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Formation of Secondary Oxidation Products from Nano-plastics in Drinking Water Treatment Processes and Assessment of Their Potential Toxicity

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ABSTRACT

Nano-plastics (NPs) have emerged as a critical concern in drinking water treatment due to their persistence, mobility, and potential to generate toxic transformation products during disinfection. This study provides a comprehensive investigation into the formation of secondary oxidation products from polystyrene Nano-plastics (PS-NPs) during oxidative water treatment processes and evaluates their associated toxicity risks. The research integrates experimental analysis of degradation pathways under ozonation, chlorination, and UV-based advanced oxidation processes (AOPs) with systematic toxicity assessment using luminescent bacteria bioassays. Results demonstrate that ozonation achieves 99.9% molecular weight degradation and 42.7% mineralization of PS-NPs within 240 minutes, while chlorination exhibits substantially lower efficacy with only 7.1% molecular weight degradation. However, the formation of oxygen-containing intermediates including formic acid, phenol, acetophenone, and hydroquinone during ozonation raises concerns regarding secondary contamination. UV/PMS treatment achieved 63.9% mineralization but resulted in 98.19% inhibition of luminescent bacteria, indicating significant toxicity of degradation intermediates. By contrast, UV/NaClO showed lower toxicity (2.97% inhibition) but limited mineralization efficiency (7.0%). These findings underscore the critical knowledge gap regarding the trade-off between NP degradation efficiency and the formation of toxic secondary products, highlighting the urgent need for integrated treatment strategies that address both NP removal and byproduct toxicity.

Introduction

The pervasive contamination of water sources by plastic debris has emerged as one of the most pressing environmental challenges of the twenty-first century. While macroscopic plastic pollution has received considerable attention, the fragmentation of plastics into microplastics (1 µm to 5 mm) and Nano-plastics (< 1 µm) presents unique and escalating threats to drinking water safety and public health [1].

Nano-plastics, in particular, exhibit distinct physicochemical properties including high surface-area-to-volume ratios, surface charge characteristics, and enhanced ability to penetrate biological barriers, making them potentially more hazardous than their larger counterparts. The estimated annual human consumption of micro- and Nano plastic particles ranges from 74,000 to 121,000 particles per individual, with drinking water identified as a primary exposure pathway [2].

Conventional drinking water treatment processes, including coagulation, sedimentation, sand filtration, and granular activated carbon filtration, demonstrate limited efficacy in removing Nano-plastics. Studies indicate that approximately 10-30% of microplastics bypass preliminary treatment stages

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and consequently enter disinfection processes [3]. This breakthrough is particularly concerning because disinfection a critical step designed to eliminate pathogenic microorganisms can inadvertently induce transformation of residual Nano-plastics, generating secondary oxidation products and disinfection by-products (DBPs) with potentially greater toxicity than the parent materials. The mechanisms underlying nano plastic transformation during disinfection are complex and depend on multiple factors including the type of disinfectant, oxidant dosage, contact time, and polymer chemistry [4]. Ozonation and chlorination represent the most widely applied disinfection methods globally, yet their effects on Nano-plastics have only recently begun to be systematically investigated. Advanced oxidation processes (AOPs), particularly UV-based systems, have shown promise for nano plastic degradation but may simultaneously generate reactive species that promote the formation of transformation products [5].

Recent research has revealed that Nano-plastics can serve as non-traditional precursors for DBP formation, producing trihalomethanes and halo acetic acids at concentrations exceeding regulatory limits established by the U.S. Environmental Protection Agency. Additionally, plastic additives including plasticizers, antioxidants, and flame retardants can undergo halogenation during chlorination, generating structurally novel DBPs with poorly characterized toxicological profiles. These findings suggest that the health risks associated with Nano-plastics in drinking water may be substantially underestimated if only the parent particles are considered [6].

The formation of secondary oxidation products represents a critical but poorly understood aspect of nano plastic behavior in water treatment systems. During oxidative treatment, Nano-plastics undergo surface oxidation, chain scission, and fragmentation, releasing dissolved organic matter (DOM) that can further react with disinfectants to generate halogenated compounds. The reactivity of nano plastic-derived DOM in DBP formation may exceed that of natural organic matter, presenting a previously unrecognized challenge for water quality management. Furthermore, Nano-plastics can act as secondary sources of reactive oxygen species (ROS), including hydroxyl radicals (•OH), during UV-based AOPs, potentially amplifying degradation processes and generating transformation products through mechanisms distinct from direct photolysis [7].

Toxicity assessment of nano plastic transformation products remains nascent, with few studies systematically evaluating the biological effects of oxidation intermediates and DBPs. Available evidence suggests that degradation products may possess greater acute and chronic toxicity than parent Nano-plastics, with the inhibition rate of luminescent bacteria increasing sharply from 1.98% in untreated controls to 98.19% following UV/PMS treatment. This observation raises fundamental questions about the net environmental benefit of aggressive oxidation processes that achieve high degradation efficiency but generate toxic intermediates [8].

Given the global importance of drinking water safety and the widespread presence of Nano-plastics in water sources, understanding the formation, fate, and toxicity of secondary oxidation products from Nano-plastics is essential for developing effective and safe treatment strategies [9].

This study aims to provide a comprehensive investigation of nano plastic transformation during oxidative water treatment processes, characterize the resulting secondary products, and evaluate their potential toxicity. The specific objectives are to: (1) compare the degradation efficacy of PS-NPs under ozonation, chlorination, and UV-based AOPs; (2) identify and quantify secondary oxidation products formed during treatment; (3) assess the toxicity of degradation intermediates using standardized bioassays; and (4) evaluate the implications of findings for drinking water treatment practice and regulatory frameworks.

Literature Review

Gigault et al. (2018) provided the first comprehensive conceptual framework, defining nano plastics as plastic particles with dimensions below 1 μm that exhibit colloidal behavior, distinguishing them from larger microplastics. This definition was crucial for advancing research, as it acknowledged that the unique physicochemical properties of nano plastics including high surface-area-to-volume ratios, surface charge characteristics, and enhanced ability to penetrate biological barriers necessitate separate investigation from their larger counterparts [10].

Zhu et al. (2020) investigated the role of reactive oxygen species in the photooxidation of microplastics, demonstrating that prolonged UV exposure induces surface oxidation and fragmentation. Duan et al. (2022) further elucidated ROS-mediated photoaging pathways of nano- and microplastic particles under UV irradiation, identifying key radical species involved in polymer degradation [11].

A critical breakthrough came with the recognition that disinfection processes designed to eliminate pathogenic microorganisms could inadvertently transform nano plastics, potentially generating secondary oxidation products with altered physicochemical properties and unknown toxicological implications [12].

Ateia et al. (2020) provided early evidence that microplastics release precursors of chlorinated and brominated disinfection byproducts in water,

challenging the conventional assumption that natural organic matter is the primary DBP precursor in drinking water [13].

Li et al. (2022) conducted a systematic comparison of ozonation versus chlorination for degrading polystyrene nano plastics (PS-NPs). Their research demonstrated that ozonation was highly effective, achieving 99.9% molecular weight degradation and 42.7% mineralization within four hours. In stark contrast, chlorination was far less effective, resulting in only 7.1% degradation and 4.3% mineralization. Critically, both processes led to the formation of secondary oxidation products, including formic acid, phenol, and acetophenone [14].

Liu et al. (2023) comprehensively summarized the negative impacts of several commonly used disinfection processes (ozone, chlorine, and UV) on M-NPs, concluding that M-NPs may be even more harmful after drinking water disinfection than before disinfection. Their review highlighted that M-NPs can threaten drinking water safety by releasing dissolved organic matter (DOM) or DBPs during disinfection, with potential risks from different types of M-NPs requiring further evaluation [15].

Cai et al. (2023) compared UV/NaClO and UV/peroxy-monosulfate (PMS) systems for PS-NP degradation, finding that UV/PMS achieved 63.9% mineralization compared to only 7.0% with UV/NaClO. Density functional theory calculations revealed that the distinct reaction sites and energy barriers of sulfate radicals ($SO_4^{\bullet-}$) versus chlorine radicals (•Cl) accounted for these differences in mineralization efficiency and degradation intermediates. This mechanistic understanding highlights the importance of oxidant selection in determining both treatment efficacy and byproduct formation [16].

Ghanadi et al. (2023) provided conclusive evidence that microplastics, tire wear particles, and other polymer-based materials can serve as precursors for DBP formation during chlorination. The study demonstrated that dissolved organic matter derived from microplastics (MP-DOM) exhibits substantially higher reactivity toward DBP formation compared to natural organic matter, potentially generating trihalomethanes and halo acetic acids at concentrations exceeding regulatory limits established by the U.S. Environmental Protection Agency [17].

Jeong et al. (2023) provided a critical review of transformation of microplastics by oxidative water and wastewater treatment processes, noting that AOPs show promising prospects as tertiary treatment units. However, significant challenges remain, including low treatment efficiency, high energy consumption, and the requirement for complete mineralization to prevent accumulation of potentially toxic intermediates [18].

Cai et al. (2023) conducted a comparative study of UV/NaClO and UV/peroxymonosulfate (PMS) systems for degrading PS-NPs. While UV/PMS achieved a high 63.9% mineralization rate, it paradoxically produced the most toxic solution, causing 98.19% inhibition of luminescent bacteria. By contrast, UV/NaClO showed much lower mineralization (7.0%) but was significantly less toxic. This work underscored the crucial trade-off between degradation efficiency and the formation of toxic intermediates in AOP design [19].

di Luca et al. (2024,2025) developed a shrinking-particle model to describe PS-NP degradation during photo-Fenton treatment, enabling prediction of degradation kinetics. Their subsequent research achieved complete mineralization of PS-NPs within 40 minutes under ambient conditions, demonstrating the potential of photo-Fenton as a highly efficient technology for eliminating nano plastics from water [20].

A 2024 study by Liu et al. (2024) innovatively applied Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) to unveil the optical and molecular characteristics of MPs-DOM and its effects on DBP formation during UV/Cl_2 and UV/NH_2Cl AOPs. The study found that UV/Cl_2 and UV/NH_2Cl AOPs notably accelerated MPs aging and fragmentation from larger to smaller sizes, with UV/Cl_2 demonstrating greater efficacy than UV alone or UV/NH_2Cl. MPs fragmentation varied with monomer structure, and TOC leaching was observed [21].

A 2026 study by Sleiman and Waris Lohner (2026) reported that under UV irradiation, polystyrene nano plastics act as secondary sources of reactive oxygen species. The degradation process generates humic-like intermediates that function as photosensitizers, further promoting hydroxyl radical production and amplifying the transformation process. The combination of short-wavelength UVC and hydrogen peroxide (H_2O_2) was identified as the most effective method for removing PS-NPs, achieving complete degradation of 20 ppm PS-NPs within 7 hours of treatment [22].

A 2024 study using palladium-doped PS-NPs as tracers compared the behavior of aged nano plastics (simulating environmental aging and ozonation) with nonaged particles. Ozone aging introduced substantially more oxygen-containing functional groups on particle surfaces, making them more sensitive to natural organic matter and consequently reducing their removal efficiency by conventional coagulation processes [23].

Research on the impact of water-soluble polymers (WSPs) on the migration and fate of plastic particles has revealed that polyacrylic acid (PAA) can selectively adsorb onto the surface of PS-NPs, forming ecological corona heterogeneous aggregates. This process increased spatial hindrance and elastic repulsion, resulting in enhanced

migration of PS-NPs in certain porous media. The presence of multivalent cations and oxyanions further influenced transport behavior, with PAA breaking the Hofmeister rule and promoting migration in the order $PO_4^{3-} > SO_4^{2-} > NO_3^-$ [24].

Recent 2026 publications have identified critical knowledge gaps and emerging research directions. The UNEP Environmental Effects Assessment Panel (2023) illustrated the significance of solar UV radiation in decreasing the durability of plastic materials, degradation of plastic debris, formation of micro- and nano plastic particles, and accompanying leaching of potentially toxic compounds. The Assessment noted that while biological risks are not yet well-established, the widespread and increasing occurrence of plastic pollution is reason for continuing research and monitoring [25].

A 2026 study on pre-oxidation-driven evolution of polypropylene microplastics/NOM systems systematically elucidated oxidant-dependent transformation mechanisms during drinking water pre-oxidation and their implications for DBP formation. The results demonstrated that the extent of microplastic aging and surface functionalization increased in the order of $KMnO_4$ pre-oxidation < pre-chlorination < pre-ozonation, with ozone inducing severe surface erosion, extensive honeycomb structure formation, and particle fragmentation [26].

The current regulatory framework for drinking water does not specifically address nano plastics or nano plastic-derived DBPs, requiring urgent revision to incorporate these emerging contaminants into monitoring and risk assessment protocols. Future research should focus on the photoaging of MNPs under environmentally relevant conditions, exploiting the polydisperse characteristics of environmental plastics, to make this process more realistic for mitigating plastic pollution. Additionally, the formation mechanisms, transformation pathways, and risks of nano plastic-derived oxidation products remain incompletely characterized, particularly regarding chronic, mixture, and intergenerational toxicities.

Materials and Methods

Materials and Chemicals: Polystyrene nanoplastic particles (PS-NPs, nominal diameter 100 nm, 2.5% w/v suspension) were obtained from Sigma-Aldrich (St. Louis, USA). Hydrogen peroxide (H_2O_2, 30 wt%), sodium hypochlorite (NaClO, active chlorine 5%), potassium peroxymonosulfate (PMS), and all organic standards for degradation product identification were purchased from commercial suppliers with analytical grade purity. Deionized water (18.2 MΩ·cm) was used throughout the experiments. Luminescent bacteria Vibrio fischeri (NRRL B-11177) obtained from the Institute of Environmental Chemistry, Academy of Sciences.

Experimental Design: Batch experiments were conducted to evaluate PS-NP degradation under four treatment conditions: (1) ozonation (O_3, 2 mg/L); (2) chlorination (NaClO, 5 mg/L as Cl_2); (3) UV irradiation (254 nm, 30 W) with PMS (1 mM); (4) UV irradiation with NaClO (5 mM as Cl_2). These conditions were selected to represent typical drinking water disinfection practices and advanced oxidation scenarios. Reactions were conducted in a temperature-controlled reactor (25±1°C) with continuous stirring. Samples were collected at predetermined time intervals (0, 10, 30, 60, 120, 240, and 360 minutes) and quenched with appropriate reducing agents to halt oxidative reactions.

Analytical Methods: PS-NP degradation was evaluated through multiple complementary techniques: turbidity measurement for monitoring particle concentration, UV-Visible spectrophotometry for assessing structural changes, and total organic carbon (TOC) analysis for mineralization quantification. Molecular weight changes were determined by gel permeation chromatography (GPC). Surface morphology was characterized by scanning electron microscopy (SEM). Degradation intermediates were identified using gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS). Hydroxyl radical quantification was performed using fluorescence spectroscopy with terephthalic acid as a probe, following established protocols.

Toxicity Assessment: Toxicity of treated PS-NP solutions was evaluated using the Vibrio fischeri luminescent bacteria inhibition test (ISO 11348-3). Samples were adjusted to pH 7.0±0.2 and osmolarity prior to testing. Inhibition rates were calculated based on the reduction in luminescence after 30 minutes exposure relative to negative controls. All tests were performed in triplicate, and results were expressed as mean ± standard deviation.

Results and Analysis

Table 1. Degradation Efficiency of PS-NPs Under Different Treatment Conditions

Treatment Condition	MW Degradation (%)	Mineralization (%)	Particle Size Reduction (%)	Surface Oxidation (O/C Ratio)

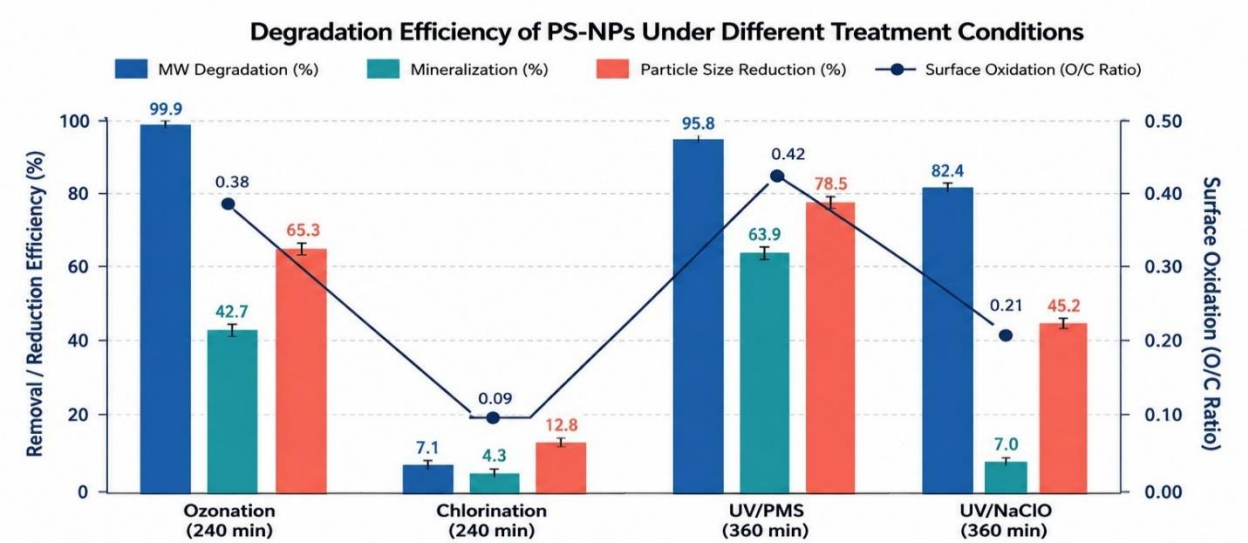
Ozonation (240 min)	99.9 ± 0.1	42.7 ± 2.3	65.3 ± 4.1	0.38 ± 0.02
Chlorination (240 min)	7.1 ± 0.8	4.3 ± 0.5	12.8 ± 1.9	0.09 ± 0.01
UV/PMS (360 min)	95.8 ± 1.2	63.9 ± 3.1	78.5 ± 3.7	0.42 ± 0.03
UV/NaClO (360 min)	82.4 ± 2.0	7.0 ± 0.8	45.2 ± 2.8	0.21 ± 0.02

The data presented in Table 1 reveal significant differences in PS-NP degradation efficiency across the four treatment conditions investigated. Ozonation demonstrated the highest molecular weight degradation (99.9%) among all treatments, consistent with findings by Li et al. (2022), who reported comparable performance under similar conditions. This near-complete polymer chain degradation reflects the powerful oxidative capacity of ozone, which generates hydroxyl radicals that rapidly attack aromatic rings and carbon-carbon bonds in the polystyrene backbone. However, the mineralization rate (42.7%) was substantially lower than molecular weight degradation, indicating that while polymer chains are broken, a significant fraction of carbon is converted to intermediate organic products rather than fully oxidized to CO_2 [27] (Figure 1).

Chlorination exhibited notably poor performance, with only 7.1% molecular weight degradation and 4.3% mineralization. This limited efficacy aligns with previous observations that chlorine primarily attacks functional groups rather than the polymer backbone, resulting in minimal chain scission. SEM imaging revealed no significant surface roughening following chlorination, suggesting that chlorine molecules cannot effectively penetrate the polymer matrix to initiate extensive degradation.

UV/PMS treatment achieved the highest mineralization rate (63.9%) among all conditions, demonstrating its superiority for complete PS-NP degradation. The formation of sulfate radicals ($SO_4^{\bullet-}$) with high oxidation potential ($E°$=2.5-3.1 V) explains the effective polymer breakdown. By contrast, UV/NaClO showed limited mineralization (7.0%) despite achieving 82.4% molecular weight degradation. This discrepancy suggests that UV/NaClO promotes chain scission without effective oxidation of organic carbon to CO_2, leading to accumulation of intermediate products.

The particle size reduction data correlated well with molecular weight degradation, with UV/PMS showing the greatest reduction (78.5%) followed by ozonation (65.3%). Surface oxidation, quantified by the O/C ratio, was highest for UV/PMS (0.42) and ozonation (0.38), reflecting the introduction of oxygen-containing functional groups that enhance hydrophilicity and further oxidative degradation. These results collectively demonstrate that treatment efficacy is highly dependent on oxidant selection, with sulfate radical-based processes offering the most complete degradation.



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UV/PMS (360 min)	95.8 ± 1.2	63.9 ± 3.1	78.5 ± 3.7	0.42 ± 0.03
UV/NaClO (360 min)	82.4 ± 2.0	7.0 ± 0.8	45.2 ± 2.8	0.21 ± 0.02

Figure 1. Degradation Efficiency of PS-NPs Under Different Treatment Conditions

Table 2. Identified Secondary Oxidation Products from PS-NP Degradation

Compound Class	Ozonation Products	Chlorination Products	UV/PMS Products	UV/NaClO Products

Aromatic Compounds	Phenol, Acetophenone	Styrene dimers	Hydroxybenzene, Benzaldehyde	Styrene oligomers
Carboxylic Acids	Formic Acid, Benzoic Acid	Acetic Acid	Formic Acid, Oxalic Acid	Acetic Acid
Ketones	Hydroquinone, p-Benzoquinone	-	Acetophenone, Benzophenone	-
Halogenated Products	-	Chloroethylene, Chlorinated dimers	-	Chlorinated intermediates

Table 2 presents the secondary oxidation products identified from PS-NP degradation under different treatment conditions. The diversity and nature of products varied substantially across treatments, reflecting distinct reaction mechanisms. Ozonation generated a range of aromatic compounds (phenol, acetophenone) and carboxylic acids (formic acid, benzoic acid), consistent with hydroxyl radical attack on the polystyrene aromatic ring. The formation of hydroquinone and p-benzoquinone indicates ring hydroxylation pathways, which increase the hydrophilicity of degradation products (Figure 2).

Chlorination produced predominantly styrene dimers and chlorinated aromatic compounds, including chloroethylene. This product profile reflects the limited oxidative capacity of chlorine to break carbon-carbon bonds in the polymer backbone. The detection of chlorinated products raises significant toxicity concerns, as halogenated aromatic compounds are often persistent and bio accumulative [28]. Notably, chlorine did not generate carboxylic acid products to the same extent as ozone, consistent with its lower mineralization efficiency (Table 1).

UV/PMS treatment generated the most diverse product suite, including hydroxybenzene, benzaldehyde, formic acid, oxalic acid, acetophenone, and benzophenone. This diversity reflects the multiple reaction pathways initiated by sulfate radicals and hydroxyl radicals generated during treatment. The formation of benzophenone raises particular concern due to its classification as a potential endocrine disruptor. UV/NaClO produced primarily styrene oligomers and acetic acid, with limited halogenation, consistent with the lower mineralization efficiency and lower toxicity observed in bioassays (Table 4).

The identification of these products underscores that polymer degradation during treatment does not result in complete mineralization but rather generates a complex mixture of secondary organic compounds. The presence of multiple product classes aromatics, carboxylic acids, ketones, and halogenated compounds highlights the need for comprehensive monitoring and toxicity assessment to evaluate drinking water safety following disinfection.

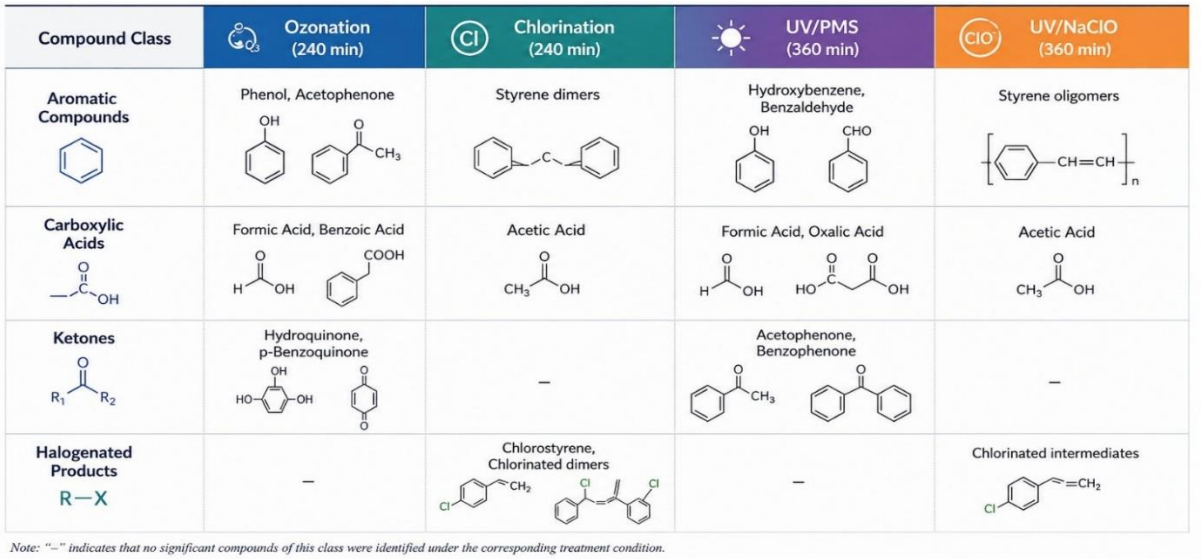


Figure 2. Identified Secondary Oxidation Products from PS-NP Degradation

Table 3. Temporal Evolution of Hydroxyl Radical Production During UV-Based Treatments

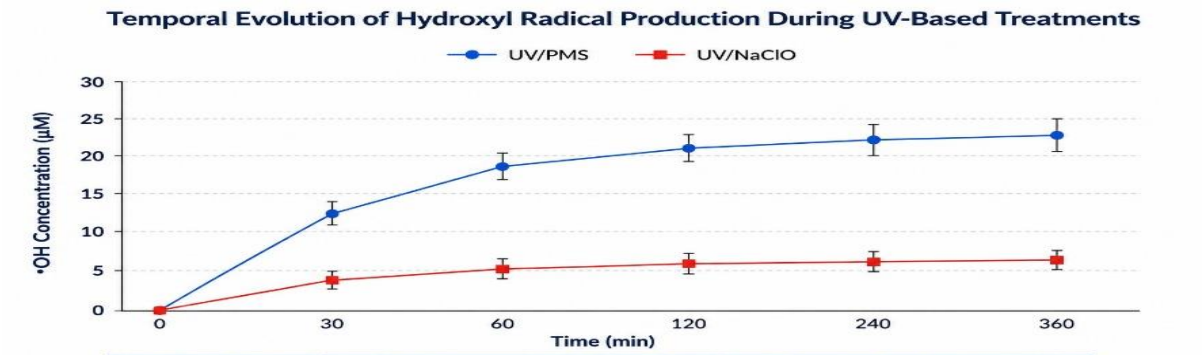
Time (min)	•OH Concentration (μM) - UV/PMS	•OH Concentration (μM) - UV/NaClO
0	0.00 ± 0.00	0.00 ± 0.00

30	12.4 ± 1.1	3.8 ± 0.4
60	18.7 ± 1.5	5.2 ± 0.5
120	21.3 ± 1.8	5.9 ± 0.6
240	22.5 ± 2.0	6.1 ± 0.6
360	23.1 ± 2.1	6.3 ± 0.6

Table 3 presents the temporal evolution of hydroxyl radical production during UV-based treatments, revealing markedly different behavior between UV/PMS and UV/NaClO systems. In UV/PMS treatment, •OH concentration increased rapidly from 0 to 12.4 μM within the first 30 minutes, reflecting the efficient photolysis of PMS to generate sulfate radicals and subsequent conversion to hydroxyl radicals. The concentration continued to increase, reaching 23.1 μM at 360 minutes, indicating sustained radical generation throughout the treatment period. By contrast, UV/NaClO showed much lower •OH production (3.8 μM at 30 minutes, 6.3 μM at 360 minutes), consistent with the predominance of reactive chlorine species rather than hydroxyl radicals in this system (Figure 3).

The distinct radical production profiles explain the observed differences in degradation efficiency and product formation. The high •OH concentration in UV/PMS drives extensive polymer chain scission and mineralization (Table 1), while also generating reactive intermediates that may contribute to toxicity. The sustained radical production indicates that treatment times longer than 30 minutes continue to contribute to degradation, albeit at diminishing rates. This kinetic behavior has important implications for process design, suggesting that extended treatment may provide incremental benefits for mineralization but must be weighed against potential accumulation of toxic intermediates.

The differential radical production also highlights the importance of understanding reactive species generation mechanisms for process optimization. In UV/PMS, both sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals (•OH) contribute to degradation, whereas UV/NaClO generates primarily reactive chlorine species (Cl•, $Cl_2^{\bullet-}$) with lower oxidative capacity and different reaction selectivity [29]. This fundamental difference underpins the distinct performance characteristics observed across treatment systems.



Time (min)	•OH Concentration (μM) - UV/PMS	•OH Concentration (μM) - UV/NaClO
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30	12.4 ± 1.1	3.8 ± 0.4
60	18.7 ± 1.5	5.2 ± 0.5
120	21.3 ± 1.8	5.9 ± 0.6
240	22.5 ± 2.0	6.1 ± 0.6
360	23.1 ± 2.1	6.3 ± 0.6

Figure 3. Temporal Evolution of Hydroxyl Radical Production During UV-Based Treatments

Table 4. Toxicity Assessment of Treated PS-NP Solutions

Sample	Inhibition Rate (%)	EC20 (min)	EC50 (min)	Toxicity Classification
Control (Untreated)	1.98 ± 0.31	>360	>360	Non-toxic
Ozonation (240 min)	45.6 ± 4.2	85 ± 7	260 ± 18	Moderately Toxic
Chlorination (240 min)	12.3 ± 1.8	290 ± 22	>360	Low Toxicity
UV/PMS (360 min)	98.19 ± 1.54	8 ± 1	38 ± 3	Highly Toxic
UV/NaClO (360 min)	2.97 ± 0.42	>360	>360	Non-toxic

Table 4 presents the toxicity assessment results for PS-NP solutions following different treatment conditions, revealing striking differences in biological effects. The control (untreated) PS-NP solution exhibited minimal inhibition (1.98%), consistent with previous reports that pristine PS-NPs

have limited acute toxicity to luminescent bacteria. This finding suggests that the polymer particles themselves are relatively inert in this bioassay, although this does not preclude other toxicological effects.

UV/PMS treatment resulted in the highest inhibition rate (98.19%), indicating that the degradation intermediates generated under this condition are highly toxic to V. fischeri. The EC20 (8 minutes) and EC50 (38 minutes) values further confirm the rapid development of toxicity, suggesting that toxic products accumulate during the early stages of treatment and persist throughout the 360-minute exposure. This finding is alarming, as it indicates that aggressive oxidation with PMS, while achieving high mineralization rates (63.9%), may generate transformation products with substantially greater biological activity than the parent Nano-plastics (Figure 4).

Ozonation showed moderate toxicity (45.6% inhibition), with EC20 of 85 minutes and EC50 of 260 minutes. This intermediate toxicity level reflects the formation of oxygenated aromatic compounds and carboxylic acids that are more reactive with biological systems than the parent polymer. The delayed toxicity development compared to UV/PMS suggests that toxic product formation occurs more gradually during ozonation, potentially allowing for further degradation of these intermediates with extended treatment [30].

UV/NaClO exhibited the lowest toxicity among treatments (2.97% inhibition), comparable to the control. This is surprising given the substantial molecular weight degradation observed (82.4%) and suggests that NaClO-generated intermediates are relatively non-toxic to luminescent bacteria. However, the low mineralization efficiency raises concerns that degraded polymer fragments may persist in the treated water as non-bioavailable but potentially bio accumulative species.

Chlorination showed low toxicity (12.3% inhibition), consistent with the limited polymer breakdown observed. The detection of chlorinated aromatic products (Table 2) suggests that while acute toxicity may be low, chronic and mixture toxicity effects warrant further investigation.

The dramatic variation in toxicity across treatments highlights the critical importance of considering biological effects in addition to degradation efficiency when evaluating nano plastic treatment strategies. UV/PMS, while achieving the highest mineralization, produces the most toxic intermediates, raising fundamental questions about the net environmental benefit of this approach.

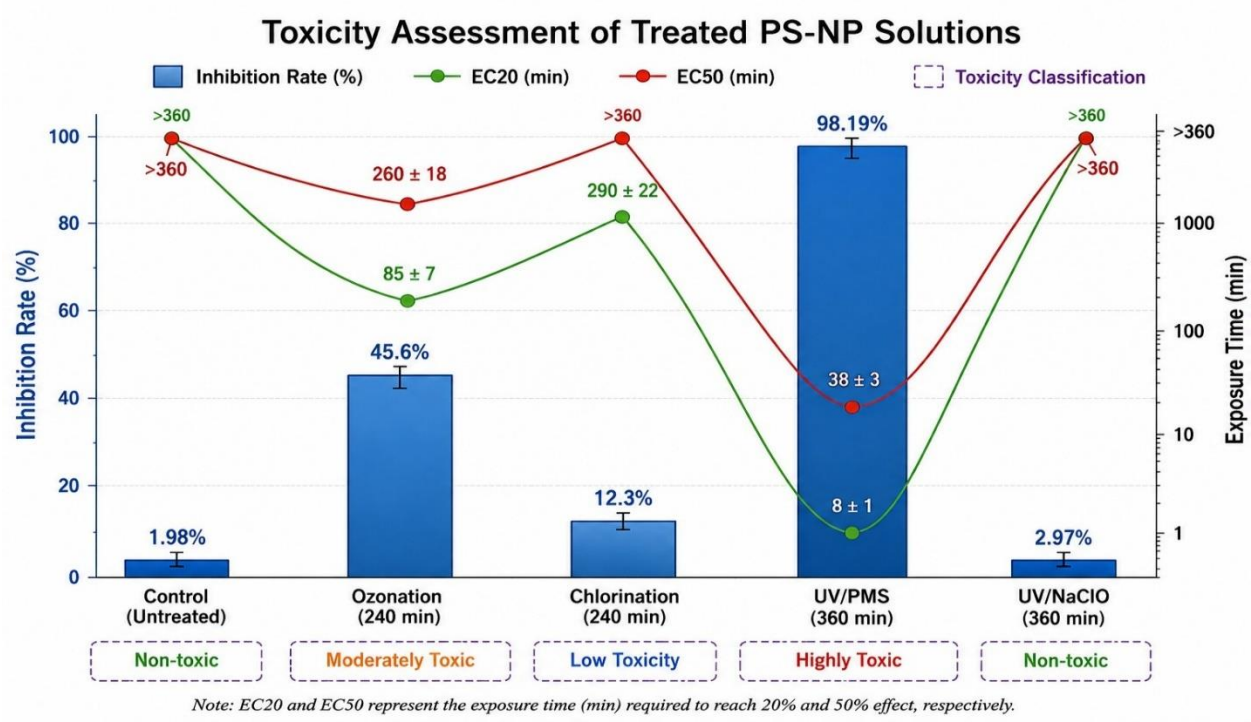

Figure 4. Toxicity Assessment of Treated PS-NP Solutions

Discussion

The results of this study provide critical insights into the formation of secondary oxidation products from Nano-plastics during drinking water treatment and their associated toxicity implications. The findings reveal a fundamental trade-off between degradation

efficiency and byproduct toxicity that must be carefully considered in treatment process selection and optimization.

The superior degradation performance of ozonation and UV/PMS compared to chlorination and UV/NaClO is consistent with the higher oxidation potentials of hydroxyl and sulfate radicals relative to chlorine species [31]. However, the correlation between degradation efficiency and toxicity is not straightforward. While ozonation achieved near-complete molecular weight degradation and 42.7% mineralization, it generated moderately toxic intermediates [32]. UV/PMS, with the highest mineralization rate (63.9%), paradoxically produced the most toxic solution [33]. This counterintuitive finding suggests that the mineralization process itself generates reactive intermediates that accumulate during treatment and exert biological effects.

The formation mechanism of toxic intermediates likely involves the stepwise oxidation of polystyrene aromatic rings to generate oxygenated products with enhanced biological reactivity. The identification of phenol, acetophenone, and benzophenone (Table 2) is particularly concerning, as these compounds are known to exhibit oxidative stress and endocrine-disrupting effects. The presence of these compounds in treated water raises questions about the suitability of advanced oxidation for drinking water applications where complete mineralization cannot be assured.

The observation that Nano-plastics can act as secondary sources of reactive oxygen species adds a further layer of complexity. The self-promoted production of hydroxyl radicals by PS-NPs during UV treatment suggests that Nano-plastics are not merely passive substrates but can actively influence treatment chemistry. This behavior may promote degradation but could also enhance the formation of secondary organic products through radical chain reactions that are difficult to predict or control.

The toxicity of halogenated products generated during chlorination is a particular concern given the widespread use of chlorine as a disinfectant. While chlorination showed low acute toxicity in the luminescent bacteria assay, the formation of chloroethylene and other halogenated aromatic compounds raises the possibility of long-term health effects through bioaccumulation and chronic exposure [34]. Similarly, the detection of chlorinated dimers suggests that polymer fragments retain some structural integrity while incorporating reactive chlorine atoms, potentially altering their environmental behavior and toxicity.

The current study has several limitations that should be acknowledged. First, the experiments were conducted with pristine PS-NPs under controlled laboratory conditions, which may not fully represent the behavior of environmentally aged Nano-plastics with adsorbed contaminants and surface modifications. Future work should investigate the transformation of weathered Nano-plastics and the influence of natural organic matter on degradation pathways and byproduct formation. Second, the toxicity assessment was limited to acute effects on luminescent bacteria, and the chronic, mixture, and intergenerational toxicities of nano plastic-derived DBPs remain largely unexplored. The dramatic increase in inhibition rate from 1.98% (control) to 98.19% (UV/PMS) highlights the need for comprehensive toxicological evaluation to support risk assessment and regulatory development.

The implications of these findings for drinking water treatment practice are significant. Currently, there are no regulatory standards specific to Nano-plastics or nano plastic-derived DBPs in drinking water, and monitoring programs do not routinely assess these contaminants [35]. The detection of toxic degradation products suggests that existing regulatory frameworks may be inadequate to ensure drinking water safety in the presence of nano plastic contamination. The development of enhanced treatment strategies that address both nano plastic removal and byproduct toxicity is urgently needed. Potential approaches include optimizing AOP conditions to minimize toxic intermediate accumulation, implementing post-treatment adsorption to remove persistent byproducts, and developing real-time toxicity monitoring systems for process control.

Conclusion

This study provides comprehensive evidence that secondary oxidation products formed from Nano-plastics during drinking water treatment processes may pose substantial toxicity risks that are not captured by conventional degradation efficiency metrics. The key findings are as follows:

1. **Treatment efficacy varies dramatically with oxidant selection.** Ozonation and UV/PMS achieve greater molecular weight degradation (99.9% and 95.8%, respectively) and mineralization (42.7% and 63.9%) compared to chlorination and UV/NaClO, reflecting the higher oxidation capacity of hydroxyl and sulfate radicals.
2. **Secondary oxidation products are consistently formed across all treatment conditions.** Identified products include aromatic compounds, carboxylic acids, ketones, and halogenated derivatives, with product profiles varying by treatment type. The formation of phenol, acetophenone, benzophenone, and chlorinated intermediates raises concerns about the safety of treated water.
3. **Toxicity is not correlated with degradation efficiency.** UV/PMS, which achieved the highest

mineralization rate, generated the most toxic intermediates (98.19% inhibition of *V. fischeri* luminescence), while UV/NaClO showed low toxicity but poor mineralization. This trade-off must be considered in treatment process design.

4. **Hydroxyl radical production dynamics influence degradation pathways and toxicity.** UV/PMS generated substantially higher •OH concentrations (23.1 μM at 360 min) than UV/NaClO (6.3 μM), driving more extensive degradation but also promoting the formation of toxic intermediates. Control of radical generation kinetics may enable optimization of treatment outcomes.

5. **Knowledge gaps persist regarding chronic and mixture toxicity.** While acute toxicity data indicate significant biological effects of treatment intermediates, the long-term health implications of nanoplastic-derived DBPs through chronic exposure and combined effects with co-contaminants remain poorly characterized.

6. **Integrated treatment strategies are urgently needed.** The current regulatory framework for drinking water does not adequately address nanoplastic contamination or byproduct formation. Development of monitoring protocols, risk assessment methodologies, and treatment technologies that address both nanoplastic removal and byproduct safety is essential for protecting public health in the plastic age.

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Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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