

Article

Degradation of Polystyrene Nanoplastics in UV/NaClO and UV/PMS Systems: Insights into Degradation Efficiency, Mechanism, and Toxicity Evaluation

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Abstract: Nanoplastics have gradually become a concern due to the wide use of plastics. Nanoplastics in aqueous phase can be exposed to users through water supply networks and cannot be efficiently removed by conventional water treatment processes. This work studied the degradation of polystyrene nanoplastics (PS-NP) by two commonly used advanced oxidation systems: UV/NaClO and UV/peroxymonosulfate (PMS). Results showed that almost no turbidity was detected in the PS-NP solution (5.00 mg/L) after treated by both UV/NaClO and UV/PMS for 360 min, suggesting the excellent turbidity removal ability. Yet, scanning electron microscope (SEM) and total organic carbon (TOC) removal tests demonstrated that PS-NP could not be completely degraded by UV/NaClO. The mineralization rate using UV/NaClO was only 7.00% even when the NaClO concentration increased to 5.00 mM, and many PS-NP particles could still be observed in SEM images. By contrast, the mineralization rate reached 63.90% in the UV/PMS system under the identical experimental conditions, and no spherical particles appeared in the SEM results. Density functional theory (DFT) calculations revealed that the different reaction sites and energy barriers of $\text{SO}_4^{\bullet-}$ and $^{\bullet}\text{Cl}$ on PS-NP resulted in the differences in mineralization rates and degradation intermediates. The degradation pathway of PS-NP by UV/NaClO and UV/PMS was proposed accordingly. Additionally, the intermediates toxicity evaluation by a luminescent bacteria test showed that the inhibition rate in the UV/NaClO system (2.97%) was not markedly different from that in the control group without any treatment (1.98%); while that in UV/PMS system increased sharply to 98.19%. This work demonstrated that UV/PMS was more effective in PS-NP degradation than UV/NaClO, and the chemical risks of degradation intermediates were non-negligible.

Keywords: nanoplastics; polystyrene degradation; mechanisms; DFT calculation; toxicity assessment

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1. Introduction

Plastic debris in the environment is an increasingly serious and growing global concern. An increasing mass of plastics has been found in natural waters around the world because of the immoderate discharge of plastic waste [1]. However, only 9% of these wastes were recycled, and over 79% of them were released into the environment or land-filled. It's predicted that 12,000 million tons of plastic wastes will be discharged into the environment by the year of 2050 [2]. The half-life period of plastics are estimated to be tens or even hundreds of years [3]. Large pieces of plastics in the environment can be fragmented into microplastics (1 μm –5 mm) and nanoplastics (1–1000 nm) under mechanical crushing, UV irradiation, hydrolysis, oxidation, and biological breakdown [4]. Nanoplastics have been found in sea water, fresh water, soil, food, and organisms [5]. Compared to microplastics, nanoplastics may cause severe ecological risks due to their large specific surface area, high colloidal stability, and mobility, facilitating them to adsorb coexisting environmental

contaminants including heavy metals and organics. Additionally, their smaller size allows them to easily penetrate into cells. At the same concentration, the number of nanoplastics with a size of 100 nm was 10^9 times that of microplastics with a size of 100 μm . Nevertheless, traditional water treatment processes failed to efficiently remove nanoplastics from aqueous phase [6]. That is, nanoplastics can reach to all the residents through urban water supply networks. Consequently, it's urgent to find a feasible and effective way to eliminate nanoplastics from water.

Advanced oxidation processes (AOP) generating strongly oxidative species have been introduced as an effective approach to degrade refractory organic contaminants from aqueous solutions. UV and chlorine are extensively applied for disinfection in drinking water treatment process [7]. The combined use of UV and chlorine (UV/chlorine) has been proposed as a powerful disinfection technology [8]. It can produce reactive species of $\bullet\text{OH}$ and $\bullet\text{Cl}$ [9], displaying a strong oxidation ability [10]. Peroxymonosulfate (PMS) based AOPs that can yield free radicals of $\text{SO}_4\bullet$ and $\bullet\text{OH}$ has attracted increasing attention for the elimination of organic compounds by virtues of a strong oxidization ability and wide pH tolerance [11]. Homogeneous catalysts including transition metals of Co^{2+} , Fe^{2+} , Mn^{2+} , and Cu^{2+} are efficient PMS activators [12]. Yet, the post-separation from treated water and accumulation of waste sludge greatly hindered its practical application. Recent studies have shown that photocatalysis assisted PMS activation could be simple and energy-saving without external chemicals requirement [13] and have a high removal efficiency for trace organic contaminants in water [14]. Although progress in the UV/chlorine and UV/PMS processes has successfully been made in treating organics-polluted water, using the two techniques to remove nanoplastics has rarely been reported to date. Especially, the underlying mechanisms involved in nanoplastics degradation by UV/chlorine and UV/PMS remains ambiguous.

As can be seen in Table 1 [15], few studies have been done to remove nanoplastic from water, and there are still many limitations. Effective methods for degrading nanoplastic in drinking water treatment need to be discovered. No literature related to the treatment of nanoplastics by UV/chlorine and UV/PMS was found herein; UV/ NaClO and UV/PMS were employed to degrade nanoplastics from aqueous solutions. Polystyrene nanoplastics (PS-NP) was selected as the representative nanoplastics, as polystyrene is one of the most extensively used plastic products with an annual production rate of multiple million tons [16]. The main objectives of this study are: (i) to investigate the removal ability of PS-NP by UV/ NaClO and UV/PMS in terms of different affecting factors in an aquatic environment, i.e., oxidant concentration, PS-NP concentration, solution pH, coexisting anions, and NOM concentration; (ii) to unveil the mechanisms of PS-NP degradation by UV/ NaClO and UV/PMS using density functional theory (DFT) calculations; and (iii) to examine the toxicity of degradation intermediates.

Table 1. Removal strategies of nanoplastics from water.

Removal Strategies	Type of Material	Time	Removal Efficiency (%)	Limitations	Reference
Filtration	0.22 μm syringe filter 3 μm Whatman filter	10 min	32 ± 12 92 ± 3	Larger nanoplastics can retain in the fractions and are not suitable for larger particles.	[17]
Ultrafiltration	0.45 μm Express PLUS PES filters	27 min	74.0	The particle may escape from the treatment and the time duration is also poor.	[18]
Flocculation	150 rpm impeller rotational speed	50 min	77 ± 15	Design parameters have to improve with studies and the order of reaction should be high.	[19]
Centrifugation	10,000 rpm speed with various steps	15 min	98.41	This process takes a longer duration to remove the plastics.	[20]
Photocatalytic reaction	UV rays	27 min	17.1 ± 0.55	Phototransformation of nanoplastics could be different and photoreactive activity can be high in the water.	[21]

2. Materials and Methods

2.1. Materials and Reagents

In this work, the size of nanoplastics is defined as 1–100 nm [22]. Polystyrene with a 50–100 nm diameter, NaCl, Na₂SO₄, and Na₂CO₃ were purchased from Aladdin, Inc. (Wallingford, CT, USA) Suwannee River NOM (Cat. 2R101N) was supplied by International Humic Substances Society (Denver, CO, USA). Sodium hypochlorite solution (NaClO, ~10% chlorine) was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Potassium peroxydisulfate was obtained from Sigma-Aldrich (St. Louis, MO, USA). All solutions were prepared using ultrapure water (18.2 MΩ cm) from a Milli-Q water purification system (Millipore, Burlington, MA, USA).

2.2. Experimental Procedure

All batch-type experiments were carried out in a 50.00 mL quartz tube at room temperature (25 °C). A 6 W low-pressure mercury UV lamp (GPH 150T5L/4, Heraeus Noblelight) emitting 254 nm light was fixed in the center of the reactor and surrounded by four quartz tubes. Generally, a quantitative amount of NaClO or PMS was added to 50.00 mL PS-NP solution, and then the UV lamp was turned on to start the degradation reaction. Within a certain time interval, a certain amount of water sample was withdrawn to test the turbidity and then returned to the tube. All experiments were conducted at least 3 times, and the relative standard deviation of different batches was usually less than 5.00%.

The photonic intensity per volume of water (I_0) and the effective light path length (L) were determined as 2.3×10^{-6} Einstein L⁻¹ s⁻¹ and 6.2 cm, respectively, corresponding to a photon fluence rate of 1.43×10^{-8} Einstein cm⁻² s⁻² and a UV intensity of 6.72 mW cm⁻² [23].

2.3. Analytical Methods

The concentration of PS-NP was determined by a turbidimeter (WGZ-200) from Shanghai INESA Physico-Optical Instrument Co., Ltd. (Shanghai, China). Solution pH was recorded by a pH meter (Thermofisher model: 8103BN, Waltham, MA, USA). The degradation products were determined using a positive electrospray ionization (ESI) HPLC (1290)-triple quadrupole MS (6460, Agilent, Santa Clara, CA, USA). Surface morphology was recorded by a scanning electron microscope (ZEISS Sigma 300, Jena, Germany). Total organic carbon (TOC) of the solution was measured by a TOC analyzer (Shimadzu, Kyoto, Japan). The toxicity was measured by a microplate multimode reader (Glomax Multi, Madison, WI, USA).

2.4. Theoretical Computation Methods

Theoretical calculations were performed using Gaussian 16 D.01 software [24]. It was reported that the B3LYP-D3BJ method in Gaussian software was suitable for calculating organic systems [25]. Thus, the B3LYP-D3BJ method with a 6-31 g(d,p) basis set was applied for geometrical optimization and vibrational frequencies calculations. The B3LYP-D3BJ method with a 6-31 g(d,p) basis set was applied for energy calculations based on the optimized structures to get more precise results. Intrinsic reaction coordinate (IRC) calculations were performed to confirm that each transition state connected with the reactants and the products.

According to transition state theory, approximate reaction rate constants for elementary reactions could be estimated based on the Eyring-Polanyi equation as follows [26]:

$$K_{TST} = (k_B T / h) \exp(-\Delta G^\ddagger / RT)$$

where k_B is the Boltzmann constant, T (K) is the reaction temperature, h is Planck's constant, R is the molar gas constant, and $\Delta G^\ddagger$ (unit: kcal/mol) is the corrected solvation activation free energy. This shows that ΔG and K_{TST} are inversely proportional. The higher the free energy barrier (ΔG) value, the more difficult this reaction will occur.

3. Results and Discussion

3.1. Turbidity Removal of PS-NP

Initially, PS-NP removal by UV/PMS, UV/NaClO, UV, PMS, and NaClO were performed as depicted in Figure 1. Turbidity variation of the PS-NP solution was recorded to represent the removal of PS-NP in different oxidation systems. As seen, the turbidity barely changed when PMS and NaClO presented alone, suggesting that PMS or NaClO could not efficiently remove PS-NP. In contrast, the turbidity removal rate in systems of UV/PMS and UV/NaClO were 94.30% and 78.20% in 360 min of reaction time under the identical experimental conditions. This could be attributed to the formed highly reactive species of $\text{SO}_4^{\bullet-}$ (2.5–3.1 V) [27], $\bullet\text{Cl}$ (2.4 V) [28], and $\bullet\text{OH}$ (1.8–2.7 V) [29], which could efficiently decompose nanoparticles.

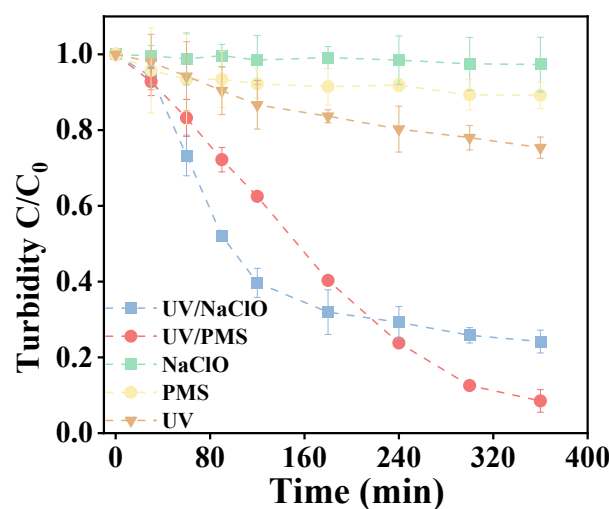


Figure 1. Turbidity variation of PS-NP degradation by systems of UV/PMS, UV/Cl, UV, PMS, and NaClO.

The factors affecting the turbidity removal of PS-NP in the UV/NaClO and UV/PMS systems were further studied in Figure 2. Figure 2a,b shows the influence of NaClO and PMS concentrations (1.25, 2.50, and 5.00 mM). In the UV/NaClO system, as expected, in 360 min of reaction time, the turbidity removal rate increased gradually from 63.41% to 94.52% with the increase of NaClO dosage from 1.25 to 5.00 mM. It slowed down after 180 min, which could be related to the complete consumption of chlorine. By contrast, in the UV/PMS system, 5.00 mM of PMS achieved a complete turbidity removal in 180 min (Figure 2b). This clearly suggested the superior performance of UV/PMS than UV/NaClO in PS-NP removal. As can be seen in Figure 2b, when the concentration of PMS increased, the reaction reached equilibrium faster. When the PMS concentration decreased to 1.25 mM, the reaction proceeded very slowly, and PS-NP could not be completely degraded within 6 h. When changing the concentration of PS-NP in Figure 2c,d, there was a similar trend in the UV/NaClO and UV/PMS systems. PS-NP was degraded faster at low concentrations, and slower at high concentrations. When the concentration of PS-NP reached 50 mg/L, neither UV/PMS nor UV/NaClO could achieve a high turbidity removal rate (72.85% for UV/PMS and 65.92% for UV/NaClO).

The solution pH is an important factor affecting the performance of AOPs as it can influence the speciation of pollutants and oxidants. In this work, the influence of initial solution pH on PS-NP removal was studied at pH values of 3, 5, 7, 9, and 11 as depicted in Figure 2e,f. In both systems, pH showed a very limited influence on turbidity removal of PS-NP. In the pH range of 3–11, the removal maintained within 75.80% to 79.00% for UV/NaClO and 91.42% to 96.49% for UV/PMS in 360 min of reaction time.

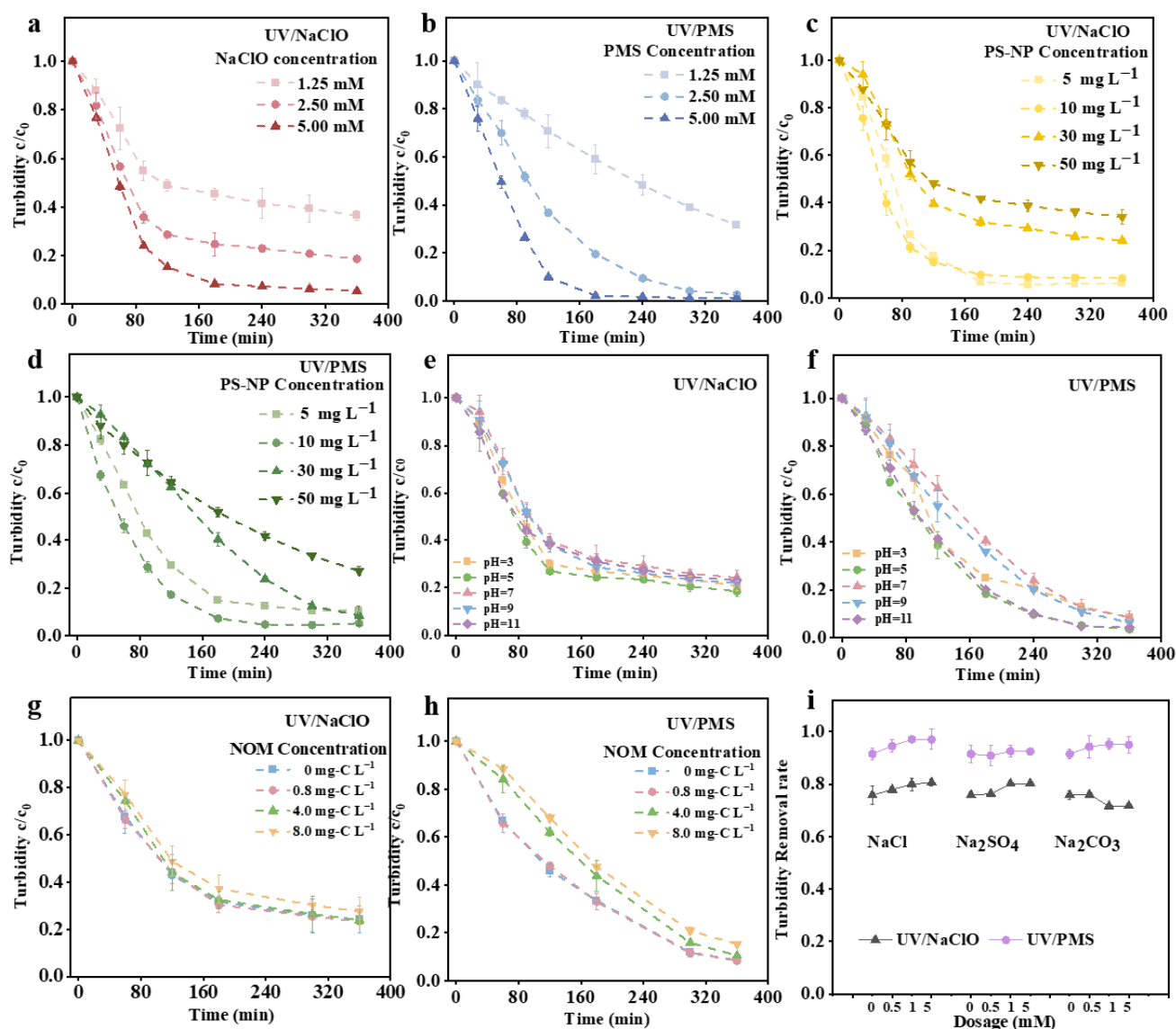


Figure 2. Effect of (a) NaClO and (b) PMS concentration on turbidity removal by UV/NaClO and UV/PMS; effect of PS-NP concentration on turbidity removal by (c) UV/NaClO and (d) UV/PMS; effect of initial solution pH on turbidity removal by (e) UV/NaClO and (f) UV/PMS; effect of NOM concentration on turbidity removal by (g) UV/NaClO and (h) UV/PMS; (i) effect of Cl^- , SO_4^{2-} , and CO_3^{2-} on turbidity removal by UV/NaClO and UV/PMS.

Figure 2g,h shows the effect of NOM on the removal of PS-NP. Low concentration of NOM (0, 0.80, and 4.00 mg-C L⁻¹) had little effect on the performance of the UV/NaClO system. Only when the NOM concentration was increased up to 8.00 mg L⁻¹, the turbidity removal decreased from 78.20% to 72.43%. This can be attributed to that NOM and PS-NP were competitive [30], and part of the chlorine and generated radicals were consumed by the reductive NOM. While in the UV/PMS system, the turbidity variation curves showed that the removal rate in the initial 180 min was slower when the concentration of NOM was set at 4 and 8 mg-C-L⁻¹. The phenomenon indicated that at the beginning, NOM competed with PS-NP to consume some of the free radicals. After 180 min, NOM was degraded completely, and the turbidity removal rate became as fast as the control sample due to the excessive dosage of PMS. Figure 2i shows the impact of three widely coexisting ions (Cl^- , SO_4^{2-} , and CO_3^{2-}) on the turbidity removal in PS-NP solution. The turbidity removal remained relatively stable when 0.50–5.00 mM of Cl^- , SO_4^{2-} , or CO_3^{2-} appeared. The

result suggested the superior performance of UV/NaClO and UV/PMS when encountering the additional common interfering anions and NOM in practical application.

3.2. Mineralization of PS-NP in Different Oxidation Systems

As the turbidity of water samples would decrease when large nanoparticles were decomposed into smaller particles, the real degradation rate of PS-NP needs to be further explored. Accordingly, the mineralization rate of water samples was determined via TOC removal tests as well. Figure 3 displays the TOC variations of PS-NP in oxidation systems of UV/PMS, UV/NaClO, UV, PMS, and NaClO. Consistent with the turbidity removal results in Figure 1, the TOC of PS-NP solution remained unchanged with the treatment of UV, PMS, and NaClO. However, after treatment by UV/PMS for 360 min, the TOC removal efficiency reached 63.90%, which was lower than the turbidity removal rate (94.30%) under the identical experimental conditions. In other words, although the turbidity decreased as PS-NP were degraded into smaller particles, PS-NP was not fully mineralized. Surprisingly, it's worth noting that a huge gap could be observed between turbidity removal (78.20%) and TOC removal (7.00%) in the UV/NaClO system.

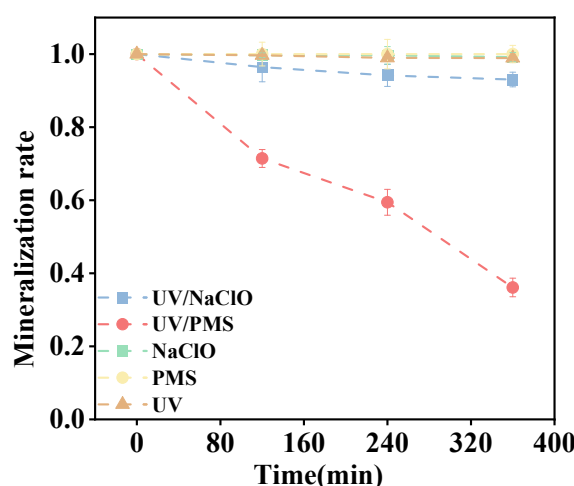


Figure 3. Mineralization rate of UV/PMS, UV/NaClO, UV, PMS, and NaClO for PS-NP degradation.

Figure 4 illustrates influences of oxidant concentrations, PS-NP concentrations, initial solution pH, coexisting anions, and NOM on the mineralization of PS-NP by the UV/NaClO and UV/PMS systems. As seen in Figure 4a, the improvement of NaClO concentration from 1.25 to 5.00 mM in solution did not lead to a significant increase in the mineralization rate of PS-NP by the UV/NaClO system. In contrast, the UV/PMS system achieved a higher mineralization rate: 80.56% in the presence of 5.00 mM PMS. A similar trend was also observed in Figure 4b–e. Comparison of Figures 3 and 4 suggested that UV/NaClO failed to mineralize PS-NP. PS-NP existing as smaller particles in water after UV/NaClO treatment would be more difficult to remove, thus posing greater risks.

Further, SEM images were recorded to examine the morphology and particle size change of PS-NP with or without the treatment by UV/NaClO and UV/PMS. As shown in Figure 5a, PS-NP exhibits a regular spherical shape, and the average diameter of PS-NP is 79.20 nm. Obviously, although the average particle size of PS-NP declined greatly to ~26.20 nm after treatment with UV/NaClO, many nanoparticles could still be observed in Figure 5b. By contrast, nearly no spherical particle in solution showed up in the UV/PMS system. This observation matched well with the results of turbidity and TOC removal, directly indicating that PS-NP could not be fully degraded by UV/NaClO.

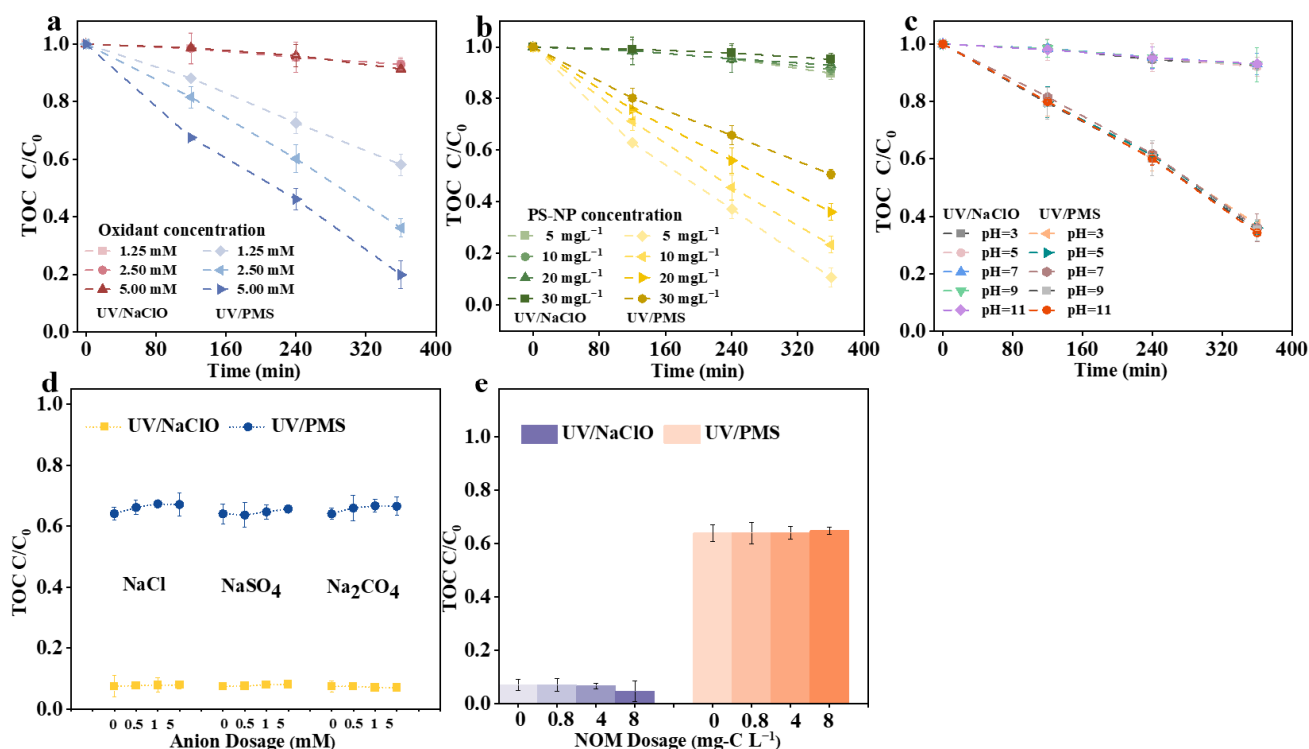


Figure 4. (a) Effect of oxidant concentrations on the mineralization of PS-NP by the UV/NaClO and UV/PMS systems; (b) effect of PS-NP concentrations on the mineralization of PS-NP by the UV/NaClO and UV/PMS systems; (c) effect of initial solution pH on the mineralization of PS-NP by the UV/NaClO and UV/PMS systems; (d) effect of Cl^- , SO_4^{2-} , and CO_3^{2-} on the mineralization of PS-NP by the UV/NaClO and UV/PMS systems; (e) effect of NOM concentrations on the mineralization of PS-NP by the UV/NaClO and UV/PMS systems.

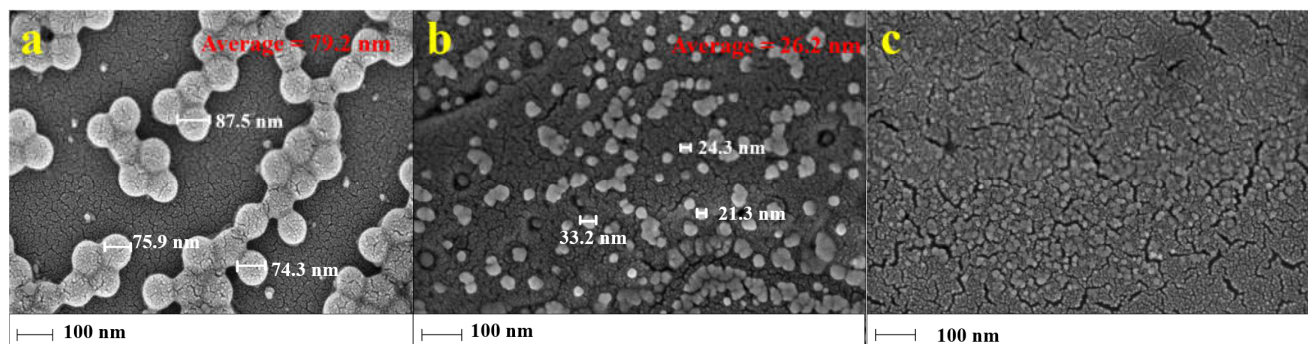


Figure 5. Surface morphology of PS-NP in aqueous phase: (a) without treatment; (b) treated by UV/NaClO; and (c) treated by UV/PMS.

3.3. Degradation Mechanisms and Pathway of PS-NP by UV/PMS and UV/NaClO

To understand degradation mechanisms of PS-NP in the UV/PMS and UV/NaClO systems, quantum chemical computations were conducted. As we know, the main difference between the two oxidative systems is that $\text{SO}_4^{\bullet-}$ is generated by UV/PMS and $\bullet\text{Cl}$ is produced by UV/NaClO. Thus, considering the symmetry structure of PS-NP, ΔG values for $\text{SO}_4^{\bullet-}$ and $\bullet\text{Cl}$ reacting at possible sites (marked as ①, ②, and ③ in Figure 6) were calculated. As for $\bullet\text{Cl}$, the ΔG values reacting at site ① and ② were determined as 11.6 and 5.7 kcal mol⁻¹. The reaction between $\bullet\text{Cl}$ and site ③ did not occur. With regard to $\text{SO}_4^{\bullet-}$, the energy at site ①, ②, and ③ were 10.3, 7.4, and 15.2 kcal mol⁻¹, respectively. As depicted in Figure 6, the reactions at site ① and ② were hydrogen atom abstraction (HAA) reaction, causing the formation of HCl molecules. In the meantime, radicals would

transfer to the PS-NP chains, and the unstable PS-NP radicals would further react with other organic compounds, leading to the chain break. The reaction at site ③ was radical adduct formation (RAF) reaction. $\text{SO}_4^{\bullet-}$ could add into the site, resulting in the benzene ring opening.

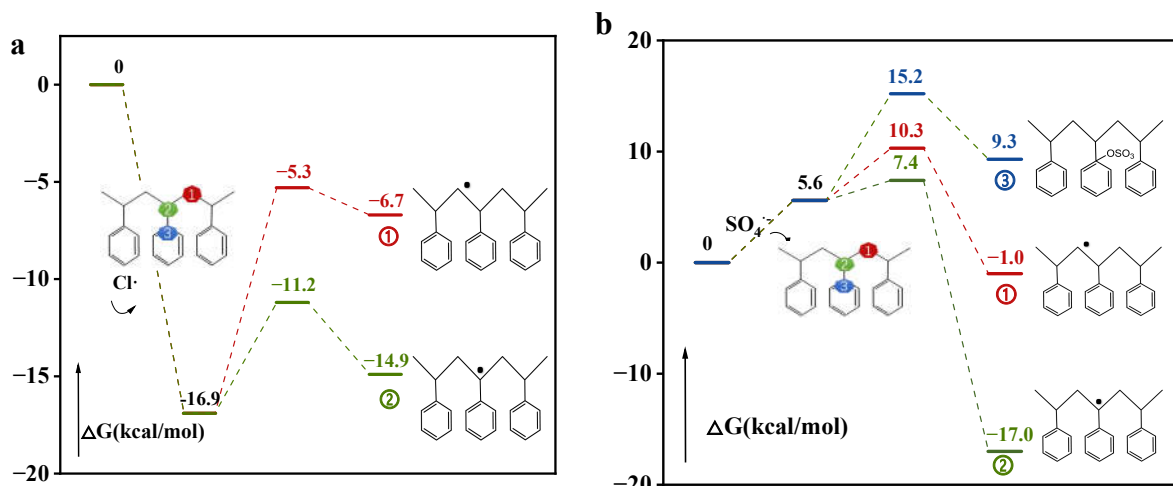
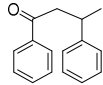
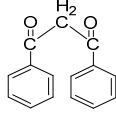
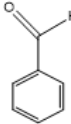
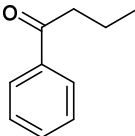
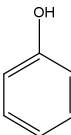
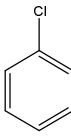
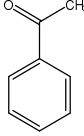
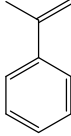
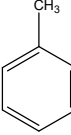
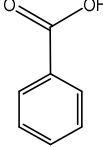


Figure 6. Free energy barrier of (a) $\bullet\text{Cl}$ and (b) $\text{SO}_4^{\bullet-}$.

Based on the DFT calculations, the long chains of PS-NP could be destroyed by $\bullet\text{Cl}$ and $\bullet\text{OH}$ generated in the UV/NaClO system, which degraded PS-NP particles into smaller ones and caused the turbidity decrease. However, as the reaction at site ③ could not happen, the stable aromatic structure would not be further decomposed, which caused the unchanged mineralization rate. By contrast, UV/PMS could open the benzene ring of PS-NP, resulting in a much higher mineralization rate. Generally, the ΔG values for these radical reactions were relatively low, which clarified the satisfactory degradation rate of PS-NP in advanced oxidation processes.

In addition, the degradation intermediates of PS-NP in the UV/NaClO and UV/PMS systems were determined using HPLC analysis as summarized in Table 2 and Figure S1. The corresponding degradation pathways were proposed in Figure 7. According to Figure S1, fourteen intermediates were detected. Affected by the electron cloud on the benzene ring, the carbon connected to the benzene ring was in a half electron losing state. So free radicals could attack the carbon connected to the benzene ring on the carbon chain first (at site ②) and destroy a small amount of C–C bonds in the main chain to produce shorter chains polymers of P1 ($m/z = 224$) [31]. The tertiary carbon sites would be attacked by $\bullet\text{OH}$ to yield P2 ($m/z = 224$), P4 ($m/z = 148$), terminal carbonyl groups, and eventually to acetophenone (P3, $m/z = 106$), phenol (P5, $m/z = 94$), and P8 ($m/z = 120$) etc. [31]. For the UV/NaClO system, $\bullet\text{Cl}$ could react with P5 to form P6 ($m/z = 112$) and P7 ($m/z = 78$). However, the reaction at site ② resulted in the generation of P9 ($m/z = 106$), then P10 ($m/z = 92$) and P11 ($m/z = 122$). The toluene could be oxidized by $\text{SO}_4^{\bullet-}$ via electron transfer from the electron-rich methyl groups, forming a carbon radical cation and producing benzoic acid (P11) [32]. The benzoic acid would be attacked by $\text{SO}_4^{\bullet-}$ to take place a ring cleavage reaction to produce P12 ($m/z = 57$), P13 ($m/z = 58$), and P14 ($m/z = 46$) [33]. And $\bullet\text{OH}$ produced in the catalytic system could also cleave aromatic rings via Criegee-type reactions [34].

Table 2. Mass spectrometry data for the identification of intermediates.

Compound List	Molecular Formula	Chemical Structure	ESI(+)MS <i>m/z</i>
P1	C ₁₆ OH ₁₆		224
P2	C ₁₅ O ₂ H ₁₂		224
P3	C ₇ OH ₆		106
P4	C ₁₀ OH ₁₂		148
P5	C ₆ OH ₆		94
P6	C ₆ ClH ₅		112
P7	C ₆ H ₆		78
P8	C ₈ OH ₈		120
P9	C ₈ H ₁₀		106
P10	C ₇ H ₈		92
P11	C ₇ O ₂ H ₆		122
P12	C ₂ O ₂ H	CH ₃ COOH	57
P13	C ₃ OH ₆	CH ₃ COCH ₃	58
P14	CO ₂ H ₂	HCOOH	46

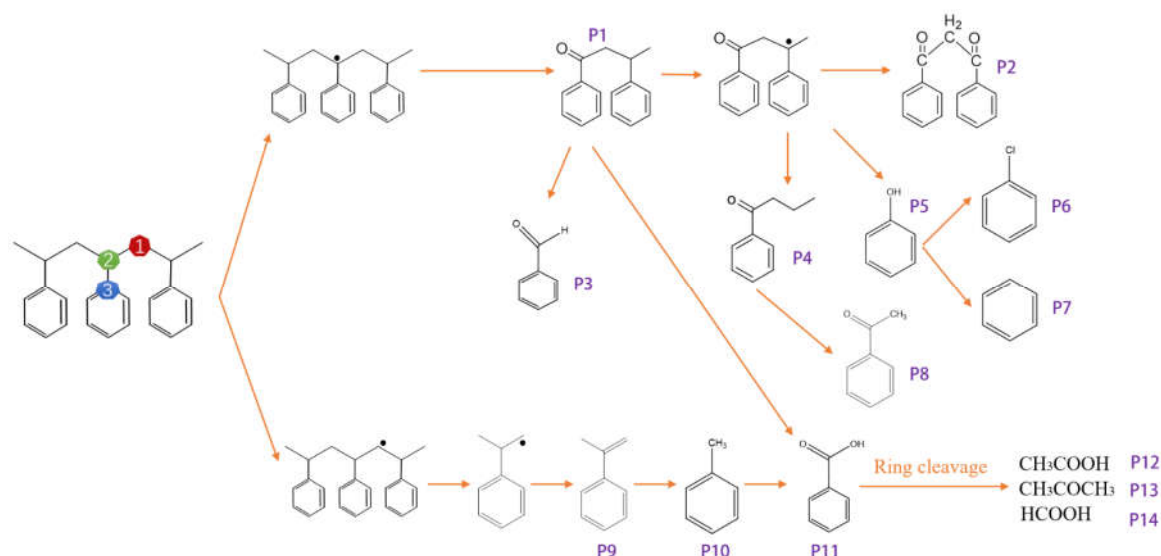


Figure 7. Proposed degradation pathways of PS-NP.

3.4. Toxicity Assessment of Degradation Intermediates

Currently, the main hazards of nanoplastics in water are thought to be chronic toxicity and long-term effects after absorption by human beings [35]. Thus, the toxicity of degradation intermediates formed in UV/NaClO and UV/PMS systems were assessed for the purpose of practical application. As shown in Figure 8, the acute toxicity of PS-NP solution after treated by UV/NaClO and UV/PMS were determined by a luminescent bacteria test. Luminescent bacteria can be inhibited by toxic compounds, and higher toxicity usually results in a higher inhibition rate. To avoid the inhibition of cellular activity by excess oxidants, the withdrawn water samples were quenched after degradation tests. The inhibition rate of PS-NP solution without any treatment was determined as 1.98%, suggesting a very limited acute toxic of PS-NP to luminescent bacteria. After treating by UV/NaClO and UV/PMS, the inhibition rates changed to 2.97% and 98.19%, respectively. This indicated that the toxicity of intermediates formed in the UV/PMS system could be more toxic than the parent PS-NP, even though the mineralization rate was high enough to fully oxidize PS-NP into small molecules.

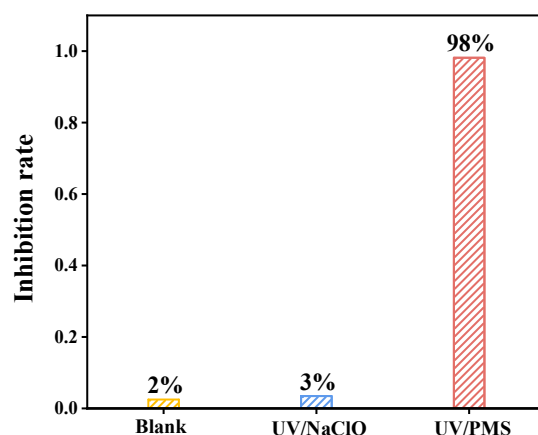


Figure 8. Inhibition rate of luminescent bacteria test.

Ecological structure activity relationship (ECOSAR) program was also carried out to analyze the toxicity of several common intermediates in two oxidative systems. As listed in Table 3, the LC50 values of P11 (benzoic acid) for fish, daphnia, and green algae were determined as 1300.78, 730.08, and 518.37 mg/L, respectively. According to the standard stipulated by the Globally Harmonized System of Classification and Labelling of Chemicals

(GHS) (Table 4), benzoic acid cannot be classified as harmful. Yet, the LC50 and EC50 values of some of the degradation intermediates including benzene, toluene, and phenol were lower than 10.00 mg/L, and these chemicals can be classified as toxic. The result indicated that although UV/PMS successfully degraded PS-NP, the intermediates' toxicity was non-negligible in practical application.

Table 3. Predicted bio-toxicity of degradation intermediates of PS-NP by ECOSAR.

Common Product	Fish (LC50, 96 h)	Daphnia (LC50, 48 h)	Green Algae (EC50, 96 h)
Butyrophenone	31.37	18.92	18.11
Benzene	5.3	10.3	29
Toluene	31.7	3.8	9.4
Phenol	8.9	3.1	150
Benzoic acid	1300.78	730.08	518.37
Acetophenone	162	106.80	70.24

Table 4. Toxicity classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) ([36]).

Toxicity Range (mg/L)	Class
LC50/EC50 $\leq$ 1	Very toxic
1 < LC50/EC50 $\leq$ 10	Toxic
10 < LC50/EC50 $\leq$ 100	Harmful
LC50/EC50 > 100	Not harmful

4. Conclusions

This work studied the degradation of PS-NP by commonly used UV/NaClO and UV/PMS systems. Results showed that UV/PMS was more efficient for PS-NP degradation from aqueous solution than UV/NaClO. However, the treated solution should be given attention as the inhibition rate of luminescent bacteria caused by the degradation intermediates from the UV/PMS system was as high as 98%. The following conclusions can be drawn.

- (1) The UV/NaClO and UV/PMS systems achieved 78.20% and 94.30% turbidity removal in 360 min of reaction time. However, the corresponding mineralization rates were 7.00% and 63.90%, indicating that UV/NaClO could not completely mineralize nanoplastics into inorganic substances, but only decompose it into smaller organic molecules.
- (2) DFT calculation coupled with HPLC analysis proposed the degradation pathways of PS-NP in two oxidative systems. The different reaction sites and energy barriers of $\text{SO}_4^{\bullet-}$ and $\bullet\text{Cl}$ on PS-NP resulted in the differences between the mineralization rate and degradation intermediates.
- (3) Toxicity assessment of degradation intermediates showed that the inhibition rate of luminescent bacteria originated by the UV/NaClO and UV/PMS systems were 2.97% and 98.19%. This suggested that the acute toxicity of PS-NP degradation intermediates using UV/PMS should be given attention.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w15101920/s1>, Figure S1: Mass spectrum of PS-NP and its degradation intermediates.

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