The influence of zero-valent iron on the photodegradation ozonation of di-2-ethylhexyl phthalate in aqueous solution

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ABSTRACT

In this study, the effect of nano zero-valent iron (NZVI) or Fe^0 on photolysis ozonation (UV/O_3) degradation of di-2-ethylhexyl phthalate (DEHP) was investigated. Applied pH, ozone dosage, NZVI dosage, reaction time, and initial concentration of DEHP were the parameters investigated under UV/O_3/Fe^0 process. The possible dominant mechanisms of DEHP degradation were also discussed. The degradation rate of DEHP gradually decreased with the increase in initial pH from 2 to 11 and increasing ozone dosage. When compared with other doses of NZVI, an NZVI dose of 200 mg/L was found to be more effective. Ozone dosage had little influence on the removal of DEHP. The reaction time of 15 min and initial DEHP concentration of 5 mg/L were optimum conditions in the combined process of UV/O_3/Fe^0. A comparison of the reaction orders of kinetic studies showed that DEHP degradation is in accordance with pseudo-second-order reaction. At the optimum conditions, the reaction time of 15 min, the major by-products of the oxidation process were phthalic acid and ethyl 5-phenyl-2-penten-4-ynoate. The NZVI photodegradation ozonation technology was capable of efficiently removing DEHP from water solutions.

Keywords: Di-2-ethylhexyl phthalate; Advanced oxidation process; Zero-valent iron; Hydroxyl radical; Aqueous solution

1. Introduction

Phthalate esters (PAEs) or phthalates are alkyl aryl esters of phthalic acid. They are the most abundantly produced plasticizers that are known as endocrine-disrupting compounds [1,2]. Owing to the widespread use of PAEs, there is deep concern about their release into the environment and their toxicity to humans and other organisms because some of them are considered to be potential carcinogens, teratogens, and mutagens. They have been associated with organ damage, birth defects, infertility, and testicular cancer [3–5]. The United States Environmental Protection Agency (US EPA) and China National Environmental Monitoring Center have categorized PAEs as environmental priority pollutants [6]. Varying concentrations of PAEs have been found in industrial wastewaters, ranging from 10 to 300 µg/L in wastewaters of a number of chemical plants and nearby rivers to 30 mg/L in wastewater near a manufacturing plant that produces plasticizers [7]. Di-2-ethylhexyl phthalate (DEHP), one of the most commonly used phthalates, is widely used as a plasticizer and solvent in toys, polyvinyl chloride products, cosmetics, medical tubing, shampoos, and other products. The Carcinogen Assessment Group of US EPA has classified DEHP as a "probable human carcinogen". The main concerns on DEHP potential toxic effects that are experimentally observed in different species are of considerable concern on the human endocrine system [8]. Over time, this compound leaches out of these commonly used products and accumulates in the environment. Therefore, PAEs are becoming ubiquitous environmental

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contaminants with significant human exposure [9]. Maximum contaminant level of 6 and 8 μg/L for DEHP in drinking water has been set by the US EPA and World Health Organization (WHO), respectively [10,11].

Advanced oxidation processes (AOPs) are the most powerful methods for minimization and degradation of PAEs [4,12,13]. They involve two stages of oxidation: (1) the formation of strong oxidants (e.g., hydroxyl radicals) and (2) the reaction of these oxidants with organic contaminants in water [14]. Among the numerous AOPs developed thus far, those 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 are readily applicable on a large scale [15]. However, a number of these processes may have other mechanisms for destroying organic pollutants; in general, the effectiveness of an AOP is proportional to its ability to generate hydroxyl radicals [14]. An increasing interest existed in the last decade in using ozone for treating effluents containing hazardous contaminants owing to the development of large-scale ozone generators along with reduced installation and operating costs. Photolytic ozonation process (UV/O_3) is an effective method for oxidation and destruction of refractory and toxic organics in water and is a potential wastewater treatment process [16]. The decay rate of ozone is approximately 1,000 times higher than that of H_2O_2 [17]. When compared with UV photolysis and ozonation process, photolytic ozonation process is more effective for degradation of some organic compounds [16,18]. Some approaches have been employed to improve the oxidizing power of ozone or UV/O_3, thus leading to a reduction in time required for the reaction and consequent reduction in energy cost [19]. Promising experiments involving ferrous or ferric ion homogeneous catalysis along with ozonation in the presence or absence of radiation have also been reported in the literature. On the other hand, Pera-Titus et al. [16] reported that when compared with single ozonation, degradation of chlorophenols (CPs) is enhanced in the presence of ferrous ions and in the presence of UV; the action of these ions improves the efficiency of the UV/O_3 method. When compared with conventional catalysis, nanocatalysis is useful for designing catalysts with excellent activity, greater selectivity, and high stability [20]. Because of economic reasons, activation of molecular oxygen by zero-valent metals, such as zero-valent iron (ZVI), to produce hydroxyl radical ($^{\bullet}OH$) is receiving increasing attention [21,22]. The use of NZVI instead of micro- and macro-scale Fe^0 (ZVI) materials

can potentially eliminate the need for permeable reactive barriers and is more effective in both cost feasibility and contaminant remediation [23].

The aim of this study was to evaluate possible improvement in an efficient combination of photodegradation, ozonation method, and NZVI for purification of solutions containing DEHP with economic and safety concerns. Thus far, the role of NZVI in DEHP degradation under photodegradation ozonation process in aqueous solutions has not been studied. Moreover, the effects of operating parameters of the $UV/O_3/Fe^0$ process, such as pH, applied ozone and NZVI dosages, reaction time, and initial concentration of DEHP were examined. Additionally, the primary intermediates of DEHP in the combined process were identified.
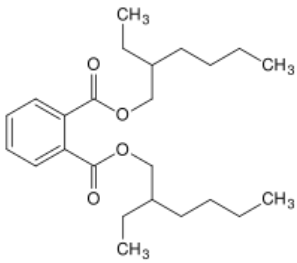
2. Materials and methods

In our previous study, we first determined the DEHP removal rate in each process (UV photolysis, ozonation, and the combination of UV and ozonation, UV/O_3) for an initial DEHP concentration of 5 mg/L and a reaction time of 30 min [18]. In the present study, for the second step, it was to investigate the influence of NZVI on the UV/O_3 process and to determine operating variables such as pH of the solution (2–11), ozone dose (50–150 mg/h), initial DEHP concentration (1–10 mg/L), NZVI dosage (50–400 mg/L), and reaction time (5–30 min) on DEHP degradation. Kinetic studies were conducted, and the intermediate products were determined.

2.1. Chemicals and instruments

In this study, analytical grade DEHP (Sigma-Aldrich Chemical Co., Fluka Co., United States) was used (Table 1). The pH was adjusted to desired values with 1 N sulfuric acid and 1 N sodium hydroxide (Merck Co., Germany). The characteristics and structure of NZVI (as powder) supplied from US Research Nanomaterials Inc. (Iran) are shown in Table 2. The stock solution of DEHP was prepared in methanol and deionized water and stored at a temperature of 4°C. Then, calibration standard was prepared by dilution of the stock solution at five concentration levels (0.01–10 mg). A linear fit of DEHP was obtained with high correlation coefficients $R^2 > 0.99$. The solid phase extraction (SPE) cartridges (CHROMABOND® C_{18}ec – 3 mL/500 mg) were purchased from Macherey-Nagel GmbH & Co. (Germany).

Table 1
Physicochemical properties of DEHP

Property	Value	Chemical structure
Chemical formula	$C_{24}H_{38}O_4$	
Molecular weight	390.62	
Vapor pressure	1.0×10^{-7} mmHg at 25°C	
Melting point	–47°C	
Boiling point	386°C	
Specific gravity	0.986	
Solubility in water	Essentially insoluble (3 g/L)	
LogK_{ow}	7.5	

An ozone generator (O & W, China) with a dosing capacity of 1 g O_3/h was used. Furthermore, a high-pressure UV lamp with 254 nm wavelength and 7.1 W/m² intensity was used in the photolysis process. A magnetic stirrer (Labinco-90-402) was used during the process to ensure adequate mixing. A Metrohm Herisau E520 pH meter was used for pH measurements of the solutions.

2.2. Experimental procedure

Degradation of DEHP was performed in a covered cylindrical batch reactor with an effective volume of 1 L and equipped with cooling water temperature control (25°C ± 3°C) to prevent the lamp from overheating, as shown in Fig. 1. A UV lamp inserted into a quartz sleeve was located at the center of the reactor.

2.3. Analysis methods

Removal efficiency (RE, %) of DEHP by UV/O_3/Fe^0 process was calculated using the following equation:

$$RE\% = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 and C (mg/L) are the initial and final DEHP concentrations, respectively.

After each process, NZVI was separated with a magnet of 20 cm height (S BMW, 0.7 Tesla) and then filtered through a syringed acetate cellulose filter with 0.2 μm pore size [24].

Table 2
Characteristics of NZVI nanoparticles

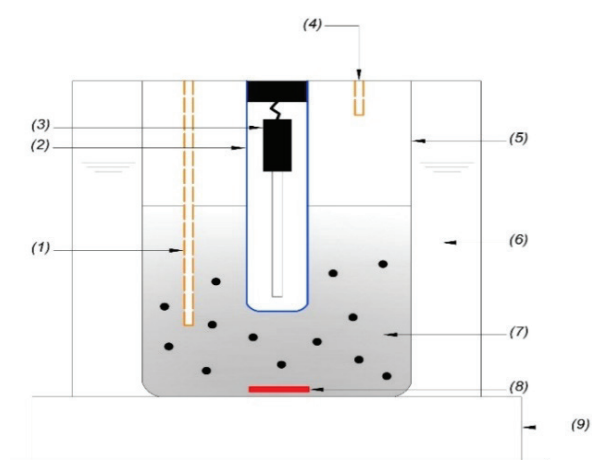| Characteristic	Value
Chemical frame	NZVI
Purity, %	>99.5
Particle size, nm	35–45

Fig. 1. Experimental setup: (1) ozone generator; (2) quartz tube; (3) high-pressure UV lamp; (4) KI solution; (5) reactor; (6) temperature-controlled bath; (7) sample content NZVI; (8) magnet; and (9) magnetic stirrer.

The DEHP was extracted from the water solutions using SPE cartridges as follows [25].

First, a C_{18} SPE column was washed with 5 mL of methanol and 10 mL of ultrapure water. Thereafter, 300 mL of the sample was passed through the column at a flow rate of 5 mL/min under vacuum. The compounds adsorbed in the C_{18} column were eluted with 2 mL of methanol. The extraction solution was dried under nitrogen gas flow, and the extracts were diluted with 100 μL of methyl tert-butyl ether in 2 mL vials for gas chromatography–mass spectrometry (GC/MS) analysis.

To determine the H_2O_2 in samples, potassium permanganate method was used [26]. We used GC for quantitative analysis and GC/mass for qualitative analysis. GC/MS analysis was performed using an Agilent technology 7890A gas chromatograph equipped with a 5975C quadrupole mass selective detector. A Phenomenex HP5 column of 30 m length with 0.32 mm i.d. (inner diameter) and 0.25 μm film thickness was used for GC separation using the following oven temperature program: 100°C hold for 1 min with heating to 210°C at 10°C/min, heating to 250°C at 5°C/min, and finally, heating to 280°C at 30°C/min (6 min hold). Both the interface and injector temperatures were 250°C. All the 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.

3. Results and discussion

The results of our previous study [18] showed that the UV/O_3 process has a positive effect on DEHP removal from aqueous solutions, and degradation percentage of DEHP was 80%. In the present study, we first evaluated the RE of DEHP by different techniques. Then, the optimum conditions and intermediates were determined.

3.1. Degradation of DEHP by different processes

Several experiments were performed with different processes, namely UV/O_3, UV/Fe^0, O_3/Fe^0, UV/O_3/Fe^0, in order to evaluate their ability to remove DEHP. Fig. 2 shows the
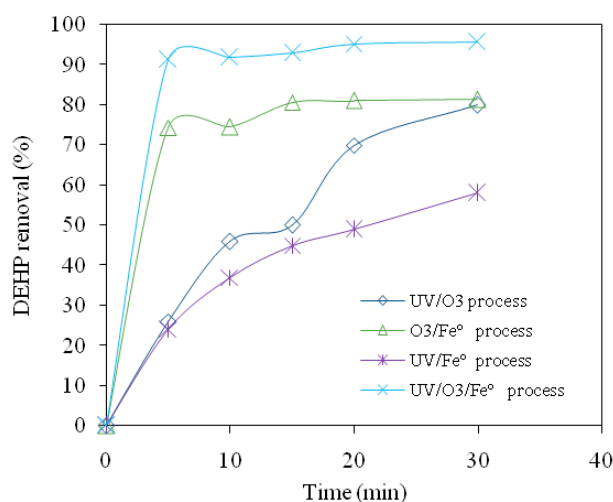

Fig. 2. DEHP degradation efficiencies in different comparable processes (DEHP concentration: 5 mg/L, ozone dosage: 100 mg/h, NZVI dosage: 200 mg/L, and pH: 7).

results of the experiments conducted under the same experimental conditions. As seen in this figure, DEHP RE increased for all processes by increasing of reaction time. Among these processes, UV/O_3/Fe^0 and UV processes had a higher and a lower efficiency removal for DEHP degradation, respectively. As indicated, the maximum DEHP removal for UV/O_3, UV/Fe^0, and O_3/Fe^0 were around 80%, 58%, and 81%, respectively. In our previous study, DEHP degradation was obtained 43% and 50% by UV photolysis and ozonation, respectively [18]. However, the present study results showed the removal percentage of DEHP was 58% after adding NZVI to UV process. Furthermore, UV/Fe^0 process could slightly improve the removal of DEHP. These results indicated the concentration of $^•$OH formed in UV/Fe^0 process is low compared with other techniques (Eqs. (2) and (3)) [27].

$$Fe^0 + h\upsilon \rightarrow Fe^{2+} + 2e^- \qquad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^•OH + OH^- \qquad (3)$$

However, DEHP degradation was significantly enhanced by the O_3/Fe^0 process. In the O_3/Fe^0 process, the electron transfer from Fe^0 to dissolved oxygen initiates the NZVI oxidative reaction; therefore, the mass transfer of O_2 onto the NZVI surface is critical. Diffusion of O_2 onto the Fe^0 surface may be accelerated during the process. The NZVI can attract oxygen, which accelerates the mass transfer process. The enhanced reduction of oxygen molecule on NZVI leads to the enhanced production of OH radicals, as given by Eqs. (4) and (5) [28,29].

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \qquad (4)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^•OH \qquad (5)$$

The effect of UV/Fe^0 on the DEHP RE compared with O_3/Fe^0 process can be explained that the source of H_2O_2 production is more various in O_3/Fe^0 than in the Fe^0 and UV reaction. Also, adding NZVI to the UV/O_3 process could increase the maximum RE up to 95%. The combination of ozone, UV, and NZVI provides numerous sources of $^•$OH such as (a) the degradation of ozone, (b) the photolysis, (c) the ozone decomposition by UV irradiation, (d) the NZVI reaction to products of ozone decomposition, and (e) the reaction between NZVI and UV irradiation.

3.2. Effect of pH

The pH of the solution is one of the most important operating parameters affecting pollutant removal rate by influencing pollutant ionization and surface properties of the system using catalyst [30,31]. The effect of the pH of the solution in the range of 2–11 on the degradation of DEHP in the UV/O_3/Fe^0 process was investigated. Fig. 3 summarizes the results of DEHP degradation as a function of the pH of the solution. As can be seen, DEHP degradation decreases from 96% to 80.5% for pH 2 and 11, respectively. Therefore, DEHP degradation increases when the pH of the solution is decreased. During the process in acidic condition, Eqs. (4) and (5) could happen. It is possible that the presence of iron
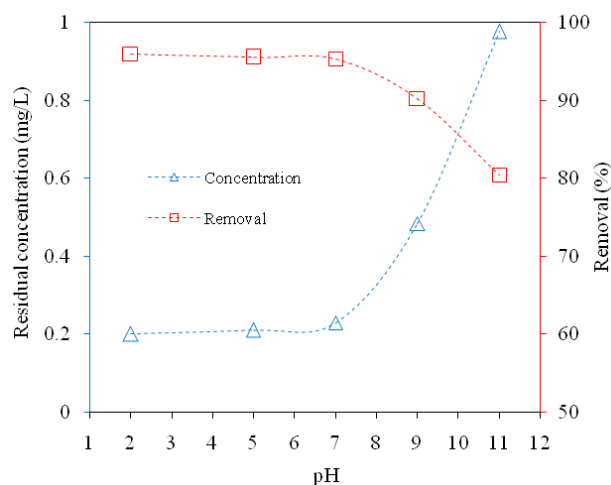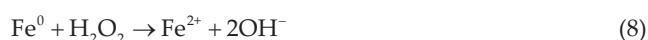

Fig. 3. Effect of pH of the solution on DEHP residual concentrations and removal efficiencies in NZVI–UV/O_3 process (DEHP concentration: 5 mg/L, NZVI dosage: 200 mg/L, ozone dosage: 100 mg/h, and reaction time: 30 min).
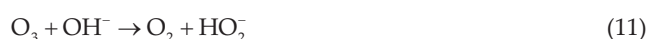
as a catalyst, which exhibits maximum activity under acidic conditions, could also be an important factor [32]. Khan et al. [33] examined the effect of two different pH values in three processes: UV/H_2O_2/Fe^{2+}, UV/HSO_5^-/Fe^{2+}, and UV/$S_2O_8^{2-}$/Fe^{2+}. In this work, all the used treatment technologies exhibited higher efficiency at pH 3 than at pH 5.8. Xu et al. [30] reported that dimethyl phthalate degradation decreases with increasing pH. Furthermore, acidic pH facilitates better RE of DEHP from aqueous solutions.

The mechanism and kinetics of the reactions are different in acidic and basic media. We can draw the reaction mechanism of systems as [34,35]:
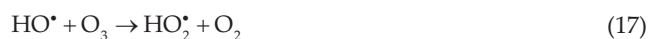
- Acidic condition:

$$O_3 + h\upsilon + H_2O \rightarrow H_2O_2 \qquad (6)$$

$$Fe^0 \xrightarrow{\ pH < 7\ } Fe^{2+} \qquad (7)$$

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2OH^- \qquad (8)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^• + OH^- \qquad (9)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^• + H^+ \qquad (10)$$

- Alkaline condition:

$$O_3 + OH^- \rightarrow O_2 + HO_2^- \qquad (11)$$

$$HO_2^- + O_3 \rightarrow HO_2^• + O_3^{•-} \qquad (12)$$

$$HO_2^• \rightleftarrows H^+ + O_2^{•-} \qquad (13)$$

$$O_2^{•-} + O_3 \rightarrow O_2 + O_3^{•-} \qquad (14)$$

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^{\bullet} \qquad (15)$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \qquad (16)$$

$$HO^{\bullet} + O_3 \rightarrow HO_2^{\bullet} + O_2 \qquad (17)$$

On the other hand, in the alkaline medium, the surface of Fe^0 can fully covered by the passivation layer. This passive film on the metal surface could affect on mass transport process [35]. In the present study, because the effect of pH in the range of 2–7 on the performance of the combined $UV/O_3/Fe^0$ process is negligible, a pH of 7 was selected as optimum for DEHP degradation. This observation is in good agreement with other studies.

3.3. Effect of ozone dosage

To determine the effect of ozone dosage on DEHP RE in $UV/O_3/Fe^0$ process, a series of experiments were performed by varying ozone dosage from 50 to 150 mg/h. Fig. 4 shows the effect of ozone dosage on the degradation of DEHP in the NZVI photodegradation ozonation process. As can be seen, in the $UV/O_3/Fe^0$ process, degradation of DEHP decreases with increasing ozone concentration. In this case, DEHP removal decreases from 97.4% to 82.6% as the ozone concentration increases from 50 to 150 mg/h for 0–30 min reaction time. Therefore, the maximum DEHP RE is 97.4% (DEHP residual concentration: 0.13 mg/L) for 50 mg/h ozone dosage in the combined process. It should be noted that both protons and O_2 molecules are competing for electron acceptors (oxidants) of Fe^0 (Eqs. (4), (5), and (8)) [28]:

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (18)$$

Therefore, O_2 molecules are oxidants for NZVI at an ozone dosage of 50 mg/h. Consequently, ZVI nanoparticles attract oxygen molecules onto their surface regions, thus,
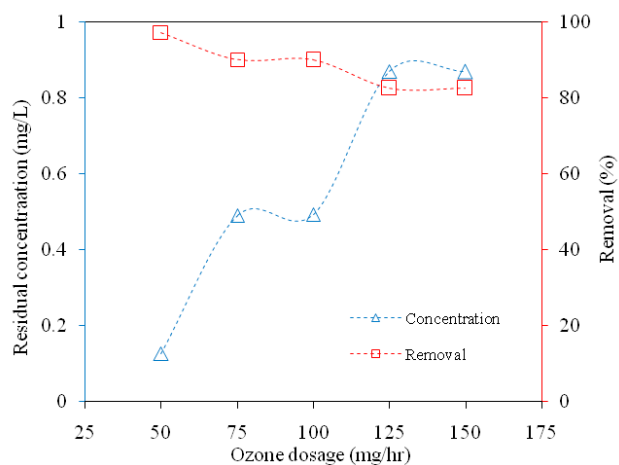

Fig. 4. Effect of ozone dosage on DEHP residual concentrations and removal efficiencies in NZVI–UV/O_3 process (DEHP concentration: 5 mg/L, NZVI dosage: 200 mg/L, pH: 7, and reaction time: 30 min).

accelerating mass transfer. The enhanced reduction of O_2 on NZVI leads to the enhanced production of OH radicals, as given by Eqs. (4) and (5). However, when ozone dosage is increased to 150 mg/h, protons are electron acceptors for NZVI.

It is possible that a small fraction of the H_2O_2 reacts with Fe(II) to produce a reactive oxidant instead of Fe^0. The reaction of Fe^0 with O_2 produces reactive oxidants capable of oxidizing organic compounds. At neutral pH (7) values, Fe(II) oxidation by O_2 produces a different oxidant, most likely the ferryl ion (Fe(IV)). Yields of the oxidant produced at pH 7 are too low and they are unable to oxidize organic compounds. In other words, Fe(IV) is a weaker oxidant than $^{\bullet}$OH [36]. Therefore, an ozone dosage of 50 mg/h is more effective for DEHP degradation.

This process may be described by the following equations [37]:

$$O_3 \xrightarrow{h\upsilon} O(1D) + O_2 \qquad (19)$$

$$O(1D) + H_2O \rightarrow H_2O_2 \qquad (20)$$

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \qquad (21)$$

$$H_2O_2 \rightarrow 2^{\bullet}OH \qquad (22)$$

$$DEHP + {}^{\bullet}OH \rightarrow products \qquad (23)$$

In order to verify experiments, we used permanganate titration method to determine the concentration of H_2O_2. To determine the effect of ozone dosage on produced H_2O_2 in $UV/O_3/Fe^0$ process, a series of experiments were performed by varying ozone dosage from 50 to 150 mg/h. Fig. 5 shows the results of experiments. As can be seen, produced H_2O_2 reduced with increasing ozone doses. Therefore, the maximum produced H_2O_2 is 0.11 mmol for 50 mg/h ozone dosage. The amount of produced H_2O_2 had no significant variation in various ozone dosages. Finally, it was noted that ozone dosage had little influence on the removal of DEHP.

3.4. Effect of NZVI dosage

The influence of ZVI nanoparticle dosage (range of 50–400 mg/L) in the $UV/O_3/Fe^0$ process was studied. The operating conditions are shown in Fig. 6. As can be seen in, an increase in nanoparticle catalyst from 50 to 200 mg/L increases DEHP oxidation efficiency from 86% to 97.4%. Oxidation mechanisms of NZVI have been described in previous sections. An increase in catalyst amount clearly leads to an increase in DEHP RE owing to the creation of greater surface area and more active sites in the nanoparticles. Therefore, more oxidation agents such as hydroxyl radicals are formed, and RE is increased. Nevertheless, the degradation rate is almost constant for an NZVI dosage of 200–400 mg/L because when the nanoparticle catalyst amount is greater than 200 mg/L, the dissolved air in the solution depletes faster, and $^{\bullet}$OH generation in the reduced time decreases during the period of the process.

Therefore, an NZVI dosage of 200 mg/L with a reaction time of 30 min is more effective for DEHP degradation. Khan et al. [33] reported that the degradation rate constant
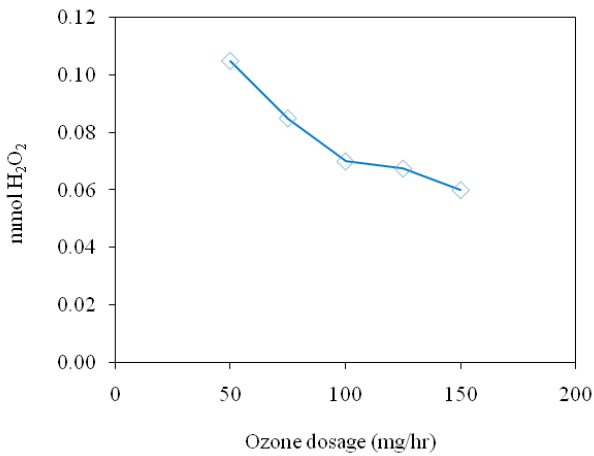
Fig. 5. Effect of ozone dosage on produced H_2O_2 in NZVI–UV/O_3 process (DEHP concentration: 5 mg/L, NZVI dosage: 200 mg/L, pH: 7, and reaction time: 30 min).
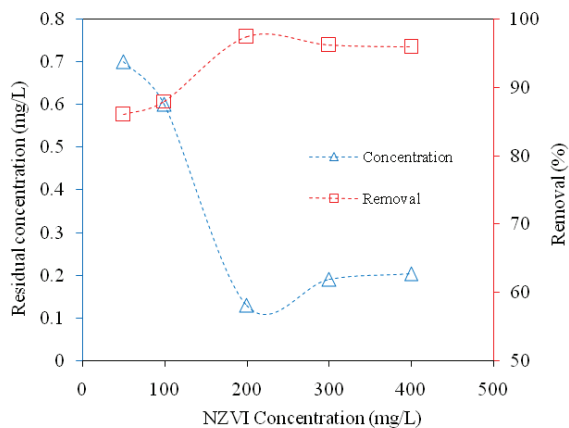

Fig. 6. Effect of NZVI catalyst dosage on DEHP residual concentrations and removal efficiencies in NZVI–UV/O_3 process (DEHP concentration: 5 mg/L, ozone dosage: 50 mg/h, pH: 7, and reaction time: 30 min).

of atrazine increases with increasing ferrous ion (Fe^{2+}) concentration. They reported that Fe^{2+} ions activate the oxidants, i.e., H_2O_2, $S_2O_8^{2-}$, and HSO_5^-, to generate reactive radicals through electron transfer mechanism.

3.5. Effect of reaction time

The effect of reaction time on DEHP degradation was evaluated, and the results are shown in Fig. 7. As can be seen, an increase in reaction time from 5 to 15 min increases DEHP degradation efficiency from 90% to 99.1%, respectively. When the reaction time is greater than 15 min, DEHP RE is constant (approximately 99%). Gaya et al. [38] also reported that reaction time has an important role in ZnO photocatalytic process. Therefore, when the reaction time is increased, 4-CPs degrades faster. Moreover, high concentrations of H_2O_2 which were produced during the reaction period could undergo self-quenching of $^\bullet$OH in the solution
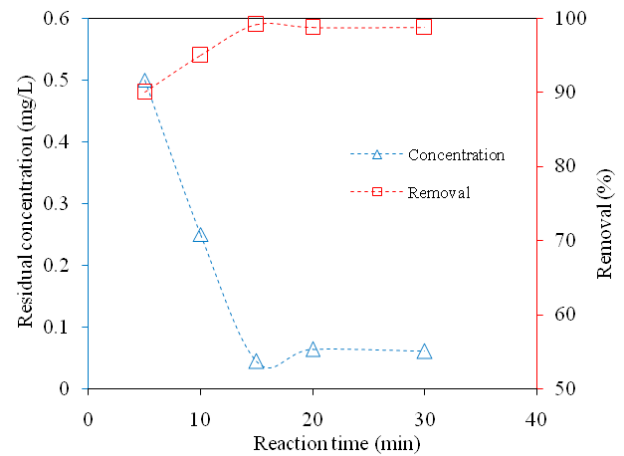

Fig. 7. Effect of reaction time on DEHP residual concentrations and removal efficiencies in NZVI–UV/O_3 process (DEHP concentration: 5 mg/L, ozone dosage: 50 mg/h, NZVI dosage: 200 mg/L, and pH: 7).

by this extra amounts of H_2O_2 to produce $OH_2^\bullet$ radicals, as given by Eq. (9) [39]:

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + OH_2^\bullet \tag{24}$$

Therefore, the optimal reaction time in these experiments is 15 min. Under these conditions, DEHP RE is 99.1%.

3.6. Effect of initial DEHP concentration

The influence of initial DEHP concentration (1–10 mg/L) in the UV/O_3/Fe^0 process was investigated. The effects of DEHP variation on DEHP degradation are shown in Fig. 8. As can be seen, DEHP degradation increases from 95.6% to 99.1% as the initial DEHP concentration increases from 1 to 5 mg/L, respectively. When DEHP concentration is increased to over 5 mg/L, DEHP RE slightly decreases to 96%. Finally, the maximum DEHP RE is 99.1% (DEHP residual concentration = 0.04 mg/L). Because the initial oxidant concentration is fixed, a high concentration of DEHP resulted in increased formation/concentration of intermediates, thus lowering the reaction rate of radicals toward DEHP. Furthermore, when the initial concentration of DEHP is increased, the number of DEHP molecules exposed to reactive radicals for degradation also increases, thus leading to higher degradation efficiency. However, for an initial DEHP concentration of 10 mg/L, the RE decreases to 96%. An increase in DEHP concentration may induce an increase in internal optical density, and the solution then gradually becomes impermeable to UV light [40]. Khan et al. [33] observed that RE increases at a fixed HSO_5^- concentration when atrazine concentration is increased.

3.7. Kinetic studies

To study the influence of UV/O_3/Fe^0 process on DEHP degradation in aqueous solutions, the kinetics of DEHP degradation were obtained (Table 3). The operating conditions
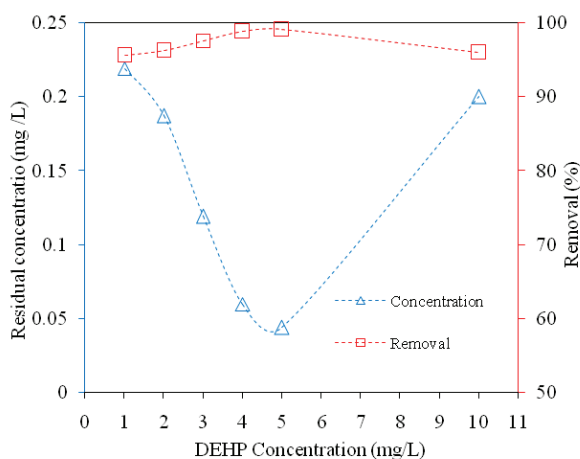
Fig. 8. Effect of initial concentration of DEHP in NZVI–UV/O$_3$ process (ozone dosage: 50 mg/h, NZVI dosage: 200 mg/L, pH: 7, and reaction time: 15 min).

were as follows: initial DEHP concentration of 5 mg/L, ozone dosage of 100 mg/h, NZVI dosage of 200 mg/L, optimal pH of 7, and a reaction time of 0–30 min. As can be seen in Table 3, the second-order model has a degree of fitness with a high regression coefficient ($R^2 > 0.95$). Further, the kinetics of combined reactions are shown in Fig. 9.

3.8. Determination of intermediate products

It is crucial to determine that the intermediate products are less toxic than DEHP. The intermediate products formed during UV/O$_3$/Fe^0 degradation of DEHP in solution were analyzed using qualitative GC/MS analysis and identified by comparing with commercially available standard GC/MS Wiley, The National Institute of Standards and Technology, and pesticide library data. Fig. 10 shows the obtained output chromatogram of UV/O$_3$/Fe^0 treatment for DEHP at optimum conditions: ozone dosage: 50 mg/h, NZVI dosage: 200 mg/L, pH: 7, and contact time: 15 min. As can be seen, phthalic acid is the primary intermediate product occurring during degradation of DEHP. Table 4 also shows the obtained results of this experiment. Chung and Chen [40] and Chen [41] have investigated DEHP degradation with UV/H$_2$O$_2$ and UV/TiO$_2$ processes, respectively. They identified some different intermediates, such as benzoic acid, phthalic acid, 2-(butoxycarbonyl)benzoic acid, 2-[(octyloxy)carbonyl]benzoic acid, mono-2-ethylhexyl phthalate, and octyl 4-hydroxybenzoate. Benzoic and phthalic acids are the common compounds detected in our study. In addition, Kaneco et al. [42] and Bajt et al. [43] analyzed DBP photocatalytic degradation and found phthalic acid to be the common intermediate produced during both DBP and DEHP photocatalytic degradation.

4. Conclusions

In this study, DEHP degradation by NZVI photodegradation ozonation process in the batch system was assayed. The process conditions and kinetic equations were obtained. The UV/O$_3$/Fe^0 process was affected by operating conditions

Table 3
Kinetic parameters for NZVI–UV/O$_3$ of DEHP

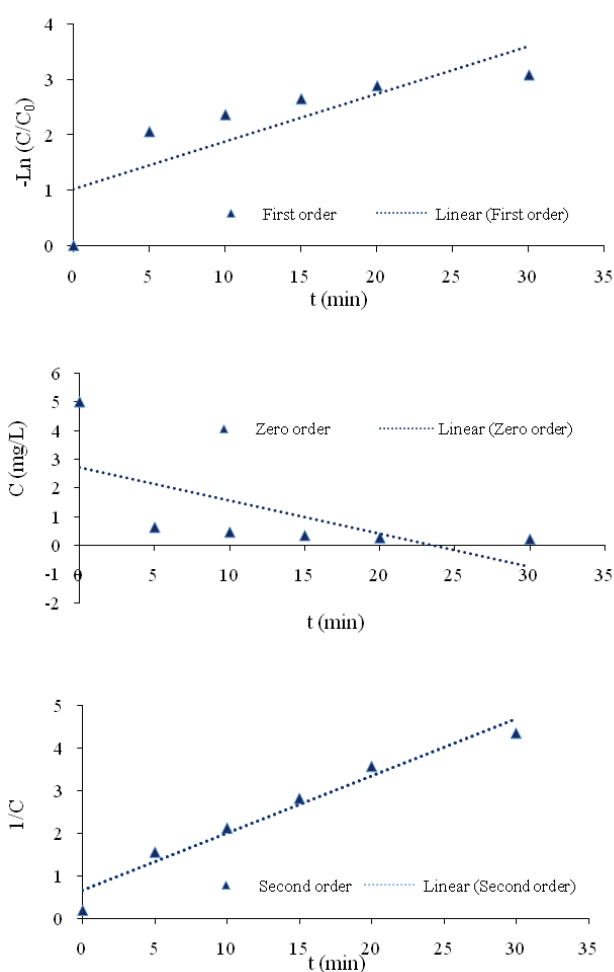| Kinetic model	Linear form	Constant	Value
Zero-order	$C - C_0 = -k_0 t$	k_0	0.1153
		R^2	0.43
First-order	$\ln \dfrac{C}{C_0} = -k_1 t$	k_1	0.0856
		R^2	0.67
Second-order	$\dfrac{1}{C} - \dfrac{1}{C_0} = k_2 t$	k_2	0.1341
		R^2	0.95

Fig. 9. Kinetic variances in NZVI–UV/O$_3$ process.

such as pH, ozone and NZVI catalyst dosages, reaction time, and initial DEHP concentration, which were the main factors investigated in this study. Initial DEHP concentration of 5 mg/L, pH of 7, ozone dosage of 50 mg/h, NZVI dosage of 200 mg/L, and reaction time of 15 min were selected as the optimum conditions for DEHP treatment, and the NZVI photodegradation ozonation process degrades to approximately 99.1% of DEHP. Oxidations by NZVI catalyst and hydroxyl radicals were the primary DEHP degradation mechanisms.
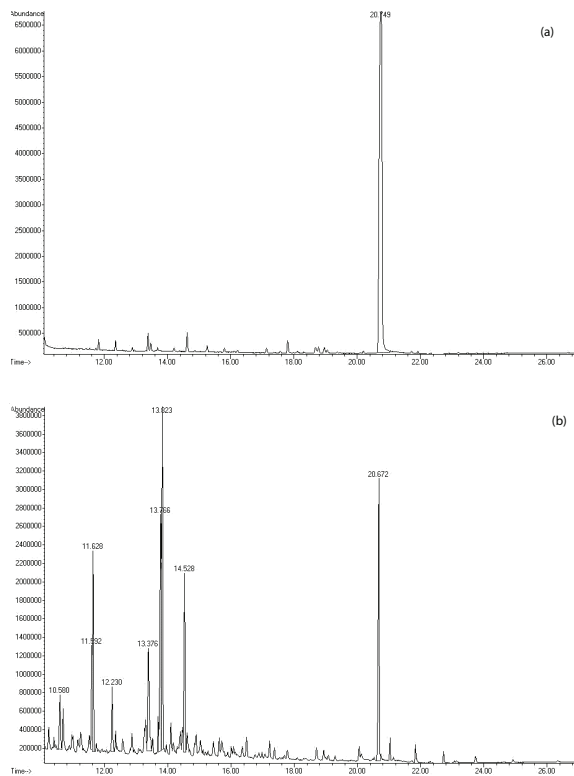
Fig. 10. Analytical results of chromatogram of (a) untreated and (b) treated solutions in NZVI–UV/O_3 process (ozone dosage: 50 mg/h, NZVI dosage: 200 mg/L, pH: 7, and contact time: 15 min).

Table 4
Intermediate products analyzed from GC–MS

Peak no.	Retention time (min)	Compound name
1	10.580	2-Cyclopropyl-2-trimethylsilyloxy cyclopropancarbonic acid
2	11.592	6-Phenyl-2-tetralone
3	11.628	Ethyl 5-Phenyl-2-penten-4-ynoate
4	12.230	Benzoic acid
5	13.823	Phthalic acid
6	14.528	3-Cyclopentylpropionic acid

The kinetics of DEHP degradation were studied by fitting data from the experiments on DEHP degradation in the UV/O_3/Fe^0 system. According to our study, DEHP degradation by the UV/O_3/Fe^0 process follows pseudo-second-order kinetics. The results of this study also show that phthalic acid is the commonly occurring intermediate during NZVI photodegradation ozonation of DEHP in the optimum condition. It is noted that the related intermediate constituents were identified for the sample withdrawn after 15 min reaction time and as the AOPs are time-dependent processes that induce stepwise decomposition of organics, it is possible to form some other intermediates and even mineralized compounds that need to additional studies. Finally, the UV/O_3/Fe^0 system

exhibits excellent oxidation capacity for organic pollutants. Therefore, NZVI can be employed as a novel technology for the treatment of solutions containing PAEs.

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