



Deposited via The University of Leeds.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/222214/>

Version: Accepted Version

Article:

Yue, J., Guo, W., Liang, S. et al. (2025) Kinetics, contributions, and pathways of the degradation of artificial sweeteners by primary and secondary radicals during UV/persulfate. *Separation and Purification Technology*, 362 (1). 131683. ISSN: 1383-5866

<https://doi.org/10.1016/j.seppur.2025.131683>

This is an author produced version of an article published in *Separation and Purification Technology*, made available under the terms of the Creative Commons Attribution License (CC-BY), which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.

Reuse

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:

<https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

**Kinetics, contributions, and pathways of the degradation of artificial sweeteners
by primary and secondary radicals during UV/persulfate**

Junhui Yue^a, Wei Guo^{a,*}, Shengxu Liang^a, Martin R. Tillotson^b, Yuhan Zhu^a, Dongyue
Li^a, Linzhu Du^a, Jun Li^a, Xu Zhao^c

^aNational Engineering Laboratory for Advanced Municipal Wastewater Treatment and
Reuse Technology, Beijing University of Technology, Beijing 100124, China

^bSchool of Civil Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom

^cInstitute of Blue and Green Development, Shandong University, Weihai 264209,
China

* Corresponding author.

Wei Guo

E-mail address: gwfybj@bjut.edu.cn

Full postal address: Beijing University of Technology, Pingleyuan 100, Chaoyang,
Beijing 100124, China.

Abstract: UV/persulfate (UV/PS) is considered an effective process for the degradation of emerging micropollutants in aquatic media. However, under the influence of complex water matrices such as wastewaters, radicals created during UV/PS will be reduced and transformed, so the chemical process of effectively obtaining the radicals in the system is very important to improving degradation efficiency. Thus, in the study, neotame (NEO, an artificial sweetener), as an emerging contaminant, was selected as the target compound to investigate in terms of its degradation and the role of free radicals in a range of water matrices during the UV/PS process. Based on the low concentration probe method (probe concentration $\leq 0.2 \mu\text{M}$, more than 3-fold improvement in radical detection accuracy), kinetic modeling was developed to determine the role of primary ($\bullet\text{OH}$ and $\text{SO}_4\bullet^-$) and secondary (e.g. $\text{Cl}\bullet$, $\text{Cl}_2\bullet^-$, $\text{CO}_3\bullet^-$, and $\text{NO}_2\bullet$) radicals. Results indicated that UV/PS was effective in decomposing NEO (>93.7%) within 7 min and was mainly attributed to $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$. Acidic environments promote NEO degradation with a greater contribution from $\text{SO}_4\bullet^-$. Natural organic matter inhibited NEO degradation by quenching radicals (especially $\bullet\text{OH}$). The k_{obs} of NEO degradation in the presence of Cl^- remained almost unchanged due to the production of $\text{Cl}\bullet$ and $\text{Cl}_2\bullet^-$ compensating the depletion of $\text{SO}_4\bullet^-$. The presence of HCO_3^- quenched a part of primary radicals, which led to a decrease in k_{obs} of NEO degradation, but $\text{CO}_3\bullet^-$ began to play a partial degradation role. In the presence of NO_3^- , UV-activated production of $\bullet\text{OH}$ and $\text{NO}_2\bullet$ promoted NEO degradation. Based on 39 transformation products obtained, 3 degradation pathways and 7 radical attack ways were proposed for NEO degradation by primary and secondary radicals in the

UV/PS system. This study provides meaningful insight into the role of primary and secondary radicals in NEO degradation using UV/PS systems.

Keywords: UV/persulfate; Secondary radicals; Artificial sweetener; Kinetics; Transformation products

1. Introduction

Artificial sweeteners (ASs) are used as sugar substitutes in a variety of foods, beverages, medications and animal feed [1,2]. However, the World Health Organization (WHO) has recently issued new guidelines noting that ASs not only have no long-term benefits for weight loss, but may also have potentially adverse effects, classifying them as possible carcinogens (IARC Group 2B) [3]. In addition, artificial sweeteners have recently been recognized as high-priority emerging contaminants due to their high frequency of detection and high concentrations in various environments [4]. Among the widely used ASs, neotame (NEO) is a second-generation AS synthesized via aspartame and 3,3-dimethylbutyraldehyde [5]. Compared to first-generation ASs (including acesulfame, sucralose, and aspartame), NEO provides higher sweetness (21–65 times), lower production costs, and greater stability [6]. Due to these commercial advantages, its use in many types of sugar substitution products is becoming more widespread [7]. Similar to first generation ASs, its impact on the environment and human health has attracted widespread attention [8,9]. For example, NEO has been detected at concentrations of 0.007–0.17 µg/L and 0.008–0.49 µg/L in aqueous environments and wastewaters, respectively [10-13]. Relatively high concentrations of NEO have also

62 been detected in sewage sludge and suspended particulate matter at 2–4 ng/g and 20–
63 51 ng/g, respectively [2,14]. Sustained exposure to NEO has been reported to alter the
64 abundance of gut microbiome, decreasing α -diversity, and modifying metabolic
65 patterns [15,16]. NEO exposure also leads to apoptosis and death of intestinal epithelial
66 cells, and can cause barrier disruption and increased monolayer leak [17]. In addition,
67 NEO interferes with enzymes involved in lipogenesis and catabolism and affects
68 neuromodulation of lipid metabolism [18]. Our recent study showed NEO is difficult
69 to remove using traditional wastewater treatment processes (such as flocculation,
70 sedimentation, and biological treatment) in sewage treatment plants (STPs), which
71 results in continuous emission into receiving waterbodies along with treated effluent,
72 thus posing a potential long-term threat to aquatic ecosystems [14]. More importantly,
73 research on effective degradation and contamination control processes for NEO
74 remains a critical knowledge gap. There is therefore an urgent need to devise efficient
75 treatment methods to supplement or replace traditional processes in STPs for improved
76 degradation of NEO in wastewater.

77 In recent decades, advanced oxidation processes (AOPs) based on the production of
78 hydroxyl radicals ($\bullet\text{OH}$) and sulfate radicals ($\text{SO}_4\bullet^-$) have been shown to be highly
79 efficient methods for removing recalcitrant organic pollutants in wastewater [19-22].
80 Amongst AOPs, $\text{SO}_4\bullet^-$ based oxidation has received the most attention. Compared with
81 $\bullet\text{OH}$, $\text{SO}_4\bullet^-$ is particularly effective at reacting with organic compounds, and this has
82 been attributed to its higher redox potential (2.5–3.1 V) and longer half-life (30–40 μs)
83 [23]. $\text{SO}_4\bullet^-$ can be generated by activation of persulfate (PS) through ultraviolet (UV)

irradiation [24], electricity [25], transition metals [26] and carbon materials [27]. Amongst these methods, UV (<300 nm) activation of PS is the most favorable since it activates PS more effectively (evidenced by a molar absorption coefficient of $16.6 \text{ M}^{-1} \text{ cm}^{-1}$), and may be integrated into current wastewater flowsheets without necessitating additional chemicals and dosage systems [22,23]. Moreover, UV/PS has been successfully applied to degradation of recalcitrant organic pollutants in wastewater, such as estrogens [28], pesticides [29], and anti-inflammatory drugs [30]. However, to date, limited information is available regarding the role of UV/PS in AS degradation, particularly concerning new ASs like NEO in wastewater.

Generally, $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ contribute to the degradation of organic pollutants in aquatic media in UV/PS systems [31]. However, in wastewaters, degradation efficiency of organic pollutants using UV/PS may be affected by water matrix components such as pH, natural organic matter (NOM) and some anions [30]. For example, pH significantly affects free radical composition in UV/PS systems, and subsequently the transformation pathways of organic pollutants. In the case of quaternary amine compound degradation using UV/PS/ Cu^{2+} , acidic conditions were found to enhance pollutant degradation, whereas alkaline conditions had an inhibitory effect [32]. Detailed investigations revealed a substantial increase (8- to 26-fold) in $\bullet\text{OH}$ contribution under alkaline conditions, whereas $\text{SO}_4\bullet^-$ played a more dominant role (1.1- to 1.2-fold increase) in acidic environments [32]. NOM and inorganic anions diminish UV flux within the system and quench some radicals, thereby impeding organic pollutant degradation [33]. In addition, $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ in UV/PS systems can

be converted to secondary radicals (*e.g.*, $\text{Cl}\cdot$, $\text{Cl}_2^{\cdot-}$, $\text{CO}_3^{\cdot-}$, and $\text{NO}_2\cdot$) by reacting with inorganic anions including Cl^- , HCO_3^- and NO_3^- [34-36]. These secondary radicals usually have high oxidation potentials (*e.g.*, 2.50 V, 2.20 V, and 1.60 V for $\text{Cl}\cdot$, $\text{Cl}_2^{\cdot-}$, and $\text{CO}_3^{\cdot-}$, respectively), which may significantly contribute to the degradation of organic pollutants [37]. Despite acknowledging the significant role of secondary radicals, there remains a shortage of detection tools to measure secondary radical concentrations during UV/PS treatments. Chemical probes are widely used to determine the concentration of radicals in photochemical-AOPs, however the probe method suffers from two drawbacks in most studies. First, the chemical processes of radicals in the system are drastically changed due to high probe concentrations [38]. Second, there is a lack of research on multiprobe coupling and detection, which has led to applications only in primary radical quantification [39]. Therefore, there is a need to develop a low concentration coupled probe method to simultaneously monitor primary and secondary radical concentrations, and to assess the specific role of secondary radicals in UV/PS for NEO degradation.

Although UV/PS is capable of removing a wide range of organic pollutants, it is difficult to fully mineralize them, thus generating a wide range of transformation products (TPs) [40,41]. TPs have greater polarity due to higher oxidation, such that they are more persistent and mobile in soil and water environments and thus may accumulate [42]. The wide distribution of TPs raises concerns about safety. For example, it has been shown that photo-induced degradation of Acesulfame results in TPs up to 500 times more toxic than the parent compound [43]. Therefore, there is a need to further

characterize the occurrence and toxicity of relevant TPs of NEO. In addition, multiple radicals in the system have different propensities to attack functional groups, and thus may play diverse roles in the induction and toxicity changes of TPs [44]. For example, during the degradation of gemfibrozil using UV/PS/ Cl^- , it was found that $\bullet\text{OH}$ hydroxylates the benzene ring, and the occurrence of phenolic functional groups may lead to increased toxicity [45]. In contrast, $\text{SO}_4\bullet^-$ breaks the ether bond of gemfibrozil and possibly aids in the removal of toxic groups [45]. Consequently, the degradation process does not necessarily reduce the toxicity of the solution, so it is necessary to evaluate the different radical-induced TPs and evaluate the toxicity of the resulting solution.

Thus, the objectives of this study were: (1) to investigate the performance and degradation kinetics of UV/PS for NEO degradation in the aquatic environment; (2) to construct a low concentration coupled probe model in UV/PS for investigating the concentration and role of primary and secondary radicals under actual matrix conditions (including pH, natural organic matter, and inorganic anions); (3) to identify possible generated TPs and degradation pathways of NEO by high-resolution mass spectrometry and density functional theory (DFT); and (4) to evaluate the toxicity risk of TPs in the system through *Vibrio fischeri* acute toxicity testing and computational toxicology. The results can provide helpful information for applicability and mechanistic understanding of AS degradation by UV/PS in real contaminated water.

2. Materials and methods

2.1 Chemicals

All chemicals used in experiments were at least analytical grade, as described in Text S1 of the Supporting Information (SI). A Milli-Q purification system (Millipore Co., France) was used to prepare deionized water to configure all solutions.

2.2 Experimental procedures

The experimental setup for photochemistry is depicted in Fig. S1. A low-pressure mercury lamp (10 W, 254 nm) with an electronic ballast was positioned at the center of the reactor, providing an irradiation intensity of 18.5 W/m². The experiment involved adding NEO (5 µM) and phosphate buffer (2 mM) to a 50 ml quartz tube reactor. UV irradiation initiated the reaction after introducing 50 µM PS. Magnetic stirring ensured proper mixing of the solution during degradation, and a water circulation cooling system keeping solution temperature at 25 ± 0.2°C. Na₂S₂O₃ solution was pre-added to 2 mL samples and used as a quencher. At predetermined intervals, 1 mL sample solution was transferred into a sample bottle. The change of pH of the solution before and after the experiment was less than 0.2.

Depending on experimental design, the pH value was adjusted within the range 6 - 8. Additionally, specific concentrations of humic acid (HA; used as a model compound for natural organic matter, at 1 and 5 mg C/L), Cl⁻ (at 1 and 5 mM), HCO₃⁻ (at 1 and 5 mM), and NO₃⁻ (at 1 and 5 mM) were introduced into the system for kinetic analysis. HClO₄ and NaOH were used to adjust the initial pH of the reaction solution. The presence of HClO₄ does not affect the removal of NEO (Fig. S2).

Radical identification was performed by quenching experiments (tert-butanol and

methanol) and electron paramagnetic resonance (EPR) experiments, which showed that the primary radicals were $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ (Text S14 for related identification analysis) [32]. Then, low concentration probe models were constructed by adding probes in pure water or water matrix systems. Bezafibrate (BZF) and p-chlorobenzoic acid (pCBA) were used as probe compounds added simultaneously to the UV/PS system to determine the concentrations of $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$. The impact of probe concentration on radicals was explored by varying the amount of probe added (0.05–2.0 μM), and then the optimum probe concentration (0.1 μM) was determined. In the UV/PS/ Cl^- system, 0.1 μM pCBA, 0.1 μM BZF, 0.1 μM 2,4,6-trimethylbenzoic acid (TMBA), and 0.2 μM naproxen (NPX) were added simultaneously as probe compounds for $\bullet\text{OH}$, $\text{SO}_4\bullet^-$, $\text{Cl}\bullet$, and $\text{Cl}_2\bullet^-$. For the UV/PS/ HCO_3^- system, 0.1 μM BZF, 0.1 μM TMBA, and 0.2 μM NPX were added simultaneously as probe compounds for $\bullet\text{OH}$, $\text{SO}_4\bullet^-$, and $\text{CO}_3\bullet^-$. In the UV/PS/ NO_3^- system, 0.1 μM aniline (AN), sulfamethoxazole (SMX), and trimethoprim (TMP) were used as probes for $\bullet\text{OH}$, $\text{SO}_4\bullet^-$, and $\text{NO}_2\bullet$. The concentration of primary and secondary radicals in the different systems was confirmed by monitoring the degradation rate constants of the probes in each system. Additionally, NEO degradation was examined in various actual waters: deionized water (DW, used as a control), river water (RW), and secondary sedimentation tank effluent from a sewage treatment plant (STPW).

To identify transformation products (TPs) of NEO, higher concentrations were used in the UV/PS system; specifically 50 μM NEO and 500 μM PS. Comparison of TPs under UV/PS, UV/ $\text{H}_2\text{O}_2/\text{Cl}^-$, UV/ $\text{H}_2\text{O}_2/\text{HCO}_3^-$, and UV/ $\text{H}_2\text{O}_2/\text{NO}_3^-$ with those under

the UV/H₂O₂ system was used to determine the proprietary TPs for SO₄•⁻, Cl•, CO₃•⁻, and NO₂•. Acute and chronic toxicity of detected TPs to three ecologically significant aquatic organisms (green algae, daphnia, and fish) was calculated using ECOSAR v2.2 software. In addition, *Vibrio fischeri* was used as a model microorganism and mixed with reacted UV/PS solution (degradation of 5 μM NEO by 50 μM PS) to determine the acute toxicity intensity of samples (see Text S2 for specific toxicity tests). All kinetic experiments were repeated in triplicate.

2.3 Analytical methods

The concentrations of NEO and probe compounds were analyzed concurrently using high-performance liquid chromatography coupled with tandem quadrupole mass spectrometry (HPLC-tqMS, Agilent Technologies Co., USA). The analysis was performed in either ESI negative or positive mode with a single injection volume of 10 μL. The instrument featured a C-18 column (2.1 × 100 mm, 1.8 μm, Agilent, ZORBAX Eclipse Plus C18, USA). Chromatographic separation of the various substances was achieved using gradient elution of methanol and 0.1% formic acid over 8 minutes at a flow rate of 0.4 mL/min. Detailed information on the organic compound assays is provided in Table S1.

TPs of NEO were analyzed using an UltiMate 3000 HPLC (Thermo Fisher, Waltham, USA) coupled to tandem orbital ion trap high-resolution mass spectrometry (Orbitrap HRMS, Thermo Fisher Scientific Co., USA) and an electrospray ion source (ESI). The instrument used was equipped with the same C-18 column as the HPLC-tqMS, and chromatographic separation was conducted at a flow rate of 0.4 mL/min with a gradient

elution time of 23 minutes. The single injection volume was 10 μL , and the instrument scanned in the range of 50–1000 m/z in ESI positive mode. Additional details of the various analytical instruments and their corresponding methods can be found in Text S3.

2.4 Kinetic model

According to the results of radical identification and the literatures, $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ are the main radicals in UV/PS activated systems [46]. Based on the assumption of steady-state concentration, the simplified kinetic model for NEO degradation by UV/PS can therefore be expressed as follows:

$$k_{\text{NEO}} = k_{\text{UV, NEO}} + k_{\bullet\text{OH, NEO}}[\bullet\text{OH}]_{\text{ss}} + k_{\text{SO}_4\bullet^-, \text{NEO}}[\text{SO}_4\bullet^-]_{\text{ss}} \quad (1)$$

where k_{NEO} is the apparent pseudo-first-order rate constant (min^{-1}) for the degradation of NEO in UV/PS expressed using the Langmuir-Hinshelwood kinetic model (see Eq. (2) for the model); $k_{\text{UV, NEO}}$ is the apparent pseudo-first-order rate constant for the degradation of NEO under direct UV irradiation (min^{-1}), which is a low and negligible value; $k_{\bullet\text{OH, NEO}}$ and $k_{\text{SO}_4\bullet^-, \text{NEO}}$ are the second-order rate constants for NEO reaction with $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ ($\text{M}^{-1} \text{s}^{-1}$); and $[\bullet\text{OH}]_{\text{ss}}$ and $[\text{SO}_4\bullet^-]_{\text{ss}}$ are the steady-state concentrations of $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ (M).

$$k_{\text{NEO}} = k_{\text{obs}} = \frac{d[\ln C_0 / C_t]}{dt} \quad (2)$$

C_0 and C_t are the initial and remaining NEO concentrations. $R_{\bullet\text{OH}}$ and $R_{\text{SO}_4\bullet^-}$ represent the percentage contributions of $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ (%), which are calculated using Eqs. (3)–(4).

$$R_{\bullet OH, NEO} = \frac{k_{\bullet OH, NEO} [\bullet OH]_{ss}}{k_{NEO}} \quad (3)$$

$$R_{SO_4^{\bullet -}, NEO} = \frac{k_{SO_4^{\bullet -}, NEO} [SO_4^{\bullet -}]_{ss}}{k_{NEO}} \quad (4)$$

In previous studies, the degradation kinetics were detected by liquid chromatography (LC) using two probes, usually nitrobenzene (NB) and p-chlorobenzoic acid (pCBA) to calculate $[\bullet OH]_{ss}$ and $[SO_4^{\bullet -}]_{ss}$, respectively [47]. However, the addition of higher concentration probes inevitably competes with target pollutants for free radicals, which reduces availability and thus affects overall results accuracy. On the other hand, the relatively low sensitivity and high detection limit of LC makes it impossible to reduce probe concentrations.

In all four systems of this study (UV/PS, UV/PS/ Cl^- , UV/PS/ HCO_3^- , and UV/PS/ NO_3^-), low concentration probes were used and LC-tqMS with very low detection limits was utilised to detect probe concentrations and minimize competing effects on the system. These more stringent criteria for probe concentrations are favorable for improving the accuracy of the evaluation of radical concentrations and relative contributions.

In the UV/PS system, 0.1 μM of pCBA and BZF were used as probes. Probe selection conditions were: (1) the second-order rate constants of the probes and radicals were as similar as to those of NEO; (2) the probes were highly ionized in the mass spectra; and (3) the second-order rate constants were measured under stringent conditions. In addition, the correction for the second-order rate constant of the probe was performed using a competitive kinetics approach (see Text S4–S9 for details of the determination).

Subsequently, $[\bullet OH]_{ss}$ and $[SO_4\bullet^-]_{ss}$ were calculated by solving the probe kinetic model, Eqs. (5)–(6):

$$k_{pCBA} = k_{UV, pCBA} + k_{\bullet OH, pCBA} [\bullet OH]_{ss} + k_{SO_4\bullet^-, pCBA} [SO_4\bullet^-]_{ss} \quad (5)$$

$$k_{BZF} = k_{UV, BZF} + k_{\bullet OH, BZF} [\bullet OH]_{ss} + k_{SO_4\bullet^-, BZF} [SO_4\bullet^-]_{ss} \quad (6)$$

where k_{pCBA} and k_{BZF} are the k_{obs} for degradation of pCBA and BZF during UV/PS (min^{-1}); $k_{UV, pCBA}$ and $k_{UV, BZF}$ are the k_{obs} for the degradation of pCBA and BZF under direct UV irradiation (min^{-1}); $k_{\bullet OH, pCBA}$ and $k_{\bullet OH, BZF}$ are the second-order rate constants for the reaction of pCBA and BZF with $\bullet OH$ ($\text{M}^{-1} \text{s}^{-1}$); and $k_{SO_4\bullet^-, pCBA}$ and $k_{SO_4\bullet^-, BZF}$ are the second-order rate constants for the reactions of pCBA and BZF with $SO_4\bullet^-$ ($\text{M}^{-1} \text{s}^{-1}$).

In the UV/PS/ Cl^- system, radicals that mainly play a role in degrading pollutants include $\bullet OH$, $SO_4\bullet^-$, $Cl\bullet$, and $Cl_2\bullet^-$ [48]. Based on our previous study [49] and recent advances in probe-based methods [48], we selected 0.1 μM pCBA, BZF, TMBA, and 0.2 μM NPX as probes and constructed kinetic models to calculate the concentration of radicals in the system (see Text S10 for specific models and calculation details). Similarly, the concentrations of primary and secondary radicals in the UV/PS/ HCO_3^- and the UV/PS/ NO_3^- systems were modeled by similar probe-based kinetic models, and the computational details are shown in Text S11 and S12, respectively. The second-order rate constants of all probes and NEO with radicals are summarized in Table S2.

It should be noted that the concentration of probe NPX (0.2 μM) was higher than the other probes (0.1 μM) due to the fact that both primary and secondary radicals have higher second-order rate constants with NPX, making it difficult to capture accurate

kinetic profiles at lower concentrations.

2.5 Theoretical calculation methods

Quantum chemical calculations were performed in the same way as in our previous study [49], using Gaussian 16 A.03 and Multiwfn 3.8 [50]. The condensed Fukui function (CFF), the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) were analyzed using density flooding theory (DFT). Detailed information on the calculations is given in Text S13.

2.6 Statistical analysis

Spearman's correlation analysis and one-way analysis of variance (ANOVA) were conducted using IBM SPSS version 19.0. All plots were generated using Origin 2022 software.

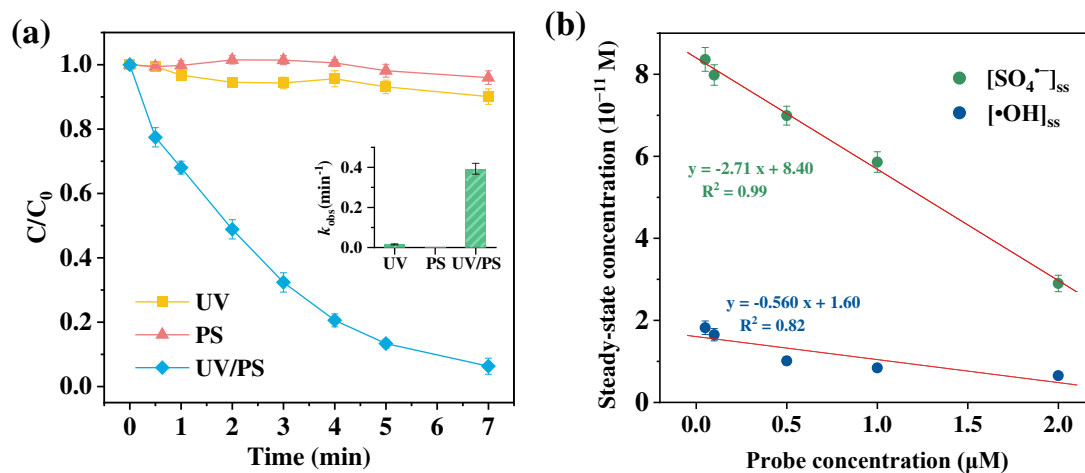


Fig. 1. (a) Degradation of NEO with sole PS in dark conditions, UV irradiation and UV/PS (Inset: the value of k_{obs} under different conditions); (b) linear relationships between the probe (pCBA and BZF) concentrations and determined steady-state

concentrations of $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ in the UV/PS system. Conditions: $[\text{PS}] = 50\ \mu\text{M}$,
 $[\text{NEO}] = 5\ \mu\text{M}$, $\text{pH} = 7$.

3. Results and discussion

3.1. Degradation kinetics of NEO in pure water

The degradation of NEO was assessed using PS, direct UV, and the UV/PS system. As depicted in Fig. 1, the removal of NEO with PS or UV alone was negligible over 7 min. However, the UV/PS system exhibited rapid degradation of NEO, with nearly 93.7% of NEO decomposed within 7 min. The degradation process in the UV/PS system followed pseudo-first-order kinetics, with k_{obs} of $0.393\ \text{min}^{-1}$ and R^2 value of 0.998. In addition, in order to assess the mineralization of the UV/PS system for the pollutants, the removal of TOC during degradation was tested. The results showed that the removal efficiency of TOC was lower than the degradation of NEO, but was able to remove 53.9% of TOC in 30 min (Fig. S3). Although complete mineralization of contaminants is very difficult, the UV/PS system achieved an acceptable level of mineralization capacity for NEO. The UV/PS system achieved a relatively high level of mineralization compared to other UV-AOPs [51,52].

The rapid degradation of NEO by UV/PS has been attributed to the involvement of highly reactive oxidizing radicals in this process. After quenching experiments (including tert-butanol and methanol) and EPR analysis, radicals in UV/PS contained $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ (see Text S14 and Fig. S4 for related identification analysis). In order to investigate $[\bullet\text{OH}]_{\text{ss}}$ and $[\text{SO}_4\bullet^-]_{\text{ss}}$ in the system, probe compounds were added to

construct kinetic models. Probe addition usually affects the free radical concentration by changing the free radical chemistry in the system. We investigated the free radical concentration of the system at probe additions of 0.05–2.0 μM (Fig. 1b). It was found that $[\bullet\text{OH}]_{\text{ss}}$ and $[\text{SO}_4\bullet^-]_{\text{ss}}$ depend on the concentration of the probe used. With an increase in probe concentration from 0.05 to 2.0 μM , $[\bullet\text{OH}]_{\text{ss}}$ and $[\text{SO}_4\bullet^-]_{\text{ss}}$ decreased linearly from 1.82×10^{-11} and 8.36×10^{-11} M to 0.65×10^{-11} and 2.90×10^{-11} M, respectively. However, the precision of probe degradation curve determination decreased when the probe concentration was lower. To address these issues, we used a mass spectrometry technique with lower detection lines, which were reduced to 32 and 11 ng/L for probes pCBA and BZF. Therefore, after balancing the effect of the probes on the radicals and the instrumental detection accuracy required for the concentration determination, we used 0.1 μM as the standard concentration of probes in the study. After calculation, $[\bullet\text{OH}]_{\text{ss}}$ and $[\text{SO}_4\bullet^-]_{\text{ss}}$ in UV/PS was 1.65×10^{-11} M and 7.98×10^{-11} M, and their percentage contribution to NEO degradation was 37.6% and 62.4%, respectively.

Under similar UV conditions, the low concentration probe method applied in this study (probe concentration of 0.1 μM) detected 1.9–51.4 times higher concentrations of radicals in the UV/PS system compared to the literature (probe concentration of 1.0–10.0 μM) [46,53,54]. Similarly, a similar phenomenon was found in the UV/H₂O₂ system, where $[\bullet\text{OH}]_{\text{ss}}$ determined using a 0.1 μM probe was more than twice as high as that determined using a 1.0 μM probe [38]. In summary, excessive probe concentration can seriously introduce errors in the determination of radical

concentration by exacerbating the competitive depletion of radicals [38]. To ensure the accuracy of radical concentration identification, the probe concentration should be selected in favor of the lower concentration as much as possible.

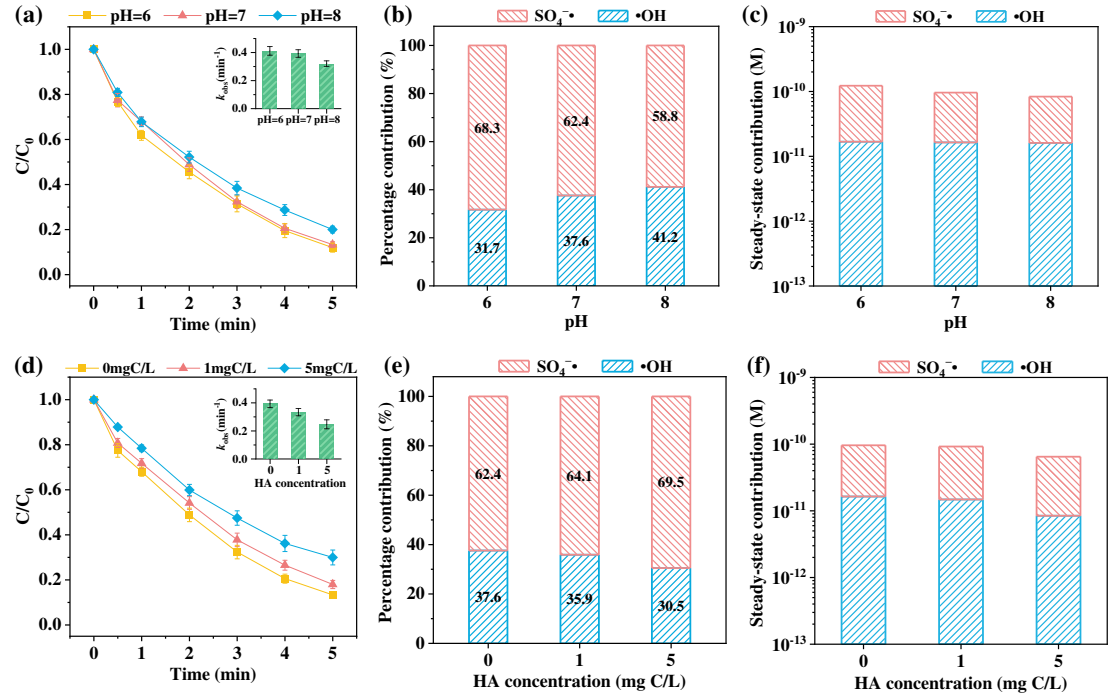


Fig. 2. Effects of pH (a) and humic acid (HA, d) (Inset: the relationship between pH, HA and the value of k_{obs}) in the degradation of NEO in the UV/PS system; trends in percentage contributions of radicals to NEO degradation during UV/PS at different pH (b) and HA (e); trends in steady-state concentration of radicals to NEO degradation during the UV/PS system at different pH (c) and HA (f). Conditions: [PS] = 50 μ M, [NEO] = 5 μ M.

3.2. Effect of pH and NOM on NEO degradation

3.2.1 pH

NEO degradation during UV/PS experiments showed a notable dependence on pH

over the range of 6 to 8 (Fig. 2a). The k_{obs} for NEO decreased from 0.412 to 0.321 min^{-1} as pH increased over this range. This suggests UV/PS degradation of NEO is more favorable at lower pH.

The impact of pH on NEO degradation during UV/PS experiments is multifaceted. First, dissociation of PS in aqueous solution is enhanced only under strongly acidic conditions, and its quantum efficiency of photo-dissociation remains stable at different pH [55]. Therefore, the effect of dissociation of PS at different pH on the system may be excluded. In addition, pH influences the dissociation of NEO. The dissociation constants ($\text{p}K_{\text{a}}$) of NEO were determined as 3.01 and 8.02. At pH 6 and 7, NEO exists as a neutral molecule, while at pH 8, 50% of NEO molecules are in an anionic form (Fig. S5). It has been reported that organic compounds (e.g., edaravone) in the anionic form may be more reactive with radicals [56]. However, the uniform decrease in k_{obs} with increasing pH demonstrates this fraction of NEO anions has less promotional effect on degradation. Furthermore, pH impacted on radicals and their transformations. As pH increased from 6 to 8, $[\bullet\text{OH}]_{\text{ss}}$ remained relatively stable, decreasing only from 1.68×10^{-11} to 1.61×10^{-11} M, while $[\text{SO}_4\bullet^-]_{\text{ss}}$ decreased from 1.06×10^{-10} to 6.72×10^{-11} M (Fig. 2c). Meanwhile, the proportion of $\text{SO}_4\bullet^-$ decreased from 68.3% to 58.8% and that of $\bullet\text{OH}$ increased from 31.7% to 41.2% (Fig. 2b). In alkaline environments, radicals may be captured by OH^- , resulting in a decrease in overall radical concentration (Eqs. (7) and (8)). Meanwhile, $\text{SO}_4\bullet^-$ is partially transformed as $\bullet\text{OH}$ after being captured by OH^- , which compensates for the partial quenching effect originally suffered by $\bullet\text{OH}$, and thus $[\bullet\text{OH}]_{\text{ss}}$ is relatively stable. pH also affects the redox potential

of radicals. Based on the Nernst equation the redox potential of $\bullet\text{OH}$ decreases with increasing pH, which leads to a higher oxidizing capacity of $\bullet\text{OH}$ under acidic conditions thus promoting NEO degradation.



3.2.2 NOM

As shown in Fig. 2d, the presence of HA inhibited NEO degradation. As HA concentration increased (0 to 5 mg C/L), k_{obs} for NEO decreased from 0.393 to 0.247 min^{-1} . The inhibitory role of HA can be assigned to two main factors: (1) Inner Filtering Effects during which HA's chromophores reduce the photon dose absorbed by PS due to competitive absorption, leading to decreased formation of $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$; and (2) Radical Scavenging in which HA scavenges various radicals in the system. As HA concentration increased from 0 to 5 mg C/L, $[\bullet\text{OH}]_{\text{ss}}$ and $[\text{SO}_4\bullet^-]_{\text{ss}}$ decreased from 1.65×10^{-11} to 8.43×10^{-12} M and from 7.98×10^{-11} to 5.63×10^{-11} M, respectively (Fig. 2f). Notably, $\text{SO}_4\bullet^-$ plays a more significant role in NEO degradation in the presence of HA. As HA concentration increased, the contribution of $\text{SO}_4\bullet^-$ to the degradation process increased from 62.4% to 69.5%, while the contribution of $\bullet\text{OH}$ decreased from 37.6% to 30.5% (Fig. 2e). Compared to $[\text{SO}_4\bullet^-]_{\text{ss}}$ (29.4%), $\text{SO}_4\bullet^-$ suffered a greater inhibitory effect (48.9%). These results are attributed to the fact that the second-order rate constants for the reaction of $\bullet\text{OH}$ with HA ($1.21\text{--}6.50 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) are much higher than those of $\text{SO}_4\bullet^-$ ($0.64\text{--}3.68 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), thus producing a more pronounced quenching effect on $\bullet\text{OH}$. In addition, recent studies have shown that HA may convert

organic radicals after hydrogen atom abstraction of pollutants, and cationic radicals after deprotonation of neutral radicals to the pollutant proper, Eq. (9). Since its reaction rate constant is $6.50 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, this may also be one of the key factors in the inhibition of NEO degradation by HA.

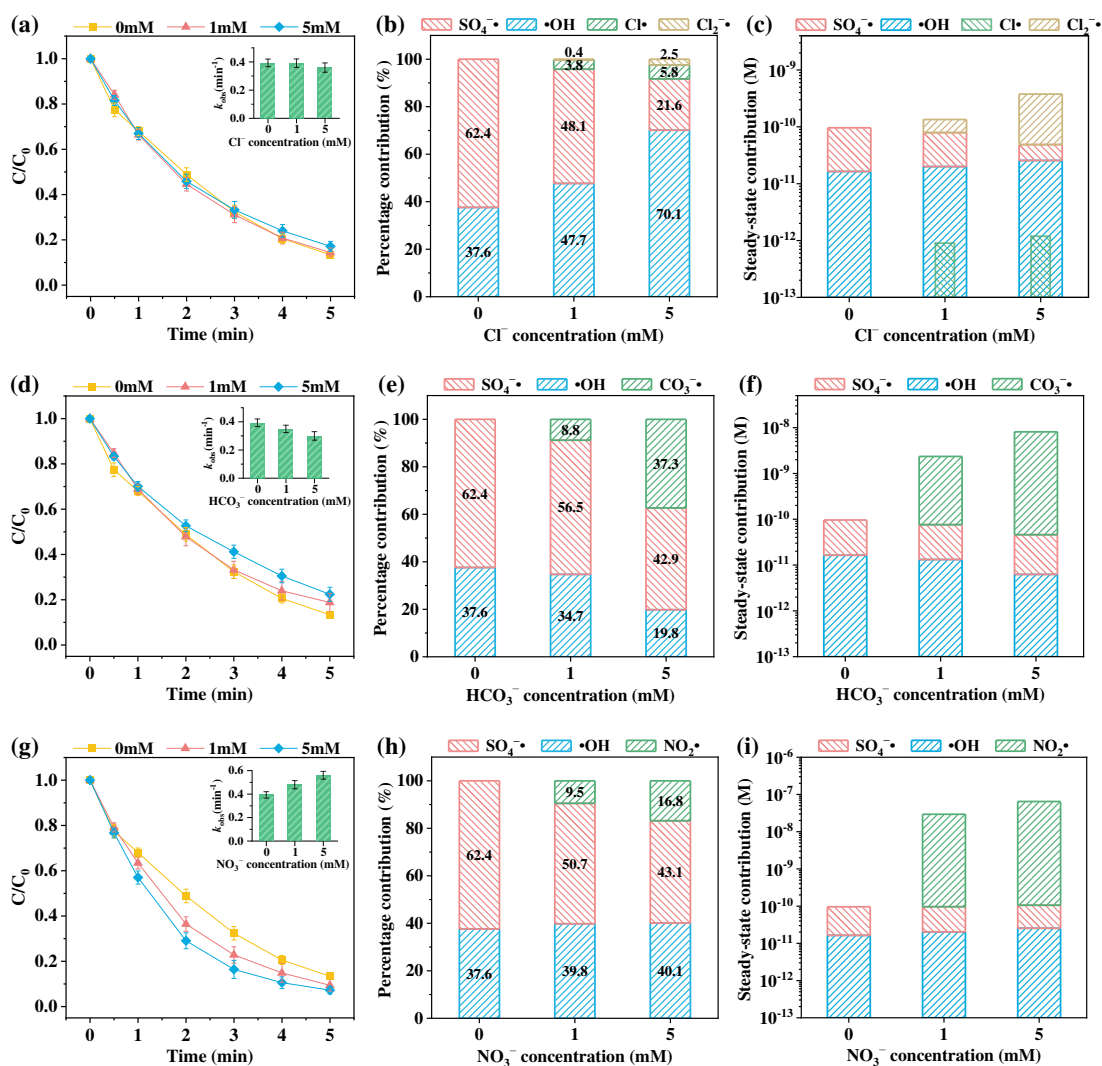
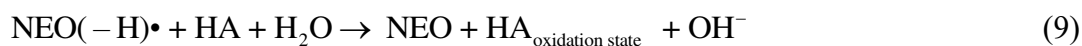


Fig. 3. Effects of (a) Cl^- , (d) HCO_3^- , and (g) NO_3^- (Inset: the relationship with Cl^- , HCO_3^- , and NO_3^- and the value of k_{obs}) in the degradation of NEO during UV/PS; trends in percentage contributions of radicals to NEO degradation during UV/PS at

different (b) Cl^- , (e) HCO_3^- , and (h) NO_3^- concentrations; trends in steady-state concentration of radicals to NEO degradation during UV/PS at different (c) Cl^- , (f) HCO_3^- , and (i) NO_3^- concentrations. Conditions: $[\text{PS}] = 50 \mu\text{M}$, $[\text{NEO}] = 5 \mu\text{M}$, $\text{pH} = 7$.

3.3. Effect of inorganic anions on NEO degradation and radical contribution

Inorganic anions are common background substances in a variety of natural waters including river water, tap water and groundwater. Their widespread presence may alter the types and radical concentrations during UV/PS, and directly impact the removal of pollutants. Therefore, the effects of inorganic anions on NEO degradation in UV/PS systems were investigated, and the types and concentrations of secondary radicals (including $\text{Cl}\cdot$, $\text{Cl}_2\cdot^-$, $\text{CO}_3\cdot^-$, and $\text{NO}_2\cdot$) produced in the system were analyzed by probe-based kinetic models.

3.3.1 Cl^-

As illustrated in Fig. 3a, the presence of 1 mM Cl^- had minimal impact on NEO degradation. However, as Cl^- concentration increased from 1 to 5 mM, NEO degradation became inhibited. As Cl^- concentration increased from 0 to 1 mM, k_{obs} decreased slightly from 0.393 to 0.391 min^{-1} , and as Cl^- concentration was further increased to 5 mM the k_{obs} value decreased to 0.360 min^{-1} . Cl^- in the environment converts radicals ($\cdot\text{OH}$ and $\text{SO}_4\cdot^-$) to a variety of reactive chlorine species including $\text{Cl}\cdot$, $\text{Cl}_2\cdot^-$, and $\text{ClOH}\cdot^-$, as shown in Eqs (10)–(13). The rapid decomposition of $\text{ClOH}\cdot^-$ (Eqs. (14) and (15)) leads to steady-state concentration usually below 10^{-16} M, and the

431 system reactive chlorine species (RCS) are dominated by $\text{Cl}\cdot$ and $\text{Cl}_2^-\cdot$ [34]. For
 432 obtaining specific information about free radical transformation, kinetic models were
 433 constructed using NPX, pCBA, BZF, and TMBA as probes to calculate $[\cdot\text{OH}]_{\text{ss}}$,
 434 $[\text{SO}_4^{\cdot-}]_{\text{ss}}$, $[\text{Cl}\cdot]_{\text{ss}}$, and $[\text{Cl}_2^-\cdot]_{\text{ss}}$ during UV/PS/ Cl^- system. The results illustrated that
 435 $[\text{SO}_4^{\cdot-}]_{\text{ss}}$ decreased from 7.98×10^{-11} M to 5.91×10^{-11} M, but $[\cdot\text{OH}]_{\text{ss}}$ increased from
 436 1.65×10^{-11} M to 2.00×10^{-11} M in the system when Cl^- concentration was 1mM (Fig.
 437 3c). Meanwhile, $[\text{Cl}\cdot]_{\text{ss}}$ and $[\text{Cl}_2^-\cdot]_{\text{ss}}$ were produced in the system with concentrations
 438 of 8.98×10^{-13} M and 5.53×10^{-11} M. At this point, Cl^- in the system scavenges $\text{SO}_4^{\cdot-}$
 439 to form $\text{Cl}\cdot$, $\text{Cl}_2^-\cdot$, and $\text{ClOH}\cdot$ which subsequently decomposes to $\cdot\text{OH}$. The generation
 440 of $\cdot\text{OH}$ ($7.71 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and highly reactive $\text{Cl}\cdot$ ($1.38 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) compensated
 441 for the reduction of $[\text{SO}_4^{\cdot-}]_{\text{ss}}$, resulting in a reduced effect of low concentrations of Cl^-
 442 on NEO degradation. At 1 mM Cl^- concentration, the $\text{SO}_4^{\cdot-}$ contribution to NEO
 443 degradation was reduced from 62.4% to 48.1%, while the $\cdot\text{OH}$ contribution increased
 444 from 37.6% to 47.7% (Fig. 3b). The newly generated $\text{Cl}\cdot$ and $\text{Cl}_2^-\cdot$ radicals contributed
 445 3.8% and 0.4% to NEO degradation, respectively. When the Cl^- concentration was
 446 increased to 5 mM it promoted further conversion of $\text{SO}_4^{\cdot-}$ to $\text{Cl}\cdot$ and $\text{Cl}_2^-\cdot$. The
 447 concentrations of $[\text{Cl}_2^-\cdot]_{\text{ss}}$ and $[\text{Cl}\cdot]_{\text{ss}}$ increased to 3.28×10^{-10} M and 1.19×10^{-12} M,
 448 which were 1.33- and 5.93-fold increases compared to that at 1mM Cl^- concentration,
 449 respectively. NEO degradation at this point was reduced due to the large decrease in
 450 $[\text{SO}_4^{\cdot-}]_{\text{ss}}$ and the relatively low reactivity of the newly generated $\text{Cl}_2^-\cdot$ with NEO (2.14
 451 $\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). The $\text{SO}_4^{\cdot-}$ contribution to NEO degradation decreased to 21.6%, and
 452 the contribution of generated $\text{Cl}_2^-\cdot$ was only 2.5%.



459 3.3.2 HCO_3^-

460 HCO_3^- inhibited NEO degradation during UV/PS system, and the inhibitory effect
 461 was enhanced with increasing HCO_3^- concentration (Fig. 3d). As HCO_3^- concentration
 462 was increased from 0 to 1 mM, k_{obs} decreased from 0.393 min^{-1} to 0.350 min^{-1} . When
 463 the concentration of HCO_3^- was further increased to 5 mM, the k_{obs} decreased to 0.301
 464 min^{-1} . As shown in Eqs. (16)–(17), HCO_3^- will produce $\text{CO}_3^{\bullet-}$ radicals by competing
 465 for $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ [36,57]. Thus, radicals in UV/PS systems were altered in two ways:
 466 First, quenching of the original radicals. As HCO_3^- concentration increased from 0 to
 467 5 mM, $[\bullet\text{OH}]_{\text{ss}}$ and $[\text{SO}_4^{\bullet-}]_{\text{ss}}$ decreased from 1.65×10^{-11} to 6.27×10^{-12} M and from
 468 7.98×10^{-11} to 3.97×10^{-11} M i.e., by 61.8% and 50.3%, respectively (Fig. 3f). Second,
 469 conversion of radicals. In order to obtain specific information on transformation
 470 between radicals, kinetic models were constructed using NPX, BZF and TMBA as
 471 probes to collectively calculate $[\bullet\text{OH}]_{\text{ss}}$ and $[\text{SO}_4^{\bullet-}]_{\text{ss}}$, and $[\text{CO}_3^{\bullet-}]_{\text{ss}}$ in UV/PS/ HCO_3^- .
 472 The results showed that $[\text{CO}_3^{\bullet-}]_{\text{ss}}$ in the system was 2.28×10^{-9} M and 8.07×10^{-9} M
 473 when HCO_3^- concentration was 1 mM and 5 mM, respectively. Meanwhile, $\text{CO}_3^{\bullet-}$ also
 474 played a partial contribution in degradation of NEO, and the percentage contribution of

CO₃•⁻ to NEO degradation was 8.8% and 37.3% when the HCO₃⁻ concentration was 1 and 5 mM, respectively (Fig. 3e). However, CO₃•⁻ has significant selectivity for organic compounds. Although CO₃•⁻ has relatively higher reactivity (10⁶–10⁷ M⁻¹ s⁻¹) with electron-rich micropollutants such as nitrogen-containing and aromatic compounds, it is still about two orders of magnitude lower than that of •OH and SO₄•⁻ [58,59]. Therefore, the generation of CO₃•⁻ prolongs the chain reaction of radicals and reduces the overall oxidizing capacity of the system.



3.3.3 NO₃⁻

The effect of NO₃⁻ concentration (0–5 mM range) on NEO degradation is shown in Fig. 3g. All concentrations of NO₃⁻ enhanced NEO degradation, with *k*_{obs} increasing from 0.393 to 0.560 min⁻¹ as NO₃⁻ concentration increased from 0 to 5 mM. The enhanced removal of NEO was mainly due to the following reasons: First, photoexcitation generates new radicals. NO₃⁻ absorbs UV irradiation and generates NO₂• and O⁻•, Eqs. (18)–(20) [60]. Subsequently, O⁻• reacts with water to form •OH which enhances NEO oxidation. In contrast to other highly unstable reactive nitrogen species (RNS, e.g., ONOOH and NO•), NO₂• is considered the only stable RNS in the presence of NO₃⁻. Therefore, SMX, AN, and TMP were used as probes to construct kinetic models to study the species, transformations, and concentrations of radicals in the UV/PS/NO₃⁻ system. The results showed that [NO₂•]_{ss} was 2.93 × 10⁻⁸ M and 6.45 × 10⁻⁸ M when NO₃⁻ concentration in the system was 1 and 5 mM, respectively (Fig.

3i). Although the $k_{\text{NO}_2\bullet\text{NEO}}$ was relatively limited ($1.28 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$), the higher $[\text{NO}_2\bullet]_{\text{ss}}$ still promoted degradation of NEO with $\text{NO}_2\bullet$ contributing 9.5% (1 mM NO_3^-) and 16.9% (5 mM NO_3^-) (Fig. 3h). Meanwhile, $[\bullet\text{OH}]_{\text{ss}}$ in the system increased to $2.04 \times 10^{-11} \text{ M}$ and $2.55 \times 10^{-11} \text{ M}$ in the presence of 1 and 5 mM NO_3^- , respectively. Second, NO_3^- also absorbs UV to generate O_2 and NO_2^- [49]. O_2 in UV/PS can be involved in the production of radicals through several pathways [61]. Third, limited quenching effect. Among other inorganic anions such as Cl^- and HCO_3^- , NO_3^- reacts with $\bullet\text{OH}$ ($k_{\bullet\text{OH},\text{NO}_3^-} < 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) and $\text{SO}_4\bullet^-$ ($k_{\text{SO}_4\bullet^-, \text{NO}_3^-} = 2.1 \times 10^0 \text{ M}^{-1} \text{ s}^{-1}$) with the smallest reaction rate, and the quenching effect on radicals was accordingly weak [62]. Fourth, minimal effects of UV luminous flux. Unlike far-UVC, there is little overlap between 254 nm UV and the NO_3^- absorption band, so the level of UV absorption shielding caused by NO_3^- is low [62].



3.4. NEO degradation in actual waters

The degradation of NEO by UV/PS in different actual waters (including DW, RW and STPW) is shown in Fig. 4a (see Table S3 for details of water quality). The k_{obs} of NEO degradation during UV/PS were in the order of DW (0.393 min^{-1}) > RW (0.098 min^{-1}) > STPW (0.071 min^{-1}). The main reasons include: (1) the chromaticity of actual waters may affect UV flux, which in turn reduces the generation of radicals; and (2) the presence of NOM and inorganic anions quenches radical availability. As mentioned

earlier, background ions in actual waters may significantly inhibit NEO degradation by scavenging radicals.

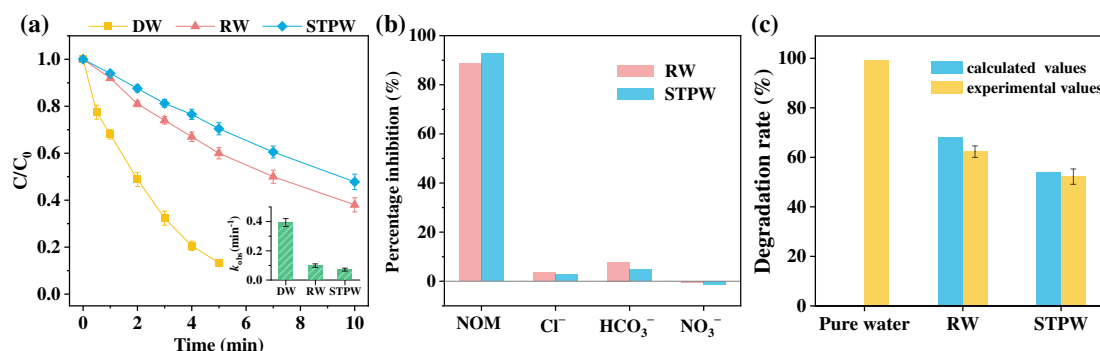


Fig. 4. (a) Degradation of NEO during UV/PS in actual waters (inset: the relationship with actual waters and the value of k_{obs}); (b) percentage contribution of NOM and inorganic anions to NEO inhibition in actual waters; (c) degradation rate after 10 min of degradation in the UV/PS process and predicted values of NEO degradation in actual waters. Conditions: [PS] = 50 μ M, [NEO] = 5 μ M, pH = 7; DW = deionized water, RW = river water and STPW = sewage treatment plant water.

In order to specifically analyze the main inducing factors for the attenuation of the degradation effect we correlated the k_{obs} with organic matter (COD and TOC), pH, inorganic anions (Cl^- , HCO_3^- , NO_3^- , and SO_4^-), and typical cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+) in the actual waters. Spearman's correlation analysis was used to determine the relevant information since the parameters of the actual waters and k_{obs} do not obey a normal distribution. The results were shown in Fig. S6, where organic matter (i.e., NOM as described previously) in water was the main factor inhibiting NEO degradation. In addition, the specific roles of different water matrix components in the UV/PS

system in real waters were traced by simulating the theoretical inhibitory (promotion) effects produced by the water matrix components, and determining their contribution in the total inhibition rate (the sum of inhibition rates of all water matrix components). Among them, impact of water matrix (NOM and inorganic anions) was predicted by interpolating their concentrations in the matrix effect fitting curves (determined by sections 3.2 and 3.3; these results are illustrated in Fig. S7). The results show that although NO_3^- promotes the degradation of NEO, the promotion effect is limited (only 0.6–1.3%). The inhibitory effects of NOM accounted for nearly 90% of the total effect, which was 11.4–34.7 times more than the effects of Cl^- and HCO_3^- (Fig. 4b). The above phenomenon was attributed to the fact that the sampling site was a major residential area in Beijing, where anthropogenic activities resulted in relatively high concentrations of NOM in actual waters. However, within 10 min, NEO in RW and STPW could still be degraded by 62.3% and 53.3% in the UV/PS system, respectively. Although NEO degradation in actual waters is not as effective as in DW, more than 53% NEO reduction can still be achieved within 10 min.

In addition, a prediction model for degradation rate of NEO in actual waters was constructed based on four major water quality factors, including NOM (x_1), Cl^- (x_2), HCO_3^- (x_3), and NO_3^- (x_4) (see Text S15 and Table S4 for specific model construction details) [63]. The output kinetic model is shown in Eq. (21), where the coefficients of the primary terms can be considered as the weights of the influence of water quality factors. The results again demonstrate that NOM is the main factor influencing the degradation of NEO, followed by HCO_3^- . The model can also predict well the

degradation of NEO in actual waters. As shown in Fig. 4c, the calculated values are lower than the experimental values, which is probably due to the complex composition of NOM and the different reactivity of different substances with radicals. In addition, other inorganic ions (e.g., NO_2^- , Br^- , etc.) and other reducing substances in actual waters can also cause partial depletion of radicals.

$$Y = 98.9 - 2.071 x_1 - 0.656 x_2 - 1.099 x_3 + 0.489 x_4 - 0.382 x_1 x_2 - 0.192 x_1 x_3 + 0.176 x_1 x_4 + 0.369 x_2 x_3 + 0.312 x_2 x_4 + 0.187 x_3 x_4 \quad (21)$$

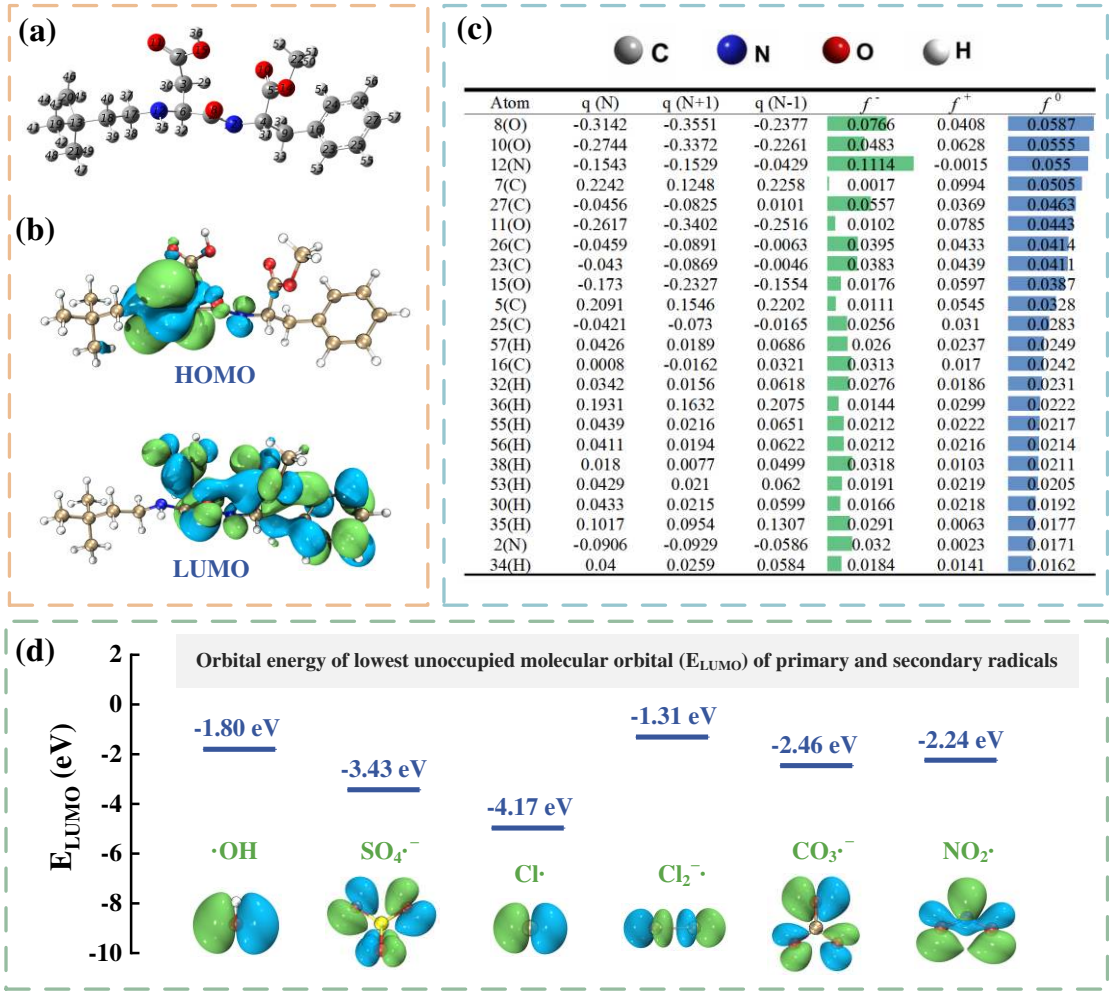
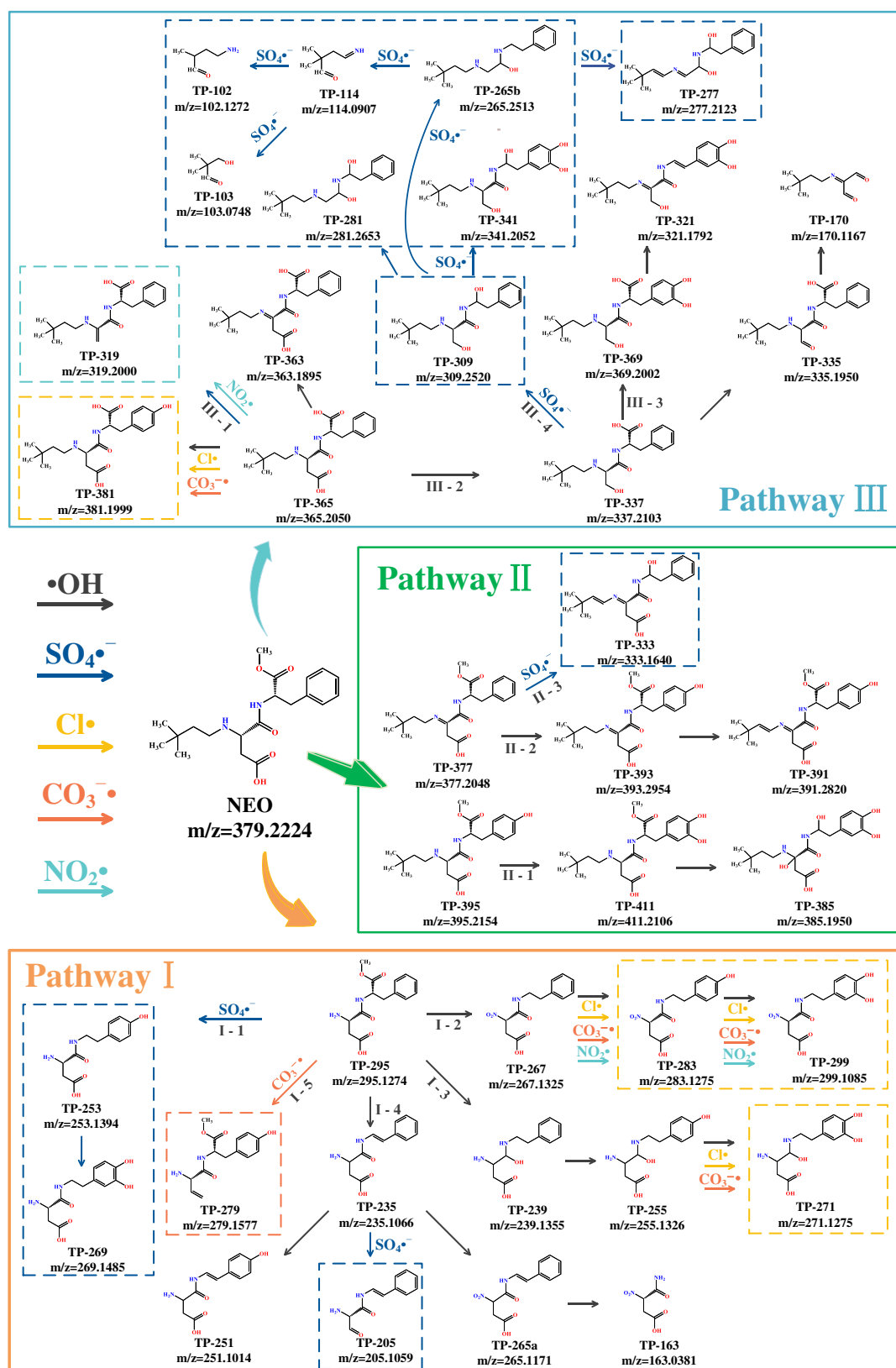


Fig. 5. (a) Molecular construction of NEO after optimization; (b) HOMO and LUMO distribution of NEO; (c) partial Hirshfeld charge distribution and CFF index; and (d) Orbital energy of LUMO (E_{LUMO}) of primary and secondary radicals.



571

572 **Fig. 6.** Potential transformation products (TPs) and degradation pathways of NEO

573 during UV/PS.

3.5. Potential transformation products and degradation pathways of NEO

In order to elucidate the potential degradation pathways of NEO, 39 TPs generated during UV/PS experiments were identified using HPLC/Orbitrap HRMS, of which 33 TPs were found for the first time and are reported in this paper. Table S5 summarizes TP various parameters such as detected molecular mass, molecular formula, magnitude of error, number of peaks, and retention time for all potential degradation products. The mass spectra and extracted ion chromatograms (EIC) of NEO and its TPs are illustrated in Figs. S8–S46. To further identify the degradation sites of NEO, HOMO, LUMO, Fukui function (f^0) and pairwise descriptors (Δf) were calculated using DFT and Multiwfn software, and the results are illustrated in Fig. 5 (Text S16) [50,64]. The HOMO orbitals were significantly concentrated near 12N and amide bonds (Fig. 5b). It is hypothesized that the two C-N bonds and amide bond sites of 12N were the main reaction sites of NEO during UV/PS degradation processes. The values of f^- , f^+ , and f^0 reflect the propensity of micropollutant molecules to be targeted by electrophiles, nucleophiles and radicals, respectively (Fig. 5c) [27]. The magnitude of these values represent the likelihood of the site being attacked [65]. $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ are strong electrophilic radicals, and mainly attack NEO electrophilically and through radical attack [31]. Thus, the 12N and O atoms close to the amide bonds have the highest f^- and f^0 ; this is the site most susceptible to electron loss and free radical attack, and is consistent with the electron-loss positions described by HOMO.

Degradation pathways of NEO during UV/PS experiments were proposed based on the measured TPs and DFT calculations. As shown in Fig. 6, three degradation

pathways were classified according to the initiating occurring functional groups of the degradation reaction, namely 5C-12N bond breaking (pathway I), hydrogen atom abstraction/hydroxylation (pathway II), and ester hydrolysis (pathway III). In addition, the UV/H₂O₂ system was used as a generator of •OH. UV/H₂O₂/Cl⁻, UV/H₂O₂/HCO₃⁻, and UV/H₂O₂/NO₃⁻ systems were used as generators of •OH and anionic radicals (Cl•, Cl₂•⁻, CO₃•⁻, and NO₂•, respectively). The attack tendencies of primary and secondary radicals in degrading NEO were distinguished by comparing the generation of TPs in different systems. The results illustrated that there were differences in the propensity of different species of radicals to attack NEO [45]: •OH was mainly involved in NEO degradation through hydroxylation, hydrogen atom abstraction (HAA), amine oxidation, ester hydrolysis, amide hydrolysis, and direct oxidation reactions, whereas SO₄•⁻ was mainly involved in hydroxylation, HAA, decarboxylation, dehydration reactions, and demethylation to attack NEO. Cl•, CO₃•⁻, and NO₂• are involved in the degradation of NEO through single electron transfer-mediated HAA, decarboxylation, and dehydration reactions.

Pathway I. Due to the highest f^- (0.1114) with 12N of the alkyl side chain, it is suggested that this is the most susceptible oxidation site for electrophilic attack. Pathway I therefore begins with the conversion of NEO to TP-295 by C-N bond breakage at 12N. In the subsequent oxidation processes there are five secondary degradation pathways, which are named as pathways I-1 to I-5, respectively. First, when the ester group attached to 5C of TP-295 is converted to a carboxyl group *via* a hydrolysis reaction, it may be further converted to the precursor substance TP-253 by

a $\text{SO}_4^{\bullet-}$ driven decarboxylation reaction. Subsequently, 57H on the benzene ring is the most likely to be converted to TP-253 by hydroxylation, due to the highest f^- and f^0 . However, TP-253 was not detected during UV/ H_2O_2 experiments. In other words, the hydroxylation reaction to TP-253 is accomplished with the participation of $\text{SO}_4^{\bullet-}$. $\text{SO}_4^{\bullet-}$ is converted to a cation free radical of NEO by plucking an electron from NEO through single electron transfer (SET) and generates hydroxylation product TP-253 by reacting with OH^- in water. Compared to $\bullet\text{OH}$ (-1.80 eV), $\text{SO}_4^{\bullet-}$ (-3.43 eV) has the lowest unoccupied molecular orbital energy (E_{LUMO}) and therefore may react with pollutants with a lower activation energy (Fig. 5d) [31]. Similar types of degradation by SET have also been found in oxidative removal processes of various pollutants such as 6-PPD, and anti-degradant used in tire manufacture [66]. Due to the localization effect of the hydroxyl group on the benzene ring, the H in the neighboring hydroxyl group (55H and 56H) becomes a potential site for hydroxylation to TP-269.

Second, in Pathway I-2, TP-295 was converted to TP-267 after an amine oxidation reaction driven by $\bullet\text{OH}$ at the 12N site. Subsequently, $\bullet\text{OH}$ converted TP-267 to TP-283 and TP-299 by successive hydroxylation reactions of the benzene ring. Degradation by amine oxidation following amine hydrolysis has also been reported in previous studies [60]. Interestingly, the yields of TP-283 and TP-299 in the presence of inorganic anions were 10.2 to 35.1-fold higher than those of the system with $\bullet\text{OH}$ alone (yields were judged by mass spectral peak Intensity). The above reason is due to the involvement of $\text{Cl}\bullet$, $\text{CO}_3^{\bullet-}$, and $\text{NO}_2\bullet$ in the degradation. The E_{LUMO} of $\text{Cl}\bullet$ (-4.17 eV), $\text{CO}_3^{\bullet-}$ (-2.46 eV), and $\text{NO}_2\bullet$ (-2.24 eV) enables the capture of electrons from NEO by

SET and subsequent hydroxylation. Pathway I-3 was the conversion of the unsaturated double bond in the amide moiety of TP-295 to TP-239 driven by an $\bullet\text{OH}$ addition reaction, as well as undergoing phenyl ring hydroxylation to TP-255 and TP-271. Then, pathway I-4 relates to the conversion of TP-295 to TP-235 by decarboxylation of 5C, followed by conversion to TP-205 by again removing the carboxyl group attached to 7C mediated by $\text{SO}_4\bullet^-$. Finally, pathway I-5 was similar to I-4 in that it is the product of the decarboxylation of 7C on TP-295. The difference is that the hydroxyl substituent formed after decarboxylation in pathway I-5 was converted to an unsaturated bond in TP-279 by a $\text{CO}_3\bullet^-$ -mediated hydrolysis reaction rather than to an aldehyde group by direct oxidation.

Pathway II. In pathway II-1 NEO was converted to TP-377 by a $\bullet\text{OH}$ -driven HAA reaction (removal of 32H and 35H), and subsequently converted to TP-393 and TP-391 by hydroxylation. NEO can also be directly converted to TP-395, TP-411, and TP-385 *via* consecutive hydroxylation reactions on the benzene ring (path II-2). NEO might also be directly converted to TP-395, TP-411, and TP-385 by three consecutive hydroxylation reactions on the benzene ring (pathway II-2). According to the activity law of carbon atoms, 32H is the most likely site of attack for a third hydroxylation reaction due to its highest reactivity, which is also verified by the abbreviated Fukui function ($f^0 = 0.0231$ and $f^- = 0.0276$). Secondly, 38H and 35H are similarly vulnerable sites for the third hydroxylation reaction (38H: $f^0 = 0.0211$ and $f^- = 0.0318$; 35H: $f^0 = 0.0291$ and $f^- = 0.0177$). The three significantly higher intensity peaks in the EIC of TP-385 also corroborates these conclusions, with retention times of 7.32 min, 8.27 min

and 9.03 min, respectively (Fig. S42). Finally, in pathway II-3, an unsaturated bond is formed at 38H by the $\text{SO}_4^{\bullet-}$ driven HAA reaction, in which $\text{SO}_4^{\bullet-}$ synchronized removal of the carboxyl group from the adjacent benzene ring is converted to TP-333.

Pathway III. Due to the instability of the ester group, NEO was converted to TP-365 either spontaneously by an ester hydrolysis reaction or by free radical attack. Similar to the first two pathways, TP-365 can also be converted to TP-381 (presence of $\text{Cl}^\bullet$ and $\text{CO}_3^{\bullet-}$ driven degradation) and TP-363 by $^\bullet\text{OH}$ driven hydroxylation and HAA reactions. TP-365 may also be converted to TP-319 by $\text{SO}_4^{\bullet-}$ (or $\text{NO}_2^\bullet$) driven decarboxylation and dehydration reactions (pathway III-1). In pathway III-2, the 7C-centered carboxyl group of TP-365 was removed by $^\bullet\text{OH}$ to produce TP-337 ($f^0 = 0.505$ above the other carboxyl group adjacent to the benzene ring). TP-337 was subsequently converted to TP-335 by a direct $^\bullet\text{OH}$ -driven oxidation reaction hence to TP-170 by an amide hydrolysis reaction to remove the benzene ring. In pathway III-3, based on TP-337, the benzene ring and 32H were attacked by $^\bullet\text{OH}$ to form the hydroxylation product TP-369 and the unsaturated bond-containing TP-321. Pathway III-4 was found to be initiated entirely by $\text{SO}_4^{\bullet-}$. TP-337 was converted to TP-309 by a second decarboxylation reaction. During subsequent oxidation, TP-309 continues to be converted to hydroxylated TP-341. At the same time, TP-309 was converted to TP-265 and TP-281 by a demethylation reaction. Subsequently, a C-N bond break at 12N of TP-265 produced small aliphatic products (TP-114, TP-102 and TP-103).

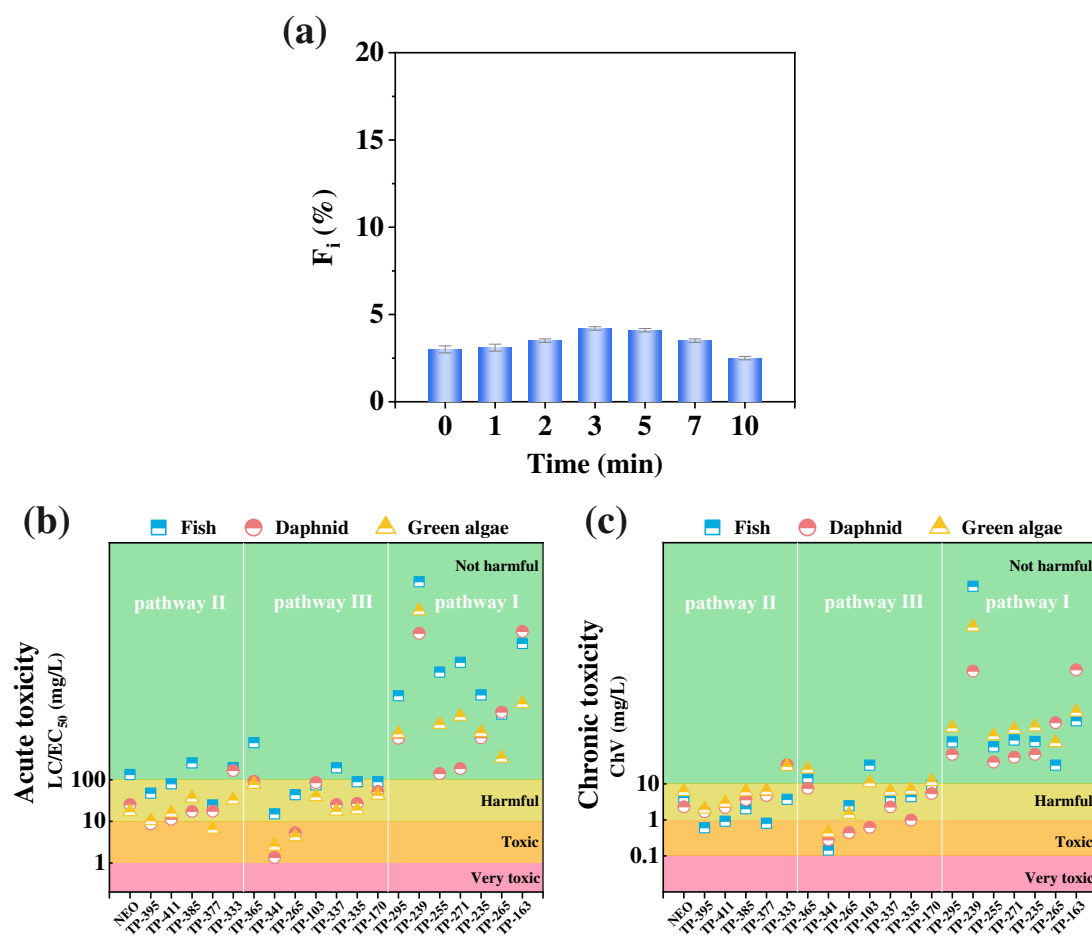


Fig. 7. (a) *Vibrio fischeri* luminescence inhibition rate accompanied by degradation of NEO during UV/PS; (b) acute and (c) chronic toxicity evolution of NEO and its transformation products. Conditions: [PS]= 50 μ M, [NEO]= 5 μ M, pH=7.

3.6. Toxicity evaluation of NEO degradation

The persistence and mobility of TPs in actual waters is often greater than that of their parent compounds which makes them potentially more widespread and enduring in the natural environment, and therefore their toxicity to organisms needs to be understood [42]. Overall solution toxicity (experimental toxicology based on *Vibrio fischeri*) and toxicity of individual TPs (computational toxicology based on ECOSAR software) have been used to comprehensively assess the toxicity levels of TPs during UV/PS

experiments. The overall toxicity of the solution was modeled using *Vibrio fischeri* as a model microorganism, and acute toxicity intensity of the samples was expressed in terms of luminescence inhibition (F_i).

As shown in Fig. 7a, F_i values of *Vibrio fischeri* showed an increasing and then decreasing trend to 10 min exposure time. Upon completion of the 10 min exposure time the F_i value of *Vibrio fischeri* was 2.5%, achieving partial detoxification compared to the original solution. In addition, the inhibition of *Vibrio fischeri* peaked at 3 min (4.2%), indicating the presence of toxic TPs at the initial stage of degradation. To further characterize toxic TPs in degradation, all TPs of the three degradation pathways were assessed using ECOSAR software (Fig. 7b, 7c and Table S6). The results illustrated that the detoxification effects of the three degradation pathways differed significantly. TPs in Pathway I were significantly less toxic to three aquatic organisms (green algae, fish, and daphnia) than those in Pathways II and III. In Pathway I, acute and chronic toxicity to the three aquatic organisms ranged from "Toxic" or "Harmful" to "Not harmful" when the degradation experiment was completed. As C-N bond breaking is the preferred initiation site for UV/PS degradation of NEO in Pathway I, it is hypothesized that the concentration of TPs in Pathway I is the highest. Therefore, most NEO was removed through pathway I and partial detoxification of the overall toxicity of the solution was achieved. In addition, in Pathways II and III, we found that the toxicity of TPs fluctuated greatly and did not decrease significantly at the end of the reaction. Part of the reason for this phenomenon was the lack of detection of small molecular weight TPs during mass spectrometry. Due to removal of the NEO carboxyl

and nitrogen-containing groups during degradation, the resulting low molecular weight alkyl compounds were difficult to load with a positive (negative) charge during the MS ionization process and could not be detected. However, it is apparent that the degradation process produces TPs with higher toxicity than the parent NEO. In Pathways II and III, the hydroxylation products (i.e., TP-395 and TP-385), decarboxylation products (TP-337 and TP-309), and aldolization products (i.e., TP-335) formed at an early stage in NEO degradation and reached increased toxicity risk levels of "Toxic" or "Harmful" in terms of the LC/EC₅₀ (acute toxicity) and ChV (chronic toxicity) of the three simulated aquatic organisms. Therefore, further attention needs to be paid to the generation and subsequent transformation of toxic TPs, and to monitoring the overall impact on the aquatic environment after NEO release.

4. Conclusion

In this study, the mechanism of NEO degradation and transformation during UV/PS degradation in pure water and actual water matrices was investigated. A kinetic model based on the low concentration probe method is proposed to determine the steady-state concentrations of primary ($\bullet\text{OH}$ and $\text{SO}_4\bullet^-$) and secondary ($\text{Cl}\bullet$, $\text{Cl}_2\bullet^-$, $\text{CO}_3\bullet^-$, and $\text{NO}_2\bullet$) radicals in a variety of systems. In the UV/PS system, the contribution of $\bullet\text{OH}$ to NEO degradation increased with increasing alkalinity, but was easily inhibited by NOM. The ranking of k_{obs} for NEO degradation in the presence of inorganic anions was: $\text{NO}_3^- >$ pure water $\approx \text{Cl}^- > \text{HCO}_3^-$. In addition, the steady-state concentration of secondary radicals produced by the system was ranked $\text{NO}_2\bullet > \text{CO}_3\bullet^- > \text{Cl}_2\bullet^- > \text{Cl}\bullet$. However,

because of the significant differences in the reactivity of different species of radicals with NEO, the final ranking of the contribution to NEO degradation is: $\text{CO}_3^{\bullet-} > \text{NO}_2^{\bullet} > \text{Cl}^{\bullet} > \text{Cl}_2^{\bullet-}$. Based on 39 detected TPs, the oxidation mechanism and the attack of primary and secondary radicals for the degradation of NEO by the UV/PS system were proposed. Toxicity assessment showed that although partial detoxification of NEO was achieved at the end of degradation reaction, the toxicity of hydroxylation products, decarboxylation products, and aldolization products formed at the initial stage of NEO degradation was relatively high.

In addition, some limitations and shortcomings still exist in this study, mainly including (1) the methods to further enhance the degradation rate in actual water still lack in-depth research; (2) the generation of toxic TPs during pollutant degradation cannot be avoided. Future studies should focus on and simulate the degradation of pollutants under actual water in order to further investigate the methods to resist the water matrix effect. Meanwhile, AOPs in practical application need to strictly monitor the formation and toxicity of TPs of the parent pollutants, especially the fate and environmental emissions of highly toxic parts of them in STPs.

Acknowledgements

This work was financially supported by the Key Technology Research and Development Program of Shandong Province (No. 2022CXGC021002-1) and the National Natural Science Foundation of China (Nos. 41977325 and 72074136).

References

- [1] Gan, Z., Sun, H., Feng, B., Wang, R., Zhang, Y., 2013. Occurrence of seven artificial sweeteners in the aquatic environment and precipitation of Tianjin, China. *Water Res.* 47(14), 4928-4937.
- [2] Guo, W., Li, J., Liu, Q., Shi, J., Gao, Y., 2021. Tracking the fate of artificial sweeteners within the coastal waters of Shenzhen city, China: from wastewater treatment plants to sea. *J. Hazard. Mater.* 414, 125498.
- [3] World Health Organization, 2023. Aspartame hazard and risk assessment results released. <https://www.who.int/news/item/14-07-2023>.
- [4] Yang, G., Cao, J., Cui, H., Zhan, X., Duan, G., Zhu, Y., 2023. Artificial sweetener enhances the spread of antibiotic resistance genes during anaerobic digestion. *Environ. Sci. Technol.* 57(30), 10919-10928.
- [5] Chattopadhyay, S., Raychaudhuri, U., Chakraborty, R., 2014. Artificial sweeteners – a review. *J. Food Sci. Technol* 51(4), 611-621.
- [6] Farag, M.A., Rezk, M.M., Hamdi Elashal, M., El-Araby, M., Khalifa, S.A.M., El-Seedi, H.R., 2022. An updated multifaceted overview of sweet proteins and dipeptides as sugar substitutes; the chemistry, health benefits, gut interactions, and safety. *Food Res. Int.* 162, 111853.
- [7] Kumari, A., Arora, S., Choudhary, S., Singh, A.K., Tomar, S.K., 2018. Comparative stability of aspartame and neotame in yoghurt. *Int. J. Dairy Technol.* 71(1), 81-88.
- [8] Subedi, B., Kannan, K., 2014. Fate of artificial sweeteners in wastewater treatment

784 plants in New York State, U.S.A. *Environ. Sci. Technol.* 48(23), 13668-13674.

785 [9] Anumol, T., Vijayanandan, A., Park, M., Philip, L., Snyder, S.A., 2016.

786 Occurrence and fate of emerging trace organic chemicals in wastewater plants in

787 Chennai, India. *Environ. Int.* 92-93, 33-42.

788 [10] Gvozdić, E., Bujagić, I.M., Đurkić, T., Grujić, S., 2023. Untreated wastewater

789 impact and environmental risk assessment of artificial sweeteners in river water and

790 sediments of the Danube River Basin in Serbia. *Environ. Sci. Pollut. Res* 30(35),

791 84583-84594.

792 [11] Li, D., Yao, Y., Sun, H., Wang, Y., Pu, J., Calderón, R., Alder, A.C., Kannan, K.,

793 2020. Artificial sweeteners in pig feed: a worldwide survey and case study in pig

794 farms in Tianjin, China. *Environ. Sci. Technol.* 54(7), 4059-4067.

795 [12] Shen, G., Lei, S., Li, H., Yu, Q., Wu, G., Shi, Y., Xu, K., Ren, H., Geng, J., 2023.

796 Occurrence and removal of four artificial sweeteners in wastewater treatment plants

797 of China. *Environ Sci Proc Imp* 25(1), 75-84.

798 [13] Yue, J., Wang, A., Zhao, Y., Zhang, Y., Guo, W., 2024. Distribution and removal

799 characteristics of typical artificial sweeteners in different process stages of sewage

800 treatment plant. *J Inner Mongolia Univ Technol (Nat Sci Ed)* 43(1), 70-76.

801 [14] Yue, J., Guo, W., Li, D., Zhu, Y., Zhao, Q., Wang, A., Li, J., 2023. Seasonal

802 occurrence, removal and mass loads of artificial sweeteners in the largest water

803 reclamation plant in China. *Sci. Total Environ.* 856, 159133.

804 [15] Lee, W., Wang, Y., 2015. Assessing developmental toxicity of caffeine and

805 sweeteners in medaka (*oryzias latipes*). *SpringerPlus* 4(1).

- 806 [16] Chi, L., Bian, X., Gao, B., Tu, P., Lai, Y., Ru, H., Lu, K., 2018. Effects of the
807 artificial sweetener neotame on the gut microbiome and fecal metabolites in mice.
808 *Molecules* 23(2), 367.
- 809 [17] Shil, A., Ladeira Faria, L.M., Walker, C.A., Chichger, H., 2024. The artificial
810 sweetener neotame negatively regulates the intestinal epithelium directly through
811 tlr3-signaling and indirectly through pathogenic changes to model gut bacteria.
812 *Front. Nutr.* 11, 1366409.
- 813 [18] Jiang, L., Yu, Z., Zhao, Y., Yin, D., 2024. Obesogenic potentials of environmental
814 artificial sweeteners with disturbances on both lipid metabolism and neural
815 responses. *Sci. Total Environ.* 919, 170755.
- 816 [19] Yin, R., Zhang, Y., Wang, Y., Zhao, J., Shang, C., 2024. Far-UVC photolysis of
817 peroxydisulfate for micropollutant degradation in water. *Environ. Sci. Technol.*
818 58(13), 6030-6038.
- 819 [20] Guo, K., Wu, Z., Chen, C., Fang, J., 2022. UV/chlorine process: an efficient
820 advanced oxidation process with multiple radicals and functions in water treatment.
821 *Acc. Chem. Res.* 55(3), 286-297.
- 822 [21] Niu, L., Lin, J., Chen, W., Zhang, Q., Yu, X., Feng, M., 2023.
823 Ferrate(VI)/periodate system: synergistic and rapid oxidation of micropollutants via
824 periodate/iodate-modulated Fe(IV)/Fe(V) intermediates. *Environ. Sci. Technol.*
825 57(17), 7051-7062.
- 826 [22] Kusic, H., Koprivanac, N., Bozic, A.L., 2006. Minimization of organic pollutant
827 content in aqueous solution by means of AOPs: UV- and ozone-based technologies.

828 Chem. Eng. J. 123(3), 127-137.

829 [23] Yang, J., Zhu, M., Dionysiou, D.D., 2021. What is the role of light in persulfate-
830 based advanced oxidation for water treatment? Water Res. 189, 116627.

831 [24] Lai, F., Tian, F., Xu, B., Ye, W., Gao, Y., Chen, C., Xing, H., Wang, B., Xie, M.,
832 Hu, X., 2022. A comparative study on the degradation of phenylurea herbicides by
833 UV/persulfate process: kinetics, mechanisms, energy demand and toxicity
834 evaluation associated with DBPs. Chem. Eng. J. 428, 132088.

835 [25] Parvizi, T., Parsa, J.B., Farnood, R., 2022. Synergetic photocatalytic fuel cell and
836 CuFe layered doubled hydroxide as photoactivator of persulfate for dramatically
837 electricity generation of organic pollutants degradation. Appl. Catal. B-Environ 319,
838 121894.

839 [26] Kusic, H., Peternel, I., Ukic, S., Koprivanac, N., Bolanca, T., Papic, S., Bozic, A.L.,
840 2011. Modeling of iron activated persulfate oxidation treating reactive azo dye in
841 water matrix. Chem. Eng. J. 172(1), 109-121.

842 [27] Jiang, Z., Wei, J., Niu, X., Cui, X., Li, Y., Cui, N., Li, J., Huo, J., Wang, L., Ji, W.,
843 Li, J., 2024. Highly dispersed Fe₇S₈ anchored on sp²/sp³ hybridized carbon boosting
844 peroxymonosulfate activation for enhanced EOCs elimination through singlet
845 oxygen-dominated nonradical pathway. J. Hazard. Mater. 461, 132607.

846 [28] Angkaew, A., Sakulthaew, C., Satapanajaru, T., Poapolathep, A., Chokejaroenrat,
847 C., 2019. UV-activated persulfate oxidation of 17β-estradiol: implications for
848 discharge water remediation. J. Environ. Chem. Eng. 7(2), 102858.

849 [29] Wang, Q., Rao, P., Li, G., Dong, L., Zhang, X., Shao, Y., Gao, N., Chu, W., Xu,

B., An, N., Deng, J., 2020. Degradation of imidacloprid by UV-activated persulfate and peroxymonosulfate processes: kinetics, impact of key factors and degradation pathway. *Ecotoxicol. Environ. Saf.* 187, 109779.

[30] Liu, X., Liu, Y., Lu, S., Wang, Z., Wang, Y., Zhang, G., Guo, X., Guo, W., Zhang, T., Xi, B., 2020. Degradation difference of ofloxacin and levofloxacin by UV/H₂O₂ and UV/PS (persulfate): efficiency, factors and mechanism. *Chem. Eng. J.* 385, 123987.

[31] Zhang, H., Xie, C., Chen, L., Duan, J., Li, F., Liu, W., 2023. Different reaction mechanisms of SO₄^{•-} and •OH with organic compound interpreted at molecular orbital level in Co(II)/peroxymonosulfate catalytic activation system. *Water Res.* 229, 119392.

[32] Lee, M., Wang, W., Du, Y., Hu, H., Huang, N., Xu, Z., Wu, Q., Ye, B., 2020. Enhancement effect among a UV, persulfate, and copper (UV/PS/Cu²⁺) system on the degradation of nonoxidizing biocide: the kinetics, radical species, and degradation pathway. *Chem. Eng. J.* 382, 122312.

[33] Cheng, S., Zhao, Y., Pan, Y., Lei, Y., Zhou, Y., Li, C., Zhang, X., Yang, X., 2022. Quantification of the diverse inhibitory effects of dissolved organic matter on transformation of micropollutants in UV/persulfate treatment. *Water Res.* 223, 118967.

[34] Wang, A., Hua, Z., Chen, C., Wei, W., Huang, B., Hou, S., Li, X., Fang, J., 2021. Radical chemistry and PPCP degradation in the UV/peroxydisulfate process in the presence of chloride at freshwater levels. *Chem. Eng. J.* 426, 131276.

872 [35] Li, B., Pan, H., Chen, B., 2023. A review of factors affecting the formation and
873 roles of primary and secondary reactive species in UV₂₅₄-based advanced treatment
874 processes. *Water Res.* 244, 120537.

875 [36] Wu, Z., Guo, K., Fang, J., Yang, X., Xiao, H., Hou, S., Kong, X., Shang, C., Yang,
876 X., Meng, F., Chen, L., 2017. Factors affecting the roles of reactive species in the
877 degradation of micropollutants by the UV/chlorine process. *Water Res.* 126, 351-
878 360.

879 [37] Lei, Y., Lu, J., Zhu, M., Xie, J., Peng, S., Zhu, C., 2020. Radical chemistry of
880 diethyl phthalate oxidation via UV/peroxymonosulfate process: roles of primary and
881 secondary radicals. *Chem. Eng. J.* 379, 122339.

882 [38] Lei, Y., Yu, Y., Lei, X., Liang, X., Cheng, S., Ouyang, G., Yang, X., 2023.
883 Assessing the use of probes and quenchers for understanding the reactive species in
884 advanced oxidation processes. *Environ. Sci. Technol.* 57(13), 5433-5444.

885 [39] Guo, Y., Long, J., Huang, J., Yu, G., Wang, Y., 2022. Can the commonly used
886 quenching method really evaluate the role of reactive oxygen species in pollutant
887 abatement during catalytic ozonation? *Water Res.* 215, 118275.

888 [40] Li, J., Zhao, L., Feng, M., Huang, C., Sun, P., 2021. Abiotic transformation and
889 ecotoxicity change of sulfonamide antibiotics in environmental and water treatment
890 processes: a critical review. *Water Res.* 202, 117463.

891 [41] Rozas, O., Vidal, C., Baeza, C., Jardim, W.F., Rossner, A., Mansilla, H.D., 2016.
892 Organic micropollutants (OMPs) in natural waters: oxidation by UV/H₂O₂ treatment
893 and toxicity assessment. *Water Res.* 98, 109-118.

894 [42] Zahn, D., Arp, H.P.H., Fenner, K., Georgi, A., Hafner, J., Hale, S.E., Hollender,
895 J., Letzel, T., Schymanski, E.L., Sigmund, G., Reemtsma, T., 2024. Should
896 transformation products change the way we manage chemicals? *Environ. Sci.*
897 *Technol.* 58(18), 7710-7718.

898 [43] Li, A.J., Schmitz, O.J., Stephan, S., Lenzen, C., Yue, P.Y., Li, K., Li, H., Leung,
899 K.S., 2016. Photocatalytic transformation of acesulfame: transformation products
900 identification and embryotoxicity study. *Water Res.* 89, 68-75.

901 [44] Wang, A., Zhu, B., Huang, C., Zhang, W., Wang, M., Li, X., Ling, L., Ma, J., Fang,
902 J., 2023. Generation mechanism of singlet oxygen from the interaction of
903 peroxymonosulfate and chloride in aqueous systems. *Water Res.* 235, 119904.

904 [45] Chen, C., Wu, Z., Hou, S., Wang, A., Fang, J., 2022. Transformation of
905 gemfibrozil by the interaction of chloride with sulfate radicals: radical chemistry,
906 transient intermediates and pathways. *Water Res.* 209, 117944.

907 [46] Fu, Y., Li, S., Shi, Y., Geng, J., Li, J., Wu, G., Xu, K., Ren, H., 2019. Removal of
908 artificial sweeteners using UV/persulfate: radical-based degradation kinetic model
909 in wastewater, pathways and toxicity. *Water Res.* 167, 115102.

910 [47] Hoang, N.T., Nguyen, V.T., Minh Tuan, N.D., Manh, T.D., Le, P., Van Tac, D.,
911 Mwazighe, F.M., 2022. Degradation of dyes by UV/persulfate and comparison with
912 other UV-based advanced oxidation processes: kinetics and role of radicals.
913 *Chemosphere* 298, 134197.

914 [48] Hong, W., Zou, J., Zhao, M., Yan, S., Song, W., 2024. Development of a five-
915 chemical-probe method to determine multiple radicals simultaneously in hydroxyl

and sulfate radical-mediated advanced oxidation processes. *Environ. Sci. Technol.* 58(12), 5616-5626.

[49] Yue, J., Guo, W., Zhu, Y., Li, D., Liang, S., Cao, R., Wang, A., Li, J., 2024. Insights on the degradation mechanism of neotame using UV/periodate: Roles of reactive species, kinetics, and pathways. *Chem. Eng. J.* 495, 153059.

[50] Lu, T., Chen, F., 2012. Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* 33(5), 580-592.

[51] Ghanbari, F., Yaghoot-Nezhad, A., Waclawek, S., Lin, K.A., Rodríguez-Chueca, J., Mehdipour, F., 2021. Comparative investigation of acetaminophen degradation in aqueous solution by UV/chlorine and UV/H₂O₂ processes: kinetics and toxicity assessment, process feasibility and products identification. *Chemosphere* 285, 131455.

[52] Xu, Y., Lin, Z., Wang, Y., Zhang, H., 2017. The UV/peroxymonosulfate process for the mineralization of artificial sweetener sucralose. *Chem. Eng. J.* 317, 561-569.

[53] Mo, C., Tian, F., Xu, B., Lai, F., Gao, Y., Ma, Y., Feng, Z., Yao, Z., Bi, D., Hu, X., 2024. Evaluation and comparison of iohexol elimination by UV/peroxymonosulfate and UV/persulfate processes: radical roles, influence factors and iodinated trihalomethanes formation. *J. Water Process. Eng.* 67, 106199.

[54] Luo, Y., Su, R., Yao, H., Zhang, A., Xiang, S., Huang, L., 2021. Degradation of trimethoprim by sulfate radical-based advanced oxidation processes: kinetics, mechanisms, and effects of natural water matrices. *Environ. Sci. Pollut. Res.* 28(44), 62572-62582.

938 [55] Wang, Z., Shao, Y., Gao, N., Lu, X., An, N., 2018. Degradation of diethyl phthalate
939 (DEP) by UV/persulfate: an experiment and simulation study of contributions by
940 hydroxyl and sulfate radicals. *Chemosphere* 193, 602-610.

941 [56] Pérez-González, A., Galano, A., 2011. OH radical scavenging activity of
942 edaravone: mechanism and kinetics. *J. Phys. Chem. B* 115(5), 1306-1314.

943 [57] Lee, M., Wang, W., Xu, Z., Ye, B., Wu, Q., Hu, H., 2019. The application of
944 UV/PS oxidation for removal of a quaternary ammonium compound of dodecyl
945 trimethyl ammonium chloride (DTAC): the kinetics and mechanism. *Sci. Total*
946 *Environ.* 655, 1261-1269.

947 [58] Zhou, Y., Chen, C., Guo, K., Wu, Z., Wang, L., Hua, Z., Fang, J., 2020. Kinetics
948 and pathways of the degradation of PPCPs by carbonate radicals in advanced
949 oxidation processes. *Water Res.* 185, 116231.

950 [59] Lian, L., Yao, B., Hou, S., Fang, J., Yan, S., Song, W., 2017. Kinetic study of
951 hydroxyl and sulfate radical-mediated oxidation of pharmaceuticals in wastewater
952 effluents. *Environ. Sci. Technol.* 51(5), 2954-2962.

953 [60] Luo, C., Li, M., Cheng, X., Wu, D., Tan, F., Li, Z., Chen, Y., Yu, F., Ma, Q., 2022.
954 Degradation of iopamidol by UV₃₆₅/NaClO: roles of reactive species, degradation
955 mechanism, and toxicology. *Water Res.* 222, 118840.

956 [61] Keen, O.S., Love, N.G., Linden, K.G., 2012. The role of effluent nitrate in trace
957 organic chemical oxidation during UV disinfection. *Water Res.* 46(16), 5224-5234.

958 [62] Ao, X., Zhang, X., Sun, W., Linden, K.G., Payne, E.M., Mao, T., Li, Z., 2024.
959 What is the role of nitrate/nitrite in trace organic contaminants degradation and

transformation during UV-based advanced oxidation processes? Water Res. 253,
121259.

[63] Fu, Y., Wu, G., Geng, J., Li, J., Li, S., Ren, H., 2019. Kinetics and modeling of
artificial sweeteners degradation in wastewater by the UV/persulfate process. Water
Res. 150, 12-20.

[64] Li, F., Borthwick, A.G.L., Liu, W., 2023. Environmental theoretical calculation
for non-periodic systems. Trends Chem. 5(6), 410-414.

[65] Pan, G., Wei, J., Xu, M., Li, J., Wang, L., Li, Y., Cui, N., Li, J., Wang, Z., 2023.
Insight into boron-doped biochar as efficient metal-free catalyst for
peroxymonosulfate activation: important role of -O-B-O- moieties. J. Hazard. Mater.
445, 130479.

[66] Chen, L., Hu, J., Borthwick, A.G.L., Sun, W., Zhang, H., Jia, D., Liu, W., 2024.
Solar-light-activated periodate for degradation and detoxification of highly toxic
6PPD-quinone at environmental levels. Nature Water 2(5), 453-463.