UV light combined with nitrate remove bisphenol A: kinetics, transformation pathways, and acute toxicity assessment

Zhiquan Li¹, Congwei Luo¹,b*, Fengxun Tan¹, Daoji Wu¹,b, Shishun Wang¹,
Xiaoxiang Cheng¹, Fumiao Zhang¹, Mingli Li¹, Qiao Ma³

¹ School of Municipal and Environmental Engineering, Shandong Jianzhu University, Jinan, 250101, P. R. China.
² Resources and Environment Innovation Institute, Shandong Jianzhu University, Jinan, 250101, P. R. China.
³ National Engineering Lab of Coal-Fired Pollution Emission Reduction, School of Energy and Power Engineering, Shandong University, Jinan 250061, P. R. China

*Corresponding authors contact details:
Doc. Congwei Luo, Phone: 86-531-86367291, email: luocongwei2009@163.com
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. ·OH played a significant role in the UV/nitrate process, and the steady-state concentration of ·OH ([·OH]ss) was calculated to be $5.26 \times 10^{-15}$ M under control conditions. Moreover, the contributions of UV irradiation (4.1%), ·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 HCO$_3^-$/CO$_3^{2-}$ (0~10 mM), which could be explained as HCO$_3^-$/CO$_3^{2-}$ scavenged ·OH resulting in the accumulation of ·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 H₂O₂, 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/H₂O₂ process (88μM H₂O₂) 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 SO₄²⁻ radicals. Over recent years, the UV/nitrate system has received growing attention because nitrate (NO₃⁻) 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).
NO$_3$ $\xrightarrow{hv}$ ·NO$_2$+O$^-$ \hspace{1cm} (1)

NO$_3$ $\xrightarrow{hv}$ NO$_2$+O( $^3$P) \hspace{1cm} (2)

O$^-$+H$_2$O $\rightarrow$ OH+OH$^-$ \hspace{1cm} (3)

NO$_2$ $\xrightarrow{hv}$ ·ON+O$^-$ \hspace{1cm} (4)

NO$_3$+H$^+$ $\xrightarrow{hv}$ ONOO$^-$+H$^+$↔ONOOH \hspace{1cm} (5)

ONOOH↔·NO$_2$+OH \hspace{1cm} (6)

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

Therefore, this work aims to achieve the following objectives: (i) to assess the proportions of direct UV, RNS, and ·OH to BPA decomposition in UV/nitrate system, (ii) to analyze the effect of NO$_3^-$ concentration, initial BPA dosage, pH values, common anions (including bicarbonate/carbonate (HCO$_3^-$/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 μL and 100 μL, 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 μm, 4.6 mm × 250 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 mW·cm$^{-2}$ after preheating for an hour. In order to facilitate the detection, the control experiment conditions were set as 30 μM BPA and 30 mM nitrate. All experiments were conducted in de-ionized water under a controlled temperature (25 ± 1 °C). The buffer used was 5 mM phosphate and pH adjusted by 0.1 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, ·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 μM, \(k_{\cdot \text{OH}, \text{NB}} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}\)) was selected to calculate the steady-state concentration of \(\cdot \text{OH}\) ([\(\cdot \text{OH}\)]\(_{ss}\)) in the UV/nitrate systems (Buxton et al. 1988, Huang et al. 2018). The calculation formula of \([\cdot \text{OH}]_{ss}\) (Eq. (8)) can be obtained by transforming Eq. (7). The \([\cdot \text{OH}]_{ss}\) at different concentrations of NO\(_3^-\) (i.e., 10mM, 20mM, 30mM, and 50mM) are shown in Table S1.

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

(7)

\[
[\cdot \text{OH}]_{ss} = \frac{k_{\text{obs}, \text{NB}}k_{\text{UV}, \text{NB}}}{k_{\cdot \text{OH}, \text{NB}}} 
\]

(8)

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

\[
- \frac{d[BPA]}{dt} = k_{\text{UV}, \text{BPA}}[BPA] + k_{\cdot \text{OH}, \text{BPA}}[\cdot \text{OH}]_{ss}[BPA] + k_{\text{RNS}, \text{BPA}}[\text{RNS}][BPA] 
\]

\[
= k_{\text{obs}, \text{BPA}}[BPA] 
\]

(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.

\[
R = R_{\text{UV}} + R_{\cdot \text{OH}} + R_{\text{RNS}} 
\]

(10)

Where \(k_{\text{UV}, \text{NB}}\) and \(k_{\text{UV}, \text{BPA}}\) represent apparent rate constants 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 $R_{UV}$, $R_{\cdot OH}$, 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 UV$_{254}$ irradiation of NO$_3^-$ generates reactive oxygen radicals (e.g., $\cdot OH$, O$^-$, O(3P)) and reactive nitrogen radicals (e.g., $\cdot NO_2$, $\cdot NO$, ONOO$^-$) (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, 50 mM 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 \([\cdot\text{OH}]_{ss}\) 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 \(\text{NO}_3^-\) concentration

The influence of \(\text{NO}_3^-\) dosage on the BPA degradation was evaluated. As shown in Fig. 4, the increase of \(\text{NO}_3^-\) dosage noteworthily accelerated the degradation of BPA. When the \(\text{NO}_3^-\) dosage was less than 30 mM, BPA decomposition followed a pseudo-first-order degradation model, indicating the \(\text{NO}_3^-\) concentration was directly proportional to the decomposition efficiency of BPA. The present results suggest that increasing \(\text{NO}_3^-\) 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 UV\(_{254}/\text{NO}_3^-\) process by Bu et al. (2020), and it reported that when the \(\text{NO}_3^-\) dosage increased by 50 folds, the ATZ degradation improved from 15.2% to 45.8%.

Nevertheless, it is noteworthy that when \(\text{NO}_3^-\) concentration increased by 50mM, a downward trend was showed up. For instance, \(k_{obs}\) just increased 3.36 time when \(\text{NO}_3^-\) rose 5 time (i.e., \(3.869 \times 10^{-5} \text{ s}^{-1}\) at 10mM \(\text{NO}_3^-\) vs. \(1.302 \times 10^{-4} \text{ s}^{-1}\) at 50mM \(\text{NO}_3^-\)). It can be explained that excessive concentration of \(\text{NO}_3^-\) can inhibit the BPA degradation due to the reaction of \(\cdot\text{OH}\) with \(\cdot\text{NO}\) and \(\text{NO}_2^-\) (see Eqs. (11)–(12)) generated in the UV/nitrate process (Buxton et al. 1988; Gonzalez & Braun 1995).

\[
\cdot\text{OH} + \text{NO}_2^- \rightarrow \text{NO}_2 + \cdot\text{OH}^- , \quad k = 1.0 \times 10^{10} \text{M}^{-1}\text{s}^{-1}
\]
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 $3.297 \times 10^4$ to $5.793 \times 10^{-5}$ 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).

$$f_{NO_3} = \frac{\varepsilon_{NO_3}[NO_3]}{\varepsilon_{NO_3}[NO_3] + \varepsilon_{BPA}[BPA]}$$

Where $f_{NO_3}$ represent the UV irradiation fraction of NO$_3^-$ absorption, $\varepsilon_{BPA}$ and $\varepsilon_{NO_3}$ represent the molar extinction coefficients of BPA ($\varepsilon_{BPA} = 750 M^{-1} cm^{-1}$) and NO$_3^-$ ($\varepsilon_{NO_3} = 3.51 M^{-1} cm^{-1}$) at 254 nm, respectively (Duca et al. 2017; Goulart de Araujo et al. 2017). The nitrate concentration and initial BPA concentration are expressed by [NO$_3^-$] and [BPA], respectively. According to the results of calculations, we can find that $f_{NO_3}$
decreased sharply as the increase of [BPA], i.e., 96.6% at 5 μM BPA vs. 73.7% at 50 μM BPA. This data revealed that the inner filter effect of BPA (5~50 μM) 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 (pKa₁ = 9.59, pKa₂=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 ·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 NO3−, 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 HCO3−/CO32−

The effect of HCO3−/CO32− (0~10mM) on BPA degradation was then explored. As
shown in Fig. 8, the decomposition rate of BPA rose as HCO3−/CO32− concentration
increasing in the solution. The kobs was 1.535×10^{-4} at 10 mM HCO3−/CO32− that was
55.92% higher than that of the control experiment. Traditionally, HCO3− and CO32− are
effectual scavengers of ·OH, as demonstrated in Eqs. (14)~(15) (Buxton et al. 1988).

HCO3−+OH→CO3−+H2O, \( k=8.5 \times 10^6 \text{M}^{-1}\text{s}^{-1} \) (14)

CO32−+OH→CO3−+OH−, \( k=3.9 \times 10^8 \text{M}^{-1}\text{s}^{-1} \) (15)

Previous studies reported that as an important one-electron oxidant, the CO3− 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 ·NO₂. From Eq. (6), it is not hard to conclude that the equilibrium shifted to the right side due to ·OH scavenged by HCO₃⁻ and CO₃²⁻. Thereby, BPA degradation was facilitated owing to accumulative ·NO₂.

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., $k_{obs}=9$–$10\times 10^{5}$ s⁻¹, Cl⁻ concentration varies from 0 to 10 mM). In general, some chlorine species, like Cl⁻, Cl₂⁻, and ClOH⁻, may be generated due to Cl⁻ reacting with ·OH (Eq. (16)–(18)) (Jayson et al. 1973; Yang et al. 2014).

$$\cdot \text{OH}+\text{Cl}^{-} \leftrightarrow \text{ClO}^{-}$$  \hspace{1cm} (16)

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

$$\text{ClO}^{-} + \text{H}^+ \leftrightarrow \text{Cl}^- + \text{H}_2\text{O}$$  \hspace{1cm} (17)

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

$$\text{Cl}^- + \text{Cl}^- \leftrightarrow \text{Cl}_2^-$$  \hspace{1cm} (18)

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

Of note, these reactions are reversible and the reaction of forming Cl⁻ (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 \( \text{Cl}^- \) 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 \( k_{\text{obs}} \) decreased with the NOM concentration increasing. Furthermore, compared with the UV/nitrate system without NOM, the \( k_{\text{obs}} \) 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 \( \cdot \text{OH} \) \( (k_{\text{NOM}, \cdot \text{OH}} = 3.3 \times 10^8 \text{ M}^{-1} \text{s}^{-1}) \) 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, ·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 ·OH and ·NO₂ 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 CO₂, H₂O, and NO₃⁻.

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/L₀). 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/L₀ 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 CaCO₃/L (i.e., 2.3mM CO₃²⁻) and the NO₃⁻ 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 NO₃⁻) limits the scope of its application. Numerous studies have shown that high concentration NO₃⁻ and generated NO₂⁻ can harm human health (e.g., causing blue baby syndrome in infants) and animals as well as eutrophication of real water bodies (Archna 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) [·OH]ₚ 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, ·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 NO₃⁻ (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 HCO₃⁻/CO₃²⁻ (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 ·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.

**References**

Ahn Y, Lee D, Kwon M, Choi I-h, Nam S-N, Kang J-W (2017): Characteristics and fate of natural organic matter during UV oxidation processes. Chemosphere 184, 960-968
Archna, Sharma SK, Sobti RC (2012): Nitrate Removal from Ground Water: A Review. E-Journal of Chemistry 9, 154616

Bergman Å, Heindel JJ, Jobling S, Kidd K, Zoeller TR, Organization WH (2013): State of the science of endocrine disrupting chemicals 2012. World Health Organization

Bu L, Zhu N, Li C, Huang Y, Kong M, Duan X, Dionysiou DD (2020): Susceptibility of atrazine photo-degradation in the presence of nitrate: Impact of wavelengths and significant role of reactive nitrogen species. Journal of Hazardous Materials 388, 121760

Burman A, Garcia-Milian R, Whirledge S (2020): Gene X environment: the cellular environment governs the transcriptional response to environmental chemicals. Hum Genomics 14, 19-19

Buxton GV, Greenstock CL, Helman WP, Ross AB (1988): Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (\(\cdot OH/\cdot O^-\)) in Aqueous Solution. Journal of Physical and Chemical Reference Data 17, 513-886

Chaves FP, Gomes G, Della-Flora A, Dallegave A, Sirtori C, Saggioro EM, Bila DM (2020): Comparative endocrine disrupting compound removal from real wastewater by UV/Cl and UV/H2O2: Effect of pH, estrogenic activity, transformation products and toxicity. Science of The Total Environment 746, 141041
Dai F, Fan X, Stratton GR, Bellona CL, Holsen TM, Crimmins BS, Xia X, Mededovic, Thagard S (2016): Experimental and density functional theoretical study of the effects of Fenton’s reaction on the degradation of Bisphenol A in a high voltage plasma reactor. Journal of Hazardous Materials 308, 419-429

de Freitas EN, Bubna GA, Brugnari T, Kato CG, Nolli M, Rauen TG, Peralta Muniz Moreira RdF, Peralta RA, Bracht A, de Souza CGM, Peralta RM (2017): Removal of bisphenol A by laccases from Pleurotus ostreatus and Pleurotus pulmonarius and evaluation of ecotoxicity of degradation products. Chemical Engineering Journal 330, 1361-1369

Diamanti-Kandarakis E, Bourguignon J-P, Giudice LC, Hauser R, Prins GS, Soto AM, Zoeller RT, Gore AC (2009): Endocrine-Disrupting Chemicals: An Endocrine Society Scientific Statement. Endocrine Reviews 30, 293-342

Ding Y, Hu Y, Peng X, Xiao Y, Huang J (2020): Micro-nano structured CoS: An efficient catalyst for peroxymonosulfate activation for removal of bisphenol A. Separation and Purification Technology 233, 116022

Duca C, Imoberdorf G, Mohseni M (2017): Effects of inorganics on the degradation of micropollutants with vacuum UV (VUV) advanced oxidation. Journal of Environmental Science and Health, Part A 52, 524-532

Fang J, Fu Y, Shang C (2014): The Roles of Reactive Species in Micropollutant Degradation in the UV/Free Chlorine System. Environmental Science & Technology 48, 1859-1868
Gao B, Lim TM, Subagio DP, Lim T-T (2010): Zr-doped TiO2 for enhanced photocatalytic degradation of bisphenol A. Applied Catalysis A: General 375, 107-115

Gao J, Duan X, O'Shea K, Dionysiou DD (2020a): Degradation and transformation of bisphenol A in UV/Sodium percarbonate: Dual role of carbonate radical anion. Water Research 171, 115394

Gao J, Luo C, Gan L, Wu D, Tan F, Cheng X, Zhou W, Wang S, Zhang F, Ma J (2020b): A comparative study of UV/H2O2 and UV/PDS for the degradation of micro-pollutants: kinetics and effect of water matrix. Environmental Science and Pollution Research 27, 24531-24541

Gewurtz SB, Tardif G, Power M, Backus SM, Dove A, Dubé-Roberge K, Garron C, King M, Lalonde B, Letcher RJ, Martin PA, McDaniel TV, McGoldrick DJ, Pelletier M, Small J, Smyth SA, Teslie S, Tessier J (2021): Bisphenol A in the Canadian environment: A multimedia analysis. Science of The Total Environment 755, 142472

Gmurek M, Olak-Kucharczyk M, Ledakowicz S (2017): Photochemical decomposition of endocrine disrupting compounds – A review. Chemical Engineering Journal 310, 437-456

Goldstein S, Rabani J (2007): Mechanism of Nitrite Formation by Nitrate Photolysis in Aqueous Solutions: The Role of Peroxynitrite, Nitrogen Dioxide, and Hydroxyl Radical. Journal of the American Chemical Society 129, 10597-10601
Gonzalez MC, Braun AM (1995): VUV photolysis of aqueous solutions of nitrate and nitrite. Research on Chemical Intermediates 21, 837-859

Gore AC, Krishnan K, Reilly MP (2019): Endocrine-disrupting chemicals: Effects on neuroendocrine systems and the neurobiology of social behavior. Hormones and Behavior 111, 7-22

Goulart de Araujo L, Santos FdS, Teixeira ACSC (2017): Degradation of bisphenol A by the UV and UV/H2O2 processes: Evaluation of process variables through experimental design. The Canadian Journal of Chemical Engineering 95, 2278-2285

Han Q, Wang H, Dong W, Liu T, Yin Y, Fan H (2015): Degradation of bisphenol A by ferrate(VI) oxidation: Kinetics, products and toxicity assessment. Chemical Engineering Journal 262, 34-40

Hu Y, Yan X, Shen Y, Di M, Wang J (2019): Occurrence, behavior and risk assessment of estrogens in surface water and sediments from Hanjiang River, Central China. Ecotoxicology 28, 143-153

Huang Y, Kong M, Westerman D, Xu EG, Coffin S, Cochran KH, Liu Y, Richardson SD, Schlenk D, Dionysiou DD (2018): Effects of HCO3− on Degradation of Toxic Contaminants of Emerging Concern by UV/NO3−. Environmental Science & Technology 52, 12697-12707

Jayson GG, Parsons BJ, Swallow AJ (1973): Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. Their formation using pulses of
radiation and their role in the mechanism of the Fricke dosimeter. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases 69, 1597

Jeong S, Jeon K-J, Park Y-K, Kim B-J, Chung K-H, Jung S-C (2020): Catalytic Properties of Microporous Zeolite Catalysts in Synthesis of Isosorbide from Sorbitol by Dehydration. Catalysts 10

Kahn LG, Philippat C, Nakayama SF, Slama R, Trasande L (2020): Endocrine-disrupting chemicals: implications for human health. The Lancet Diabetes & Endocrinology 8, 703-718

Kang Y-M, Kim M-K, Zoh K-D (2018): Effect of nitrate, carbonate/bicarbonate, humic acid, and H2O2 on the kinetics and degradation mechanism of Bisphenol-A during UV photolysis. Chemosphere 204, 148-155

Kong X, Jiang J, Ma J, Yang Y, Liu W, Liu Y (2016): Degradation of atrazine by UV/chlorine: Efficiency, influencing factors, and products. Water Research 90, 15-23

Kosky PG, Silva JM, Guggenheim EA (1991): The aqueous phase in the interfacial synthesis of polycarbonates. Part 1. Ionic equilibria and experimental solubilities in the BPA-sodium hydroxide-water system. Industrial & Engineering Chemistry Research 30, 462-467

Lee Y, von Gunten U (2012): Quantitative structure–activity relationships (QSARs) for the transformation of organic micropollutants during oxidative water treatment.
Water Research 46, 6177-6195

Lu N, Lu Y, Liu F, Zhao K, Yuan X, Zhao Y, Li Y, Qin H, Zhu J (2013): H3PW12O40/TiO2 catalyst-induced photodegradation of bisphenol A (BPA): Kinetics, toxicity and degradation pathways. Chemosphere 91, 1266-1272

Luo C, Ma J, Jiang J, Liu Y, Song Y, Yang Y, Guan Y, Wu D (2015): Simulation and comparative study on the oxidation kinetics of atrazine by UV/H2O2, UV/HSO5− and UV/S2O82−. Water Research 80, 99-108

Luo C, Gao J, Wu D, Jiang J, Liu Y, Zhou W, Ma J (2019): Oxidation of 2,4-bromophenol by UV/PDS and formation of bromate and brominated products: A comparison to UV/H2O2. Chemical Engineering Journal 358, 1342-1350

Luo C, Gao J, Ma Q, Wu D, Cheng X, Jiang J, Zhou W, Yang Z, Ma J (2020): The bromate formation accompanied by the degradation of 2,4-bromophenol in UV/peroxymonosulfate. Separation and Purification Technology 233, 116028

Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Zhang J, Liang S, Wang XC (2014): A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Science of The Total Environment 473-474, 619-641

Mack J, Bolton JR (1999): Photochemistry of nitrite and nitrate in aqueous solution: a review. Journal of Photochemistry and Photobiology A: Chemistry 128, 1-13

Mohajeri P, Smith CMS, Chau HW, Lehto N (2021): ALLODUST augmented activated sludge single batch anaerobic reactor (AS-SBAAnR) for high concentration
nitrate removal from agricultural wastewater. Science of The Total Environment 752, 141905

Newbold RR, Padilla-Banks E, Snyder RJ, Phillips TM, Jefferson WN (2007): Developmental exposure to endocrine disruptors and the obesity epidemic. Reproductive Toxicology 23, 290-296

Rodríguez-Chueca J, García-Cañibano C, Sarro M, Encinas Á, Medana C, Fabbri D, Calza P, Marugán J (2019): Evaluation of transformation products from chemical oxidation of micropollutants in wastewater by photoassisted generation of sulfate radicals. Chemosphere 226, 509-519

Rosenfeldt EJ, Linden KG (2004): Degradation of Endocrine Disrupting Chemicals Bisphenol A, Ethinyl Estradiol, and Estradiol during UV Photolysis and Advanced Oxidation Processes. Environmental Science & Technology 38, 5476-5483

Sato Y, Ishihara M, Fukuda K, Nakamura S, Murakami K, Fujita M, Yokoe H (2018): Behavior of Nitrate-Nitrogen and Nitrite-Nitrogen in Drinking Water. Biocontrol Science 23, 139-143

Scholes RC, Prasse C, Sedlak DL (2019): The Role of Reactive Nitrogen Species in Sensitized Photolysis of Wastewater-Derived Trace Organic Contaminants. Environmental Science & Technology 53, 6483-6491

Sharma J, Mishra IM, Kumar V (2015): Degradation and mineralization of Bisphenol A (BPA) in aqueous solution using advanced oxidation processes: UV/H2O2
and UV/S2O82− oxidation systems. Journal of Environmental Management 156, 266-275

Sharma J, Mishra IM, Kumar V (2016): Mechanistic study of photo-oxidation of Bisphenol-A (BPA) with hydrogen peroxide (H2O2) and sodium persulfate (SPS). Journal of Environmental Management 166, 12-22

Vilarinho F, Sendón R, van der Kellen A, Vaz MF, Silva AS (2019): Bisphenol A in food as a result of its migration from food packaging. Trends in Food Science & Technology 91, 33-65

Vione D, Maurino V, Pelizzetti E, Minero C (2004): Phenol Photonitration and Photonitrosation upon Nitrite Photolysis in basic solution. International Journal of Environmental Analytical Chemistry 84, 493-504

Welshons WV, Nagel SC, vom Saal FS (2006): Large Effects from Small Exposures. III. Endocrine Mechanisms Mediating Effects of Bisphenol A at Levels of Human Exposure. Endocrinology 147, s56-s69

Wu L, Jin X, Zhao T, Wang H, Dai Z (2021): Impact factors of the degradation of bisphenol A by nitrocellulose membrane under illumination. Journal of Environmental Sciences 100, 193-202

Wu W, Shan G, Wang S, Zhu L, Yue L, Xiang Q, Zhang Y, Li Z (2016a): Environmentally relevant impacts of nano-TiO2 on abiotic degradation of bisphenol A under sunlight irradiation. Environmental Pollution 216, 166-172

Wu Z, Fang J, Xiang Y, Shang C, Li X, Meng F, Yang X (2016b): Roles of reactive
chlorine species in trimethoprim degradation in the UV/chlorine process: Kinetics and transformation pathways. Water Research 104, 272-282

Yang Y, Pignatello JJ, Ma J, Mitch WA (2014): Comparison of Halide Impacts on the Efficiency of Contaminant Degradation by Sulfate and Hydroxyl Radical-Based Advanced Oxidation Processes (AOPs). Environmental Science & Technology 48, 2344-2351

Zellner R, Exner M, Herrmann H (1990): Absolute OH quantum yields in the laser photolysis of nitrate, nitrite and dissolved H2O2 at 308 and 351 nm in the temperature range 278–353 K. Journal of Atmospheric Chemistry 10, 411-425

Zhou S, Li L, Wu Y, Zhu S, Zhu N, Bu L, Dionysiou DD (2020): UV365 induced elimination of contaminants of emerging concern in the presence of residual nitrite: Roles of reactive nitrogen species. Water Research 178, 115829