UV Light Combined with Nitrate Remove Bisphenol A: Kinetics, Transformation Pathways, and Acute Toxicity Assessment

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Research Article

Keywords: Bisphenol A, Nitrate, Photodegradation, Kinetics, Degradation pathway

Posted Date: August 13th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-509991/v1>

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2 **transformation pathways, and acute toxicity assessment**

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ABSTRACT

As a powerful endocrine disruptor, bisphenol A (BPA) is a serious threat to human health. In this study, low-pressure UV lamp (LP-UV) photolysis nitrate was used to degrade BPA in different aqueous solutions. Results showed that BPA could be decomposed efficiently in the UV/nitrate process. $\cdot\text{OH}$ played a significant role in the UV/nitrate process, and the steady-state concentration of $\cdot\text{OH}$ ($[\cdot\text{OH}]_{\text{ss}}$) was calculated to be 5.26×10^{-15} M under control conditions. Moreover, the contributions of UV irradiation (4.1%), $\cdot\text{OH}$ (52.7%), and reactive nitrogen species (43.2%) were obtained. The observed rate constant of BPA degradation (k_{obs}) increased with nitrate concentration since more activity species were generated in high nitrate concentration. BPA degradation rate significantly accelerated as the pH value rose, it was ascribed to the increase of the molar absorption coefficient and the portion of ionic BPA. However, k_{obs} declined with increasing BPA concentration result from the inner filter effect and the competition of more generated intermediate products. The increasing decomposition of BPA with the addition of $\text{HCO}_3^-/\text{CO}_3^{2-}$ (0~10 mM), which could be explained as $\text{HCO}_3^-/\text{CO}_3^{2-}$ scavenged $\cdot\text{OH}$ resulting in the accumulation of $\cdot\text{NO}_2$. The effect of Cl^- (0~20 mM) can be ignored, which suggested reactive chlorine radicals degraded BPA effectively. The k_{obs} reduced acutely when NOM (0~5mg-C/L) existed in the solution, this could be ascribed to the dual role of NOM inner filter effect and reactive radicals scavenging effect. Further, several degradation products were detected and possible transformation pathways were put forward. Remarkably, the acute toxicity

of BPA was slightly enhanced then decayed in the UV/nitrate process.

Keywords: Bisphenol A; Nitrate; Photodegradation; Kinetics; Degradation pathway

1. Introduction

Various man-made chemicals, such as pesticides, flame retardants, plastic additives, cosmetics, are widely distributed in this century (Burman et al. 2020). Endocrine disruptors (EDCs) may be released from these various chemicals, affecting the endocrine (hormonal) system of wild animals, even leading to human diseases like diabetes mellitus, obesity, autoimmune diseases, and cancer (Bergman et al. 2013; Diamanti-Kandarakis et al. 2009). Bisphenol A(BPA), as an important endocrine disruptor possessed estrogenic activity, is a high-volume chemical and a widespread plasticizer (Gore et al. 2019; Kahn et al. 2020). Food and drinking water could be contaminated through migration after BPA is released from chemical products (Newbold et al. 2007). Although the BPA concentration detected in surface water and sediments are low (i.e., nd~30ng/L in surface water, 5.3~6.1 ng/g dry weight in sediments, respectively), a great danger to biological health can be presented by it (Hu et al. 2019; Welshons et al. 2006).

For this reason, the European Commission updated the new regulation on BPA in food packaging in 2018. The Specific Migration Limit (SML) of bisphenol A was set as 0.05 mg per kilogram of eatables (Vilarinho et al. 2019). Besides, the government of Canada limited the concentration of BPA released in wastewater to no more than 1750

ng/L in 2012 and 2013 (Gewurtz et al. 2021). Moreover, the United States, France, and other countries have forbidden the usage of BPA in infant feeding bottles and toys for a long time, because infants are more sensitive to its estrogenic activity (Jeong et al. 2020). Despite the above measures, the global volume of BPA usage is estimated to achieve 10.6 million tons by 2022 (de Freitas et al. 2017).

Conventional methods of water purification (e.g., coagulation, filtration, adsorption, and biodegradation) are insufficient for completely degrade EDCs, especially BPA made up of strong bonds hence (Gmurek et al. 2017; Luo et al. 2014). However, many advanced oxidation processes (AOPs) especially the UV-based AOPs can be selectively applied to degrade BPA, such as UV combined with H_2O_2 , chlorine, persulfate (PS), or peroxymonosulfate (PMS) (Chaves et al. 2020; Rodríguez-Chueca et al. 2019; Sharma et al. 2015). Chaves et al. (2020) found that the BPA decomposition rate reached 55% in UVA/ H_2O_2 process ($88\mu M H_2O_2$) for 120 min. Sharma et al. (2016) have pointed out that the BPA degradation increased in UV-C/SPS oxidation system as a result of the BPA molecules attacked by the $SO_4^{\cdot -}$ radicals. Over recent years, the UV/nitrate system has received growing attention because nitrate (NO_3^-) is a naturally occurring ion involved in the nitrogen cycle in the environment and it can effectively decompose EDCs (e.g., estrone, and 17α -ethynylestradiol) (Huang et al. 2018; Sato et al. 2018). With further studies, reactive oxygen species (ROS) and reactive nitrogen species (RNS) are generated in the UV/nitrate process, as shown in Eqs. (1)~(6) (Goldstein & Rabani 2007; Mack & Bolton 1999).

93 Among the reactive species, hydroxyl radical ($E_0 = 2.73\text{V}$ vs NHE) shows strong non-
 94 selective, which can destroy BPA molecular structure at a fairly high second-order rate
 95 constant (Luo et al. 2015). Some ROS (e.g., O^- , O_2^- , and $\text{O}(^3\text{P})$) are not be taken into
 96 account in the UV/nitrate system because of their relatively low concentration and weak
 97 oxidability (Huang et al. 2018). RNS, such as $\cdot\text{NO}_2$ and $\cdot\text{NO}$, have relatively weaker
 98 oxidation ability ($E_0 = 1.03\text{ V}$ and $E_0 = 0.39\text{V}$, respectively) (Huang et al. 2018). However,
 99 these weak oxidizing radicals can selectively react with some electron-donating
 100 moieties compounds via electrophilic substitution (Vione et al. 2004). Overall, it could
 101 be predicted that BPA should be degraded effectively in the UV/nitrate process.
 102 However, the degradation kinetics, transformation pathways, and acute toxicity
 103 assessment of BPA degradation by the UV/nitrate have not been investigated.

104 Therefore, this work aims to achieve the following objectives: (i) to assess the
 105 proportions of direct UV, RNS, and $\cdot\text{OH}$ to BPA decomposition in UV/nitrate system,
 106 (ii) to analyze the effect of NO_3^- concentration, initial BPA dosage, pH values, common
 107 anions (including bicarbonate/carbonate ($\text{HCO}_3^-/\text{CO}_3^{2-}$) and chloride ions (Cl^-)), and

natural organic matter (NOM) on BPA decomposition in the UV/nitrate process, (iii) to analyze intermediate products and explore the possible transformation pathways, (iv) to assess the acute toxicity and evaluate application significant of UV/nitrate system in actual waters.

2. Materials and methods

2.1 Chemicals

Bisphenol A (99%), nitrobenzene (NB) (99%), sodium nitrate (99%), and perchloric acid were from Aladdin. Sodium chloride, sodium bicarbonate, disodium hydrogen phosphate, sodium dihydrogen phosphate, sodium hydroxide, and acetic acid (HPLC grade) were from Sinopharm Chemical Reagent Company. Natural organic matter (NOM) was from the International Humic Substances Society. Methanol (HPLC grade) and was from Tedia Company. Groundwater and surface water were obtained from Baotu Spring and Xiaoqing River in Jinan, China. Drinking water was taken from the municipal tap and left for two days before use. De-ionized water was obtained from the Milli-Q Biocel water system.

2.2 Analytical methods

The concentrations of BPA, NB were detected using high-performance liquid chromatography (HPLC, Waters 2695) reported in the previous study (Gao et al. 2020b). The constituents of the mobile phase were methanol and 0.1% acetic acid (70:30 for BPA, NB), with a flow rate of 1.0 mL min⁻¹. The sample injection volume of BPA and NB were 50 μ L and 100 μ L, respectively. UV absorption of BPA and NB were

monitored at 278 nm, and 262 nm, respectively. The concentrations of NO_3^- and NO_2^- of actual waters were determined by a double beam ultraviolet-visible spectrophotometer (Metash, UV9000). The concentration of NOM and total organic carbon (TOC) was obtained using a Shimadzu TOC analyzer (TOC-L), and the pH values were detected by a pH meter (Sartorius, PB-10). A Waters alliance 2695 XELC/MS/MS (Waters, Watford, UK) and Zobax SB-C18 ($5\ \mu\text{m}$, $4.6\ \text{mm} \times 250\ \text{mm}$, Agilent, USA) were combined as the LC/MS/MS system to detect intermediate products. Detailed LC-MS/MS information is elucidated in Text S1.

2.3 Experimental methods

The photochemical experiment was conducted using four 10 W low-pressure Hg UV lamps (peak wavelength output at 254 nm, Heraeus, GPH212T5L/4) in a closed box. The UV light intensity was $0.172\ \text{mW}\cdot\text{cm}^{-2}$ after preheating for an hour. In order to facilitate the detection, the control experiment conditions were set as $30\ \mu\text{M}$ BPA and $30\ \text{mM}$ nitrate. All experiments were conducted in de-ionized water under a controlled temperature ($25 \pm 1\ ^\circ\text{C}$). The buffer used was $5\ \text{mM}$ phosphate and pH adjusted by $0.1\ \text{M}$ NaOH or HClO_4 . The samples were withdrawn at predetermined time intervals. Based on the methods reported by Wu et al. (2016b), toxicity assessment was carried out by using *Vibrio fischeri* strains. Detailed methods of the acute toxicity test are shown in Text S1.

2.4 Calculation of contributions of UV, $\cdot\text{OH}$, and RNS

As illustrated in Fig. 1, the NO_3^- concentration did not decrease significantly after

the 3600 s process, and a very small amount of nitrite produced was detected. This result was the same as that of Huang et al, so the steady-state assumption can be used to calculate the concentration of radicals in this experiment (Huang et al. 2018). As a result of negligible reacting between nitrobenzene (NB) and RNS, NB ($50 \mu\text{M}$, $k_{\cdot\text{OH}, \text{NB}} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) was selected to calculate the steady-state concentration of $\cdot\text{OH}$ ($[\cdot\text{OH}]_{\text{ss}}$) in the UV/nitrate systems (Buxton et al. 1988, Huang et al. 2018). The calculation formula of $[\cdot\text{OH}]_{\text{ss}}$ (Eq. (8)) can be obtained by transforming Eq. (7). The $[\cdot\text{OH}]_{\text{ss}}$ at different concentrations of NO_3^- (i.e., 10mM, 20mM, 30mM, and 50mM) are shown in Table S1.

$$-\frac{d[\text{NB}]}{dt} = k_{\text{UV}, \text{NB}}[\text{NB}] + k_{\cdot\text{OH}, \text{NB}}[\cdot\text{OH}]_{\text{ss}}[\text{NB}] = k_{\text{obs}, \text{NB}}[\text{NB}] \quad (7)$$

$$[\cdot\text{OH}]_{\text{ss}} = \frac{k_{\text{obs}, \text{NB}} - k_{\text{UV}, \text{NB}}}{k_{\cdot\text{OH}, \text{NB}}} \quad (8)$$

Similarly, the degradation of BPA can be expressed by Eq. (9).

$$\begin{aligned} -\frac{d[\text{BPA}]}{dt} &= k_{\text{UV}, \text{BPA}}[\text{BPA}] + k_{\cdot\text{OH}, \text{BPA}}[\cdot\text{OH}]_{\text{ss}}[\text{BPA}] + k_{\text{RNS}, \text{BPA}}[\text{RNS}][\text{BPA}] \\ &= k_{\text{obs}, \text{BPA}}[\text{BPA}] \end{aligned} \quad (9)$$

Because of the following relationship (Eq. (10)), the contribution ratios of UV, $\cdot\text{OH}$, and RNS for BPA decomposition in the UV/nitrate process can be calculated, respectively.

$$\text{R} = \text{R}_{\text{UV}} + \text{R}_{\cdot\text{OH}} + \text{R}_{\text{RNS}} \quad (10)$$

Where $k_{\text{UV}, \text{NB}}$ and $k_{\text{UV}, \text{BPA}}$ represent apparent rate constant of NB and BPA in the direct UV process, respectively, and $k_{\cdot\text{OH}, \text{NB}}$, $k_{\cdot\text{OH}, \text{BPA}}$, and $k_{\text{RNS}, \text{BPA}}$ are the second-order rate constants of $\cdot\text{OH}$ with NB, $\cdot\text{OH}$ with BPA, and RNS with BPA, respectively.

Where R_{UV} , R_{OH} , and R_{RNS} are the contributions of UV, $\cdot OH$, RNS on BPA decomposition. Based on studies of Huang et al, the details of calculations about contributions in the control experiment are shown in Text S2 and Table S2 (Huang et al. 2018; Zhou et al. 2020).

3. Results and discussion

3.1 Contributions of reactive species on BPA decomposition.

In the work, BPA degradation efficiencies in direct UV and UV/nitrate processes were quite different. Fig. S1 demonstrates that 30 μM BPA was efficiently degraded in the UV/nitrate process while direct UV had a little effect and the degradation of BPA in sole NO_3^- was negligible. In reality, the root cause of this phenomenon is that UV₂₅₄ irradiation of NO_3^- generates reactive oxygen radicals (e.g., $\cdot OH$, $O^\cdot$, $O(^3P)$) and reactive nitrogen radicals (e.g., $\cdot NO_2$, $\cdot NO$, $ONOO^\cdot$) (Mack & Bolton 1999). What is more important, the second-order rate constant of $\cdot OH$ with BPA is $1.02 \times 10^{10} M^{-1} s^{-1}$ and $\cdot OH$ plays a crucial part in the UV/nitrate process (Rosenfeldt & Linden 2004).

The NB degradation in different dosages of NO_3^- is shown in Fig. 2. And the calculated $[\cdot OH]_{ss}$ in Table S1 shows the increase of $[\cdot OH]_{ss}$ with the concentration of NO_3^- , i.e., $5.64 \times 10^{-16} M$, $1.15 \times 10^{-15} M$, $5.26 \times 10^{-15} M$, and $7.45 \times 10^{-15} M$ at 10, 20, 30, 50mM NO_3^- , respectively.

As demonstrated in Fig. S2, after 3600 s of irradiation, the removal ratio of BPA in UV/nitrate control experiment system was 30.39%. Obviously, RNS played a significant role and UV, $\cdot OH$, and RNS accounted for 4.1%, 52.7%, and 43.2% (Fig. 3)

of the total removal ratio, respectively. Therefore, although the $[\cdot\text{OH}]_{\text{ss}}$ was low in the control experiment, the contribution of $\cdot\text{OH}$ to BPA was larger than that of RNS can attribute to their superhigh second-order reaction rate constant.

3.2 Effect of NO_3^- concentration

The influence of NO_3^- dosage on the BPA degradation was evaluated. As shown in Fig. 4, the increase of NO_3^- dosage noteworthyly accelerated the degradation of BPA. When the NO_3^- dosage was less than 30 mM, BPA decomposition followed a pseudo-first-order degradation model, indicating the NO_3^- concentration was directly proportional to the decomposition efficiency of BPA. The present results suggest that increasing NO_3^- concentration can generate more reactive oxygen species (ROS) and reactive nitrogen species (RNS). A comparable finding was mentioned in the study for atrazine(ATZ) degradation in the $\text{UV}_{255}/\text{NO}_3^-$ process by Bu et al. (2020), and it reported that when the NO_3^- dosage increased by 50 folds, the ATZ degradation improved from 15.2% to 45.8%.

Nevertheless, it is noteworthy that when NO_3^- concentration increased by 50mM, a downward trend was showed up. For instance, k_{obs} just increased 3.36 time when NO_3^- rose 5 time (i.e., $3.869 \times 10^{-5} \text{ s}^{-1}$ at 10mM NO_3^- vs. $1.302 \times 10^{-4} \text{ s}^{-1}$ at 50mM NO_3^-). It can be explained that excessive concentration of NO_3^- can inhibit the BPA degradation due to the reaction of $\cdot\text{OH}$ with $\cdot\text{NO}$ and NO_2^- (see Eqs. (11)~(12)) generated in the UV/nitrate process (Buxton et al. 1988; Gonzalez & Braun 1995).

3.3 Effect of the initial BPA concentration

The influence of the initial BPA concentration (5~50 μM) was also examined in the UV/nitrate process. According to the results of Fig. 5, the k_{obs} decreased from 3.297×10^{-4} to 5.793×10^{-5} with the BPA concentration rose from 5 μM to 50 μM . This result of inhibiting effect on degradation BPA because of increasingly BPA concentration mainly explained by (i) The intermediate oxidation products of BPA in the UV/nitrate process would be generated inevitably and increasingly, and they can efficiently scavenge reactive radicals. The high reactivity of various unintended products (e.g., nitrophenol) with RNS proposed by R.C. Scholes et al. (2019) also confirmed this view. (ii) Excessive addition of BPA weakened the penetration ability of UV, and the subsequent effect was to reduce the photon absorption efficiency of NO_3^- . This phenomenon is usually explained as the inner filter effect (Luo et al. 2020). To confirm this effect resulted from BPA, the UV irradiation fraction absorbed by NO_3^- was determined and the method is shown as Eq. (13).

$$f_{\text{NO}_3^-} = \frac{\epsilon_{\text{NO}_3^-} [\text{NO}_3^-]}{\epsilon_{\text{NO}_3^-} [\text{NO}_3^-] + \epsilon_{\text{BPA}} [\text{BPA}]} \quad (13)$$

Where $f_{\text{NO}_3^-}$ represent the UV irradiation fraction of NO_3^- absorption, ϵ_{BPA} and $\epsilon_{\text{NO}_3^-}$ represent the molar extinction coefficients of BPA ($\epsilon_{\text{BPA}} = 750 \text{M}^{-1} \cdot \text{cm}^{-1}$) and NO_3^- ($\epsilon_{\text{NO}_3^-} = 3.51 \text{M}^{-1} \cdot \text{cm}^{-1}$) at 254 nm, respectively (Duca et al. 2017; Goulart de Araujo et al. 2017). The nitrate concentration and initial BPA concentration are expressed by $[\text{NO}_3^-]$ and $[\text{BPA}]$, respectively. According to the results of calculations, we can find that $f_{\text{NO}_3^-}$

decreased sharply as the increase of [BPA], i.e., 96.6% at 5 μ M BPA vs. 73.7% at 50 μ M BPA. This data revealed that the inner filter effect of BPA (5~50 μ M) in this study should be greatly appreciated.

3.4 Effect of pH value

Different pH values (5, 7, 9, 10, and 11) were selected to assess the effect of varying solution pH values on BPA degradation. The pH values were chosen according to the pKa of BPA ($pK_{a1} = 9.59$, $pK_{a2} = 10.2$) for the reason that the pH value can change the charge of the compound resulting in altering the molar extinction coefficient of the compound and sometimes even alter the transformation pathway (Gao et al. 2010; Kang et al. 2018; Kosky et al. 1991; Lu et al. 2013). As presented in Fig. 6, the k_{obs} had a slight increase (i.e., 8.687×10^{-5} to 9.969×10^{-5}) with the pH value from 5 to 9. Nevertheless, early studies have shown that solution pH (ranging from 4 to 9) does not affect the quantum yield of $\cdot OH$ (Zellner et al. 1990). Therefore, characteristics and existing forms of BPA at different pH values were given more attention in this study. Actually, the absorption coefficient of BPA increased remarkably with pH 4 to 11 at 254 nm reported by Kang et al. (2018). Therefore, it is not difficult to explain that when the photon absorption capacity of BPA increased, the UV direct degradation efficiency naturally rose.

However, when solution pH higher than or equal to 10, k_{obs} rapidly grow, and the k_{obs} at pH 10 was almost twice times as high as that at pH 9. It seems that only the change of molar absorption coefficient can not perfectly illustrate this phenomenon. Through

an enormous amount of previous studies, it was found that, as the solution pH exceeded the pKa of BPA, the deprotonation degree of BPA enhanced and the concentration of ionic BPA rose as the pH value increasing (Lu et al. 2013; Wu et al. 2021). Furthermore, the ionic form of BPA (i.e., bisphenolate anion) is more likely to be attacked by reactive species, resulting in structural destruction (Ding et al. 2020; Kosky et al. 1991; Lee & von Gunten 2012; Wu et al. 2021). As further shown in Fig. 7, without NO_3^- , the removal ratio of BPA by UV photolysis at pH 11 was so much more than that at pH 7. These results also indicate that the above elucidated about the reason of pH value affecting the degradation of BPA is reasonable. Additionally, comparable results were stated in previous studies in which alkaline conditions can facilitate BPA degradation (Wu et al. 2016a).

3.5 Effect of $\text{HCO}_3^-/\text{CO}_3^{2-}$

The effect of $\text{HCO}_3^-/\text{CO}_3^{2-}$ (0~10mM) on BPA degradation was then explored. As shown in Fig. 8, the decomposition rate of BPA rose as $\text{HCO}_3^-/\text{CO}_3^{2-}$ concentration increasing in the solution. The k_{obs} was 1.535×10^{-4} at 10 mM $\text{HCO}_3^-/\text{CO}_3^{2-}$ that was 55.92% higher than that of the control experiment. Traditionally, HCO_3^- and CO_3^{2-} are effectual scavengers of $\cdot\text{OH}$, as demonstrated in Eqs. (14)~(15) (Buxton et al. 1988).

Previous studies reported that as an important one-electron oxidant, the $\text{CO}_3^{\cdot-}$ has relatively high reaction rates with electron-rich aromatic compounds (e.g., phenolic and

aromatic amine moieties) mainly through electron transfer (Gao et al. 2020b; Huang et al. 2018). What is more, this result also can be ascribed to $\cdot\text{NO}_2$. From Eq. (6), it is not hard to conclude that the equilibrium shifted to the right side due to $\cdot\text{OH}$ scavenged by HCO_3^- and CO_3^{2-} . Thereby, BPA degradation was facilitated owing to accumulative $\cdot\text{NO}_2$.

3.6 Effect of Cl^-

As a common anion in the environment, the effect of Cl^- in UV/nitrate was also explored. Fig. 9 represented the result that Cl^- had not outstanding inhibition or acceleration BPA degradation (i.e., $k_{\text{obs}}=9\sim 10\times 10^{-5}\text{ s}^{-1}$, Cl^- concentration varies from 0 to 10 mM). In general, some chlorine species, like $\text{Cl}\cdot$, $\text{Cl}_2\cdot^-$, and ClOH^- , may be generated due to Cl^- reacting with $\cdot\text{OH}$ (Eq. (16)~(18)) (Jayson et al. 1973; Yang et al. 2014).

$$k_+=4.3\pm 0.4\times 10^9\text{ M}^{-1}\text{ s}^{-1}, k_-=6.1\pm 0.8\times 10^9\text{ M}^{-1}\text{ s}^{-1}$$

$$k_+=2.1\pm 0.7\times 10^{10}\text{ M}^{-1}\text{ s}^{-1}, k_-=1.3\times 10^3\text{ M}^{-1}\text{ s}^{-1}$$

$$k_+=2.1\times 10^{10}\text{ M}^{-1}\text{ s}^{-1}, k_-=1.1\pm 0.4\times 10^5\text{ M}^{-1}\text{ s}^{-1}$$

Of note, these reactions are reversible and the reaction of forming $\text{Cl}\cdot$ (Eq. (17)) usually is significant at low pH. While this experiment was conducted in neutral conditions. Additionally, despite the above reaction occurred, those chlorine radicals do

not make a noteworthy affection because their reactivity with BPA may be equal to $\cdot\text{OH}$ (Fang et al. 2014; Kong et al. 2016). Hence, the effect of Cl^- on BPA degradation can be neglected in this work.

3.7 Effect of NOM

As widespread substances in the environment, the effect of NOM on degradation efficiency was also investigated (0~5mg-C/L). As depicted in Fig. 10, the k_{obs} decreased with the NOM concentration increasing. Furthermore, compared with the UV/nitrate system without NOM, the k_{obs} with NOM of 5 mg-C/L was lower 62.0%. This phenomenon that NOM inhibited BPA degradation in UV/nitrate process can be interpreted as follows:

On the one hand, NOM is an effective scavenger of $\cdot\text{OH}$ ($k_{\text{NOM}, \cdot\text{OH}} = 3.3 \times 10^8 \text{ Mc}^{-1}\text{s}^{-1}$) which lead to decrease $[\cdot\text{OH}]_{\text{ss}}$ and reduct reacting opportunities of $\cdot\text{OH}$ with BPA or intermediate products (Ahn et al. 2017). Although some organic radicals may produce resulting from electron transfer reaction of $\cdot\text{OH}$ with NOM, the reactivities of those radicals are lower than $\cdot\text{OH}$ (Luo et al. 2019). On the other hand, NOM, whose molar absorption coefficient is $\epsilon = 3.15 \text{ L} \cdot \text{mg}^{-1} \cdot \text{m}^{-1}$, served as an inner filter for UV (Fang et al. 2014). Therefore, the ability of nitrate to absorb photons was reduced extremely, which led to the decrease of the reaction efficiency of producing $\cdot\text{OH}$.

3.8 Intermediate products and proposed transformation pathways

The changes of TOC of BPA before and after reaction in the UV/nitrate process are depicted in Fig. S3, indicating that mineralization was little in this study. BPA

predominantly transformed small organic compounds. Based on the results of LC/MS/MS, the possible transformation pathways of BPA in the UV/nitrate process are elucidated in Fig. 11. Intermediate products and detailed information are supplied in Table. S4 and Fig. S4. According to Gao et al's (2020a) reaction mechanism study on BPA degradation in UV/SPC, the BPA transformation pathways can be divided into four aspects in this study (i.e., (1) isopropylidene bridge cleavage, (2) isopropylidene modification, (3) ring modification, and (4) ring cleavage.). First, $\cdot\text{OH}$ could attack the electron-rich isopropyl C atom of BPA, resulting in the formation of 4-isopropyl phenol (B_{135} , $m/z=135.19$) and phenol (B_{93} , $m/z=93.1$). Therefore, B_{199} ($m/z=199.11$), a nitrobenzene derivative, could be produced because of the rapid reaction of $\cdot\text{OH}$ and $\cdot\text{NO}_2$ with phenol. Based on the consideration of the reaction activation energy and Gibbs free energy, the ortho position of BPA is more likely to be hydroxylated than the meta and para positions (Dai et al. 2016). Hence, B_{151} ($m/z=151.19$) generated by hydroxylation. And through further oxidation and possible degradation of BPA, B_{131} ($m/z=131.16$) and B_{136} ($m/z=136.14$) were generated. Besides, with the aromatic ring of B_{151} H-abstraction and further oxidation, a benzoquinone derivative (i.e., B_{181} , $m/z=181.17$) formed. All the above products were further oxidated and occurred ring cleavage, some small-molecule organic compounds (e.g., B_{97} ($m/z=97.14$), B_{79} ($m/z=79.13$), and B_{92} ($m/z=92.09$)) formed. Besides, the mineralization of partial organic compounds could produce inorganic compounds such as CO_2 , H_2O , and NO_3^- .

3.9 Acute toxicity and effect of actual waters components

The change regularity in acute toxicity of BPA in the UV/nitrate process is demonstrated in Fig. 12. The acute toxicity is represented using the ratio of bioluminescence of the solution before and after treatment (i.e., L/L_0). When *Vibrio fischeri* contacted with BPA solution for 900 s and 1800 s, the inhibition percentages were about 10.2% and 12.1%, respectively. These data show nonnegligible acute toxicity of BPA to *V. fischeri*. As expected, the toxicity increased obviously in the initial reaction time. In detail, the L/L_0 decreased from 0.88 to 0.74 when reaction time increased from 0 to 1200 s. The formation of more toxic transformation products, including those containing aromatic ring compounds (e.g., phenol), benzoquinone derivatives, and nitrobenzene derivatives was to blame for this result (de Freitas et al. 2017; Han et al. 2015). Subsequently, the acute toxicity gradually decayed as the experiment time was longer than 1200 s. This phenomenon indicated that lower toxic products were formed with the further reaction.

To investigate the application of the UV/nitrate system in the real environment, BPA degradation experiments were also conducted in several actual waters. As is demonstrated in Fig. 13, compared with de-ionized water, BPA degradation in surface water was inhibited. From Table. S3, the possible reason for this phenomenon is the relatively high concentration of NOM (TOC=4.115mg-C/L). Although the total alkalinity was as high as 230.63 mg CaCO_3/L (i.e., 2.3mM CO_3^{2-}) and the NO_3^- concentration was 10.418mg-N/L (i.e., 0.744mM), the inhibition effect can not be offset. In contrast, BPA decomposition rates in groundwater and drinking water were

accelerated. The results can be ascribed to their high total alkalinity and low TOC (Table. S3). Consequently, the decomposition of BPA and other EDCs in the UV/nitrate process could become a reality theoretically. But the strict condition (e.g., needing a relatively high concentration of NO_3^-) limits the scope of its application. Numerous studies have shown that high concentration NO_3^- and generated NO_2^- can harm human health (e.g., causing blue baby syndrome in infants) and animals as well as eutrophication of real water bodies (Archana et al. 2012; Mohajeri et al. 2021). Besides, the generation of harmful intermediate products (e.g., benzoquinone and nitrobenzene derivatives) and possible enhanced acute toxicity results should be taken into consideration. As a result, the UV/nitrate process is not a suitable technology to apply in drinking water treatment plants, and its applications in the treatment of wastewater rich in nitrate also need further studies.

4. Conclusions

In this work, the degradation of BPA in different effect factors was investigated, and intermediate products and possible transformation pathways were proposed. The conclusions are as follows:

(i) $[\cdot\text{OH}]_{\text{ss}}$ was 5.26×10^{-15} M at control conditions in UV/nitrate process. When BPA was degraded in the UV/nitrate process for 3600 s, the contributions of UV, $\cdot\text{OH}$, and RNS accounted for 4.1%, 52.7%, and 43.2%, respectively.

(ii) BPA could be effectively degraded in UV/nitrate process, k_{obs} increased with increasing addition of NO_3^- (0~50 mM) while decreased with increasing of BPA

concentration (5~50 μM).

(iii) The degradation efficiency of BPA promoted with pH value rise in the range of 5 to 11.

(iv) Increasing the concentration of $\text{HCO}_3^-/\text{CO}_3^{2-}$ (0~10 mM) can accelerate the BPA degradation, while the effect of Cl^- (0~20mM) could be ignored when the Cl^- dosage less than 20 mM, and adding NOM (0~5mg-C/L) acutely reduced the BPA degradation due to the dual role of $\cdot\text{OH}$ scavenged and serving as an inner filter.

(v) BPA decomposition was mainly divided into four aspects, and many intermediate products including benzoquinone and nitrobenzene derivatives could form in the UV/nitrate process.

(vi) The acute toxicity of BPA in the UV/nitrate process increased slightly in the initial 1200 s because of more toxic intermediate products produced and then gradually declined due to the further decomposition of intermediates. UV/nitrate process is not very suitable to apply in drinking water treatment plants and its application with other technology needs to be studied further.

Author contributions All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Zhiquan Li, Shishun Wang, Fumiao Zhang, and Mingli Li. The first draft of the manuscript was written by Zhiquan Li, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Congwei Luo has made significant contributions to the experimental research ideas,

finalized the version to be published, and provided project funding support for this paper. Xiaoxiang Cheng and Qiao Ma have made in-depth revisions to the manuscript on important technical content and finalized the version to be published. Fengxun Tan and Daoji Wu supervised the implementation of research activities and finalized the version to be published.

Funding This study was supported by the Central Government Guides the Local Science and Technology Development Special Project (Grant Nos. 2020ZY0068), China Postdoctoral Science Foundation (Grant Nos. 2020M672085), National Natural Science Foundation of China (Grant Nos. 51908335), the post-doctoral innovation project of Shandong Province (Grant Nos. 317202002023).

Availability of data and materials The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests The authors declare no competing interests.

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Figures

Figure 1

(a) Changes of NO_3^- concentration in the UV/nitrate process. (b) Changes of NO_2^- concentration in UV/nitrate process. Experimental conditions: $[\text{BPA}] = 30 \mu\text{M}$, $[\text{NO}_3^-] = 10\sim 50 \text{ mM}$, $\text{pH} = 7$, $[\text{phosphate}] = 5 \text{ mM}$, $\text{time} = 3600 \text{ s}$, $I = 0.172 \text{ mW cm}^{-2}$.

Figure 2

Degradation of NB in different concentrations of NO_3^- . Experimental conditions: $[\text{NB}] = 50 \mu\text{M}$, $[\text{BPA}] = 30 \mu\text{M}$, $[\text{NO}_3^-] = 0 \sim 50 \text{ mM}$, $\text{pH} = 7$, $[\text{phosphate}] = 5 \text{ mM}$, $\text{time} = 3600 \text{ s}$, $I = 0.172 \text{ mW} \cdot \text{cm}^{-2}$.

Figure 3

Proportions of UV, ·OH, and RNS in the total removal ratio. Experimental conditions:[BPA] = 30 μM, [NO3-] = 30 mM, pH = 7, [phosphate] = 5 mM, time = 3600 s, I = 0.172 mW cm-2.

Figure 4

The changes of kobs with NO3- concentration in UV/nitrate process. Experimental conditions:[BPA] = 30 μM, [NO3-] = 0~50 mM, pH = 7, [phosphate] = 5 mM, time = 3600 s, I = 0.172 mW·cm-2.

Figure 5

The changes of k_{obs} with BPA concentration in UV/nitrate process. Experimental conditions: [BPA] = 5~50 μM , $[NO_3^-]$ = 30 mM, pH = 7, [phosphate] = 5 mM, time = 3600 s, $I = 0.172 \text{ mW} \cdot \text{cm}^{-2}$.

Figure 6

Effect of pH on BPA degradation in UV/nitrate process. Experimental conditions:[BPA] = 30 μ M, [NO₃⁻] = 30 mM, pH = 5,7, 9, 10, and 11, [phosphate] = 5 mM, time = 3600 s, I = 0.172 mW·cm⁻².

Figure 7

Effect of pH on BPA degradation in direct UV process. Experimental conditions:[BPA] = 30 μ M, [NO₃⁻] = 30 mM, pH = 7,9,10, and 11, [phosphate] = 5 mM, time = 3600 s, I = 0.172 mW·cm⁻².

Figure 8

Effect of $\text{HCO}_3^-/\text{CO}_3^{2-}$ on BPA degradation in UV/nitrate process. Experimental conditions: $[\text{BPA}] = 30 \mu\text{M}$, $[\text{NO}_3^-] = 30 \text{ mM}$, $\text{pH} = 7$, $[\text{phosphate}] = 5 \text{ mM}$, $\text{time} = 3600 \text{ s}$, $I = 0.172 \text{ mW}\cdot\text{cm}^{-2}$.

Figure 9

The changes of k_{obs} with Cl^- concentration in UV/nitrate process. Experimental conditions: $[\text{BPA}] = 30 \mu\text{M}$, $[\text{NO}_3^-] = 30 \text{ mM}$, $\text{pH} = 7$, $[\text{phosphate}] = 5 \text{ mM}$, $\text{time} = 3600 \text{ s}$, $I = 0.172 \text{ mW}\cdot\text{cm}^{-2}$.

Figure 10

Effect of NOM on BPA degradation. Experimental conditions: [BPA] = 30 μ M, [NO₃⁻] = 30 mM, pH = 7, [phosphate] = 5 mM, time = 3600 s, I = 0.172 mW·cm⁻².

Figure 12

Variation of bioluminescence of *Vibrio fischeri* during BPA degradation by UV/nitrate process.

Experimental conditions: [BPA] = 1 μ M, [NO₃⁻] = 30 mM, pH = 7, [phosphate] = 5 mM, time = 7200 s, I = 0.172 mW·cm⁻².

Figure 13

Effect of actual waters components on BPA degradation in the UV/nitrate process. Experimental conditions: [BPA] = 30 μ M, [NO₃⁻] = 30 mM, pH = 7, [boric acid buffer] = 5 mM, time = 3600 s, I = 0.172 mW·cm⁻².

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