Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.827297

52 (2014) 797–804
January

Taylor & Francis
Taylor & Francis Group

Effect of nitrate on the degradation of bisphenol A by UV/H_2O_2 and ozone/H_2O_2 oxidation in aqueous solution

C.G. Park[a,]*, E.S. Choi[a], H.W. Jeon[b], J.H. Lee[a], B.W. Sung[b], Y.H. Cho[a], K.B. Ko[b]

[a]*Green Environmental Industry Division, Korea Testing Laboratory, Guro-gu, Seoul 152-718, Korea*
Tel. +82 2 860 1678; Fax: +82 2 860 1639; email: parkcg@ktl.re.kr
[b]*School of Civil & Environmental Engineering, Yonsei University, 134 Shinchondong, Seoul 120-749, Korea*

Received 9 March 2013; Accepted 30 March 2013

ABSTRACT

The goal of the present study was to investigate the effect of nitrate on the removal of bisphenol A (BPA) by conducting bench-scale UV/H_2O_2 and O_3/H_2O_2 operations under a variety of reaction time and initial concentrations of H_2O_2 and NO_3^-–N. Also, this study evaluated the advanced oxidation process processes and determined the optimal conditions, for removing BPA. The practical reaction time and initial H_2O_2 concentration for the more than 85% removal of BPA proved to be 2.0 min and 150 mg/L, respectively, in the presence or absence of nitrate. The removal efficiency of BPA was improved by the hydroxyl radicals produced from nitrate photolysis in the absence of H_2O_2. In the presence of H_2O_2, however, nitrate hindered the BPA removal by acting as $^{\cdot}OH$ scavengers under the operating conditions described above. Also, H_2O_2 acts as free-radicals scavenger at concentrations above optimum required. In O_3/H_2O_2 process with nitrate addition, more than 75% of the BPA was removed under the conditions of an initial O_3 concentration of 7.5 mg/L and H_2O_2 concentration of more than 150 mg/L.

Keywords: AOPs; BPA; Hydroxyl radical; Nitrate; Scavenger

1. Introduction

The revolutionized development of resources and technologies has produced more chemicals and compounds which consequently increased the number of compounds that were identified as possessing potential environmental threats to the livings. This ever-increasing number of surreptitious compounds poses potential environmental threat to the living organisms [1]. An example is bisphenol A [2,2-bis(4-hydroxyphenyl)propane; BPA], which is widely used as a raw material for polycarbonate and epoxy resins and is known to accumulate in nature without decomposition causing reproductive damages to a variety of animal species [2]. BPA and other endocrine disrupting chemicals (EDCs) manage to enter surface waters through wastewater from BPA production factories and/or by agricultural runoff and irrigation return waters [3]. BPA was detected at considerably high levels ranging from 0.44 to 53 nmol/L in surface waters [4] and 5.7 to 75 mmol/L

---

*Corresponding author.

Presented at the Fifth Annual International Conference on "Challenges in Environmental Science & Engineering—CESE 2012" Melbourne, Australia, 9–13 September 2012

in landfill leachates [5]. Persistent EDCs appear to remain for periods ranging from days to months in the surface waters into which they are discharged [6]. Therefore, in the last decade, there is an increasing interest in effective remediation technologies for the destruction of BPA in contaminated water environments [7].

Advanced oxidation process (AOP) employing hydrogen peroxide with UV or O_3 is an effective method in the degradation of organic pollutants. In UV/H_2O_2 or O_3/H_2O_2 process, the oxidation of H_2O_2 generates oxidizing species hydroxyl radical ($^{\cdot}OH$), which oxidize various organic compounds quickly [8]. 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 [9]. Hydroxyl radicals can oxidize a broad range of organic pollutants quickly and nonselectively [10]. In addition, the advanced H_2O_2 oxidation process has been found to be very effective in the degradation of endocrine disruptors [11]. Typical concentrations of NO_3^-–N are known to range from 2 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 [12], 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 $^{\cdot}NO_2$. One of these mechanisms is the direct route to NO_2^- formation from NO_3^- photolysis, with a low quantum yield [12,13]. The considerable production of NO_2^- can be expected via the two other reactions, which produce the intermediates ONO_2^- and $^{\cdot}NO_2$. These intermediates are eventually undergone thermal reactions to NO_2^- form as a stable product [12,14]. The formation of hydroxyl radicals $^{\cdot}OH$ can also be expected, together with one of the intermediates, $^{\cdot}NO_2$, from nitrate photolysis. As NO_2^- accumulates, it can acts as an $^{\cdot}OH$ scavenger. The mechanisms involving H_2O_2 photolysis have been critically reviewed [12,15]. 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 [15]. The literature review conducted 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 $^{\cdot}OH$ producers or, at some point in time, as $^{\cdot}OH$ scavengers, in an aqueous solution [16].

There were 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 and O_3/H_2O_2 process [17–20]. In our previous studies [16,21–23], effects of nitrate on the UV photolysis were investigated for the degradation of volatile organic compounds, 2,4-dichlorophenol, DEP, DEHP in aqueous solutions.

The goal of the present study was to investigate the effect of nitrate on the removal of BPA by conducting bench-scale UV/H_2O_2 and O_3/H_2O_2 operations under a variety of reaction time and initial concentrations of H_2O_2 and NO_3^-–N. Also, this study evaluated the AOP processes (UV alone, UV/H_2O_2, and O_3/H_2O_2) and determined the optimal conditions, for removing BPA. Therefore, the results of this study can provide the referable information about the proper application of ozonation and UV irradiation with hydrogen peroxide for the removal of BPA. The identification of the intermediates from the BPA oxidation was not within the scope of this study.

2. Materials and methods

2.1. Bench-scale AOP system for advanced H_2O_2 oxidation

All the solvents and reagents used in this study, including bisphenol A (99%, Sigma–Aldrich, USA), hydrogen peroxide (28% w/w, Duksan, Korea) and KNO_3 (99%, Samchun, Korea), were of analytical grade. All experiments (UV alone, UV/H_2O_2, O_3/H_2O_2) were carried out in a bench-scale AOP system (Fig. 1), which consisted of a 28 L raw water tank, a 1 m^3/h capacity raw water feed pump, a 18 L UV and O_3 reactor, and a maximum 2 g/h capacity O_3 generator. An O_3 generator (Wony Machinery Co., LTD), an O_3 injector (Mazzel, USA) and reactor were installed, and connected to the bench-scale AOP system to study the BPA's oxidation. The reactor and tank are made of a stainless steel (STS316L). Also, they were interconnected with stainless steel pipes. The UV lamp in the reactor (HanSung Ultraviolet co. LTD) with a nominal power of 65 W, emitted radiation at 254 nm. 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.

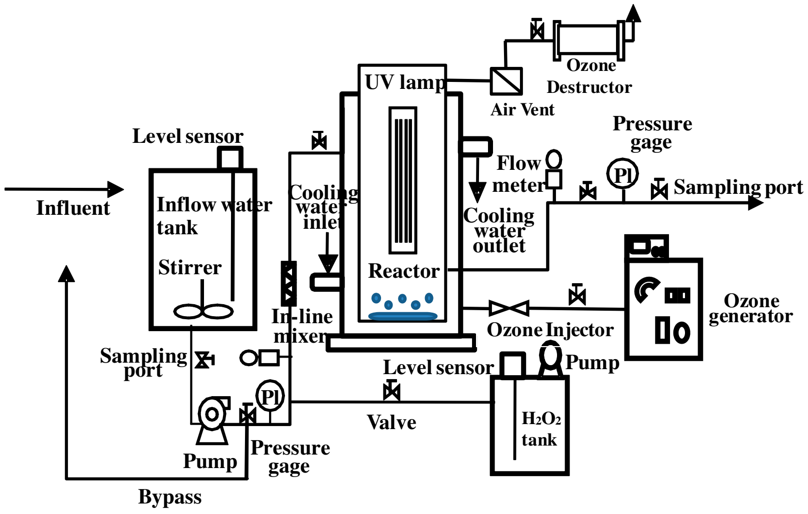

Fig. 1. Schematic diagram of the bench-scale AOP system for advanced H_2O_2 oxidation.

The aqueous solution (28 L) that was poured into the raw water tank was prepared by dissolving 0.256 g of BPA standard power and 1.01 g of KNO_3 in 28 L double-distilled water. To completely mix the solution, the mixture was carefully performed with a stirrer and was circulated in the raw water tank with the use of the installed agitator (IKA-RW 20, IKA-Werke GmbH, & Co.KG) for 2 min. Aliquots (799.93 μL) of H_2O_2 were injected before the aqueous solution was circulated to the UV and O_3 reactor, and the UV and O_3 reactor was filled with the aqueous solution to prevent any head-space inside it. This aqueous solution was again completely mixed for a period of time circulated in the UV and O_3 reactor, without UV irradiation and O_3 injection. The UV lamp in the reactor was turned on to initiate the oxidation reaction. Samples (2 mL) were regularly collected according to the predetermined schedule.

2.2. Analytical methods

BPA separation and quantification was performed using high-performance liquid chromatography system (HPLC), which is an Infinity 1290 liquid chromatography from Agilent Technology (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 Eclipse Plus C18 column (2.1 × 100 mm, 1.8 μm particle size) supplied by Agilent Technology was used for the separation of BPA. Only 100% of acetonitrile was used as a binary mobile phase. The flow rate and the injection volume were 0.3 mL/min and 1 μL, respectively. Under these conditions, the separation time was less than 2 min. These optimal conditions are shown in Table 1. The samples were injected directly into the chromatograph, without any previous sample preparation process.

3. Results and discussion

3.1. Effect of nitrate on the UV alone and UV/H_2O_2 processes to degrade BPA

Fig. 2(a) shows the profiles of the removal of BPA as functions of reaction time in the two UV photolysis operations, into which any H_2O_2 was not supplied. However, it was added into the one operation as an initial NO_3^-–N concentration of 5 mg/L, and no NO_3^- was added into the other operation. The profiles clearly indicate that BPA was removed by the UV photolysis without any H_2O_2 and NO_3^-–N addition, and the removal efficiency of BPA gradually increased as the reaction time increased in this UV photolysis operation. In the UV photolysis without any H_2O_2 addition, the removal efficiency at a reaction of 30 min was about 42.8% with nitrate addition and about

Table 1
Operational conditions for HPLC

HPLC (Agilent 1290)	
Column	Agilent Eclipse Plus C18 (2.1 × 100 mm, 1.8 μm)
Column temperature	35 ℃
Mobile phase	100% acetonitrile
Flow rate	0.3 mL/min
Injection volume	1 μL

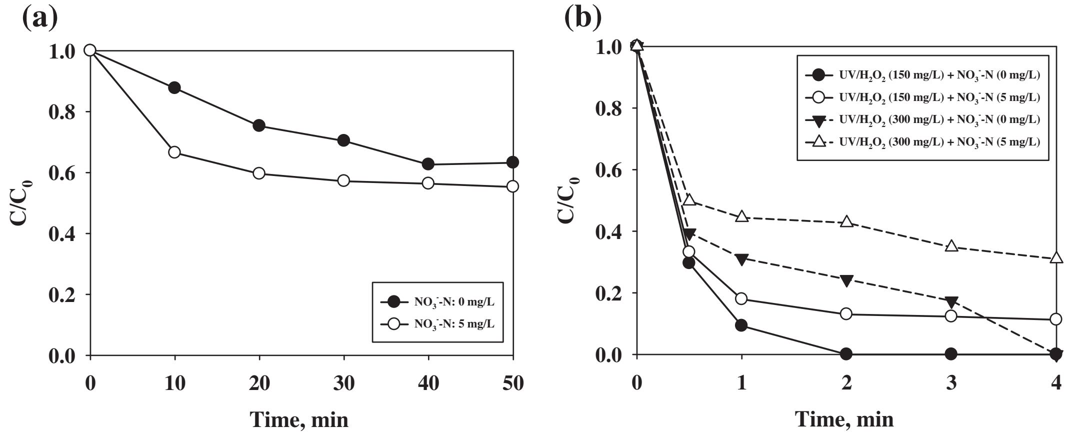

Fig. 2. (a) Profiles of the removal of BPA as a function of time with respect to different initial concentrations of NO_3^-–N; initial concentration of BPA: 4×10^{-5} mol/L; UV intensity: 20 mW/cm^2, (a) UV irradiation alone, (b) UV irradiation with initial H_2O_2 concentrations of 150 and 300 mg/L.

29.6% without nitrate addition, respectively. It is quite interesting to compare the removal efficiencies in the two operations. The removal efficiencies in the reactor, where NO_3^- was present were higher than those in the reactor where NO_3^- was absent, and these results were observed for the tested operation time. It is possibly due to the oxidation of BPA by hydroxyl radicals, and NO_3^- can be attributed to the OH radical production from the NO_3^- absorption of UV [24], even when no H_2O_2 dissolved in the solution was present in the operations. The results indicate that NO_3^- clearly has enhanced the removal of BPA through the following nitrate photolysis [13,19,25]:

$$NO_3^- + hv + H^+ \rightarrow {}^{\cdot}NO_2 + {}^{\cdot}OH \qquad (1)$$

As shown in Fig. 2(b), BPA was rapidly degraded for the first 0.5 min of UV irradiation with H_2O_2 addition and was completely removed at a reaction time of 2 min with an initial H_2O_2 concentration of 150 mg/L, and in the absence nitrate addition. Also, with an initial H_2O_2 concentration of 300 mg/L, and in the absence of nitrate, BPA was completely removed at a reaction time of 4 min. The results indicated that the UV photolysis of H_2O_2 was a more effective method for removing BPA 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 [15].

$$H_2O_2 + hv \rightarrow 2{}^{\cdot}OH \qquad (2)$$

However, the removal efficiency of the BPA was about 87.0% with an initial H_2O_2 concentration of 150 mg/L and NO_3^-–N concentration of 5 mg/L at a reaction time of 2 min and about 69.0% at s reaction time of 4 min with an initial H_2O_2 concentration of 300 mg/L and NO_3^-–N in the UV/H_2O_2 operation. The adverse effect of NO_3^- on the removal of BPA could clearly be shown under the operating conditions. The noticeable scavenging effect of nitrate on the H_2O_2 photolysis of BPA was the photolysis of NO_3^- produced NO_2^- ions, which were accumulated during the reaction, as mentioned earlier [13,24]. The observed removal efficiencies of BPA consequently decreased due to the OH-radical scavenging of the photo-chemically generated NO_2^-, as shown in the following chemical reactions (see (3), (4)) [15]. 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 [13]. It is very interesting that the longer the reaction time is, the larger the scavenging effect is.

$$NO_3^- + hv \rightarrow NO_2^- + O \qquad (3)$$

$$NO_2^- + {}^{\cdot}OH \rightarrow {}^{\cdot}NO_2 + OH^- \qquad (4)$$

3.2. Effect of initial H_2O_2 concentration on UV/H_2O_2 process to degrade BPA

The effects of the initial H_2O_2 concentration on the removal of BPA are shown in Fig. 3(a). The effects of the initial H_2O_2 concentrations on the removal of BPA (4×10^{-5} mol/L) investigated at five different H_2O_2 concentrations of 50,100, 150, 200, and 300 mg/L, with respect to two initial NO_3^-–N concentrations of 0 and 5 mg/L, at a reaction time of 2 min. About 60.7 and 70.5% of the BPA were removed by UV irradiation without nitrate addition, with initial H_2O_2 concentrations of 50 and 100 mg/L, respectively.

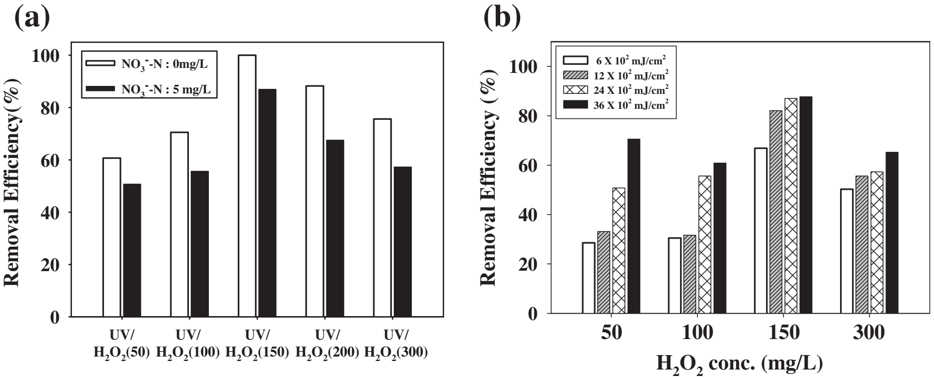

Fig. 3. (a) Profiles of the removal efficiencies (%) of BPA as a function of the initial concentrations of H_2O_2 with respect to different initial concentration of NO_3^-–N in the bench-scale UV/H_2O_2 operation; reaction time: 2 min; initial concentration of BPA: 4×10^{-5} mol/L; UV intensity: 20 mW/cm^2. H_2O_2 concentration for each treatment is given in parentheses. (b) Removal efficiencies (%) of BPA as functions of initial H_2O_2 concentrations (50, 100, 150 and 300 mg/L) at the four different UV doses in the bench-scale UV/H_2O_2 operation; initial concentration of BPA: 4×10^{-5} mol/L; UV intensity: 20 mW/cm^2; NO_3^-–N concentration: 5.0 mg/L.

The complete removal of BPA was achieved with initial H_2O_2 concentration of 150 mg/L in the absence of nitrate. The enhancement of removal by addition of H_2O_2 is due to the increase in the hydroxyl radical concentration. At low H_2O_2 concentration, H_2O_2 cannot generate enough hydroxyl radical and the removal rate is limited [10]. However, the removal efficiency of BPA decreased with increasing initial H_2O_2 concentration of more than 150 mg/L; the addition of 150–300 mg/L H_2O_2 decreases the removal efficiency from 100 to 75.7% in the same operating conditions. It was reported that high concentration of H_2O_2 could restrain the reaction [26]. At the high H_2O_2 concentration, H_2O_2 can act as a free-radical scavenger [27].

$$H_2O_2 + {}^{\cdot}OH \rightarrow {}^{\cdot}HO_2 + H_2O \tag{5}$$

In the presence of nitrate (Fig. 3(b)), the removal efficiencies of BPA by UV irradiation, at the initial H_2O_2 concentrations of 50, 100, and 150 mg/L, were 50.8, 55.6, and 87.0%, respectively. In the case of initial H_2O_2 concentration of 150 mg/L, the removal efficiencies of BPA were lower than previous those obtained. The removal efficiencies of BPA were 65.5 and 57.3%, with nitrate addition, at the initial H_2O_2 concentrations of 150 and 300 mg/L, respectively. It is suggested that H_2O_2 act as a free-radicals scavenger at concentrations above optimum required. The removal efficiencies of BPA in the H_2O_2 photolysis with nitrate were lower than those without nitrate. The scavenging effect of nitrate was remarkable in the H_2O_2 photolysis under the tested operating conditions. Also, the largest difference of the removal efficiency due to the scavenging effect of nitrate was about 20.7% with initial H_2O_2 concentration of 200 mg/L. The impact of initial H_2O_2 concentration on the removal of BPA has been investigated by varying the initial H_2O_2 concentration from 50 to 300 mg/L. The results clearly show that the practical initial concentration of H_2O_2 for more than 85% removal turned out to be 150 mg/L in the presence or absence of nitrate.

Fig. 3(b) shows the removal efficiencies (%) of BPA as functions of initial H_2O_2 concentrations (50, 100, 150, and 300 mg/L) at four different UV doses of 6×10^2, 12×10^2, 24×10^2 , and 36×10^2 mJ/cm^2 in the presence of nitrate. The BPA concentration into the UV/H_2O_2 system was 4×10^{-5} mol/L with an average NO_3^-–N concentration of 5.0 mg/L. The highest efficiency at the H_2O_2 concentrations of 150 mg/L was shown at all tested UV doses. It appears because nitrate reacted least as hydroxyl radical scavenger at the H_2O_2 concentrations of 150 mg/L under tested conditions. These show that the UV photolysis of H_2O_2 was most effective for BPA oxidation with the H_2O_2 concentration of 150 mg/L at the UV dose of 36×10^2 mJ/cm^2 in the aqueous solution containing nitrate of 5 mg/L. It is noted that about 87.7% of BPA was removed under these operating conditions, even if the relatively high NO_3^-–N concentration of about 5.0 mg/L was observed in the influent.

3.3. *Effect of initial nitrate concentration on UV/H_2O_2 process to degrade BPA*

Fig. 4(a) shows the removal efficiencies (%) of BPA as functions of time at the three different NO_3^-–N concentrations (0, 2, and 5 mg/L) with UV irradiation and no H_2O_2 addition. The removal efficiencies of BPA by UV irradiation with nitrate addition were higher than those without nitrate addition. Nitrate could be attributed to the OH radicals production from the nitrate absorption of UV, in the case of no dissolved H_2O_2, as previously discussed above. The removal efficiencies rather linearly increased, as the NO_3^-–N concentration increased. About 24.7, 38.0, and 40.4% of the BPA wereRemoved by UV irradiation without H_2O_2 addition, at a reaction time of 20 min, with initial NO_3^-–N concentrations of 0, 2, and 5 mg/L, respectively. Fig. 4(b), on the other hand, the removal efficiencies (%) of BPA as functions of time at the three different NO_3^-–N concentrations (0, 2 and 5 mg/L) with UV irradiation and H_2O_2 addition. The removal efficiencies rather linearly decreased, as the NO_3^-–N concentration increased due to the scavenging effect of nitrate. The removal efficiencies of the BPA were 70.5, 60.4, and 55.6% in the H_2O_2 photolysis, at a reaction time of 2 min, with initial NO_3^-–N concentrations of 0, 2, and 5 mg/L, respectively. Experiment results from this study clearly describe that nitrate ions act as producers of OH radicals in the UV irradiation and absence of H_2O_2; however, as scavengers of OH radicals in the UV photolysis and presence of H_2O_2. Also, the producing and scavenging effects of nitrate increased, as the NO_3^-–N concentration increased.

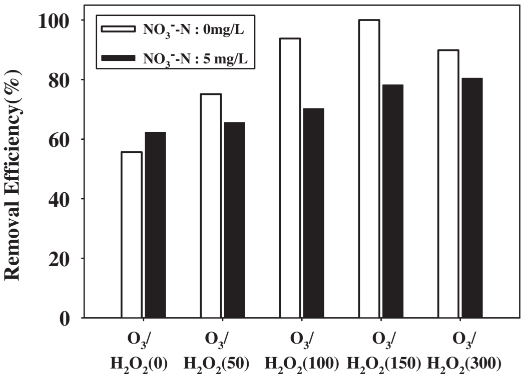

Fig. 5. Profiles of the removal efficiencies (%) of BPA as a function of the initial concentrations of H_2O_2 with respect to different initial concentration of NO_3^-–N in the bench-scale O_3/H_2O_2 operation; initial concentration of BPA: 4×10^{-5} mol/L; O_3 concentration: 7.5 mg/L. H_2O_2 concentration for each treatment is given in parentheses.

3.4. Effect of initial H_2O_2 concentration on O_3/H_2O_2 process to degrade BPA

Fig. 5 shows the effect of H_2O_2 concentration on oxidation enhancement for an initial BPA concentration (4×10^{-5} mol/L) in the O_3/H_2O_2 operation. About 55.7 and 62.3% of the BPA were oxidized by O_3 process only without H_2O_2 addition, with and without nitrate addition, respectively. The removal efficiencies increased with increasing H_2O_2 concentration; addition of 0–150 mg/L increased the removal efficiencies from 55.7 to 100% and from 62.3 to 78.2%, without and with nitrate addition, respectively. One reason for this significant increase in the oxidation efficiencies in the O_3/H_2O_2 process is the possible acceleration of the decomposition of ozone with the addition of H_2O_2, as the following chemical reactions suggest [28,29]:

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{6}$$

$$O_3 + HO_2^- \rightarrow {}^{\cdot}OH + {}^{\cdot}O_2^- + O_2 \tag{7}$$

$$2O_3 + H_2O_2 \rightarrow 2{}^{\cdot}OH + 3O_2 \tag{8}$$

It was shown that the conjugate base of H_2O_2 could initiate the composition of ozone much more rapidly into hydroxyl radicals than hydroxide ion.

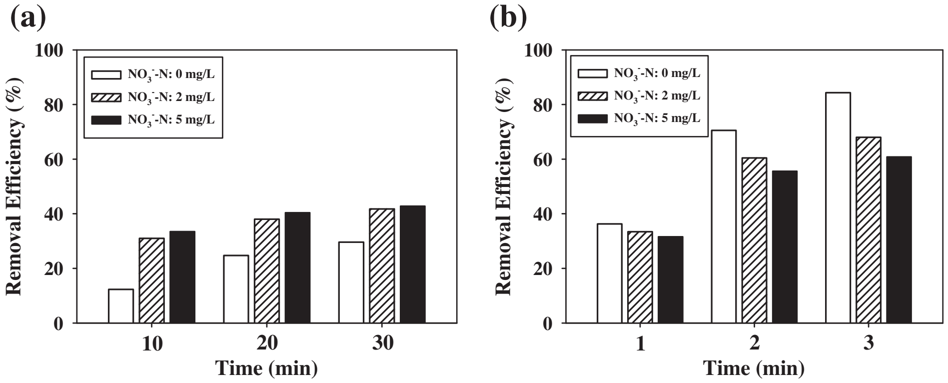

Fig. 4. Removal efficiencies (%) of BPA as functions of time at the three different NO_3^-–N concentrations (0, 2, and 5 mg/L) in the bench-scale UV/H_2O_2 operation; initial concentration of BPA: 4×10^{-5} mol/L; UV intensity: 20 mW/cm^2, (a) UV irradiation alone, (b) UV irradiation with initial H_2O_2 concentration of 100 mg/L.

However, further increase in initial H_2O_2 concentration induced a decrease in removal efficiency. The removal efficiency of BPA with the initial H_2O_2 concentration of 300 mg/L was 89.9%. It was also noted that both ozone and hydrogen peroxide appear to act, at some time, as hydroxyl radical scavengers in an aqueous solution, as shown in the following reactions [30,31]:

$$^{\cdot}OH + O_3 \rightarrow {}^{\cdot}HO_2 + O_2 \tag{9}$$

$$H_2O_2 + {}^{\cdot}OH \rightarrow {}^{\cdot}HO_2 + H_2O \tag{10}$$

$$HO_2^- + {}^{\cdot}OH \rightarrow {}^{\cdot}HO_2 + OH^- \tag{11}$$

These reactions consider consumption of OH radical to the formation of less reactive perhydroxyl radical $^{\cdot}HO_2$.

4. Conclusions

It was found that BPA (4×10^{-5} mol/L) was removed in very limited amounts through the direct UV photolysis, without addition oxidation by hydroxyl radicals. However, BPA could completely be removed with an initial H_2O_2 concentration of 150 mg/L in the H_2O_2 photolysis and absence of nitrate. It is indicated that the UV photolysis of H_2O_2 is a more effective method for removing BPA than the direct UV photolysis. The practical reaction time and initial H_2O_2 concentration for the more than 85% removal of BPA proved to be 2.0 min and 150 mg/L, respectively, in the presence or absence of nitrate. The removal efficiency of BPA was improved by the hydroxyl radicals produced from nitrate photolysis in the absence of H_2O_2.In the presence of H_2O_2, however, nitrate hindered the BPA removal by acting as $^{\cdot}OH$ scavengers under the operating conditions described above. The removal efficiency of BPA was clearly hindered with initial H_2O_2 concentration of more than 150 mg/L. It is noted that H_2O_2 acts as free-radicals scavenger at concentrations above optimum required. In O_3/H_2O_2 process with nitrate addition, more than 75% of the BPA was removed under the conditions of an initial O_3 concentration of 7.5 mg/L and H_2O_2 concentration of more than 150 mg/L.

These findings suggest that the UV/H_2O_2 process would likely be more appropriate method compared with O_3/H_2O_2 process for removing BPA in the presence of nitrate.

References

[1] N. Bolong, A.F. Ismail, M.R. Salim, T. Matsuura, A review of the effects of emerging contaminants in wastewater and options for their removal, Desalination 239 (2009) 229–246.

[2] A. Krishnan, P. Stathis, S. Permuth, L. Tokes, D. Feldman, Bisphenol-A: An estrogenic substance is released from polycarbonate flasks during autoclaving, Endocrinology 132 (1993) 2279–2286.

[3] E. Rosenfeldt, K. Linden, Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes, Environ. Sci. Technol. 38 (2004) 5476–5483.

[4] D. Kolpin, E. Furlong, M. Meyer, E. Thurman, S. Zaugg, L. Barber, H. Buxton, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance, Environ. Sci. Technol. 36 (2002) 1202–1211.

[5] T. Yamamoto, A. Yasuhara, H. Shiraishi, O. Nakasugi, Bisphenol A in hazardous waste landfill leachates, Chemosphere 42 (2001) 415–418.

[6] J.H. Kang, F. Kondo, Bisphenol A degradation in seawater is different from that in river water, Chemosphere 60 (2005) 1288–1292.

[7] R. Wang, D. Ren, S. Xia, Y. Zhang, J. Zhao, Photocatalytic degradation of Bisphenol A (BPA) using immobilized TiO_2 and UV illumination in a horizontal circulating bed photocatalytic reactor (HCBPR), J. Hazard. Mater. 169 (2009) 926–932.

[8] C.-Y. Chen, The oxidation of Di-(2-Ethylhexyl) phthalate (DEHP) in aqueous solution by UV/H_2O_2 photolysis, Water Air Soil Pollut. 209 (2010) 411–417.

[9] Metcalf & Eddy, Inc., Wastewater Engineering: Treatment and Reuse, 4th ed., McGraw-Hill, New York, 2003.

[10] B. Xu, N.Y. Gao, X.F. Sun, S.J. Xia, M. Rui, M.O. Simonnot, C. Causserand, J.F. Zhao, Photochemical degradation of diethyl phthalate with UV/H_2O_2, J. Hazard. Mater. B. 139 (2007) 132–139.

[11] O.M. Alfano, R.J. Brandi, A.E. Cassano, Degradation kinetics of 2,4-D in water employing hydrogen peroxide and UV radiation, Chem. Eng. J. 82 (2001) 209–218.

[12] F.A. Momani, C. Sans, S. Esplugas, A comparative study of the advanced oxidation of 2,4-dichlorophenol, J. Hazard. Mater. 107 (2004) 123–129.

[13] J. Mack, J.R. Bolton, Photochemistry of nitrite and nitrate in an aqueous solution: A review, J. Photochem. Photobiol. Chem. 128 (1999) 1–13.

[14] P. Warneck, C. Wurzinger, Product quantum yields for the 305 nm photodecomposition of NO_3^- in aqueous solutions, J. Phys. Chem. 92 (1988) 6278–6283.

[15] J.W. Coddington, J.K. Hurst, S.V. Lymar, Hydroxyl radical formation during peroxynitrous acid decomposition, J. Am. Chem. Soc. 121 (1999) 2438–2443.

[16] J.H. Park, C.G. Park, J.W. Lee, K.B. Ko, Degradation of diethyl phthalate in treated effluents from an MBR via advanced oxidation processes: Effects of nitrate on oxidation and a pilot-scale AOP operation, Environ. Technol. 31 (2010) 15–27.

[17] M. Sorensen, F.H. Frimmel, Photochemical degradation of hydrophilic xenobiotics in the UV/H_2O_2 process: Influence of nitrate on the degradation rate of EDTA, 2-amino-1-naphthallenesulfonate, diphenyl-4-sulfonate, and 4,4´-diaminostilbene-2–2´-disulfonate, Water Res. 31 (1997) 2885–2891.

[18] K.B. Ko, S.H. Kang, J.Y. Lee, J.H. Park, Z. Yun, S.K. Yim, Effects of nitrate ions on the UV photolysis of H_2O_2 for VOC decomposition, in: Proceedings of Special Optics: Recalcitrant and Anthropogenic Micropollutants, IWA 4th International Conference on Oxidation Technologies for Water and Wastewater, Goslar, Germany, 2006.

[19] K.B. Ko, J.Y. Lee, Y.H. Yoon, T.H. Moon, Y.H. Ahn, C.G. Park, K.S. Min, K.T. Kim, J.H. Park, Effects of nitrate on the UV photolysis for 2,4-dichlorophenol degradation in treated effluents, Desalin. Water Treat. 2 (2009) 6–11.

[20] J.H. Park, T.H. Moon, Y.H. Ahn, Y.K. Oh, Y.H. Yoon, C.G. Park, H.D. Park, K.B. Ko, Effects of nitrate on the UV photolysis of H2O2 for diethyl phthalate degradation in treated effluents, 4th IWA Leading Edge Conference and Exhibition on Water and Wastewater Technologies, Singapore, 2007.

[21] J.H. Park, S.H. Kang, J.Y. Lee, S.H. Lim, Z. Yun, S.K. Yim, K. B. Ko, Effects of nitrate on the UV photolysis of H_2O_2 for VOC degradation in an aqueous solution, Environ. Technol. 29 (2008) 91–99.

[22] K.B. Ko, C.G. Park, T.H. Moon, Y.H. Ahn, J.H. Park, J.K. Lee, K.H. Ahn, I.T. Yeom, Advanced H_2O_2 oxidation for diethyl phthalate degradation in treated effluents: Effect of nitrate on oxidation and a pilot-scale AOP operation, Water Sci. Technol. 58 (2008) 1031–1037.

[23] C.G. Park, J.C. Kim, Effects of nitrate on the advanced UV photolysis of di(2-ethylhexyl) phthalate degradation in aqueous solution, Desalin. Water Treat. 47 (2012) 163–170.

[24] C.M. Sharpless, M.A. Page, K.G. Linden, Impact of hydrogen peroxide on nitrite formation during UV disinfection, Water Res. 37 (2003) 4730–4736.

[25] C.M. Sharpless, D.A. Seidold, K.G. Linden, Nitrate-photo-sensitized degradation of atrazine during UV water treatment, Aquat. Sci. 65 (2003) 359–366.

[26] M. Muruganandham, M. Swaminathan, Photochemical oxidation of reactive azo dye with UV-H_2O_2 process, Dyes Pigm. 62 (2004) 269–275.

[27] H. Kusic, N. Koprivanac, A.L. Bozic, Minimization of organic pollutant content in aqueous solution by means of AOPs: UV- and ozone-based technologies, Chem. Eng. J. 123 (2006) 127–137.

[28] J. Rivas, O. Gimeno, F. Beltran, Wastewater recycling: Application of ozone based treatments to secondary effluent, Chemosphere 74 (2009) 854–859.

[29] B. De Witte, J. Dewulf, K. Demeestere, H. Van Langenhove, Ozonation and advanced oxidation by the peroxone process of ciprofloxacin in water, J. Hazard. Mater. 161 (2009) 701–708.

[30] J. Staehelin, J. Hoigné, Decomposition of ozone in water: Rate initiation by hydroxide ions and hydrogen peroxide, Environ. Sci. Technol. 16 (1982) 676–981.

[31] J. Staehelin, J. Hoigné, Decomposition of ozone in water in the presence of organic solute acting promoters and inhibitors of radical chain reaction, Environ. Sci. Technol. 19 (1985) 1206–1213.