEHP (1 μg/mL) was oxidized in very limited amounts through the direct UV photolysis, without addition oxidation by hydroxyl radicals. However, the DEHP could be oxidized more than twice by adding H_2O_2 because H_2O_2 photolysis provides another source of hydroxyl radicals. It is indicated that the UV photolysis of H_2O_2 is a more effective method of DEHP oxidation than the direct UV photolysis. It was observed that the DEHP oxidation efficiency of about 85.0% or higher could be achieved at a UV dose of 800 mJ/cm^2 with an initial H_2O_2 concentration of more than 30 mg/L in the absence of nitrate. Nitrate hindered the DEHP oxidation by acting as ·OH scavengers under the operating conditions described above. The adverse effect by nitrate in the UV/H_2O_2 process was significantly greater than that in the UV oxidation alone, and its oxidation was almost reduced to half by nitrate under some operating conditions. However, it is noted that the DEHP oxidation efficiency of more than 70% could be expected at a UV dose 600 mJ/cm^2 with an initial H_2O_2 concentration of 50 mg/L while considering the nitrate scavenging effect. These findings suggest that UV/H_2O_2 process seem to be suitable method for DEHP oxidation at the presence of nitrate.

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