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UV/ozone induced physicochemical transformations of polystyrene nanoparticles and their aggregation tendency and kinetics with natural organic matter in aqueous systems

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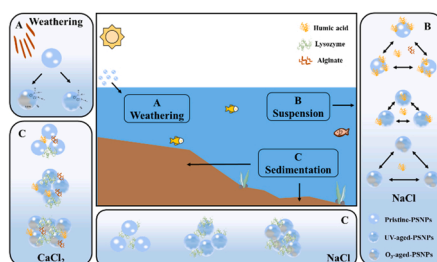
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HIGHLIGHTS

- Aggregation of PSNPs as affected by aging, NOM, and solution chemistry was studied.
- Different aging processes induced distinct physicochemical transformations of PSNPs.
- The enhanced hydrophilicity contributed to the high stability of aged-PSNPs in NaCl.
- The interaction between PSNPs and NOM varied with the surface properties of PSNPs.
- UV and O₃ aging enhanced the mobility of PSNPs in natural waters.

GRAPHICAL ABSTRACT



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ABSTRACT

Once discharged into the environment, plastics debris are unavoidably subjected to natural weathering processes. Unfortunately, the impact of weathering on the aggregation tendency and kinetics of nanoplastics in complex environmental matrices is poorly understood. Here, we investigated the influence of weathering as induced by UV and O₃ treatments, on the aggregation of polystyrene nanoparticles (PSNPs) in simulated waters containing representative organic molecules (humic acid, lysozyme, and alginate) and in natural waters. Results showed that UV/O₃ weathering-induced physicochemical transformations of PSNPs, particularly the formation of oxygen-containing functional groups and the increase in hydrophilicity, altered the aggregation state of PSNPs to different extents. The presence of organic molecules destabilized the UV-aged PSNPs with strength of lysozyme > alginate > humic acid, owing to the decrease of sorption of macromolecules on their surface. Differently, the O₃-aged PSNPs displayed strong stability in the absence or presence of organic molecules (except for lysozyme), probably due to steric repulsion arising from the leakage of endogenous organic matters. This work demonstrates that the aggregation behavior of PSNPs is determined by the complex interplays among weathering, natural

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organic matter, and solution chemistry, and provides significant insights into the fate and transport of PSNPs in realistic scenarios.

1. Introduction

The huge demand and wide application of products containing plastics (e.g., personal care products, waterborne paints, and biomedical products), and the improper plastic wastes disposal has resulted in plastics contamination rapidly becoming a pressing and global environmental concern (Hernandez et al., 2017; Toussaint et al., 2019). As one of the emerging contaminants, the environmental behavior (including aggregation, transport, and adsorption) and toxic effects of nanoplastics have recently been examined under experimental conditions (Brennecke et al., 2016; Rezanian et al., 2018; Banerjee and Shelver, 2021; Liu et al., 2020). However, the majority of these studies used commercial nanoplastics, which lack representative of naturally occurring particles in the actual environment, and thus limit our understanding in predicting the environmental behavior and potential risks of nanoplastics in general. As noted in recent studies, plastics debris inevitably undergo aging processes during their life-cycle (Liu et al., 2019a; Wang et al., 2020a). These processes reduce their sizes, increase their hydrophilicity, and induce the formation of persistent free radicals and endogenous pollutants leaching, and finally enhance their mobility, facilitate contaminant cotransport, and elevate the toxicity of polystyrene plastics to organisms (Liu et al., 2019a; Wang et al., 2020a; Alimi et al., 2021). As the fate and toxic effects of nanoplastics in aquatic environments are highly dependent on their aggregation state, it is imperative to elucidate the influence of aging on the aggregation behavior and colloidal stability of nanoplastics under environmentally relevant conditions.

To date, only two studies have examined the effects of weathering processes on the aggregation kinetics of nanoplastics which have both focused on UV irradiation in simulated solutions (Liu et al., 2019b; Wang et al., 2020b). Liu et al. (2019b) found that prolonged UV irradiation time increased the stability of nanoplastics in NaCl solutions, but accelerated their aggregation in CaCl₂ containing medium. Wang et al. (2020b) reported that the influence of UV exposure on the colloidal stability of nanoplastics depends on their surface modifications and the type of the electrolyte used. Although these studies yielded important insights, the aggregation behavior of aged nanoplastics in simulated aquatic systems is not equivalent to their behavior in natural, complex aquatic environments. In the latter systems, the ubiquitous presence of natural organic matter (NOM) has been demonstrated to be a crucial factor affecting the aggregation behavior of nanoparticles (Liu et al., 2020; Li et al., 2020a, 2020b; Tan et al., 2019). Our previous studies showed that particle size and surface coating of nanoplastics influenced their interaction with proteins, leading to distinct aggregation behaviors (Li et al., 2020a, 2020b). Since the physicochemical properties of nanoplastics can be altered during aging processes, it is reasonable to hypothesize that the impacts of NOM on aged nanoplastics might be distinctly different from the impacts of NOM on pristine plastics. However, there is a paucity of information on the effects of NOM on the aggregation and stability of aged nanoplastics, which is important for evaluating the environmental fate and potential impacts of nanoplastics in realistic scenarios.

Humic substances, proteins, and polysaccharides are the most important fractions of NOM in natural water (Nebbioso and Piccolo, 2013). However, the composition and concentration of NOM depend on the water type. For instance, the polysaccharide content of the NOM in lake is 10–30%, while it may be as high as 50% of NOM in marine environments (Buffle et al., 1998; Engel et al., 2004). The concentration of protein in surface water is in general relatively low, but could reach a value of up to 30.2 mg/L in an urbanized river or in wastewater (Feng et al., 2011). Liu et al. (2020) found that different macromolecules

exhibited different extent of stabilization effects on pristine nanoplastics, but the influence of various types of NOM on the fate of aged nanoplastics is largely unknown. Furthermore, the physicochemical parameters of surface waters such as ionic strength and cation type could influence the interaction of particles and NOM by electrostatic interaction and cation bridging, which in turn changes the aggregation process of nanoplastics (Li et al., 2020a, 2020b; Tan et al., 2019). Thus, considering that the composition of NOM and ion varies greatly in different water bodies, it is an intriguing question whether or not aged nanoplastics would behave differently in different water bodies.

In this study, polystyrene nanoplastics (PSNPs) were chosen as the representative model nanoplastics in view of the wide detection of their debris in the environment (Auta et al., 2017). Pristine PSNPs were chemically treated with UV irradiation or O₃ exposure to obtain aged PSNPs. The UV irradiation and O₃ exposure were selected to simulate the photo aging and oxidation process of plastics in realistic environments (Liu et al., 2019b). Humic acid (HA), lysozyme (Lys), and sodium alginate (SA) were employed to represent three major components of NOM (humic substance, protein, and polysaccharide) (Philippe and Schaumann, 2014). It was hypothesized that the aging process influenced the interaction between PSNPs and NOM due to the alterations in the surface properties of PSNPs, thus influencing the aggregation state and colloidal stability of PSNPs. To test this hypothesis, the aggregation kinetics of PSNPs before and after aging in a diverse array of synthetic and natural waters were systematically investigated by using time-resolved dynamic light scattering (TR-DLS). The pristine and aged PSNPs were comprehensively characterized to understand the physicochemical changes induced by aging processes. Extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) interaction energies were calculated to better understand the mechanisms of PSNPs stability. The mechanisms responsible for the aggregation of PSNPs in the presence of NOM were proposed and explored using three dimensional-excitation emission matrix spectra (3D-EEM), and laser scanning confocal microscopy (LSCM).

2. Materials and methods

2.1. Nanoplastics and organic matters

The pristine PSNPs of 100 nm nominal diameter (5% w/v) were purchased from Shanghai Huge Biotechnology Co., Ltd. (Shanghai, China). Aged PSNPs were chemically treated with UV and O₃ before aggregation experiments out of consideration for the following reasons. Firstly, large amounts of nanoplastics are originating from plastics products, which undergo oxidation process during they are used and disposed (Alimi et al., 2018; Li et al., 2018). Secondly, once primary nanoplastics discharged into aquatic environments, they would be suspended in the column water, and thus oxidation would be the dominating factor influencing their physicochemical properties and subsequently environmental behaviors (Singh et al., 2019; Wang et al., 2020). To obtain UV-aged PSNPs, a 100 mL quartz tube containing a PSNPs suspension (500 mg/L) were exposure to a mercury lamp (500 W) at room temperature (25 °C) for 12 and 24 h with constant stirring, respectively. The O₃-aged PSNPs were prepared by bubbling O₃ gas into 100 mL PSNPs suspension (500 mg/L) at a rate of 100 mg/min for 15 and 30 min, respectively. The aged PSNPs suspensions were preserved in the dark at 4 °C before use.

HA, Lys, and SA were obtained from Sigma-Aldrich (Shanghai, China). A stock suspension of HA was prepared as described in our previous study (Li et al., 2020a, 2020b). The Lys and SA suspensions were obtained by dissolving a pre-specified amount of powder into 100

mL Milli-Q water. These stock solutions were stored at 4 °C in the dark to prevent degradation before use.

2.2. Natural water samples

Natural water samples, including seawater, river water, lake water, and groundwater were collected and preserved at – 80 °C before use. After filtering through a 0.45 µm mixed cellulose ester membrane, these samples were subjected to ionic chromatography analysis (ICS-5000, Thermo Fisher Co., USA) and TOC analysis (TOC-V, Shimadzu, Japan) (Li et al., 2020a, 2020b). The compositions of the dissolved organic matter in each sample were analyzed by F-7000 fluorescence spectrometry (Hitachi, Japan). The detailed sampling information and physicochemical properties of these samples are shown in the [Supplementary Material \(Table S1 and S2\)](#).

2.3. Characterization of pristine and aged PSNPs

The surface morphology of pristine and aged nanoplastics was characterized by transmission electron microscopy (TEM, Talos L120C G2, Thermo Fisher Co., USA) and scanning electron microscopy (SEM, JSM-7800 F, JEOL, Japan). The zeta potential of PSNPs before and after aging was recorded at pH 5.0 by using a zeta potential analyzer (Zetasizer Nano-ZS 90, Malvern Instruments Ltd, UK). Fourier transformed infrared spectroscopy with an optical microscopy approach (Micro-FTIR, Nicolet iN10 Thermo Fisher Co., USA) and X-ray photoelectron spectroscopy (XPS) were employed to investigate the change of surface functional groups of PSNPs under different aging treatments. The hydrophobicity of PSNPs was measured using a contact angle analyzer (DSA100, Kruss, Germany) at 25 °C.

2.4. Aggregation experiments

Time-resolved dynamic light scattering (TR-DLS, Nano ZS 90, Malvern, UK) equipped with a He-Ne 633 nm laser and a detected angle of 90° was applied to investigate the aggregation kinetics of pristine and aged PSNPs in eight natural waters. Before each measurement, a suspension of PSNPs was sonicated in an ice water bath for 15 min. Then, an equal volume of the suspension of the PSNPs and a water sample were pipetted into a cuvette. After vortexing by hand, the cuvette was inserted into a Malvern Zetasizer instrument for the TR-DLS measurement. The hydrodynamic diameter (D_h) was recorded at intervals of 30 s for 15 min. The aggregation kinetics of PSNPs before and after aging were also conducted in different solutions containing different ionic strength and different cation type, with or without NOM following similar procedures. In these experiments, the final concentration of PSNPs in the mixture was 10 mg/L, which meets the DLS detection, and may represent the contaminant concentration in natural water bodies (Liu et al., 2020). The NOM concentration was investigated at a fixed concentration (2 mg C/L), which is within the range of NOM concentrations (0.01 ~ 10 mg C/L) typically detected in surface water (Nebbioso et al., 2013). The pH of these suspensions was maintained at 5.0 by adjusting with 0.1 M HCl or NaOH. Each sample were measured in triplicate.

The initial aggregation stage was defined as the period from aggregation initiation (t_0) to the time when the recorded D_h values reached 2 times its initial value. The aggregation rate (k) of PSNPs is proportional to the size growth rate ($dD_h(t)/dt$) and inversely proportional to the PSNPs concentration (N_0) (Chen and Elimelech, 2008):

$$k \propto \frac{1}{N_0} \left(\frac{dD_h(t)}{dt} \right)_{t \rightarrow 0} \quad (1)$$

To assess the stability of PSNPs under different conditions, the attachment efficiency (α) was calculated by normalizing the k in the reaction-limited regime to that in the k_{fast} in the diffusion-limited regime as follows:

$$\alpha = \frac{k}{k_{fast}} = \frac{\frac{1}{N_0} \left(\frac{dD_h(t)}{dt} \right)_{t \rightarrow 0}}{\frac{1}{(N_0)_{fast}} \left(\frac{dD_h(t)}{dt} \right)_{t \rightarrow 0, fast}} \quad (2)$$

2.5. Calculation of the interaction energy

The interaction energy (including Van der Waals forces, electrostatic double-layer interactions and Lewis acid-base interactions) between particles was calculated according to the XDLVO theory for better understanding the effects of aging processes on PSNPs aggregation. Detailed calculations are presented in the [Supplementary information \(Text S1\)](#).

2.6. Interactions between PSNPs and NOM

The NOM solutions before and after interacting with pristine/aged PSNPs were placed on an excitation-emission-matrix (EEM) spectroscopy (FLS1000, Edinburgh Instruments) to characterize the interaction of NOM and PSNPs. The slit size was set as 5 nm, and the scan speed was 2400 nm/min. Laser scanning confocal microscopy (LSCM, TCS SP8 STED 3X, Leica, Germany) was applied to reveal the attachment of NOM on the surface of PSNPs. The details of the sample preparation and the instrumental settings are given in the [Supplementary Information \(Text S2\)](#).

3. Results and discussion

3.1. Characteristics of pristine and aged PSNPs

The TEM and SEM images show that the pristine and aged PSNPs are regularly-shaped spherical particles with ~100 nm in diameter (Fig. S1). Previous studies indicated that the aging processes (e.g., UV irradiation, O₃ oxidation, and photo-Fenton treatment) could significantly influence the morphological features of polystyrene particles by the generation of reactive radical oxidants (e.g., •OH, O₂•⁻, and SO₄•⁻) (Liu et al., 2019b, 2019c). However, no obvious difference in the size, and shape of the PSNPs before and after aging were found in this study. This can be ascribed to the different aging methods and the aging time used compared with other studies. Despite of the unchanged shape and size, the contrast of the PSNPs was weakened after being aerated with O₃ for 30 min, while a thin film of most likely organic matter was formed around the PSNPs. We subsequently measured the amount of dissolved organic carbon (DOC) in the suspensions of pristine and aged PSNPs. The DOC concentration in the PSNPs suspensions was drastically elevated after exposure with O₃ gas (Fig. 1a). O₃ treatment is thus shown to induce the release of organic matters as arising from PSNPs because of decreased affinity of additives with PSNPs due to the increased surface hydrophilicity (Fig. 1e), and micropores formation on the PSNPs surface (Liu et al., 2019c; Wang et al., 2020a).

The change in the surface functional groups of PSNPs before and after aging were characterized by Micro-FTIR and XPS (Fig. 1b and c, Fig. S3). Typical adsorption peaks of the pristine PSNPs were observed at the range of 2800 ~ 3200 nm, 1400 ~ 1600 nm, and 500 ~ 700 nm, corresponding to C-H, C=C, and benzene ring moieties, respectively (Kaczmarek et al., 2008). After UV irradiation, new peaks assigned to O-containing functional groups (-OH, O-C=O, C-O-C, and -C-OH) were formed on the surface of the PSNPs (Fig. 1b, and Table 1). This result was consistent with previous studies, which reported that the C-H bonds within the polymer chain can react with oxygen under UV irradiation, resulting in the formation of hydroxyl (-OH) and carbonyl groups (C=O) (Yousif and Haddad, 2013; Mao et al., 2020). The generation of O-containing functional groups subsequently increased the surface charge of UV-irradiated PSNPs, as evident from the measured zeta potential (Fig. 1d). In contrast, the aeration with O₃ gas obviously broke

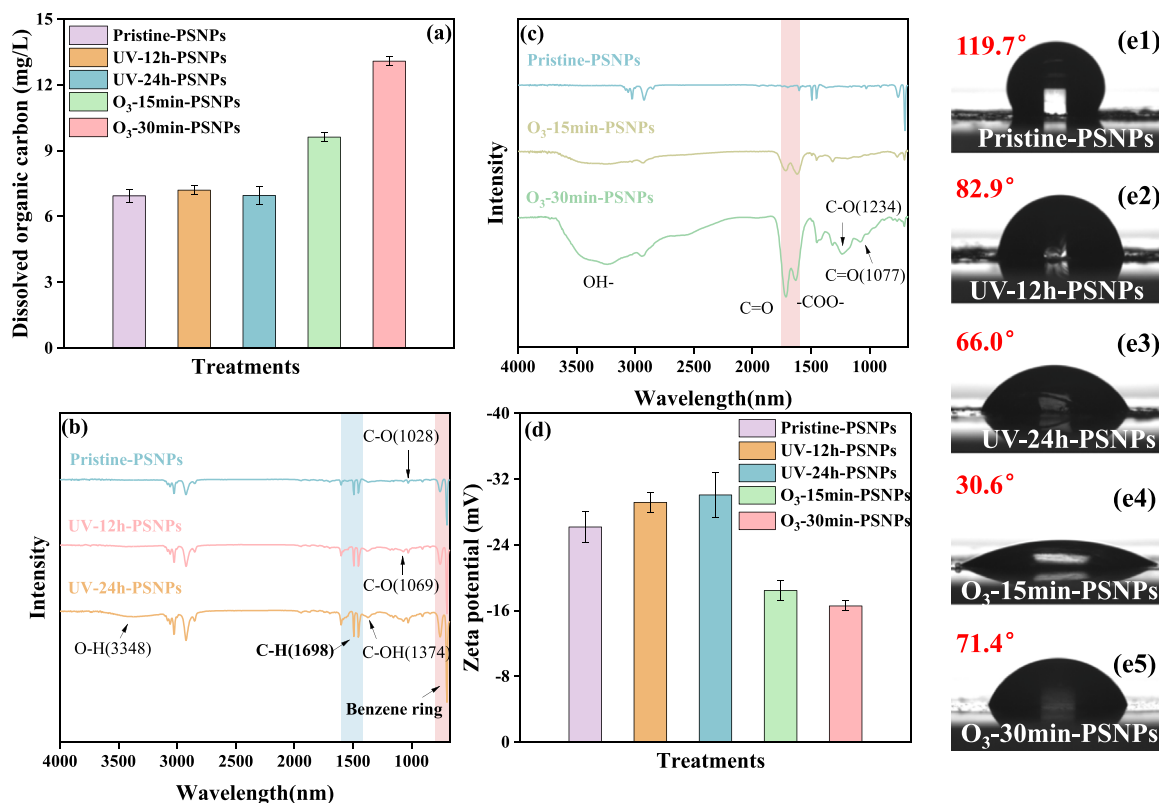


Fig. 1. Dissolved organic carbon (a), FTIR spectra (b and c), zeta potential (d), and water contact angle (e1-e5) of PSNPs before and after aging.

Table 1

Surface functional groups and element content of PSNPs before and after aging.

	Aromatic rings (C-C/C=C)	Epoxy/hydroxyl (C-O-C/C-OH)	Carboxyl (O-C=O)	Total C ^a (%)	Total O ^a (%)	C/O ratio
Pristine-PSNPs	94.82	5.19	BDL ^b	97.81	2.19	44.66
UV-12 h-PSNPs	89.05	10.06	0.80	94.12	5.09	18.49
UV-24 h-PSNPs	77.79	20.7	1.44	85.58	14.43	5.93
O ₃ -15 min-PSNPs	69.27	24.21	6.32	81.33	18.67	4.36
O ₃ -30 min-PSNPs	57.43	31.15	11.43	75.77	24.24	3.12

^a : Analyzed using XPS.

^b : Below detection limit.

the C-H bonds and the benzene ring structure of the PSNPs, accompanied with the formation of large amounts of O-containing functional groups. Nevertheless, the absolute value of the zeta potential of O₃-oxidized PSNPs did not further increase (Fig. 1c and d). The different trends in zeta potential between UV treatment and O₃ treatment may be ascribed to the released organic matters from O₃-oxidized PSNPs into the suspension, which subsequently attached on the surface of PSNPs, and finally modified their surface properties (Li et al., 2020a, 2020b). Moreover, the water contact angle of PSNPs decreased gradually as UV irradiation time increased. This was due to the introduction of hydrophilic functional groups (Fig. 1e1-e3, Fig. S2) (Liu et al., 2019a, 2019b). This finding was in line with the trends of the measured zeta potential, XPS spectra and the FTIR spectra, meaning that prolonged UV irradiation time aggravated the change of the surface physicochemical properties of PSNPs. Similarly, the hydrophilicity of O₃ oxidized PSNPs was significantly higher than that of pristine PSNPs (Fig. 1e4 and e5). However, an extension of the ozonation time did not further increase the hydrophilicity of PSNPs, but actually decreased their hydrophilicity. The relatively low hydrophilicity of O₃-30 min-PSNPs may result from the adsorption of organic matter on the surface of the particles. Furthermore, the C/O ratio of PSNPs decreased gradually as aging time increasing, and the relative degrees of surface oxidation followed the

order of O₃-30 min-PSNPs > O₃-15 min-PSNPs > UV-24 h-PSNPs > UV-12 h-PSNPs (Table 1). Overall, it is shown that UV irradiation and O₃ oxidation can accelerate the aging of PSNPs, and the physicochemical properties of the aged PSNPs were highly dependent on aging times and aging modes.

3.2. Effects of aging processes on the stability of PSNPs

The aggregation kinetics of pristine-PSNPs, UV-12 h-PSNPs, and O₃-15 min-PSNPs were firstly investigated in a wide concentration range of NaCl solutions (100 ~ 500 mM) (Fig. S4). Upon increasing the electrolyte concentration, the attachment efficiency (α) of pristine-PSNPs and UV-12 h-PSNPs increased gradually due to electrostatic screening, which can be corroborated by the decreasing zeta potential (Figs. 2a, and S5a). At high ionic strength, the α of pristine-PSNPs and UV-12 h-PSNPs was close to 1 and remained unchanged, meaning that the energy barrier among particles was completely shielded under high salt levels (Liu et al., 2019b). The observed two regimes generally are defined as the reaction-limited regime (RLR) and the diffusion-limited regime (DLR), indicating that the aggregation behavior of pristine-PSNPs and UV-12 h-PSNPs may follow the DLVO theory (Liu et al., 2019b; Li et al., 2021b). Differently, the D_h of O₃-15 min-PSNPs remained constant even

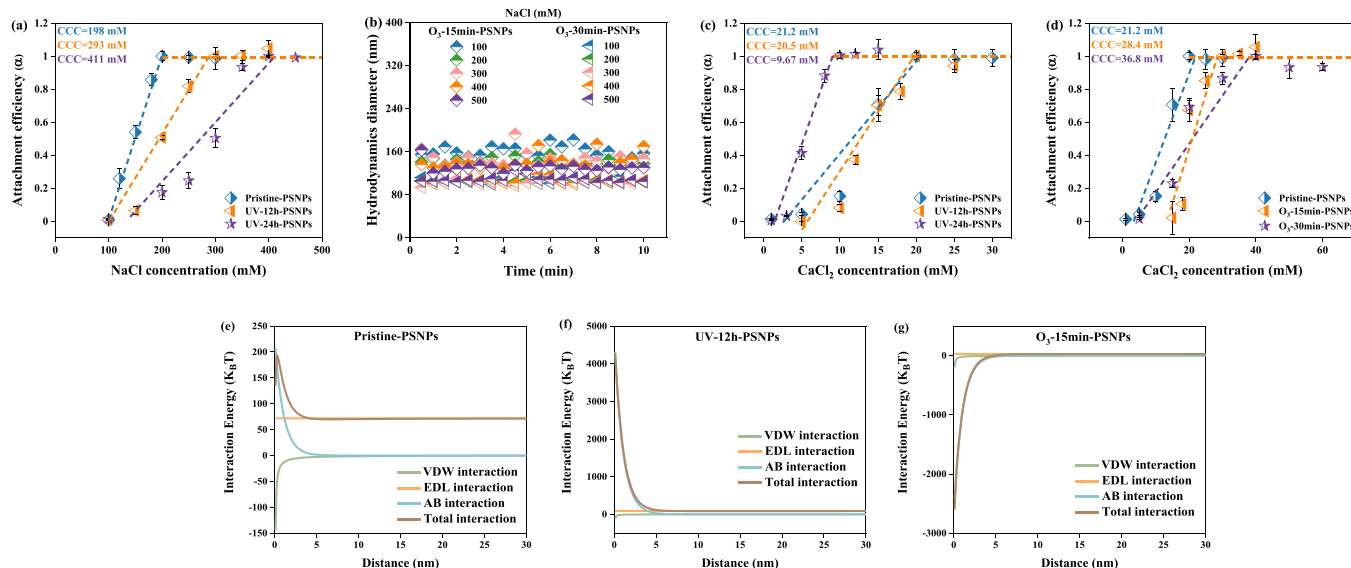


Fig. 2. Attachment efficiency of Pristine-PSNPs, UV-12 h-PSNPs, UV-24 h-PSNPs, O₃-15 min-PSNPs, and O₃-30 min-PSNPs as a function of NaCl, and CaCl₂ concentrations (a, c, and d). Representative aggregation kinetics of O₃-15 min-PSNPs and O₃-30 min-PSNPs in the presence of NaCl (b). The interaction energy of Van der Waals force (VDW), electrostatic force (EDL), Lewis acid-base interactions (AB), and the total interaction energy (Total) of Pristine-PSNPs (e), UV-12 h-PSNPs (f), and O₃-15 min-PSNPs (g) in 100 mM NaCl solutions.

in 500 mM NaCl (Fig. 2b), suggesting that the stability of aged PSNPs depends on the specific aging process. Furthermore, the critical coagulation concentration (CCC) was further calculated for assessing the colloidal stability of PSNPs before and after aging. The CCC_{Na} of Pristine-PSNPs, UV-12 h-PSNPs, and O₃-15 min-PSNPs was 198, 293, and > 500 mM, respectively (Table 2). This indicated that UV-irradiation and O₃-oxidation significantly enhanced the stability of PSNPs. A similar trend was also reported by Liu et al. (2019a) who concluded that the strong stability of aged-PSNPs was derived from increasing surface charge due to the formation of O-containing functional groups on their surface. In the current study, new functional groups were observed in UV-12 h-PSNPs and O₃-15 min-PSNPs, but the surface charge of aged-PSNPs was not significantly higher than in the case of pristine-PSNPs (Fig. 1d). This finding suggests that other mechanisms contributed to the enhanced stability of the aged-PSNPs. Thus, we further calculated the energy barrier between particles based on the XDLVO theory (Fig. 2e-g). Results showed that the aging treatments significantly increased Lewis acid-base interactions among PSNPs, meaning that hydration forces were responsible for the stabilization of UV-12 h-PSNPs and O₃-15 min-PSNPs (Fig. 1e-g) (van Oss, 2003; Xu et al., 2017). These findings were consistent with previous studies, which reported that the hydrophilicity of aged carbon-based particles (PSNPs, and dissolved black carbon) played a predominant role in their stability (Liu et al., 2019a; Xu et al., 2017).

In contrast to PSNPs in NaCl solutions, Pristine-PSNPs, UV-12 h-

PSNPs, and O₃-15 min-PSNPs aggregated to a higher extent in CaCl₂ solutions (Fig. S4d, 4e and 4g). This can be explained by the high performance of Ca²⁺ in double layer compression, as verified by the measured zeta potential (Fig. S5b) (Li et al., 2020a, 2020b; Sun et al., 2018). It is worth noting that prolonged UV-irradiation time (from 12 h to 24 h) significantly decreased the CCC_{Ca} of PSNPs ($p < 0.05$), whereas enhanced O₃-exposure time (from 15 min to 30 min) significantly increased this value ($p < 0.05$) (Fig. 2c and d, and Table 2). This observation showed that the aggregation of aged PSNPs relies both on the aging modes and the cation types present in suspension. Such distinct aggregation behaviors as observed for UV-12 h-PSNPs, and O₃-15 min-PSNPs in CaCl₂ solutions can be explained by their different surface properties. As aforementioned, UV-irradiation induced the formation of O-containing functional groups on the surface of the PSNPs, which can specifically interact and bridge with Ca²⁺ and consequently destabilized PSNPs (Liu et al., 2019b). Additionally, a comparison between the surface charges of the Pristine-PSNPs and the UV-12 h-PSNPs revealed that UV-12 h-PSNPs were less negatively charged than the Pristine-PSNPs over the entire tested range of CaCl₂ concentrations (Fig. S5b). This implies that Ca²⁺ was more effective in neutralizing negative charges on the UV-12 h-PSNPs surface than on the Pristine-PSNPs (Qu et al., 2010). Although O₃-15 min-PSNPs contained more O-containing functional groups on their surface, accompanied with high efficiency in interacting with Ca²⁺ (Fig. 1c and Fig. S5b), the bridging effect and charge neutralization did not reduce their stability.

Table 2

The critical coagulation concentrations (mM) of PSNPs before and after aging at different conditions.

Treatments	NaCl electrolyte solution				CaCl ₂ electrolyte solution			
	Without NOM	Humic acid	Lysozyme	Sodium alginate	Without NOM	Humic acid	Lysozyme	Sodium alginate
Pristine-PSNPs	198 ± 14a ^a	705 ± 22b	169 ± 48c	494 ± 39b	21.2 ± 0.9b	12.3 ± 0.4a	10.2 ± 1.2a	23.0 ± 2.2a
UV-12 h-PSNPs	293 ± 10b	480 ± 43a	73.9 ± 9.0b	200 ± 6.0a	20.5 ± 0.8b	14.1 ± 2.3a	12.7 ± 0.4b	17.7 ± 0.9b
UV-24 h-PSNPs	411 ± 17c	ND ^b	ND	ND	9.67 ± 0.8a	ND	ND	ND
O ₃ -15 min-PSNPs	> 500	> 700	46.3 ± 19a	> 700	28.4 ± 2.0c	19.6 ± 1.8b	10.4 ± 1.2a	20.4 ± 1.4a
O ₃ -30 min-PSNPs	> 500	ND	ND	ND	36.8 ± 3.0d	ND	ND	ND

^a : Values in each column with different letters (a, b, c or d) indicate significant ($p < 0.05$) differences among different treatments. The critical coagulation concentrations in some treatments cannot be calculated in the studied concentration ranges of NaCl solution, thus the statistical analysis cannot be performed for these treatments.

^b : Not determined.

The highest CCC_{Ca} (28 mM) for O₃-15 min-PSNPs can be ascribed to their high hydrophilicity as aforementioned. In addition, the released organic matter from PSNPs may attach on the surface of the PSNPs and provide a strong steric hindrance to restrain particles aggregation, as evident from the increased DOC content in O₃-15 min-PSNPs suspension (Wang et al., 2020a; Liu et al., 2019b).

We further explored the influence of aging time on the aggregation kinetics and colloidal stability of PSNPs (Figs. S4c, 4f, 4h and 2). The calculated CCC_{Na} and CCC_{Ca} demonstrated that prolonging UV-irradiation time inhibited the aggregation of PSNPs in NaCl solutions, while accelerated PSNPs aggregation in CaCl₂ solutions (Table 2). Contrary to the observations in UV-aged PSNPs, PSNPs tended to be stabilized in NaCl as well as in CaCl₂ solutions with increasing O₃ exposure time. This difference can be mainly attributed to the different oxidation ability between UV irradiation and O₃ oxidation, where UV irradiation is primarily confined to the top layer of polymers, while O₃ not only interacts with the polymer surface, but also causes the oxidation within particles (Halle et al., 2017). Although CaCl₂ significantly destabilized UV-irradiated PSNPs in the present study, this trend may be more appropriate for evaluating the aggregation behavior of primary nanoplastics (under short-term aging process as investigated in this study) other than secondary nanoplastics (under long-term aging process) fragmented from microplastics. In realistic scenarios, plastics debris which encountered long-term natural aging processes (i.e., UV irradiation, oxidation, and microbe degradation) can have an enhanced mobility attributed to the enhanced hydrophilicity and a strong steric hindrance arising from the adsorption of the leaked endogenous organic matters (Liu et al., 2019b), which is not the case from the short-term observations. Hence, further studies should be conducted to characterize the compositions of endogenous organic matters leaching from nanoplastics, identify the key components influencing the environmental behavior of nanoplastics, and explore the underlying mechanism of key endogenous organic matters controlling the aggregation of nanoplastics.

3.3. Type dependent effects of NOM on the aggregation of pristine and aged PSNPs

The presence of three types of NOM (HA, Lys, and SA) significantly affected the aggregation state of Pristine-PSNPs, UV-12 h-PSNPs, and O₃-15 min-PSNPs, as indicated by the different CCC values (Fig. S6-S8, Fig. 3, and Table 2). In NaCl solutions, the addition of HA greatly enhanced the CCC of Pristine-PSNPs and UV-12 h-PSNPs, whereas Lys adding markedly decreased the CCC values of Pristine-PSNPs, UV-12 h-PSNPs, and O₃-15 min-PSNPs. Such distinct observations highlighted that environmental behavior of nanoplastics also depends on the type of NOM and their properties in the surrounding environment (Huangfu et al., 2013). The presence of SA can stabilize Pristine-PSNPs in comparison with those exposed in pure NaCl solutions, while UV-12 h-PSNPs exhibited lower stability in the presence of SA. This discrepancy may have been caused by the differences in surface compositions between PSNPs before and after aging, suggesting that natural aging processes may strongly alter their behavior in the aqueous environment (Liu et al., 2019c; Wang et al., 2020b). The specific interactions between PSNPs and NOM were further investigated using LSCM. The LSCM images clearly showed that the green fluorescence of HA, FITC-Lys, and FITC-SA was colocalized with the red fluorescence of PSNPs, confirming that these environmental macromolecules were adsorbed on the surface of PSNPs (Fig. 4) (Wang et al., 2020c). Based on these observations, it can be concluded that the steric hindrance arising from the adsorption of HA and SA on the particles (i.e., Pristine-PSNPs and UV-12 h-PSNPs for HA, Pristine-PSNPs for SA) contributed to their high stability (Huangfu et al., 2013). Conversely, the attractive patch-charged interaction and bridging effect induced by the adsorption of Lys onto three PSNPs might be the dominating force for the decreased CCCs (Dong et al., 2020; Li et al., 2021b). However, the underlying mechanism for the high stability of O₃-15 min-PSNPs in the presence of HA and SA may be different from the mechanisms most relevant for Pristine-PSNPs because of their distinct hydrophobicity. It can be assumed that very limited numbers of

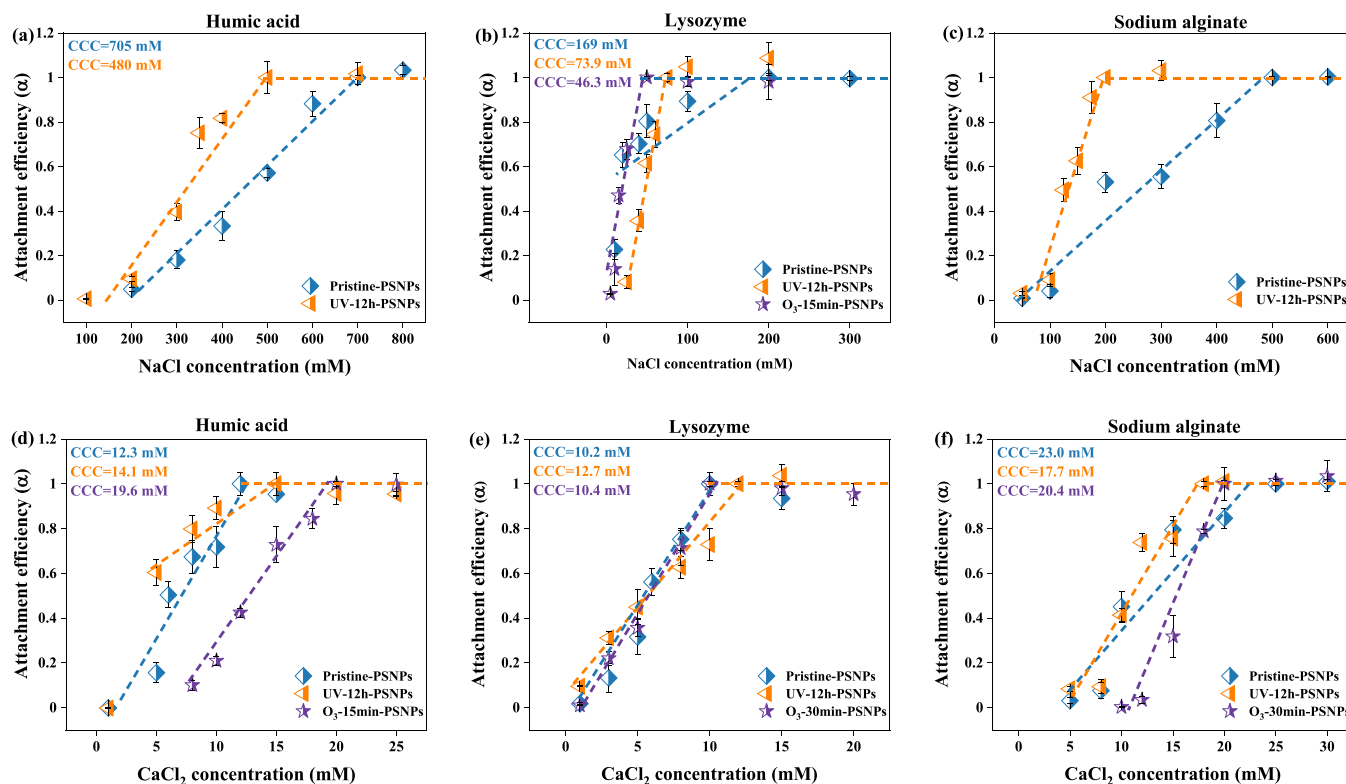


Fig. 3. Attachment efficiency of Pristine-PSNPs, UV-12 h-PSNPs and O₃-15 min-PSNPs as a function of NaCl, and CaCl₂ concentrations in the presence of 2 mg C/L humic acid (a and d), lysozyme (b and e), and sodium alginate (c and f), respectively.

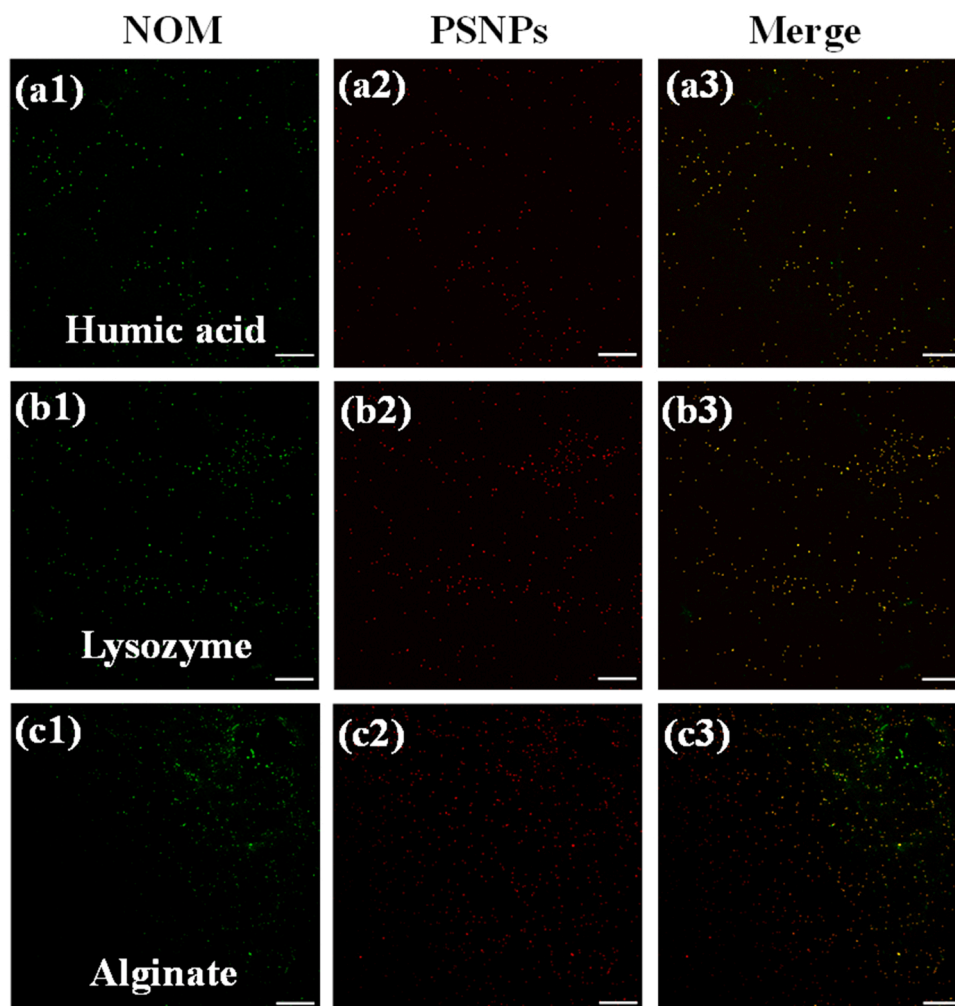


Fig. 4. Laser scanning confocal microscope images of humic acid, FITC-lysozyme, and FITC-sodium alginate incubated fluorescence-labeled PSNPs. Scale bar = 7.5 μm .

HA and SA molecules can attach to the surface of highly hydrophilic O₃-15 min-PSNPs (Qu et al., 2010). Hence, the increase in hydrophilicity and steric hindrance arising from endogenous organic matter were most likely the primary cause for the enhanced O₃-15 min-PSNP stability in the presence or absence of HA and SA (Liu et al., 2019a).

With respect to the CaCl₂ suspensions, the presence of HA decreased the CCC_{Ca} of Pristine-PSNPs, UV-12 h-PSNPs, and O₃-15 min-PSNPs, which is different from the observations in NaCl solutions (Table 2). This confirmed that the colloidal stability of PSNPs strongly depended on the electrolyte valence, as described by the Schulze-Hardy Rule (Tan et al., 2019). Conversely, Qu et al. (2010) found that 1 mg C/L HA enhanced the stability of fullerene before and after aging in CaCl₂ solutions due to steric repulsion. Various researchers confirmed that the aggregation behavior of colloids depends mainly on their surface physicochemical properties (size, shape, and surface functional groups), environmental conditions (IS, cation type, and source of NOM), and interactions between particles and naturally occurring colloids (Dong et al., 2020; Sun et al., 2020; Li et al., 2021a). Hence, this difference can be ascribed to differing physicochemical properties between PSNPs and fullerene (e.g., surface functional groups), and the different sources of humic substances used in different studies. Similarly, the addition of Lys in the CaCl₂ solutions reduced the CCC_{Ca} of PSNPs before and after aging. To better distinguish whether bridging flocculation of NOM could accelerate the aggregation of PSNPs, the aggregation kinetics of HA, Lys and SA in the absence and presence of CaCl₂ (10 mM) were investigated (Fig. S9). Results showed that Ca²⁺ could enhance the hydrodynamics diameter

of these NOM, confirming that divalent cations are helpful in pulling together individual NOM molecules into a more flocculated state via cation bridge (Xu et al., 2016; Hou et al., 2018). Hence, the decreased CCC_{Ca} of Pristine-PSNPs, UV-12 h-PSNPs, and O₃-15 min-PSNPs in the presence of HA or Lys could be attributed to the high efficiency of Ca²⁺ in neutralizing surface charges, and the Ca²⁺-bridging effect, which overcame the steric hindrance resulting from NOM adsorption on particles (Sun et al., 2018; Yang et al., 2019; Liu et al., 2020). However, addition of SA slightly enhanced the stability of Pristine-PSNPs, but decreased the stability of aged PSNPs. This can be explained by the linear semi-flexible structure of SA, which will be discussed in the later part.

In the presence of HA, Lys, and SA, UV-irradiation significantly reduced the CCC_{Na} of PSNPs, meaning that the stabilization effects of NOM on PSNPs can be reduced by UV aging. The reduced influence of NOM on the colloidal stability of UV-12 h-PSNPs can be ascribed to the decrease in NOM adsorption due to increased hydrophilicity of PSNPs after UV irradiation. This finding is in line with the results of Sun et al. (2021), who reported that the influence of protein on the stability of UV-irradiated graphene oxide was much weaker than in the case of pristine graphene oxide because of reduced adsorption of protein molecules. However, in NaCl solutions, the introduction of HA and SA had no effects on the D_h of O₃-15 min-PSNPs (Fig. S6c and S8c), meaning that O₃ treated PSNPs exhibited a high stability. This can be interpreted by the high hydrophilicity and steric repulsion arising from leached organic matter as aforementioned, and signified that colloidal stability

of nanoplastics highly depends on the extent of surface and inner oxidation.

In contrast to the decrease of the CCC_{Na} , the UV and O_3 aging treatments increased the CCC_{Ca} of PSNPs at different extents in the presence of HA and Lys. This suggested that the addition of HA and Lys enhanced the stability of aged-PSNPs in $CaCl_2$ solutions, which was in accordance to the report of Qu et al. (2010). Ca^{2+} may facilitate the adsorption of HA and Lys on aged-PSNPs, which subsequently provided steric repulsions to retard the aggregation of aged-PSNPs. Here, two potential mechanisms contributed to the enhanced NOM adsorption on the surface of UV-12 h-PSNPs and O_3 -15 min-PSNPs. On the one hand, Ca^{2+} can specifically interact with the oxygen-containing functional groups on the surface of UV-12 h-PSNPs and O_3 -15 min-PSNPs, neutralizing surface charges of particles as evidenced by the less negative zeta potential (Fig. S5). Meanwhile, Ca^{2+} can form complexes with HA/Lys and consequently decrease their charge (Chen et al., 2008; Li et al., 2020a, 2020b). Therefore, the presence of Ca^{2+} reduced the electrostatic repulsion between particles and HA/Lys, facilitating adsorption of NOM. On the other hand, divalent Ca^{2+} can connect the oxygen-containing functional groups on the surface of aged-PSNPs to HA/Lys because of the bridging effect. Furthermore, the 3D-EEM results clearly showed that UV-irradiation and O_3 -exposure influenced the interaction pattern between PSNPs and HA/Lys (Fig. S10). For example, O_3 treatment significantly quenched the fluorescence of HA (peak A, Ex/Em = 450/525). The O_3 -15 min-PSNPs addition exerted higher efficiency in decreasing the fluorescence of peak B of Lys (Ex/Em = 260/330), while Pristine-PSNPs tended to reduce the intensity of peak A of Lys (Ex/Em = 295/325). The difference in interaction pattern may be responsible for their distinct stability, which thus deserves further investigation. However, the influence of aging processes on the CCC_{Ca} of PSNPs in the presence of SA was not in agreement with the case of HA and Lys. Such distinct results can be interpreted by their different molecular structure. With respect to SA, it is known that SA displays a linear semi-flexible structure, which favors the adsorption of particles in $CaCl_2$ solutions (Saleh et al., 2010).

Under realistic conditions, NOM also undergoes oxidation, which would transform molecular weights (MW) fractions of NOM to small MW fractions (Gan et al., 2015). Li et al. (2020a, 2020b) reported that the reduction in the MW of Suwannee River NOM could accelerate the aggregation of ferrihydrite nanoparticles due to the low adsorption mass of NOM on particles surface and patch-charge attraction. Additionally, the oxidation of NOM would result in the cleavage of C=C bonds, and the formation of O-containing functional groups, which would further influence their hydrophobicity (Lim et al., 2019; Liu et al., 2019a). The change in the hydrophobicity of NOM can affect the adsorption amounts of NOM on the surface of nanoparticles (Ratpukdi et al., 2021). In general, higher stability of nanoplastics can be induced by the increased adsorption of NOM on NPs surface due to the steric repulsion (Sun et al., 2018). In addition, NOM types also play significant roles on the stability of nanoplastics. For instance, the stabilization of nanoplastics in NaCl followed the order of bovine serum albumin > humic acid > extracellular polymeric substance > sodium alginate (Liu et al., 2020). In the real aquatic environment, different types of NOM coexist while undergoing the same oxidation process with varying extents. This complexity alone could increase the difficulty to disentangle the aggregation behavior of nanoplastics without considering their interactions nor the status of nanoplastics. Hence, comprehension of the aggregation of nanoplastics under more real conditions where both nanoplastics and NOM are oxidized together requires step-by-step investigations. Our study here belongs to the very-first step where only the type of NOM was considered during their interactions with nanoplastics and subsequent aggregation behaviors. Overall, aging extent of nanoplastics, heterogeneity in NOM composition, and ion types should be all considered when each of their effects were individually elucidated when trying to predict the environmental behavior of nanoplastics.

3.4. Aggregation kinetics of pristine and aged PSNPs in natural water

To further understand the stability of aged PSNPs in the real environments, the aggregation kinetics of Pristine-PSNPs, UV-12 h-PSNPs, and O_3 -15 min-PSNPs in eight different natural aqueous matrices were explored (Fig. 5). Negligible aggregation of Pristine-PSNPs, and UV-12 h-PSNPs was perceived in lake water, river water, and groundwater, while significant aggregations were observed in seawater. Such distinct phenomena were mainly ascribed to the distinct ionic strength and NOM composition of eight waters (Table S2) (Yu et al., 2019; Wang et al., 2021). The fast aggregation of UV-12 h-PSNPs in two types of seawater can be interpreted by the high ionic strength (534 and 600 mM), which were far above the CCCs measured in electrolyte solutions. Moreover, 3D-EEM results showed that polysaccharide was the dominating NOM in seawater (Fig. S11), which could accelerate the aggregation of UV-12 h-PSNPs as evidenced by the lower CCCs of UV-12 h-PSNPs after SA addition. Nevertheless, the aggregation rates of UV-12 h-PSNPs (32 nm/min in SW-1, and 34 nm/min in SW-2) were lower than that of Pristine-PSNPs (41 nm/min in SW-1, and 37 nm/min in SW-2), meaning that PSNPs would become more stable after UV irradiation. Different from UV aged PSNPs, O_3 -15 min-PSNPs were well dispersed in the seawater samples. This was consistent with the observation on O_3 -15 min-PSNPs in the presence of SA and NaCl solutions, where the size of the O_3 -15 min-PSNPs remained unchanged in pure NaCl solutions as high as 700 mM. Similar to UV-12 h-PSNPs and Pristine-PSNPs, the D_h of O_3 -15 min-PSNPs was constant in lake water, river water, and groundwater, all of which contained NOM (i.e., humic substance, polysaccharide, and protein), whilst having a low ionic strength. Although some studies concluded that the high dispersity of PSNPs in fresh water could mainly be ascribed to steric repulsion arising from the NOM corona (Li et al., 2021a; Wang et al., 2021), this explanation is not applicable to aged-PSNPs investigated in this study. Aging processes may decrease the amount of NOM adsorbed on PSNPs surface by altering

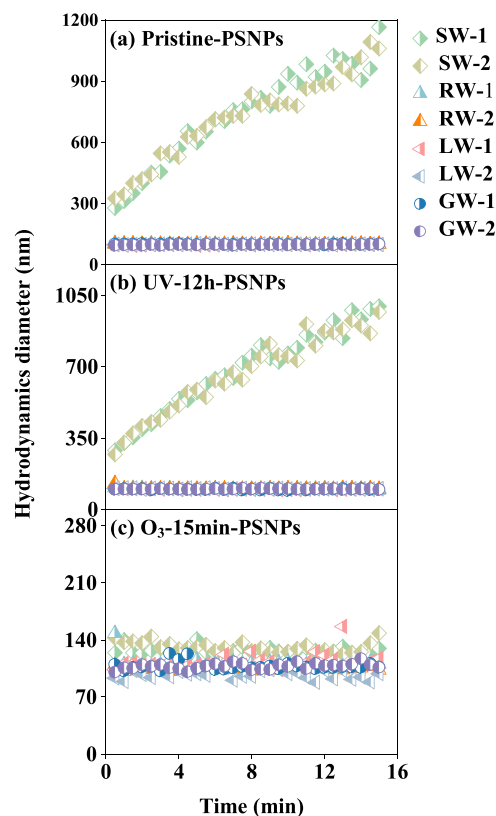


Fig. 5. Aggregation profiles of Pristine-PSNPs (a), UV-12 h-PSNPs (b), and O_3 -15 min-PSNPs (c) in different types of natural water.

their surface charge and hydrophilicity (Qu et al., 2010), and thus influencing NOM corona formation. According to our results obtained in synthetic waters, we postulate that the increase in hydrophilicity is the primary reason for the high stability of UV-12 h-PSNPs in fresh water. The combination of high hydrophilicity and steric repulsion resulting from leaching of endogenous organic matter should be responsible for the high dispensability of O₃-15 min-PSNPs in the waters studied.

4. Conclusions

The current study devoted to uncover the environmental behavior of nanoplastics, and demonstrated that the aggregation behavior of PSNPs can be affected by the complex interplays among aging factor, NOM type, and solution chemistry. The surface physicochemical properties of aged PSNPs were much altered in comparison to the properties of pristine PSNPs, and this has significant impacts on their aggregation behavior in aquatic environments. The oxygen-containing functional groups at the particle surface and the hydrophilicity of the PSNPs are crucial factors that govern the interactions with naturally occurring NOM and ions, implying that the aggregation state of nanoplastics varied across their life cycle. Considering the significant implications of the colloidal stability of nanoplastics on the growth and development of aquatic organisms, and the potential environmental risk imposed by their associated metals and persistent organic pollutants, more attention is warranted on the environmental behavior and ecological impact of aged-nanoplastics under environmentally relevant exposure conditions. Additionally, although UV and O₃ aging suppressed the aggregation of PSNPs in our investigated natural water, the encounter with biomacromolecules (such as lysozyme) may destabilized aged-PSNPs, as evidenced by the decreased CCC in the presence of Lys. This difference highlights the important role of environmental heterogeneity, particularly in NOM compositions and ion types, which also should be taken into consideration when evaluating and predicting the environmental risk associating with emerging nanoplastics. In realistic scenarios, microorganisms that are ubiquitously present can easily colonize the surfaces of plastics debris in the form of biofilms, which consequently alter their physical and chemical properties (such as surface morphology and roughness, surface charge, and particle size). Hence, further studies should address the influence of biological aging on the aggregation and stability of nano-sized plastics, and ascertain the key factors determining bio-aged nanoplastics aggregation.

Environmental Implication

Nanoplastics undergo aging processes in aqueous systems, altering their physicochemical properties and affecting their fate and transport. This study investigated the effects of aging via UV irradiation and O₃ oxidation on the aggregation kinetics of nanoplastics. Results showed that the aggregation tendency of nanoplastics was highly dependent on the aging degree and the type of natural organic matter. The increase in hydrophilicity and the leaching of endogenous organic matters manipulated the interactions of nanoplastics with NOMs, and subsequently influenced their aggregation states. These findings enrich our understanding on the aggregation of nanoplastics with important implications for environmental fate and risk.

CRedit authorship contribution statement

Xing Li: Investigation, Data curation, Formal analysis, Writing – original draft. **Sitong Ji:** Data curation. **Erkai He:** Supervision, Writing – review & editing, Funding acquisition. **Willie J.G.M. Peijnenburg:** Writing – review & editing. **Xinde Cao:** Resources, Project administration. **Ling Zhao:** Writing – review & editing. **Xiaoyun Xu:** Writing – review & editing. **Peihua Zhang:** Writing – review & editing. **Hao Qiu:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.128790.

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