

Article

Aged Polystyrene Microplastics Accelerate the Photo-Reduction of Chromium(VI)

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Abstract: Microplastics (MPs) and hexavalent chromium (Cr(VI)) are typical environmental pollutants, yet their interactions in aquatic systems remain poorly understood. This study investigates the mutual influence between Cr(VI) and both virgin and aged polystyrene microplastics (PS-MPs) under light conditions. Concentration kinetics revealed that the total chromium concentration remained stable across all systems, while Cr(VI) concentrations decreased over time, indicating that PS-MPs accelerate the reduction of Cr(VI) to Cr(III). Conversely, it had been found that Cr(VI) promoted the aging of PS-MPs, and this was evidenced by an increase in surface roughness and the generation of oxygen-containing functional groups. Cr(VI) led to a rise in the O/C ratio and carbonyl index, providing additional evidence for the aging of PS. Two-dimensional correlation spectroscopy (2D-COS) elucidated that under Cr(VI) exposure, the order of functional group alterations in PS and aged PS exhibited an opposite trend. Additionally, three-dimensional fluorescence spectroscopy revealed distinct changes in the fluorescence characteristics of leached substances from aged and pristine PS, both with and without Cr(VI), under light and dark conditions. These results furnish innovative understandings of environmental behavior and risks associated with the co-occurrence of MPs and heavy metals, highlighting the complex interplay between Cr(VI) and PS-MPs in aquatic environments.

Keywords: polystyrene microplastics; Cr(VI) reduction; photoaging; interaction



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1. Introduction

Plastics, renowned for their exceptional durability, flexibility, and processability, have become indispensable materials in modern human life [1]. Global plastic production soared to 390.7 million tons in 2021 [2], yet only a fraction of this is recycled [3]. Alarming, it is estimated that 4 to 12 million tons of plastics are discharged into aquatic systems annually, with projections suggesting that plastic waste will outweigh marine fish by 2050 [4]. Under natural conditions, prolonged mechanical abrasion, physicochemical processes, thermal exposure, and oxidative reactions fragment plastics into fine particles. These particles, defined as microplastics (MPs) when smaller than 5 mm [5], have permeated global ecosystems, including the atmosphere, oceans, soils, and biota [6,7]. MPs have the potential to bioaccumulate within food webs, and this can pose significant risks to human health, thereby attracting substantial scientific attention [8,9].

Notably, the diminutive size, extensive specific surface area, and pronounced hydrophobic nature [10] enable MPs to act as vectors for various environmental pollutants [11], including organic compounds, heavy metals, and antibiotics [12]. Among these pollutants, heavy metals are particularly pernicious inorganic pollutants [13]. MPs can adsorb heavy metals [14], facilitating their migration and engendering cumulative and synergistic toxic effects [15]. Environmental weathering processes, such as physical abrasion, thermal exposure, ultraviolet irradiation, and chemical oxidation, have a substantial impact on altering the physicochemical properties of MPs [16]. These changes include the incorporation of oxygen-containing functional groups [17] and modifications to surface morphological features [18,19], leading to the aging of MPs. Aged MPs typically exhibit enhanced adsorption capacities for metal ions compared to their pristine counterparts [20]. Consequently, elucidating the mechanisms through which MPs influence the migratory and transformative behaviors of heavy metals is crucial for environmental and health risk assessments.

Chromium (Cr), a prevalent heavy metal, exists primarily as Cr(III) and Cr(VI) in aquatic environments. Anthropogenic activities such as industrial metallurgy, coal combustion, pesticide application, tanning, and wood preservation are major sources of Cr(VI). Cr(VI) is notably more soluble, mobile [21], and toxic than Cr(III), posing significant carcinogenic risks to humans and aquatic organisms [22]. Recent studies have indicated that Cr is rapidly adsorbed onto MPs, with a higher affinity compared to other heavy metals [23]. The adsorption efficiency is influenced by MP type, solution pH, and temperature. However, the broader interactions between MPs and Cr remain underexplored. Polystyrene (PS) MPs, a ubiquitous thermoplastic polymer, serve as an ideal model for MP studies due to their chemical inertness, low moisture absorption, and widespread environmental occurrence [24]. Therefore, this study systematically investigates the mutual effects between Cr(VI) and PS-MPs, including both virgin and aged forms, under UV irradiation. By integrating advanced spectroscopic techniques (e.g., 2D-COS, XPS, and 3D-EEM) with kinetic modeling, this work elucidates the synergistic process governing Cr(VI)-MP co-behavior, offering novel perspectives on the environmental fate and risks associated with the combined pollution of MPs and heavy metals.

2. Materials and Methods

2.1. Materials and Chemicals

Granular PS-MPs exhibiting a mean particle size of $100.35 \pm 6.78 \mu\text{m}$ were obtained from Thai Petrochemical Industry Public Co., Ltd. (Bangkok, Thailand), and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, $\geq 99.8\%$) was purchased from Xilong Scientific Co., Ltd. (Shantou, China). All PS-MPs were homogenized through an 80-mesh stainless steel screen, followed by solvent cleaning with anhydrous ethanol and deionized water prior to the aging experiments. Then, part of the PS-MPs was aged in air for 5 days under ultraviolet (UV) light conditions and recorded as APS. All other relevant chemicals are detailed within Text S1.

2.2. Experimental Procedures

First, 0.8 g of PS and APS each was placed into separate special quartz tubes, each filled with 200 mL of deionized water under UV light conditions for 24 h, and recorded as PS (L) and APS (L), respectively. The same experimental groups as above were set up again, and Cr(VI) solution was added to them at a concentration of 100 μM and recorded as Cr(VI) + PS (L) and Cr(VI) + APS (L). The light reaction experiment was carried out in a closed reaction chamber. Meanwhile, dark control groups were set up and recorded as PS (D), APS (D), Cr(VI) + PS (D), and Cr(VI) + APS (D). All samples were regulated to pH 3.0 with 1.0 mol/L NaOH and 1.0 mol/L HNO_3 . Samples of the PS-MPs and solution were collected at 6, 12, and 24 h through a 0.45 μm filter membrane. Additionally, a pseudo-first-

order model was constructed to evaluate the Cr(VI) amount in the aging process and the first-order rate constant (k), derived from the linear regression slope, was employed to compare the reduction efficiency as follows:

$$\ln(C/C_0) = -kt \quad (1)$$

2.3. Filtrate Analysis

The concentration of Cr(VI) was measured through a UV-Vis spectrophotometer (GEN10S, Thermo Fisher, Waltham, MA, USA) at 540 nm, based on the purple complex of Cr(VI) and 1,5-diphenylcarbazide (DPC). An atomic absorption spectrophotometer (AAS, PinAAcle 900T, Perkin Elmer, Waltham, MA, USA) was used to analyze the total Cr. Moreover, a three-dimensional excitation emission matrix (3D-EEM) spectroscopy analysis of dissolved organic matters derived from the MPs (MP-DOM) was conducted through a fluorescence spectrometer (RF-6000, Shimadzu, Kyoto, Japan). The emission (Em) spectra were recorded across a wavelength range of 250 to 650 nm, with a step length of 5 nm, while the excitation (Ex) spectra were captured over a wavelength interval of 200 to 600 nm, also at a step length of 5 nm.

2.4. Characterization of MPs

X-ray diffraction (XRD, D8 Advance, Bruker, Karlsruhe, Germany) was utilized to achieve the crystallinity assessment of PS-MPs, and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher, Waltham, MA, USA) was employed to analyze the elemental composition present in PS-MPs, as well as oxygen-containing groups (Text S2). The functional groups were assessed using Fourier transform infrared (FTIR, Vetex70, Bruker, Karlsruhe, Germany) with spectral recordings made in the 4000–500 cm^{-1} region. The parameters included a resolution of 4 cm^{-1} and 64 scanning times. For the quantification of the aging extent of PS-MPs, the carbonyl index (CI) was calculated, involving comparing the absorbance values of carbonyl stretching vibration and methylene vibration within the FTIR spectra. Two-dimensional correlation spectroscopy (2D-COS) was conducted to describe the sequence of functional groups (Text S3). To analyze environmentally persistent free radical (EPFR) signals on the surface of the PS-MPs, electron paramagnetic resonance (EPR, EMXmicro-6/1/P/L, Bruker, Karlsruhe, Germany) was applied.

3. Results and Discussion

3.1. The Effect of PS-MPs on Cr(VI)

The interactive behavior of Cr(VI) with PS-MPs was investigated by monitoring the changes in total Cr and Cr(VI) concentrations under both dark and light conditions. As shown in Figure 1a, the total Cr concentration remained nearly constant across all reaction systems, indicating negligible adsorption of Cr by PS-MPs. However, the measured concentration of Cr(VI) underwent a continuous decline over time (Figure 1b). According to previous studies, Cr(VI) undergoes a reduction to Cr(III) under PS-MP mediation, rather than other Cr species such as Cr(II) or Cr^0 [25]. The reduction kinetics of Cr(VI) were fitted using a pseudo-first-order model (Figure 1c). The reduction efficiency of Cr(VI) under the addition of pristine PS ($0.69 \pm 0.17 \text{ min}^{-1}$) was significantly lower than that in the presence of APS ($2.04 \pm 0.41 \text{ min}^{-1}$) (Figure 1d), indicating that aging enhanced the reduction capacity of PS-MPs. Furthermore, under light conditions, the reduction rates of Cr(VI) mediated by pristine PS and APS increased to 5.73 ± 1.11 and $12.93 \pm 0.97 \text{ min}^{-1}$ (Figure 1d), respectively, highlighting the critical role of light in driving Cr(VI) reduction. This phenomenon is consistent with that in previous studies, where PS-MPs were shown to capture electrons or act as electron carriers under light irradiation, generating superoxide

anions O_2^-) that facilitate the reduction of Cr(VI) to Cr(III) [25,26]. The enhanced reduction capacity of APS can be rooted in the increased oxygen-containing functional groups formed during aging, which improve light absorption and promote the generation of reactive oxygen species (ROS) [27].

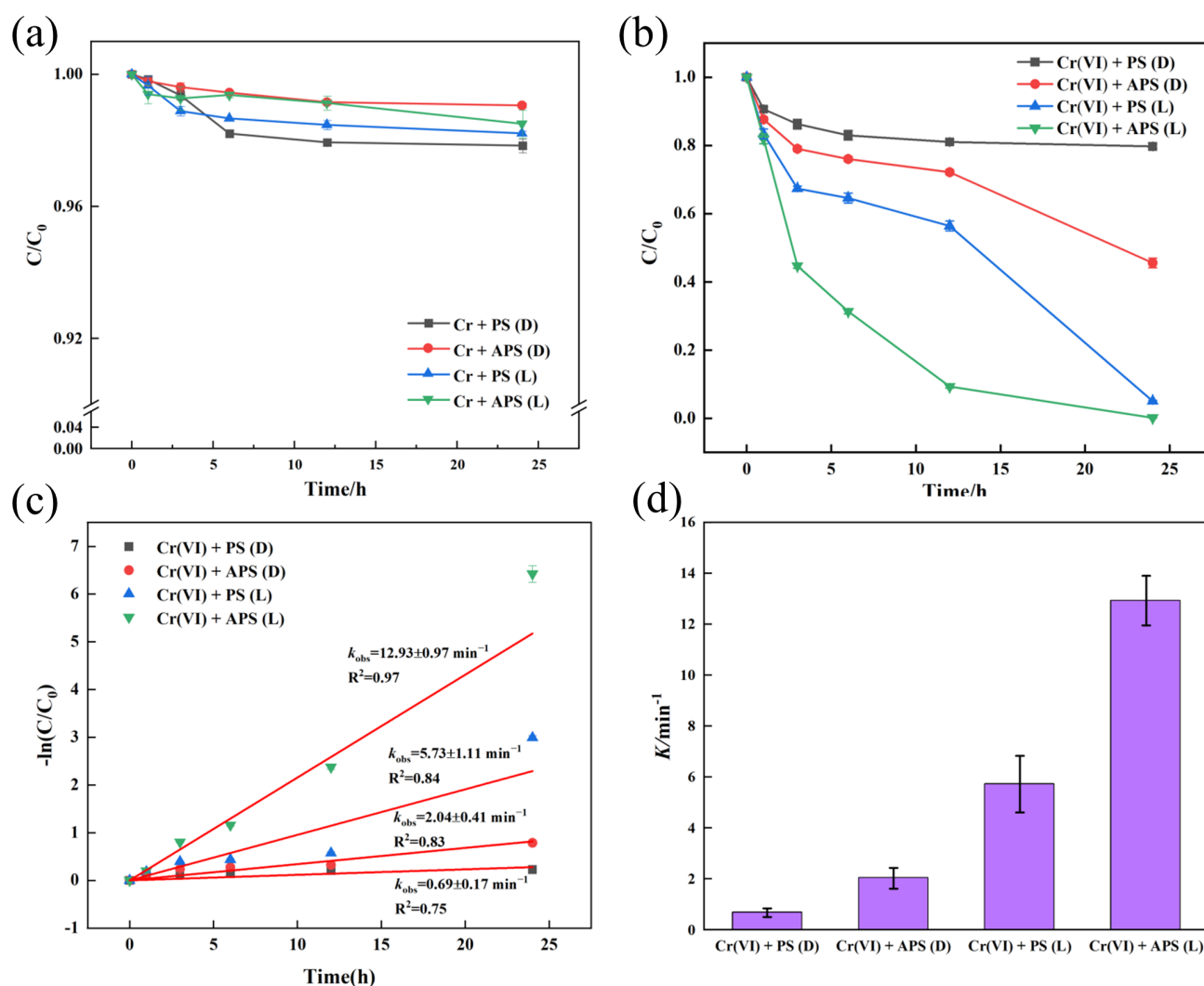


Figure 1. Concentration kinetics of (a) total Cr and (b) Cr(VI) with PS-MPs in the dark or under light conditions at different time points. (c) Pseudo-first-order kinetic curves for the valence conversion of Cr(VI) by PS-MPs; (d) The reduction rate of Cr(VI) in different reaction systems. Reaction condition: $[\text{Cr(VI)}] = 100 \mu\text{M}$, $[\text{PS-MPs}] = 4.0 \text{ g/L}$.

3.2. Characterization of Representative MPs

3.2.1. Dynamic Alterations in the Physical Properties of MPs

Generally, the surface of virgin PS is relatively smooth. Light irradiation leads to the formation of cracks on the PS surface, and the surface roughness thus significantly increases. Meanwhile, light exposure induces polymer chain scission in MPs, generating free radicals and initiating oxidation reactions that ultimately degrade their surface structure [28]. Notably, with the addition of Cr(VI), the presence of Cr(VI) might alter the surface chemical structure of PS-MPs and increase their degree of oxidation. Furthermore, the crystallinity of PS-MPs in different systems was analyzed by XRD, and the impact of Cr(VI) on the morphological and microstructural features of both PS and aged PS was further investigated. As clearly illustrated in Figure 2a, under illumination conditions, the characteristic diffraction peaks of PS and APS appeared at 9.8° and 19.1° , with the intensity of the diffraction peak of APS being lower than that of PS. In contrast, the characteristic

diffraction peaks of Cr(VI) + PS and Cr(VI) + APS disappeared, showing a further decrease in crystallinity. Previous studies have shown that a decrease in the crystallinity of MPs indicates degradation of their structured portions, accompanied by chain scission and a reduction in molecular weight, which confirmed the promoting role of Cr(VI) during the aging process of PS-MPs [29].

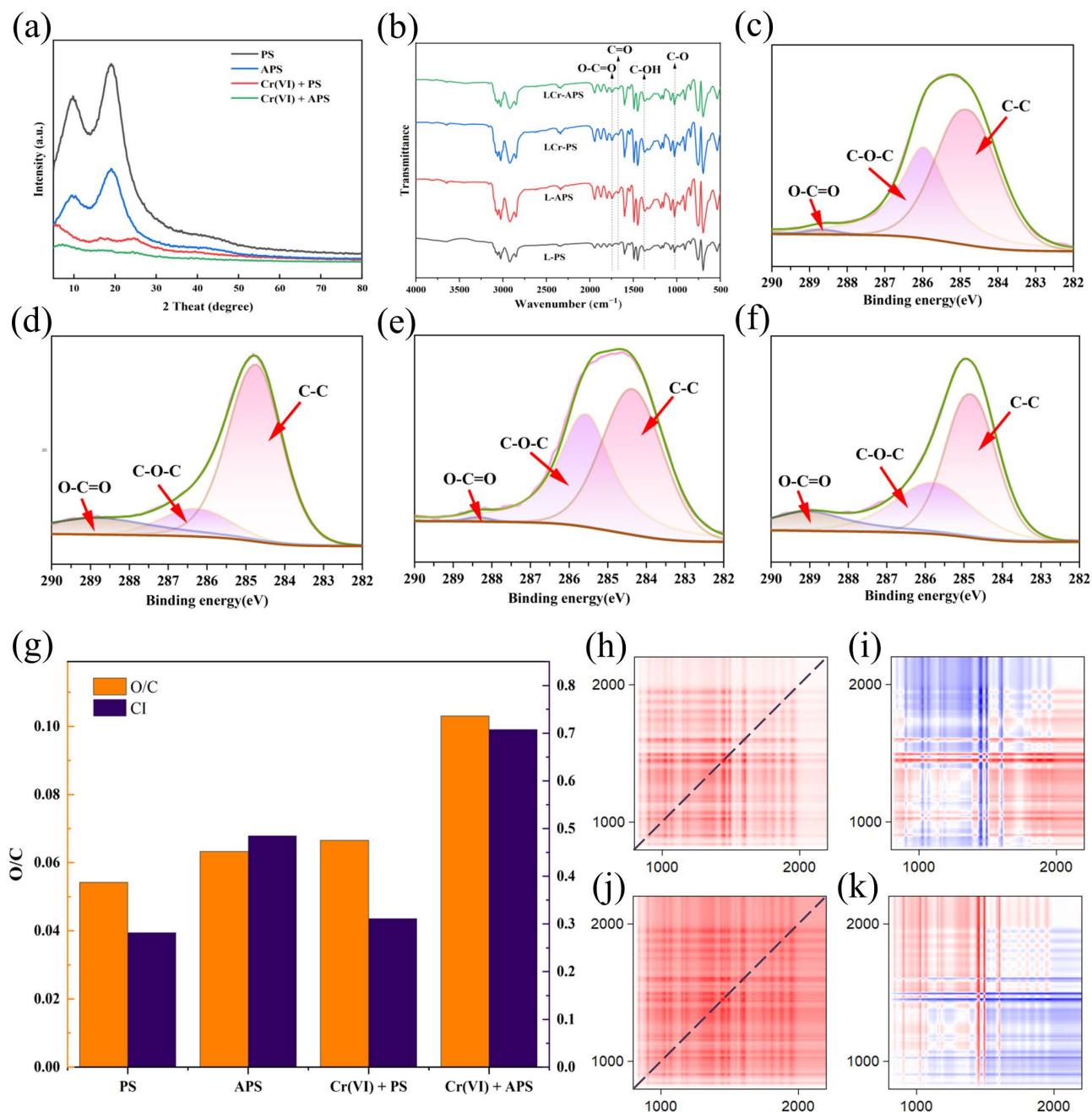


Figure 2. (a) XRD patterns and (b) FTIR spectra of PS, APS, PS + Cr(VI), and APS + Cr(VI) under light conditions; XPS spectra of (c) PS, (d) APS, (e) PS + Cr(VI), and (f) APS + Cr(VI); (g) O/C and Cl ratios of PS, APS, PS + Cr(VI), and APS + Cr(VI) under light conditions; synchronous (h,j) and asynchronous (i,k) 2D correlation maps of PS (h,i) and APS (j,k) with Cr(VI) under light conditions in the region of 900–2100 cm⁻¹. Red and blue colors denote positive and negative correlations, respectively, with darker colors indicating stronger correlations.

3.2.2. Changes in Chemical Properties of MPs

To delve more profoundly into the impact of Cr(VI) on PS-MPs, FTIR was employed to analyze the structural features and functional groups of PS-MPs. Figure 2b showed

that the absorption peaks of PS-MPs occurred at 756, 1023, 1375, 1446, 1493, 1601, 1673, 1745, and 3645 cm^{-1} and the peaks associated with C-H deformation and skeletal vibration were discernible at 756, 1446, 1493, and 1601 cm^{-1} . The peaks at 1023, 1375, and 1673 cm^{-1} were due to the tensile vibration of C-O, C-OH, and C=O, respectively [19]. The peak at 1744 cm^{-1} was attributed to the presence of γ -lactone (tensile vibration of O-C=O). A significant increase in the intensity of oxygen-containing functional groups was observed in APS compared to pristine PS-MPs. This phenomenon could be attributed to the cleavage of C-H bonds on the PS-MPs surface during aging, which generated carbon-centered radicals. These radicals subsequently reacted with oxygen to form peroxy radicals ($\text{ROO}\bullet$), followed by assimilating hydrogen to produce hydroperoxides (ROOH). The hydroperoxides ultimately decomposed or further oxidized to generate carboxyl groups (COOH) and other oxygenated functionalities [28]. It is crucial to note that Cr(VI) exerted a significant influence on the functional groups of PS-MPs. With the introduction of Cr(VI), the peak intensity of oxygen-containing functional groups exhibited an upward trend and this observation aligned well with the results of previous studies about the aging of PS-MPs [30]. Figure 2c–f presents the composition and functional groups of PS-MPs characterized by XPS. The C1s spectra reveal that, in the presence of Cr(VI), the relative content of the C-O-C and O-C=O groups increased, indicating that Cr(VI) influenced the surface chemistry of the PS-MPs. Previous studies have demonstrated that the oxygen-to-carbon ratio (O/C) and carbonyl index (CI) are useful indicators for evaluating the degree of aging in MPs [31–33]. As shown in Figure 2g, the O/C and CI values of PS-MPs varied under distinct conditions, highlighting the impact of Cr(VI) and illumination on the aging of PS-MPs. The O/C ratio of the virgin PS was 0.0142, whereas after illumination treatment, the O/C of APS increased to 0.0542, indicating that light exposure promoted the generation of oxygenated functional groups. Moreover, the addition of Cr(VI) further increased the O/C ratio. Specifically, the O/C of Cr-PS was 0.0097 higher than that of PS, while the O/C of Cr-APS nearly doubled, reaching 0.10303 compared to 0.0633 for APS. These results suggest that Cr(VI) not only enhances the formation of oxygen-containing groups but also interacts with the illuminated PS-MPs to further accelerate aging processes. The XPS results align with the FTIR analysis, which also indicates the formation of oxygenated groups such as carbonyl and hydroxyl functional groups. This consistency supports the conclusion that Cr(VI) exerts a substantial effect on the aging of PS-MPs, enhancing the generation of oxygenated functional groups.

However, one-dimensional FTIR spectra provided limited information for analyzing the arrangement of functional groups in MPs during the process of aging [34]. In order to uncover the sequential changes of functional groups in PS and APS under the influence of Cr(VI), a 2D-COS analysis was performed in the low wavenumber region ($900\text{--}2100\text{ cm}^{-1}$) of the FTIR spectra. The synchronous 2D correlation maps of Cr-PS and Cr-APS (Figure 2h,j) show that the peak distributions were essentially the same. Seven prominent peaks along the diagonal of the synchronous maps were located at 1023, 1375, 1446, 1493, 1601, 1673, and 1745 cm^{-1} , corresponding to C-O, C-OH, C-H, C-H, C-H, C=O, and O-C=O, respectively. Furthermore, positive signs were observed for the cross peaks in the synchronous map (Tables S1 and S2), illustrating that these functional groups change simultaneously over time with the aging of PS-MPs [35]. According to the Noda Rule [36], asynchronous maps can further reveal the sequential transformation of functional groups in PS-MPs throughout the aging progression. Figure 2i,k clearly illustrates substantial discrepancies in the cross-peak symbols between Cr-PS and Cr-APS. Under the influence of Cr(VI), the order of functional group changes in PS was $1493/1446/1601(\text{C-H}) > 1023(\text{C-O}) > 1375(\text{C-OH}) > 1745(\text{O-C=O}) > 1673(\text{C=O})$. Interestingly, the sequence of the functional group change in Cr-APS and Cr-PS was essentially opposite, with carbonylation and carboxylation taking precedence: in the order

1673(C=O) > 1745(O-C=O) > 1375(C-OH) > 1023(C-O) > 1601/1446/1493(C-H). The results demonstrated that the addition of Cr(VI) exerted a significant promotional effect on the aging of APS.

3.3. Specific Alterations in Fluorescence Properties

In this study, the fluorescence properties of MP-DOM with and without Cr(VI) under light and dark conditions were compared (Figures 3 and S1). The 3D-EEM analysis showed that PS-MPs derived low levels of matter in the dark [37]. The great difference of fluorescence intensity between PS (D) and APS (D) treatments indicated that aged PS-MPs could produce a lot of substance under dark condition, obviously more than virgin PS-MPs, and this was consistent with previous reports (Figure S1) [38]. Compared to the PS (L) and APS (L) treatments, the fluorescence intensity of PS (D) and APS (D) treatments was significantly higher, indicating that a portion of the substances derived from PS-MPs and aged PS-MPs underwent degradation under light conditions (Figures 3a–f and S1). It has been reported that the fluorescence loss of PS-DOM occurred one day after irradiation, which is in line with the results that the fluorescence intensity of both PS (L) and APS (L) treatments decreased gradually with time in this study [39].

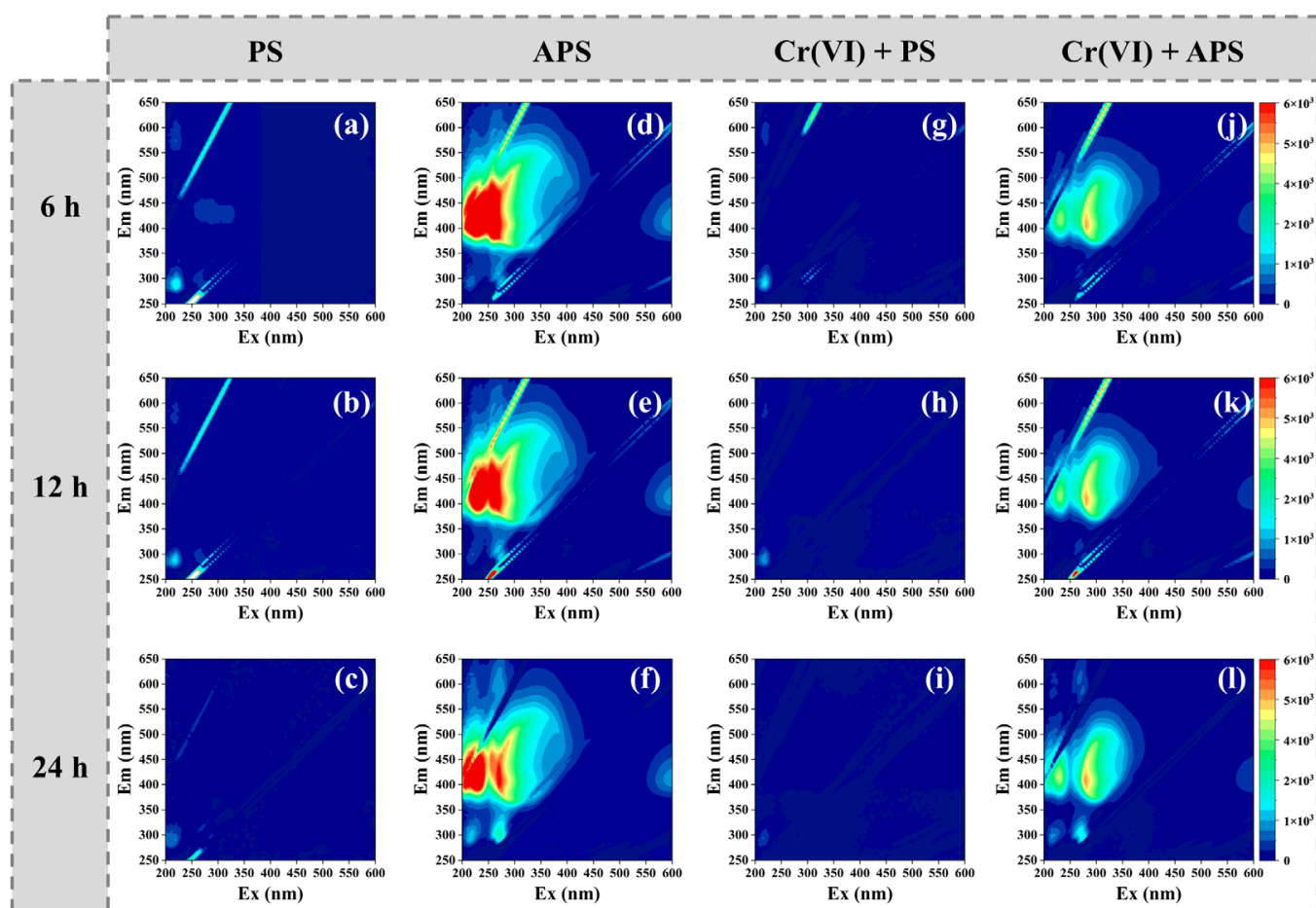


Figure 3. Variation of 3D-EEM images of (a–c) PS, (d–f) APS, (g–i) Cr(VI) + PS, and (j–l) Cr(VI) + APS under light conditions.

Furthermore, the addition of Cr(VI) made the fluorescence intensity of the Cr(VI) + PS and Cr(VI) + APS treatments smaller than that of the corresponding treatments without Cr(VI) at each time and condition, respectively (Figures 3g–l and S1). From the above discussion, it could be seen that there is no adsorption of Cr(VI) onto MPs in this

study, which was contrary to the existing view [40,41], presumably because the interaction between MP-DOM and Cr(VI) along with Cr(III) was more intense. It has been reported that humic acid (typical model DOM) contains protein components rich in reducing groups, such as amino and phenolic groups, allowing the reduction of Cr(VI) to Cr(III) [42]. Moreover, the findings from previous investigations have indicated that carboxyl and phenolic groups within DOM play a crucial role as binding sites or ligands for metals [43,44], and the interaction between Cu and DOM has also been confirmed [45]. This suggests that Cr(III) resulting from Cr(VI) reduction might be further incorporated by MP-DOM [46]. Therefore, the above phenomenon in this study was the result of PS-MPs reducing Cr(VI) and binding Cr(III). By comparing the fluorescence intensities of APS (D), APS (L), and Cr(VI) + APS (D) (Figures 3d–f,j–l and S1), it was shown that the fluorescence regions of PS-DOM under light and Cr(VI) conditions were almost the same, and this demonstrated that there was a synergistic effect between the two on the fluorescence intensity of PS-DOM, consistent with the lower fluorescence intensity in Cr(VI) + APS (L). Curiously, the fluorescence intensity of Cr(VI) + APS (L) did not decrease significantly with time, unlike that of Cr(VI) + PS (L). Prior studies demonstrated that UV irradiation serves as a driving force for promoting the formation or release of fluorescent substances within MPs but induces photo-degradation at the same time [37]. Therefore, due to the fact that aged PS-MPs has the ability to leach more material than virgin PS-MPs under light conditions [31,47], it was hypothesized that the rate of leachate and photo-degradation of APS-DOM were almost equal, along with the effect of Cr(VI) on some of the APS-DOM in the Cr(VI) + APS (L) treatment, distinct from the Cr(VI) + PS (L) treatment. Therefore, there was a binding or reduction between PS-DOM and Cr(VI), which affected the transformation process of both.

3.4. The Reduction Process of Cr(VI) Mediated by PS-MPs

Previous studies have confirmed that the PS-MP-mediated reduction of Cr(VI) primarily relies on O_2^- , yet the origin of these reactive species remains unclear [25]. Existing studies indicate that MPs, including PS, can generate EPFRs under light irradiation [28]. These EPFRs transfer single electrons to molecular oxygen (O_2), thereby generating superoxide anions. Consequently, it is reasonable to hypothesize that the O_2^- involved in Cr(VI) reduction originates from PS-MP-derived EPFRs. To further elucidate the interaction mechanism between PS-MPs and Cr(VI), we conducted EPR analyses to detect EPFR signals across different experimental systems. The stability of EPFRs on PS-MPs exhibited significant variations between virgin PS and APS, as depicted in Figure S2. An EPR spectroscopy analysis demonstrated that APS exhibited markedly stronger EPFR signals than virgin PS, attributed to the photochemical cleavage of C-H bonds in the benzene rings of PS-MPs, which generates stable oxygen-centered free radicals. This effect is further amplified in APS, where prior photochemical or oxidative aging disrupts the polymeric structure, thereby enhancing its propensity to form free radicals. Notably, under light conditions, the EPFR signals on APS diminished following the addition of Cr(VI). The reason is that EPFRs act as electron donors, transferring electrons to Cr(VI) ions and reducing them to the less toxic Cr(III) form. Interestingly, compared to APS, pristine PS exhibited a greater capacity to form stable EPFRs under light conditions, which may be attributed to its relatively intact chemical chains, allowing more chemical bonds to break and generate EPFRs under illumination. This process highlights the dual role of light and aging in promoting the reduction of Cr(VI) through the generation of EPFRs. These findings highlight that the conversion of Cr(VI) into Cr(III) with the addition of PS-MPs is predominantly driven by EPFRs, particularly under light conditions.

4. Conclusions

This study elucidated the dynamic interaction between Cr(VI) and PS-MPs and found that while PS-MPs promoted the reduction of Cr(VI) to Cr(III), the presence of Cr(VI) would further accelerate the aging of PS-MPs. Pseudo-first-order kinetics governed the reduction process, with light exposure and MP aging critically enhancing Cr(VI) reduction efficiency. This could be ascribed to the generation of EPFRs on the surface of PS through light-induced chemical bond breaking, which can provide lone pair electrons and thus facilitate the reduction of Cr(VI) to Cr(III). Advanced characterization further confirmed that Cr(VI) interactions accelerated PS-MP aging, triggering DOM release. Fluorescence quenching indicated effective Cr(VI)-DOM coordination, while light simultaneously degraded DOM-derived fluorophores. These findings highlight the necessity of integrating environmental factors and MP aging states when assessing contaminant–MP interactions. This work advances our mechanistic understanding of co-pollutant behaviors in aquatic systems and underscores actionable strategies for mitigating the combined risks of MPs and heavy metals in environmental management.

Despite the fact that this research has achieved certain advancements in understanding the interaction mechanism between MPs and heavy metals, several limitations remain. First of all, this experimental system focused exclusively on PS-MPs, while environmental MP pollution typically comprises diverse polymer types (such as polyethylene (PE), polypropylene (PP), and so on). The physicochemical variations of different MPs, including surface functional groups, crystallinity, and so on, may fundamentally alter their interaction mechanisms with heavy metals. Second, although short-term experimental design can clarify key processes, potential synergistic effects such as the accelerated fragmentation of MPs and the secondary release of heavy metals under long-term exposure still need to be systematically verified. Third, this work specifically addressed chromium species interactions, yet the broader applicability to other heavy metals (e.g., Pb, Cd, and Hg) necessitates verification. Differential behaviors may emerge due to variations in metal oxidation states, reduction potentials, and complexation capacities with MP-DOM. Therefore, future research is recommended to further explore the MP–heavy metal composite pollution system by constructing multi-type MP composite systems and design long-term exposure experiments.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/w17071102/s1>, Text S1: Chemicals used in experiments. Text S2: XPS analysis of PS-MPs. Text S3: Characterizations of PS-MPs with two-dimensional correlation spectroscopy. Figure S1: 3D-EEM of each group at different time points under dark conditions; Figure S2: The EPR signals of EPFRs on the PS, APS, Cr(VI)+PS and APS, Cr(VI)+APS under the light condition; Table S1: 2D–COS data on the assignment and sign of each cross-Peak in synchronous (Φ) and asynchronous (Ψ , in the Brackets) maps of Cr(VI) + PS (L) with increasing aging time; Table S2: 2D–COS data on the assignment and sign of each cross-Peak in synchronous (Φ) and asynchronous (Ψ , in the Brackets) maps of Cr(VI) + APS (L) with increasing aging time. References [48–50] is cited in the Supplementary Materials.

Author Contributions: Conceptualization, P.Z., Q.W. and Z.O.; methodology, Y.C. and S.Q.; software, Y.C.; formal analysis, Y.C.; writing—original draft preparation, Y.C. and S.Q.; writing—review and editing, P.Z., Q.W. and Z.O.; supervision, Z.O. and Q.W.; funding acquisition, Z.O. and Q.W. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data generated and analyzed during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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