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Review

Adsorption of environmental contaminants on micro- and nano-scale plastic polymers and the influence of weathering processes on their adsorptive attributes

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ABSTRACT

Increases in plastic-related pollution and their weathering can be a serious threat to environmental sustainability and human health, especially during the present COVID-19 (SARS-CoV-2 coronavirus) pandemic. Planetary risks of plastic waste disposed from diverse sources are exacerbated by the weathering-driven alterations in their physical-chemical attributes and presence of hazardous pollutants mediated through adsorption. Besides, plastic polymers act as vectors of toxic chemical contaminants and pathogenic microbes through sorption onto the 'plastisphere' (i.e., plastic-microbe/biofilm-environment interface). In this review, the effects of weathering-driven alterations on the plastisphere are addressed in relation to the fate/cycling of environmental contaminants along with the sorption/desorption dynamics of micro-/nano-scale plastic (MPs/NPs) polymers for emerging contaminants (e.g., endocrine-disrupting chemicals (EDCs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pharmaceuticals and personal care products (PPCPs), and certain heavy metals). The weathering processes, pathways, and mechanisms governing the adsorption of specific environmental pollutants on MPs/NPs surface are thus evaluated in relation to the physicochemical alterations based on several kinetic and isotherm studies. Consequently, the detailed evaluation on the role of the complex associations between weathering and physicochemical properties of plastics should help us gain a better knowledge with respect to the transport, behavior, fate, and toxicological chemistry of plastics along with the proper tactics for their sustainable remediation.

1. Introduction

Global-scale contamination by plastic polymers is occurring at an alarming pace, especially during present novel coronavirus (SARS-CoV-2) outbreak (Patrício Silva et al., 2021). Based on global regulatory institutions like the United Nations Environment Program (UNEP), plastic contamination and associated weathering mechanisms are an emergent environmental and human health concern (UNEP, 2014; Klingelhöfer et al., 2020). This is because of the weathering driven high surface reactivity of microplastics (MPs) and nanoplastics (NPs) that allow adsorption of hazardous chemical contaminants on 'plastisphere' (i.e., novel human-made ecosystem with close interface of plastic litter and microbiome) (Rochman et al., 2013; Rocha-Santos and Duarte, 2015; Jakubowska et al., 2020; Cortés-Arriagada, 2021). Further, the weathering induced physical-chemical changes are inextricably linked with the adsorption of hazardous pollutants on MPs and NPs to pose human health risks (Duan et al., 2021; Fu et al., 2021; Luo et al., 2022).

Among diverse environmental matrices, the pronounced weathering

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processes in marine ecosystems can serve as main depositories and reservoirs of MPs (with expected storage potential of 250 Mt (metric tons)) by 2025 (Sun et al., 2020). In the marine environment, increased weathering induced adsorption of inorganic, organic, and emerging contaminants on plastisphere and their subsequent desorption at biotic interface threatens the build-up of a 'Blue Economy' (i.e., ocean resources underpinning the economy and human well-being) (da Costa, 2018; Peng et al., 2020). Nonetheless, the terrestrial ecosystem is also not free from such a problem as it also represents a large fraction (14%) of global plastic pollution, which is further exacerbated through weathering processes and adsorption of environmental contaminants (Horton et al., 2017a, 2017b; Wanner, 2020; Vieira et al., 2021).

Plastic weathering processes can increase the environmental abundance of MPs/NPs to perturb the environmental sustainability and planetary public health due to their role as effective adsorbents/vectors of toxic inorganic contaminants such as heavy metals (Bradney et al., 2019), organic (Agboola and Benson, 2021; Fu et al., 2021), emerging pollutants (e.g., bisphenol A: BPA) (Cortés-Arriagada, 2021), and pathogenic microbes (Zettler et al., 2013; Wu et al., 2019a, 2019b; Zhang et al., 2020a, 2020b; Luo et al., 2022). It is well known that the weathering of plastic particles can allow microbial adhesion or colonization (Sun et al., 2020). Therefore, the plastisphere can act as a potential vector of pathogenic microbes such as *Pseudomonas* and *Vibrio* to pose human health risks (Koelmans et al., 2019). Also, weathered plastic surface associated with biofilm or microbial substrata can adsorb more pollutants relative to virgin MPs (Wang et al., 2021). In addition to the weathering induced hazardous effects, uncontrolled incineration of medical plastic waste as management option may contribute to the release of greenhouse gases (GHG) and other potentially dangerous pollutants such as polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), dioxins, furans, and heavy metals (Patrício Silva et al., 2021). The recent outburst of the SARS-CoV-2 pandemic has substantially raised the consumption and disposal rates of plastic products by the general public and para-medical/medical personals due to the increased global demand for PPE products (e.g., single-use face mask, medical gloves, gowns, etc.), packaged meals, plastic cups, and home-delivered groceries (Adyel, 2020; Prata et al., 2020; Patrício Silva et al., 2021). Therefore, the weathering of disposed plastic products (e.g., especially during COVID-19) can further enhance the chemical adsorption on plastisphere to exacerbate their hazardous effects.

The weathering linked physical-chemical factors (e.g., pH, temperature, solar irradiation, and the presence of salts such as NaCl and $CaCl_2$) and biotic factors (e.g., microbial diversity) influence the sorption-desorption mechanism of chemicals and pathogens on MPs/NPs surface (Zhang et al., 2019a). Therefore, adsorption of pollutants on plastic polymers and consequential physical-chemical processes are also controlled by weathering (Bradney et al., 2019; Rodrigues et al., 2019). Plastic weathering results in the formation of MPs/NPs in specific particle size ranges (e.g., MPs less than 5 mm in diameter and NPs with less than 100 nm) with salient physical-chemical and adsorptive attributes (Rocha-Santos and Duarte, 2015; da Costa et al., 2019; Hoang and Kim, 2020; Harraq and Bharti, 2021; Luo et al., 2022).

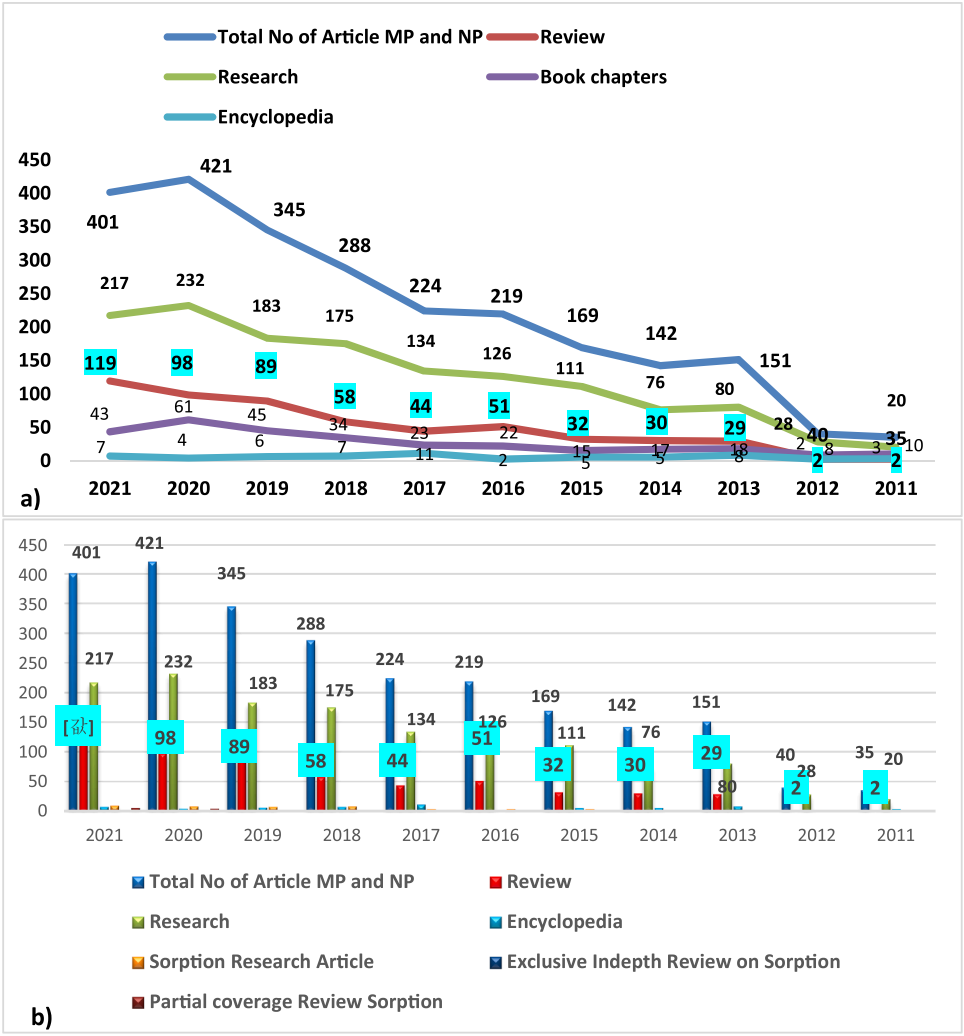

Fig. 1. Trends in the research publications related to MPs/NPs emphasizing lesser studies on pollutants adsorption on plastisphere, especially in terms of empirical or critical reviews during the last decade. (a) The number of experimental researches, review, book chapters, and encyclopedia publications pertaining to wide health/analytical or multiple prospects of MPs and NPs (duration 2011-ongoing 2021; Source-Science direct using the keywords: "Microplastics" and "Nanoplastics"; values in cyan color represent reviews in multiple aspects of MPs/NPs). (b) The number of research articles related to chemicals sorption on MPs/NPs in proportion to the total number and lack of a holistic review on sorption of diverse contaminants on plastics (keyword: 'chemical sorption on plastics); values in cyan color represent reviews which partially mentioned sorption of pollutants on MPs/NPs.

Our basic knowledge of the sorption chemistry of environmental contaminants on the plastisphere has been upgraded by enormous efforts in this research field (Yu et al., 2019; Fred-Ahmadu et al., 2020; Seeley et al., 2020; Rai et al., 2021a, 2021b, 2021c). Nevertheless, useful information is yet scanty to elucidate the influence of plastic weathering on adsorptive attributes. In this respect, a survey on the 'Science Direct' search engine also reveals the rapid increase in the number of articles (research, reviews, book chapters, and encyclopedia articles) on MP and NP pollution in the recent decade (2011 to on-going 2021) (Fig. 1a). Notably, there is a considerable increase in the research concerning the sorption chemistry of MPs/NPs for various emergent chemicals over the past five years (Fig. 1(a,b)). However, the number of research articles related to sorption of chemicals on the plastic surface is relatively low in proportion to the total number of publications covering the diverse aspects of MPs and NPs (Fig. 1b). Further, only 11 reviews are found to be made over the last five years that cover the sorption of contaminants on MPs and NPs surfaces to a large degree (e.g., Ribeiro et al., 2019; Yu et al., 2019; Mammo et al., 2020; Fred-Ahmadu et al., 2020; Wang et al., 2021). Such efforts were confined by their quest on plastisphere adsorption of organic/emerging pollutants (Agboola and Benson, 2021; Fu et al., 2021; Vieira et al., 2021) or the interactive role of plastic-microbes as vector of pollutants (Wang et al., 2021; Luo et al., 2022). As such, the past research efforts were inadequate to empirically address the effects of weathering on the adsorptive attributes of MPs and NPs.

The lack of our knowledge in the weathering-physical-chemical interface operating in tandem is yet significant not to gain an integrated overview as previous adsorption studies on MPs/NPs did not encompass a broad range of environmental pollutants. Therefore, our knowledge horizon on the influence of weathering on adsorptive and physical-chemical attributes is still narrow despite the noticeable progress made in the recent past.

To the best of our knowledge, the explicit holistic reviews on the sorption of diverse environmental contaminants on plastisphere are scanty (Fig. 1b). Besides, there is a knowledge gap in elucidating the role of weathering and subsequent alterations in physical-chemical/environmental processes on the sorption kinetics/isotherms of hazardous pollutants over MPs/NPs surfaces. Henceforth, the present review aims to fill the knowledge voids in weathering-plastisphere sorption interrelationship under different physical-chemical conditions. The recent increase in the global plastic pollution under the event of COVID-19 pandemic further exacerbated the investigation of their sorption processes and related mechanisms in relation to their interrelationship with weathering and physical-chemical properties (particle size and surface chemistry). A detailed analysis of these interactive factors (e.g., pollutant adsorption, sorption kinetics, environmental behavior, and ecotoxicity of MPs/NPs) is also made to allow the comparative evaluation of pollutant adsorption on plastic particles and non-plastic environmental substrata (e.g., biochar and nano-adsorbents). This review is thus expected to offer a better knowledge on the plastic weathering and their influence on adsorption mechanism of diverse hazardous chemicals.

2. Influence of weathering on adsorption chemistry of plastic particles

2.1. Weathering pathway/mechanisms and influence on plastisphere adsorption

Weathering is one of the most critical processes affecting the physical-chemical attributes of plastic particles (MPs/NPs) and their sorption affinity for contaminants in the surrounding environment (Lambert et al., 2017; Duan et al., 2021; Vieira et al., 2021; Luo et al., 2022) (Fig. 2a and b). Thus, the weathering and physical-chemical attributes operate in tandem to influence the pollutant adsorption on MPs/NPs surface. Although both weathering and alterations in physical-chemical attributes act in concert, each of them is discussed in separate sections to explicitly elucidate their influence on pollutant adsorption by MPs/NPs. There are several weathering, physical-chemical, and environmental stress processes that exert controls on plastisphere adsorption in several respects: (i) physical factors (*via* abrasion by sand particles), (ii) chemical factors (e.g., pH, ionic strength, and oxidizing agents), (iii) photo/thermal-oxidative factors (e.g., the climate in terms of light and heat), and (iv) biological factors by microbial degradation (Fig. 2b). Notably, the effect of weathering on plastic physico-chemical properties is a more complicated process in the real environment due to the simultaneous action of environmental attributes (in terms of climate, regional conditions, and biological factors) (Luo et al., 2022). Hence, the individualistic effects of a single environmental stress factor on plastic weathering initiated the physical-chemical attributes and their influence on pollutant adsorption are commonly investigated under controllable laboratory simulations (Sun et al., 2020). In this scenario, the effects of physical and chemical environmental stress factors on plastic weathering and sorption capability are frequently elucidated in laboratory research. For instance, MPs released into real field conditions are expected to undergo physical abrasion and chemical reaction accelerated by increasing temperature, in line with the Arrhenius relationship (Geburtig et al., 2019). In addition to abrasion, thermal oxidation and photo-oxidation are projected to trigger polymeric yellowing when exposed to near-UV and visible radiation via various free-radical reaction mechanisms that proceed according to the following steps (Gardette et al., 2013).

A. Chain initiation

$$RH + h\gamma \rightarrow \mathrm{R}\bullet + \mathrm{H}\bullet \quad (1)$$

B. Propagation (chain growth and branch formation)

$$R\bullet + O_2 \rightarrow ROO\bullet \quad (2)$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet \quad (3)$$

$$ROOH + h\gamma \rightarrow \mathrm{RO}\bullet + \quad \bullet\mathrm{OH} \quad (4)$$

$$2ROOH + h\gamma \rightarrow \mathrm{ROO}\bullet + RO\bullet + H_2O \quad (5)$$

C. Termination of the chain

$$R\bullet + R\bullet \rightarrow R - R \quad (no \quad free \quad radical \quad products) \quad (6)$$

$$R\bullet + ROO\bullet \rightarrow ROOR \quad (no \quad free \quad radical \quad products) \quad (7)$$

$$ROO\bullet + ROO\bullet \rightarrow ROOR + R\bullet + O_2 \quad (no \quad free \quad radical \quad products) \quad (8)$$

Photo-oxidative processes could also lead to significant alterations in the MPs surface chemistry, mainly by forming new functional groups such as -C =O; -C –O, and –OH in the presence of O/N oxides, OH radicals, and other photo-generated radicals (Chandra and Rustgi, 1998; Bandow et al., 2017; Duan et al., 2021). Ageing under photo-oxidative reactions may also induce microscopic surface cracks and polymeric plastic backbone fragmentation induced by light and oxygen radical reactions with their internal layers (H. Luo et al., 2020; H. Luo et al., 2020; Y. Luo et al., 2020). MPs aged under these weathering conditions showed increased surface area (Lambert et al., 2017). For instance, the surface area of polyethylene (PE) MPs increased from 3.4 ± 0.1–$5.8 \pm 0.3\ m^2g^{-1}$ as a result of cracking and fragmentation after exposure to Xenon light- (ZH-XD-150 Xenon-lamp aging test chamber) for 8 weeks (H. Luo et al., 2020; H. Luo et al., 2020; Y. Luo et al., 2020). In this case, the environmental factors were tightly regulated at 60 °C, 50% humidity, and light irradiance 1200 Wm^{-2} to demonstrate the influence of photo-oxidative ageing on PE MP surface area (H. Luo et al., 2020; H. Luo et al., 2020; Y. Luo et al., 2020).

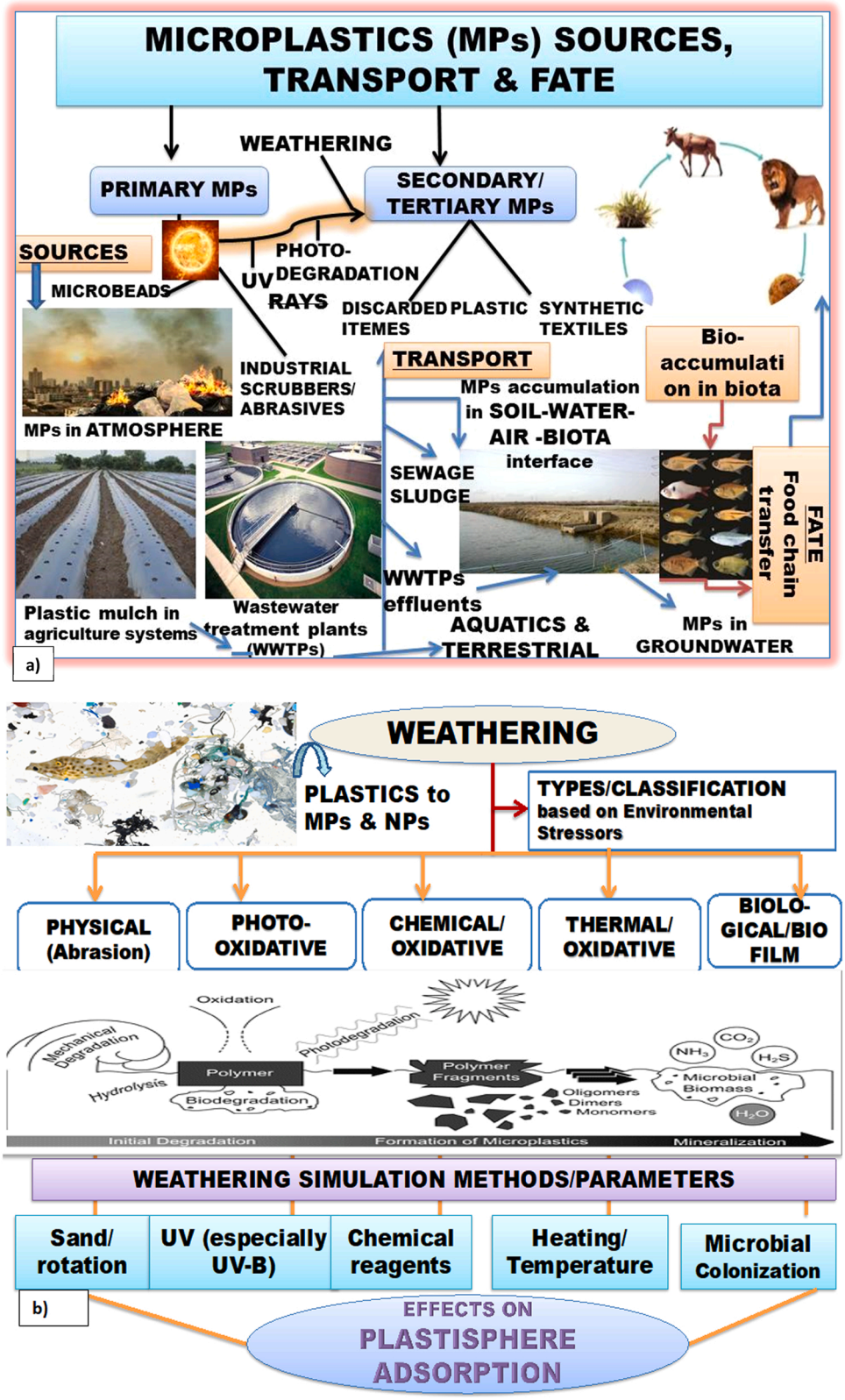

Fig. 2. Influence of weathering on adsorption and environmental fate of MPs (a) sources and the fate of MPs under the event of weathering and (b) classification of MP weathering caused by multiple abiotic/biotic environmental stressors and their influence on chemical sorption, environmental fate, and eco-toxicity (Modified 2b after Klein et al., 2018).

Similarly, in another study, the specific surface area of the naturally weathered plastic debris (polystyrene (PS) MPs) collected from the coastal beaches of North China was increased from 2.0 ± 0.1–7.9 ± 0.2 m^2 g^{-1} due to fragmentation upon oxidative weathering under solar irradiation when compared with virgin PS MPs foams (Zhang et al., 2018a)

However, it was noted that weathered PS MPs had a smaller average pore diameter (5.1 ± 0.2 nm) relative to virgin PS MPs with an average pore size of 39.3 ± 0.5 nm due to the pore deformation under solar weathering effects (Zhang et al., 2018a). In this context, the aged or weathered MP pellets offer a larger surface area for the sorption of multiple toxic organic contaminants (F. Wang et al., 2018; Z. Wang et al., 2018). Concomitantly, aged MP pellets allow better diffusion and transfer mechanisms for hazardous chemicals to penetrate deep inside their internal structure (Fries and Zarfl, 2012; Fries et al., 2013; Mendoza and Jones, 2015). In marine environments, it was observed that the sorption affinity of MP for organic chemicals (e.g., PCBs, PAHs, and DDT) decreased in the order PE > PP (polypropylene)> PS due to the weathering effects (F. Wang et al., 2018; Z. Wang et al., 2018). Moreover, the weathering of aged PS pellets also leads to the leaching of toxic chemicals such as hexabromocyclododecanes (HBCDDs) as the result of the photooxidation process (Z. Liu et al., 2019; G. Liu et al., 2019; Liu et al., 2020a, 2020b, 2020c).

As the weathering proceeds actively, the changes in physical-chemical characteristics of plastic particles take place to influence their potential for chemical adsorption (H. Luo et al., 2020; H. Luo et al., 2020; Y. Luo et al., 2020; Agboola and Benson, 2021; Fu et al., 2021). For example, exposure to UV radiation reduced the average molecular weight of PVC MPs while increasing their surface roughness and size to impact the adsorption behavior of triclosan (Ma et al., 2019). In contrast to photo-oxidation, biological weathering by *Chlorella pyrenoidosa* could improve plastic stability through biological secretions of extracellular polymeric substances (EPS) through the formation of a plastic-microbe biofilm (Mao et al., 2020). The formed plastic-microbe biofilm should reduce the aggregation of MP and NP particles in the surrounding environment, thereby improving their chemical stability (Mao et al., 2020). A study on the aggregation kinetics using Derjaguin–Landau–Verwey–Overbeek (DLVO) calculations revealed that the energy barrier of PS NPs (in water) was dependent on electrostatic repulsion, van der Waals forces, and the pH of the surrounding media (Mao et al., 2020). Additionally, chemical kinetic models indicated that a number of factors (e.g., DLVO/xDLVO ratio, ionic strength, and the PS NPs/chemical additives ratio) could impact PS NPs mobility and stability in the environment due to a charge shielding effect (Hu et al., 2020). Therefore, in addition to weathering, aggregation of MPs is a vital attribute governing their life cycle in real environmental conditions. This may be estimated using a set of chemical interactions.

$$V_T(d) = V_{vdw}(d) + V_{edl}(d) \tag{9}$$

$$V_{vdw}(d) = -\frac{A}{6}\left\langle \frac{2a^2}{d(4a+d)} \right| + \left| \frac{2a^2}{(2a+d)^2} \right\rangle + ln\left[\frac{d(4a+d)}{(2a+d)^2}\right] \tag{10}$$

$$V_{edl}(d) = \frac{32\pi\psi\varepsilon\varepsilon_0 K^2 T^2 a}{q_e^2 z^2} \times tanh^2\left(\frac{zq_e\psi}{4kT}\right) \times e^{-\kappa d} \tag{11}$$

Here, $V_T(d)$ represents the total interaction energy, $V_{vdw}(d)$ denotes van der Waals interaction energy, and $V_{edl}(d)$ is the electric double layer interaction energy in Eq. (9). In Eq. (10), A is the Hamaker constant for the NP dispersion system, a is the radius of NPs, and d is the separation distance between NPs. In Eq. (11), ε denotes the dielectric constant of the aqueous phase, ε_0 reflects the dielectric constant of vacuum, k is the Boltzmann constant, T is the absolute temperature, q_e is the electron charge, z denotes the charge number, ψ represents the surface potential of NPs, and κ denotes the Debye length.

The above equations of DLVO theory are vital in explaining the role of environmental factors such as inorganic ions, pH, organic matter, ionic strength, and natural minerals in controlling the aggregation of NPs (Mao et al., 2020; Wang et al., 2021). For example, a positive charge on NPs under low solution pH (acidic conditions) can reduce ψ value and stimulate the aggregation process. Conversely, a negative charge on NPs at a higher pH (alkaline medium) with negative ε –potentials can cause an increase in ψ value, which results in increased stability of PS NPs (Mao et al., 2020). Furthermore, an increased ionic strength could reduce the V_{edl} (d) factor, thereby facilitating the aggregation process of NPs (Wu et al., 2020a, 2020b, 2020c, 2020d; Wang et al., 2021). In this respect, natural minerals also facilitate hetero-aggregate formation by increasing the electrostatic interactions between the particles of NPs (Singh et al., 2019). The hydrophobic MPs with net surface zero charges increased the capability of MPs to attract and adsorb various substances (nutrients, biomolecules, organic matter, environmental contaminants, and pathogenic microbes) from the surrounding environment (Galloway et al., 2017). The layer of organic matter formed on the MPs surface can lead to eco-corona formation that enhances NPs stability while the aggregation process decreased with an increase in the ψ value (Saavedra et al., 2019; Wang et al., 2021). Accordingly, a MP surface covered with bio-molecules (eco-corona) potentially acts as a vehicle for transferring pathogens and persistent organic pollutants (POPs) through the environmental media as mediated through the adsorption process (Galloway et al., 2017). Similarly, NPs can also interact with biomolecules like protein, leading to the generation of eco-corona/"coronal protein rings", which had a remarkable impact on endocytosis in biota (Huang et al., 2018). Therefore, the formation of an eco-corona can influence the adsorption, fate, and eco-toxicity of MPs/NPs.

Fig. 2b shows the effects of weathering on the environmental fate and ecotoxicity of MPs. For example, solar radiation can enhance photo-oxidation, physicochemical abrasion, and microbial colonization of plastic polymers (Sun et al., 2020). These weathering attributes remarkably influence their environmental stability, transport/migration processes, sorption behavior, and toxicological chemistry. In some cases, long-term weathering could also increase the leaching rate of some chemical additives added during MP manufacturing (e.g., antioxidants or brominated flame retardants) and/or other adsorbed contaminants on plastic polymers (e.g., HBCDD) into the surrounding environment (Brandon et al., 2016). Note that antioxidant plastic additives are frequently added to increase plastic stability upon long-term aging through capturing the generated photo-oxidative free radicals. However, brominated flame retardants (categorized as POP) have been of particular interest given their potential to cause environmental damage and human health effects (Rai et al., 2021a). For instance, leaching of HBCDD from PS MPs increased in open seawater (42.9 mg g^{-1}; 61%) under photo-oxidative weathering compared with dark exposure (25.6 mg g^{-1}; 37%) after five days of aging (Rani et al., 2017). Furthermore, according to the simulation of weathering processes in several plastic polymers, photo-oxidative ageing promoted the leaching of many contaminants (e.g., Cu, Zn, Ca, Cl, and total organic carbon), compared to thermal oxidation (Bandow et al., 2017). In this context, the photo-oxidative ageing of MPs was also observed by introducing new adsorption bonds (e.g., C-O, C═O, and OH), unlike thermally induced oxidation (Bandow et al., 2017).

The sorption affinity of aged MPs for chemical contaminants is complex and depends on various factors such as contaminant types, chemical structure of plastic polymers, weathering conditions, and sorption mechanism. In principle, the weathering factors could decrease or increase MP adsorption affinity for target contaminants by altering the physicochemical attributes of MPs along with their textural and surface properties by the action of reactive oxygen species, as described in Eqs. 1–8 (Wang et al., 2021). For instance, beach-weathered MPs were found to have more oxygen-mediated functional groups than pristine MPs (Turner and Holmes, 2015; Huffer et al., 2018; Tiwari et al., 2019; Agboola and Benson, 2021). Furthermore, during the initial stages of photooxidative weathering, the crystallinity of aged MPs can increase

due to plastic degradation (amorphous polymers) associated with oxidative chain scission reactions and subsequent rearrangement into shorter segments (Carrasco et al., 2001; Lv et al., 2015; Rouillon et al., 2016; Fu et al., 2021). Unlike photo-oxidation, thermal oxidation of pre-degraded PE MPs in the marine environment did not significantly affect crystallinity (Karlsson et al., 2018). In contrast, thermal oxidation was found to increase the extent of biofouling and density of pre-degraded PE MPs in a marine environment. This indicates that the variations in the weathering factors (e.g., photo or thermal-oxidation processes) can have different influences on the physicochemical features of plastics in the real environment.

The sorption chemistry of environmental contaminants is inextricably linked with multiple weathering and ageing factors controlling the alterations in physical-chemical process (e.g., particle size). For instance, the sorption capacity of 2, 2 ', 4, 4'-tetrabromodiphenyl ether (BDE-47) on virgin PS MPs (6.16 ng g^{-1}) was reduced to 4.96, 3.75, and 3.53 ng g^{-1} upon ageing PS plastics for 90 days under seawater, seawater with UV irradiation, and UV irradiation alone, respectively (Wu et al., 2020a, 2020b, 2020c, 2020d). The low sorption of BDE-47 on PS aged in seawater was due to surface biofilm formation, which reduces the MPs hydrophobicity and the number of available sorption sites. However, the sorption of BDE-47 on PS MPs was further reduced in seawater irradiated with UV due to the increased number of oxygen-containing functional groups (Wu et al., 2020a, 2020b, 2020c, 2020d). These oxygen-mediated functional groups formed hydrogen bonds between the MP surface and the surrounding water molecules, increasing surface hydrophilicity and reducing hydrophobic BDE-47 sorption (Wu et al., 2020a, 2020b, 2020c, 2020d). In several other studies, an enhancement in the adsorption of chemical contaminants on MPs surface was observed with the progress of plastic weathering (P. Liu et al., 2019; Z. Liu et al., 2019; G. Liu et al., 2019). Herein, the increased adsorption was ascribed to increased surface area and formation of more favorable active sorption sites on the plastisphere. For example, the laboratory simulated weathering of PS and polyvinylchloride (PVC) plastic wastes enhanced the adsorption of hydrophilic antibiotics contaminants (e.g., ciprofloxacin) by 123.3% and 20.4%, respectively (P. Liu et al., 2019; Z. Liu et al., 2019; G. Liu et al., 2019). The enhanced adsorption performance of the antibiotics was ascribed to the increased negative surface zeta potential that enhances electrostatic interaction and hydrogen bonding between ciprofloxacin and the weathered plastic surface (P. Liu et al., 2019; Z. Liu et al., 2019; G. Liu et al., 2019). The physical abrasion (cryo-milled) and chemically induced (acid-treated) weathering factors also enhanced the sorption of difenoconazole and metformin pollutants on aged polyamide (PA), polypropylene (PP), and PS MPs (Goedecke et al., 2017). Furthermore, surface modifications of MPs through mechanical weathering (etching) also facilitated the sorption of PAHs (logK 3.85–5.18) more than UV-induced ageing (logK 3.71–4.98) when compared with pristine MPs (logK 3.80–4.95) (Li et al., 2020a, 2020b). Herein, the etching process accelerated intraparticle diffusion, π-π interactions, and hydrogen bonding mechanisms between MP and PAH aromatic rings.

In addition to organic chemical adsorption, the weathered PVC MPs were demonstrated to have a high adsorption capability against inorganic contaminants such as silver and copper ions when aged over 502 days in marine ecosystems (Kedzierski et al., 2018). Notably, the adsorption of metallic contaminants onto aged PVC MPs was induced after the desorption of estrogenic compounds from PVC plastics to the aquatic environment. The sorption of inorganic contaminants (e.g., Cr, Ni, Zn, Cd, Pb, Mn, and Al) also increased upon aging PVC, PP, PE, and PET MPs over one year in the natural aquatic environment of San Diego Bay (Rochman et al., 2014). Other inorganic contaminants (like Cd, Pb, and Br) were also associated with MPs during field and lab-based weathering studies at two different beaches of southwest England (Massos and Turner, 2017). Inorganic contaminants (e.g., Ag, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn) were strongly adsorbed on weathered or beached PE MPs relative to the virgin plastic particles of suspended river sediments. (Turner and Holmes, 2015). In this study, the higher adsorption of metallic contaminants on beached PE MPs than virgin pellets was attributed to surface modification by photooxidation (i.e., improved electrostatic interactions with increasing oxygenated surface functionalities) (Turner and Holmes, 2015; Turner et al., 2020). Further, these authors observed an adsorption isotherm of virgin PE against Hg and Pb with a maximum distribution coefficient of 6.0 mL g^{-1}. Conversely, the weathered or beached plastic pellets adsorbed with Pb and Ag (instead of Hg) recorded comparatively higher distribution coefficients on the order of 1.0×10^2 mL g^{-1} (Turner and Holmes, 2015). Interestingly, an increase in photo-oxidative weathering duration (from 200 to 500 h UV exposure) promoted the adsorption of metallic contaminants on PE MPs like Cu^{2+} (from 55 to 60–160–175 μg g^{-1}) and Zn^{2+} (from 45 to 50–75–80 μg g^{-1}) (Turner and Holmes, 2015; Wang et al., 2020a, 2020b).

In a laboratory simulation, it was observed that the addition of external chemical stimuli such as Fenton's reagent (a combination of H_2O_2 and ferrous ions with catalytic potential) could efficiently accelerate the aging process of MPs to subsequently alter the sorption potential for various chemical contaminants (Lang et al., 2020). In this context, Fenton's reagent can induce a more substantial aging effect on PS MP surfaces than H_2O_2, while the aging of PS MPs via a photo-mediated Fenton's reagent reaction was reported to decrease the adsorption efficiency for atorvastatin (Liu et al., 2020a, 2020b, 2020c). Conversely, oxygen-mediated functional groups such as carbonyl or carboxyl released during the aging of PS MPs increased the adsorption of amlodipine due to the high surface charge, hydrophilicity, and electrostatic/hydrogen bonding interactions on the MPs surface (P. Liu et al., 2019; Z. Liu et al., 2019; G. Liu et al., 2019). Compared with aged PS MPs, the adsorption of pharmaceuticals onto pristine PS MPs is mainly controlled by hydrophobic and π-π interaction mechanisms. In another report, the sorption potential of BDE-47 on aged PS MPs was reduced relative to pristine MPs, irrespective of changes in pH and DOM concentration (Wu et al., 2020a, 2020b, 2020c, 2020d). The decreased BDE-47 sorption was attributed to the reduced number of hydrophobic sorption sites on the aged PS MPs surface due to the increased oxygen-mediated surface functionalities during aging. Zhang et al. (2020b, 2020b), H. Zhang et al. (2020), J. Zhang et al. (2020), and W. Zhang et al. (2020) noted a decline in sorption potential of all the MPs after their UV-induced photooxidative weathering as new oxygenated functional groups occupied the available sorption sites. As discussed in this section, the weathering of MPs is of paramount importance in driving the changes in physical-chemical processes and plastic properties/attributes which remarkably influence the pollutants adsorption on their surface. Therefore, an explicit evaluation on the effects of weathering on the alterations in physical-chemical attributes or properties of plastics can better elucidate the adsorption chemistry of pollutant, as described below.

2.2. Physical-chemical changes on plastisphere and their influence on pollutant adsorption

It is well-known that the chemical interactions of emerging contaminants with plastic surfaces are affected by both intrinsic (plastic characteristics) and extrinsic (environmental/biotic) attributes (Fig. 3a, b). These intrinsic/extrinsic attributes regulate the sorption affinity of plastic polymers for contaminants and their toxicological chemistry (Fig. 3c). In this respect, the physical-chemical characteristics of MPs/NPs play a vital role in determining their sorption chemistry (Ma et al., 2020).

2.2.1. Physical attributes

2.2.1.1. Effect of size and shape. It is well-known that the sorption affinity and ecotoxicity of plastics are dependent on their size and shape

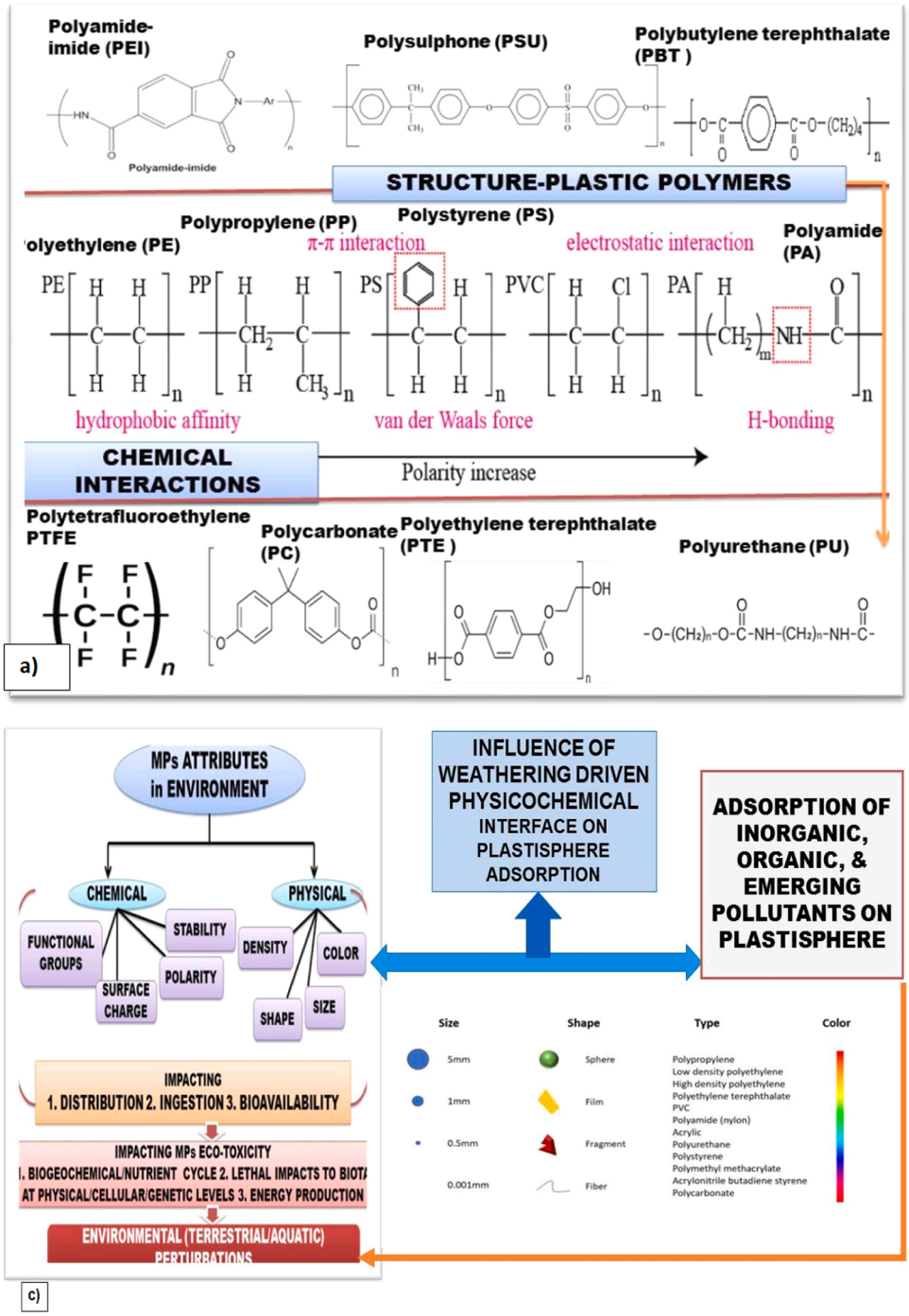

Fig. 3. Chemical interactions within plastic particles and sorption chemistry of inorganic, organic, and emerging environmental contaminants on plastisphere (a) Chemical interactions among MP plastic polymers, structure, and trends in polarity, (b) explanation of plastic-chemical interactions considering POP as a model example in elucidating adsorption mechanisms, and (c) weathering driven changes in physical-chemical factors affecting pollutant adsorption on plastic (MPs and NPs) surface which further influence their environmental fate, behavior, and eco-toxicity.

(Wright et al., 2013; Lambert et al., 2017; Ma et al., 2020; Fu et al., 2021). Weathering factors could cause fragmentation of larger MPs to smaller (nano-scale) particles and alter their surface functionalities (i.e., active sorption sites) and affinity for target adsorbates in the surrounding environmental matrices (Sun et al., 2020; Duan et al., 2021; Luo et al., 2022). For example, the downsizing of virgin PP MPs (of size 3–5 mm) by cryo-milling to 0.2–0.6 mm increased the plastic surface area (about 5–14 times) and its sorption capacity for difenoconazole by approx. 4 times (Goedecke et al., 2017). Furthermore, the sorption rates of PCBs on PS NPs were 1–2 fold higher than PE MPs, demonstrating the synergistic role of size and surface area of plastic polymers on the adsorption process (Velzeboer et al., 2014). The distribution coefficient of phenanthrene on NPs (log K_d: 5.82 ± 5.23) in freshwater was also higher than MPs (log K_d: 4.23 ± 3.04) (Ma et al., 2016). Accordingly, the toxic effects of NPs on biota (*Daphnia magna* and feathered minnow) might be greater than MPs (Ma et al., 2016; Hoang and Kim, 2020), thereby emphasizing the effect of size on ecotoxicity. It was also noted that MPs could be manufactured in different shapes (e.g., fibers, fragments, film, foam, and pellets) (Bond et al., 2018; Zhang et al., 2019a, 2019b). In addition, the plastic shape can also influence the adsorption and eco-toxicity of chemical pollutants (Koelmans et al., 2019). Among these shapes, fiber-shaped PP MPs are more toxic to *Hyalella azteca* (an amphipod) than PP beads (Au et al., 2015). Plastic particles of irregular and needle shapes bind to biotic surfaces more readily and have a greater toxic potential, which is ascribed to increased specific surface area (Lambert et al., 2017).

2.2.1.2. Effect of plastic color. The visual appearance of MPs may be linked with pseudo-ingestion by biota and may influence the sorption and toxicological chemistry of several organic contaminants (Ma et al., 2020). The color could also be altered by the extent of weathering of plastic polymers. In this respect, lighter color beached plastic pellets exhibit a higher affinity to absorb lower-molecular-weight PAHs, while darker plastics tend to preferentially adsorb higher-molecular-weight PAHs (Fisner et al., 2013). Black beached MPs adsorbed more organic chemical contaminants (e.g., PCBs and PAHs) compared to white MPs (Frias et al., 2013; Ma et al., 2020). Greater adsorption on black MPs was ascribed to the enhanced-photo-oxidative weathering under solar light irradiation (relative to aged white MPs). As such, the surface area of weathered black MPs increased for organics or chemical additive adsorption. Furthermore, white-colored MPs demonstrated differential growth inhibition for green algae (*Scenedesmus obliquus*) due to the presence of ethanol residue (toxic agent for microbial pathogen) in white-colored MPs (Chen et al., 2020). Therefore, the color of plastic particles can also impact the pollutants' adsorption and biotic eco-toxicity.

2.2.1.3. Effect of plastic density and polymer type. The MP density plays a key role in controlling the sorption dynamics of plastics for various organic and inorganic contaminants (Cole et al., 2013; Song et al., 2014; Desforges et al., 2015; Rummel et al., 2017; Carbery et al., 2018). For instance, lower-density PE (LDPE) MPs were seen to exhibit higher adsorption affinity for PCBs, phenanthrene, and PAHs than the higher-density PE (HDPE) MPs (Mato et al., 2001; Karapanagioti and Klontza, 2008; Fries and Zarfl, 2012). Similarly, the LDPE MPs displayed a higher diffusion coefficient for PAHs when compared to the higher-density MPs such as PVC and PP (Seidensticker et al., 2017; Chen et al., 2018; Lee et al., 2018; F. Wang et al., 2018; Z. Wang et al., 2018). The lower sorption of PP and PVC MPs for PAHs can be ascribed to their glassy attributes (with a glass transition temperature of > 80 °C) and the increased surface hydrophilicity (e.g., lower hydrophobic and π-π interaction with PAHs). In addition, LDPE MPs have a large free volume between the molecules (relative to high-density MPs (PVC/PP)) with fewer void spaces of 0.2–10% (George and Thomas, 2001; Mammo et al., 2020). Such textural properties increase the free volume and available adsorption sites onto LDPE MPs, accelerating the PAH sorption process by a diffusion mechanism. Accordingly, PE MPs recorded a higher partition coefficient for PAHs (log K_d: 4.58 ± 3.75) than PP (log K_d: 3.34 ± 2.23) and PVC MPs (log K_d: 3.22 ± 2.30) (F. Wang et al., 2018; Z. Wang et al., 2018). The types of plastic polymer affect the adsorption kinetics of Cd(II) ions on PE, PP, PVC, and PS MPs in conjunction with other factors such as pH, humic acid concentration, and ionic strength of the solution (Guo et al., 2020). In this respect, the adsorption capacity of Cd(II) ions was ranked as follows: PVC (151.4 mg Kg^{-1}) > PS (134.1 mg Kg^{-1}) > PP (123.6 mg Kg^{-1}) > PE (113.5 mg Kg^{-1}).

2.2.2. Chemical attributes

2.2.2.1. Effect of plastic surface chemistry. The surface chemistry of plastics profoundly controls their sorption and eco-toxicity mechanisms in the relevant environmental matrix. This is due to the effect of plastic surface chemistry on the interaction between MPs and chemical contaminants as well as bioaccumulation/bioavailability processes. The adsorption patterns of emerging pharmaceutical contaminants (e.g., sulfadiazine, amoxicillin, tetracycline, ciprofloxacin, and trimethoprim) on five MPs (i.e., PE, PP, PS, PVC, and polyamide [PA]) were studied as a function of their surface functionalities (Li et al., 2018). Accordingly, PA was found to have the highest adsorption capacity for all pharmaceutical contaminants due to H-bond formation between the amide groups of PA and the pharmaceuticals. Likewise, the adsorption affinity of 18 perfluoroalkyl substances (PFASs) on MPs decreased in the order of PS > PS-COOH > PE (Llorca et al., 2018). This resulted from the extent of the hydrophobic interactions between MPs and PFASs. Naphthalene (NAP) MPs with charged functional groups such as -NH_2, -OH, and -COOH also demonstrated lower adsorption of PAHs (e.g., K_d: 4.5–6.3 L/g) than uncharged naphthalene derivatives (with -CH_3; K_d: 11.6–12.0 L/g) (Yu et al., 2020a, 2020b). The lower sorption of PAHs on charged naphthalene derivatives was ascribed to the higher NAP MPs surface polarity (i.e., lower hydrophobicity in terms of Log K_{OW}). The charged functional groups tend to attenuate the π- π interactions and enhance the repulsion between NAP/NAP derivative molecules and MP particles, leading to reduced sorption capacity of PAHs on charged NAP MP derivatives (Yu et al., 2020a, 2020b).

PS-MPs with carboxylated functional groups (PS-COOH) increased the toxicity of inorganic chemical contaminants (e.g., Ni) in *D. magna* relative to unmodified PS due to the contribution of PS-COOH for concentrating Ni pollutants on its surface via a sorption process (Kim et al., 2017). Similarly, the exposure of mysid shrimp to PS-COOH produced a more toxic outcome than exposure to fresh PS due to their bio-accumulation in the stomachs of mysid shrimp (Wang et al., 2020a, 2020b). Upon exposing sea-urchin embryos to two functional derivatives of 40-nm PS (PS-COOH and PS-NH_2), only PS-NH_2 caused potential oxidative stress and apoptosis (Vega and Epel, 2004). Similarly, another eco-toxicity study in sea urchins also noted higher toxicity of positively charged 40-nm PS-NH_2 NPs when compared with negatively charged PS-COOH NPs (Della et al., 2014). It is suggested that PS-NH_2 disrupts the lysosomal membrane stability and induces oxy-radical production, causing cellular apoptosis and forming a PS-NH_2 protein corona. In contrast, PS-COOH NPs tend to micro-aggregate in ambient media, resulting in lower bioavailability and ecotoxicity (Canesi et al., 2016).

2.2.2.2. Effect of plastic microstructure. The crystalline structure and molecular composition of plastic polymers are crucial to understanding the sorption-desorption mechanism of various chemical contaminants (Teuten et al., 2007; Wang et al., 2015). This is due to the effects of molecular composition and structural crystallinity (relates to cross-linking, glass transition temperature, and packing) on the density and permeability of plastic polymers (Lambert et al., 2017). In general, more ordered and firmer structures of plastic polymers have a higher degree of crystallinity (Rodrigues et al., 2019). On this basis, it was noted that amorphous PE and PP polymers with a low degree of packing and greater free volume demonstrated a stronger propensity for chemical sorption of many organics, such as PCBs (Cornelissen et al., 2005; Pascall et al., 2005), PBDEs (Rochman et al., 2014a), PAHs, hexachlorocyclohexanes, and chlorinated benzenes (Lee et al., 2014) in comparison to crystalline PS polymers. Based on glass transition temperature, amorphous polymeric regions are subdivided into glassy and rubbery. Glassy PE/PS polymers have lower diffusivity and more accessible adsorption sites for hydrophobic organic contaminants (e.g., phenanthrene, lindane, and naphthalene) when compared to rubbery polymers (Guo rt al, 2012; Rodrigues et al., 2019). Highly crystalline plastic polymers do not facilitate the sorption of pharmaceuticals (such as ciprofloxacin) because of the requirement for significant energies to stabilize their highly ordered polymer chain regions (P. Liu et al., 2019; Z. Liu et al., 2019; G. Liu et al., 2019). It has also been suggested that more crystalline PE MPs usually exhibit smoother, cleaner surfaces with a reduced number of adsorption sites for chemical contaminants (e.g., they demonstrate lower sorption for phenanthrene, lindane, and naphthalene pollutants) (Guo et al., 2012). Herein, Guo et al. (2012) noted that the adsorption of phenanthrene, lindane, and naphthalene was increased when the crystallinity of PE MPs decreased from 59% to 26%. In this context, the PS MPs with high crystallinity showed higher adsorption for ciprofloxacin than PVC MPs with lower crystallinity (P. Liu et al., 2019; Z. Liu et al., 2019; G. Liu et al., 2019). Further, glassy polymers with a high degree of cross-linking (e.g., PVC and PS) exhibit nano-holes, which serve as strong adsorption sites for organic chemical

contaminants (Hüffer and Hofmann, 2016; Hartmann et al., 2017).

2.2.2.3. Effect of environmental parameters (water pH and ionic strength). The external environment (biotic and abiotic) also plays a vital role in controlling the adsorption behavior of plastics and their ecotoxicity. In general, the sorption capacity and ecotoxicity of chemical contaminants sorbed onto MPs are remarkably influenced by variations in water pH and ionic strength. For instance, at alkaline pH (> 8), the adsorption of sulfamethoxazole (SMX) on PE MPs greatly declined due to the electrostatic repulsion between the negatively charged PE surface and the anionic SMX (Xu et al., 2018a, 2018b). The adsorption efficiency of Triclosan on PS MPs was significantly decreased from 80% to 10% as solution pH increased from 4 to 10 (Seidensticker et al., 2018). The reduced adsorption at higher pH was ascribed to alterations in Triclosan ionic charge that induced electrostatic repulsion with PS MP. The chemical adsorption of positively charged sertraline and propranolol on negatively charged PE MPs also increased at neutral pH (6.85) due to the accelerated electrostatic attraction mechanism during the adsorption process (Razanajatovo et al., 2018).

The effects of salinity on chemical adsorption onto the plastisphere were demonstrated by the difference in values of partitioning coefficients in seawater (log $K_{MP\text{-}SW}$) and water (log $K_{MP\text{-}W}$) (F. Wang et al., 2018; Z. Wang et al., 2018). Nevertheless, salinity does not demonstrate a consistent pattern in relation to its effect on chemical adsorption (i.e., a consistent increase or decrease) (Mammo et al., 2020). For example, the PAH partition coefficient in seawater (log $K_{MP\text{-}SW}$) is higher than for water (log $K_{MP\text{-}W}$) due to the 'salting-out effect' (F. Wang et al., 2018; Z. Wang et al., 2018). This explains the decreased solubility of organic chemicals following an increase in salinity, leading to enhanced chemical availability for sorption on MPs surfaces. Similarly, the $K_{MP\text{-}SW}$ values of phenanthrene and pyrene were 7% and 5% greater than their $K_{MP\text{-}W}$ (Bakir et al., 2014). In contrast, hexachlorobenzene's partition coefficient in seawater was lower than its partition coefficient in pure water. A higher water salinity also significantly increased the sorption of Triclosan on PE MPs. However, no effect was observed on the sorption of other emerging chemical contaminants (e.g., carbamazepine, 4-methylbenzylidene camphor, and 17α-ethinyl estradiol) (Wu et al., 2016). Under a saline effect of NaCl and $CaCl_2$ addition, the sorption of PFOS on PE/PS MPs increased due to its existence in anionic form (Wang et al., 2015). Accordingly, the insignificant effects of salinity on chemical sorption of organic compounds on MP surfaces can be attributed to the predominant physisorption mechanism via hydrophobic and van der Waals interactions, which are not key factors in solution pH or salinity.

Accordingly, the sorption of hazardous inorganic/organic chemicals on MPs is also dependent on weather factors, NOM concentration, salinity, pH, and biofilms due to their influence on MP crystallinity, oxygen groups, surface area, and physical-chemical attributes (Liu et al., 2020a, 2020b, 2020c). The chemical stability of MPs and NPs in the aquatic environment also depends on surrounding conditions such as pH, aging, metal cations, and EPS (Mao et al., 2020). The interactions of MPs/NPs with environmental particulates and organic matter also influence their sorption affinity for chemical contaminants, aggregation, and fate behavior. Shiu et al. (2020) observed that the hydrophobic interactions of 25 nm PS NPs with DOM in freshwater led to microgel formation, accelerating the DOM-particulate organic matter (POM) transition. These interactions result in the development of large organic particles. Thus, the settling of NPs can alter the dynamics of aquatic ecosystems. In a real terrestrial environment, it was also noted that the identification/separation of plastics is complicated due to their similar or comparable physical-chemical attributes to that of soil organic matter (SOM) (Hidalgo-Ruz et al., 2012; Dekiff et al., 2014; Lima et al., 2014). The plastic-microbe interactions ('biofilms') release EPS, which influences the chemical adsorption and biodegradation (Rai et al., 2021b). Further, microbial exposure to MPs sorbed with environmental contaminants (heavy metals/ antibiotics) significantly alters their antibiotic resistance profile (Mammo et al., 2020). In the absence of biofilms, microbes on MPs can pave the way to degrade plastic polymers into metabolites of the tricarboxylic acid (TCA) cycle (Ghosh et al., 2019; Mammo et al., 2020). As such, the changes in physical-chemical properties of MPs/NPs during the weathering process are found to remarkably influence the potential of pollutant adsorption. Unraveling the interactive role of 'weathering-physicochemical processes' and 'pollutant adsorption' in an interrelated framework can remarkably help expand our knowledge horizon of MPs/NPs sorption chemistry.

3. Adsorption chemistry of pollutants on the plastic surface and eco-toxic effects

3.1. Sorption of environmental contaminants onto plastics and effects on biota

A good number of organic chemical additives (e.g., BPA, parabens, benzophenones, organotins, phthalates, polybrominated flame retardants) are used to manufacture plastic polymers with improved quality and higher chemical stability under various environmental conditions (i.e., making plastics more resistant to radiative and microbial degradation). However, it was noted that some of these additives might bind/absorb to MPs and NPs surfaces during their manufacturing stage and be released to biota under harsh weathering conditions (Lithner et al., 2009, 2011; Sofia et al., 2015; Y. Luo et al., 2020; Duan et al., 2021). Most of these released organic additives act as harmful chemicals which are categorized as endocrine-disrupting chemicals (EDCs), which are hazardous to the environment and human health (Gallo et al., 2018; Rai et al., 2018a, 2018b, 2019, 2020; Amereh et al., 2020; Cortés-Arriagada, 2021). This fact was verified by a 48 h microcosm study on the movement of *Daphnia* exposed to 32 plastic leachates (EC_{50}: 5–80 g plastic material L^{-1}) (Lithner et al., 2009). The results showed no impact on *Daphnia* mobility even at high concentrations up to 70–100 g L^{-1}. In contrast, the dramatic accumulation of phenanthrene in *Arenicola marina* (lugworm) was seen when exposed to ambient concentrations of only 1 μg PE/g sediment (Teuten et al., 2007). Similar findings were observed in *Nitocra spinipes* (marine copepod), where 38% of 21 plastic samples showed negative effects (Sofia et al., 2015). Further, it was noted that di (2-ethylhexyl) phthalate (DEHP) and other phthalates are EDCs with potential renal, reproductive, cardio, and neuro-toxic effects on biota (Rowdhwal and Chen, 2018). In Bohai and the Yellow Sea of China, phthalate concentrations of 6.09 ng/g were recorded for MPs (PE, PP, and PS) in beach samples, of which 64% consisted of DEHP (Zhang et al., 2018a).

BPA is also a chemical additive that constitutes 65% of polycarbonate (PC) and 30% of epoxy resin plastics as monomeric units with potential estrogenic properties (Fred-Ahmadu et al., 2020). The maximum BPA adsorption on PVC MPs was 0.19 ± 0.02 mg g^{-1} at the initial plastic concentration of 1.5 g L^{-1} (Wu et al., 2019a, 2019b). Likewise, flame retardants (such as polybrominated diphenyl ethers (PBDE)) have been demonstrated to be carcinogenic, mutagenic, and teratogenic with potential reproductive, liver, and neurotoxicity in mice (USEPA, 2017; Fred-Ahmadu et al., 2020). In light of these toxic effects, adsorption studies of PBDE on MPs were emphasized in biota such as a marine amphipod *Allorchestes compressa* (Chua et al., 2014). Accordingly, MP adsorption was greater in higher PBDE congeners (BDE-154/-153) than in lower brominated congeners such as BDE-28/-47. Likewise, a significant correlation was found between the density of MPs and the absorbed concentration of PBDE (BDEs 183–209) in the biomass of marine myctophid fish (Rochman et al., 2014). Similarly, the sorption of PBDEs (congeners BDE 47, 99, and 153) was demonstrated to occur on several MPs (PE, PP, PS, and PE) under different conditions (e.g., experimental pHs, temperatures, salinities, and organic matter concentrations) (Xu et al., 2019). In field conditions in Swiss lakes, several plastic additives (phthalates, BPA, PBDEs, and NP) were measured in collected MPs samples at concentrations above

detection limits (Faure et al., 2015). These NPs are often considered as other examples of toxic EDCs that leach from MPs (e.g., PET, high-density PE, and PVC bottles), yielding concentrations ranging from 180 ng/L (from HDPE) to 300 ng/L (from PVC) (Loyo-Rosales et al., 2004). The hazardous impact of NP leaching from plastics inhibits mitochondrial complex 1, perturbing normal respiratory chain functioning (Belaiche et al., 2009). Plastic polymers can also act as potential vectors or sources of organic/inorganic/emerging contaminants in biota, which can pose serious threats to biota (Kaposi et al., 2014; Rochman et al., 2015; Avio et al., 2015; Agboola and Benson, 2021; Fu et al., 2021; Vieira et al., 2021). Table 1 summarizes a list of the emerging contaminants adsorbed on plastic particles under the event of weathering and methods used for their measurement. Further, the list of organic and inorganic contaminants adsorbed on the weathered plastic particles and their associated eco-toxicity is compiled in Table 2. Thus, the chemical additives associated with plastic particles can be released into environmental matrices under the event of weathering. The release or leaching of additives can potentially act as hazardous pollutants with adverse effects on biota.

The weathering driven degradation of plastics and consequential leaching of fluorescent additives (such as 3,3′-diaminobenzidine and similar substances) from PUMPs (of 1.6 g L^{-1} concentration) was also reported to inhibit microalgae (*Chlorella vulgaris*) photosynthesis (Luo et al., 2019). Note that the leaching or desorption of these chemical/additive contaminants depends on the MPs' physicochemical and textural attributes and other environmental factors during the process of weathering (Fred-Ahmadu et al., 2020). Recently, Gu et al. (2020) also found that the presence of polybrominated diphenyl ethers (BDE-47) on

Table 1
Sorbed chemical contaminants on several weathered plastic particles (MP and NP) investigated in microcosm (M)/lab and field (F) conditions with the instrumental techniques used.

S. No.	MPs/NPs polymer types in the environment/ Organism	MPs-size	Organic sorbed chemicals	Detection techniques	Study type [Microcosm (M)/ Field (F)]	Reference
1.	PE & PS *M. galloprovincialis*	< 100 μm	Pyrene	HPLC-Fluorimetric detection	M	Avio et al. (2015); Rodrigues et al. (2019)
2.	PS	5 μm	Dibutyl phthalate (DBP)	SEM & Flow cytometer	M	Li et al. (2020, 2020b)
3.	PA, PE, PVC, PS	< 250 μm	n-Hexane, Cyclohexane Benzene Toluene Chlorobenzene Ethylbenzoate Naphthalene	GC-MS	M	Hüffer and Hofmann (2016)
4.	PET, PE-HD, PP, PVC PE-LD	Pellets (<5 mm)	Acenaphthalene, Acenaphthene Fluorene, Phenanthrene Anthracene, Fluoranthene Pyrene, Benz(a)anthracene Chrysene, Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene, Indeno(123-cd) pyrene, Dibenzo(ah)anthracene Benzo(ghi)perylene, CB congeners: 8, 18, 28, 52, 44, 60, 101, 81, 77, 123, 118, 114, 153, 105, 138, 126, 187, 128, 167, 156, 180, 169, 170, 189, 196, 206, 209	GC-MS	F	Rochman et al. (2013); Rodrigues et al. (2019)
5.	PP	0.45–0.85 mm	Tonalide, Musk xylene, Musk ketone	GC-MS	M	Zhang et al. (2017)
6.	PE	10–180 μm	PCB 118 PCB 126	GC-MS	M	Velzeboer et al. (2014); Rodrigues et al. (2019)
7.	PS	70 nm (nano)	Phenanthrene, Anthracene, Fluoranthene, Pyrene Benzo(a)anthracene, Chrysene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Benzo[g,h,i]perylene	HPLC-fluorescence Detector	M	Liu et al. (2016)
8.	PE	10–20 μm Zebrafish (*Danio rerio*)	Benzo(a)pyrene	Fluorescence spectroscopy	M	Batel et al. (2018)
9.	PVC PE	200–250 μm *A.marina,* Fish, Seabird (*Fulmarus glacialis*)	Dichlorodiphenyltrichloroethane Phenanthrene Bis(2-ethylhexyl)phthalate	LSC	M	Bakir et al., (2016)
10.	PE-LD	20–25 μm *M. galloprovincialis*	Benzo(a)pyrene	GC-MS	M	Pittura et al. (2018)
11.	PE	212–250 μm Bacteria	Phenanthrene, Anthracene	GC-MS	M	Kleinteich et al. (2018)
12.	PE	Pellets (<5 mm)	PCBs (38 PCB congeners)	GC-MS	M	Rodrigues et al. (2019)
13.	PE, PP, PS	< 250 μm	Phenanthrene, Fluoranthene Anthracene, Pentachlorobenzene Chrysene, Benzo(a)pyrene, Dibenz(a,h)anthracene, Benzo(ghi)perylene, Pyrene αß-HCH, ß¥-HCH, ¥–HCH, £ -HCH Hexachlorobenzene	GC-ECD (HCHs, PCBs) HPLC-Fluorescence detector (PAHs)	M	Lee et al. (2014); Rodrigues et al. (2019)

Table 2
Chemical contaminants (organic/inorganic) adsorbed on MPs under the event of weathering and their eco-toxic impacts.

S. No.	CHEMICAL CONTAMINANTS	MPs	Model organism/ species	Eco-toxicity (cumulative-MPs+ adsorbed chemical)	Reference
ORGANIC CHEMICAL CONTAMINANTS					
1.	PAHs/PCBs/PBDEs	PE; PS; PSNPs and humic acid-PS-matrix	Japanese medaka (*Oryzias latipes*); Mussel (*Mytilus galloprovincialis*); *Daphnia magna; Gammarus roeseli*	Adsorption of PAHs led to genotoxicity, neurotoxicity, oxidative stress, and endocrine disruption	Rochman et al. (2014); Avio et al. (2015); Ma et al. (2020); Lin et al. (2020); Bartonitz et al. (2020)
2.	Procainamide and doxycycline (pharmaceuticals)	Red fluorescent polymer microspheres	*Tetraselmis chuii* (marine microalga)	Adsorbed pharmaceutical chemicals enhanced reduction in chlorophyll	Prata (2018)
3.	Triclosan (TCS)	PE;PS;PVC; PVC800	*Skeletonema costatum* (microalga)	The adsorption of TCS led to reduced growth	Zhu et al. (2019)
4.	^{14}C Phenanthrene	PS MPs	*Daphnia magna*	Enhanced the eco-toxicity	Ma et al. (2020)
5.	Perfluorinated compounds (PFCs), PCBs, methyl-mercury	LDPE	Zebrafish	Adsorbed LDPE caused acute liver toxicity in fish	Rainieri et al. (2018)
6.	Organic pyrethroid insecticide (deltamethrin)	PE MPs	*Daphnia magna*	Enhanced eco-toxic responses	Felten et al. (2020)
7.	Tetrabromobisphenol a (TBBPA)	Cosmetic-derived MP (PE microbeads)	Zebrafish	Enhanced oxidative stress	Yu et al. (2020a, 2020b)
8.	Decabromodiphenyl ether (BDE-209)	PS MPs	Marine scallop (*Chlamys farreri*)	Adverse impacts on hemocyte phagocytosis and ultrastructural changes in gills and digestive gland	Xia et al. (2020)
9.	Polybrominated diphenyl ethers (BDE-47)	PS MPs	Marine mussel (*Mytilus coruscus*)	Elevated respiration rate and antioxidant enzyme levels	Gu et al. (2020)
INORGANIC CHEMICAL CONTAMINANTS					
10.	Hg	Fluorescence red polymer microspheres	European seabass (*Dicentrarchus labrax*)	Hg adsorption on polymer enhanced the eco-toxic impact in the form of oxidative stress and neuro-toxicity	Antao Barboza et al. (2018); Ma et al. (2020)
11.	Cu	PS	Zebrafish	MPs associated with natural organic matter (NOM) elevated the toxicity of Cu, manifested through increased levels of malonaldehyde and metallothionein while reducing super-oxide dismutase (SOD)	Qiao et al. (2019)
12.	Ni	PS; PS-COOH	*Daphnia magna*	Adsorption of Ni on PS demonstrated antagonistic effect on eco-toxicity, whereas PS-COOH had a synergistic effect with Ni	Kim et al. (2017)
13.	Pb & Cr	Powdered MPs	*Microcystis aeruginosa*	Concentrations (>10 μg L^{-1}) led to inhibition of photosynthesis	Y. Luo et al. (2020); H. Luo et al. (2020)
14.	Pb	polyolefins & PVC	Avian physiologically-based extraction test (PBET)	Bioaccessible concentrations of added Pb (as chemical additive) were significantly higher than environmentally adsorbed	Turner et al. (2020)
15.	Ag	PE microbeads from cosmetics	*L. minor* and *Daphnia magna*	Ag on aged microbeads exhibited eco-toxicological impacts	Kalčíková et al. (2020)

the PS MPs surface should cause anti-oxidative stress in marine mussels (Table 2). Further, the common herbicide glyphosate, combined with PS-NP-NH_2, exhibited increased toxicity in *M. aeruginosa* relative to glyphosate alone. In contrast, PS-NP-NH_2 particles alone showed no toxicity (Zhang et al., 2018a, 2018b; Q. Zhang et al., 2018). Further, Yu et al. (2020a, 2020b) investigated the sorption of flame retardant tetrabromobisphenol A [TBBPA] on cosmetic-MPs (PE μBs) and noted an elevated production of harmful free radicals to put oxidative stress on zebrafish.

The association of MPs with other environmental contaminants (e.g., natural organic matter (NOM), minerals and nano-scale particles) can enhance their ecotoxicity (Oriekhova and Stoll, 2018; Qiao et al., 2019). In addition to the surface charge on the plastic polymeric surface, the charges on NOM and nanoscale particles are mainly responsible for increases in toxicity. For instance, neutral or positively charged MPs exacerbated the toxic impact of synthetic nanoparticles (e.g., TiO_2) on marine algae *Chlorella* sp. (Thiagarajan et al., 2019). Conversely, negatively charged PS-COOH MPs decreased TiO_2 NP toxicity which was ascribed to hetero-aggregation between PS MPs and synthetic nanoparticles, unlike positively charged MPs. It was also found that the oxidative stress trend was dependent on the surface charge of PS (PS-NH_2/TiO_2 > PS-COOH/TiO_2), signifying its significant effect on the adsorption potential of environmental contaminants on the plastisphere (Thiagarajan et al., 2019).

As heavy metals also adsorb on plastic particles, their subsequent release can take place to increase algae toxicity (H. Luo et al., 2020; H. Luo et al., 2020; Y. Luo et al., 2020; Capolupo et al., 2020). In this regard, high concentrations of Pb and Cr (e.g., greater than 10 μg·L^{-1}) inhibited photosynthesis in blue-green algae (H. Luo et al., 2020; H. Luo et al., 2020; Y. Luo et al., 2020). In addition to contaminants, microbiomes (such as bacteria and algae) could also be adsorbed onto MPs/NPs. Subsequent ingestion of these microbiomes may exertharmful effects on higher trophic level biota (Xu et al., 2018a, 2018b; Shen et al., 2019). The majority of the studies describing the eco-toxic effects of plastic weathering and subsequent leaching of pollutants were regulated under controlled environment at laboratory scale. However, the effects of weathered plastic particles on the trophic level/food chain can be pragmatically assessed with prioritization of eco-toxic studies in field environment. In light of these hazardous biological impacts, the influence of weathering on the association between MPs and environmental contaminants through several adsorptive attributes should be investigated more thoroughly (Zhang et al., 2019b; Luo et al., 2022),especially based on the scenario of the coronavirus (COVID-19) pandemic.

3.2. Sorption chemistry of environmental contaminants onto plastics

The sorption chemistry of environmental contaminants on MPs involves both absorption and adsorption processes. The adsorptive attributes of plastic particles and associated chemistry are tightly regulated by weathering processes. Each of those processes influences the transport, fate, and toxicity of MPs and other environmental contaminants (Fig. 4) (Duan et al., 2021). In absorption, the chemical contaminant penetrates through MPs/NPs solid molecules by diffusion or osmosis processes and becomes associated within the solid phase matrix (Endo and Koelmans, 2016; Fu et al., 2021). However, in the case of adsorption, the chemical contaminant adheres to the MP and NP solid surfaces through physical attachment. Further, the adsorbate interacts with a sorbent at the sorbent-sorbate interface. In contrast, the sorbate (e.g., liquid) interacts internally with the sorbent of different medium (usually a solid matrix) in absorption. Hence, the partitioning of the chemical contaminants takes place due to the chemical forces within MPs (Fotopoulou and Karapanagioti, 2012; Endo and Koelmans, 2016; Agboola and Benson, 2021). Therefore, in the case of MPs, the chemical partitioning is usually synonymous with absorption. In contrast, a wide array of physical (reversible bonds) and chemical (irreversible covalent bonds) interactions are involved in the case of the adsorption process (Fig. 3a). However, it should be noted that the sorption mechanism of chemical contaminants on plastic particles is dependent on various physicochemical and environmental abiotic/biotic factors (Fig. 3b), such as the type and characteristics of pollutants, free energy relationships, and the textural and surface chemistry of the MP/NP solid phase (Fred-Ahmadu et al., 2020).

The variance in polarity and hydrophobicity of organic chemicals is also an important factor that influences adsorption chemistry on MPs/NPs (Wang et al., 2021). Specifically, hydrophobic organic chemicals tend to adsorb on NPs with $K_{pw} > 1$ to reflect their greater enrichment on plastispheres than in the aqueous phase (Liu et al., 2018). Furthermore, the sorption of polar chemical contaminants frequently occurs on the surfaces of aged NPs according to the polarity (i.e., surface interaction mechanisms) (Liu et al., 2018). Conversely, non-polar or less polar chemicals are adsorbed within the inner matrices of plastic polymers (i.e., pore diffusion mechanism) (Liu et al., 2018; Wang et al., 2021). Such differences in adsorption chemistry of weathered plastics, as driven by the polarity/hydrophobicity of chemicals, can also lead to changes in their mobility and bioavailability.

The sorption affinity of MPs/NPs for organic contaminants is influenced strongly by weathering effects (such as UV- photo-oxidation and microbial degradation processes) through which alterations are induced in their surface chemistry, texture, and crystallinity (Fotopoulou and Karapanagioti, 2012; Endo and Koelmans, 2016; Yu et al., 2019; Harraq and Bharti, 2021). In this context, the PVC MP exhibited a high efficiency for adsorbing five BPAs via physical adsorption mechanisms such as hydrophobic interactions, electrostatic force, and non-covalent bonds (Wu et al., 2019a, 2019b). It has also been recognized that UV-induced weathering increased the surface area of PVC (1.85 times) and PLA MPs (2.66 times) when compared with the virgin PVC/PLA pellets (Fan et al., 2021). Herein, this increase in surface area of weathered PVC/PLA MPs enhanced the adsorption potential of antibiotics (ciprofloxacin and tetracycline) due to the increased number of oxygen-containing surface functionalities (e.g., carbonyl groups) (Fan et al., 2021). This is supported by the decrease in the zeta potential of PLA (from −7.79 to −13.51 mV) and PVC MPs (from −4.96 to −8.34 mV) when compared with the virgin PVC/PLA pellets due to UV-weathering effects (Fan et al., 2021). Accordingly, weathering can also cause alterations in the chemical interactions between MPs/NPs and chemical contaminants (Reichel et al., 2021). In this sense, the π-π-interactions were the primary adsorption mechanism of organic chemicals on virgin PS NPs. In contrast, the sorption mechanisms for aged PS NPs were altered to electrostatic interactions and hydrogen bonding (Liu et al., 2020a, 2020b, 2020c). Such alteration in the adsorption mechanism was attributed to the change of MPs/NPs surface chemistry under weathering conditions (i.e., increased oxygen functional groups on aged PS NPs) (Liu et al., 2020a, 2020b, 2020c). The nucleophilic nature of the outer surface of PET NPs can remarkably facilitate the mass transfer and intraparticle diffusion of emerging contaminants (e.g., BPA) into their inner matrices to form stable complexes with a maximum adsorption

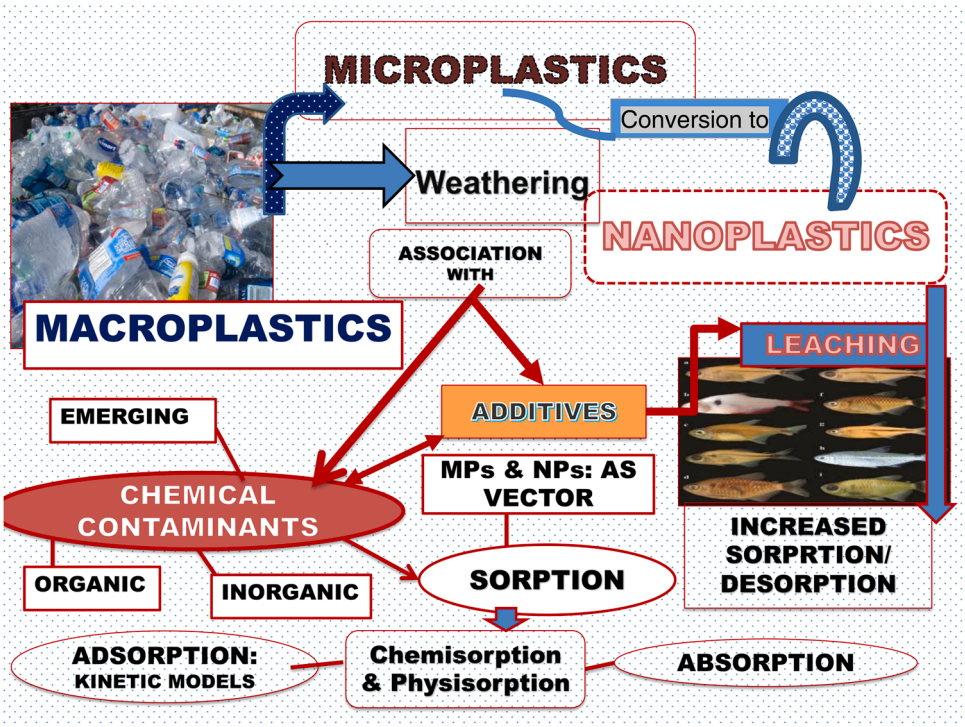

Fig. 4. Weathering mediated transformation of macroplastics to microplastics (MPs) and eventually nanoplastics (NPs) and their interactions with different chemical contaminants through sorption processes (adsorption and/or absorption) (i.e., effects on biota and the food chain).

energy of 19 kcal/mol (Cortés-Arriagada, 2021). The adsorption energy of BPA onto PET NP complexes was comparable or even higher than those of synthetic or engineered nano-scale adsorbents like graphene, carbon nanotubes, and activated carbon. Further, higher adsorption of BPA-PET NP complexes was mainly attributed to dispersion (38–49%) and electrostatic energies (43–50%) with the lowest role of π-π-interactions (Cortés-Arriagada, 2021). Notably, the BPA adsorption on PET NPs can increase the potential of their leaching and transport into aquatic ecosystems, thereby posing a severe threat to the environment, biota, and human health (Cortés-Arriagada, 2021).

Plastic debris can act as a reservoir for several organic contaminants like PAHs (e.g., fluoranthene, chrysene, pyrene, and phenanthrene) and PCBs (e.g., congeners: 18, 31, 138, and 187) in aquatic ecosystems (Zhang et al., 2019a). Many types of environmentally hazardous organic chemicals such as perfluorinated compounds, PCBs, PAHs, methyl-mercury, pharmaceutical antibiotics, and DDT adsorb on the surfaces of plastic particles (Rainieri et al., 2018; Sun, 2018; Zhou et al., 2018; Yu et al., 2020a, 2020b). In this context, the sorption strength of phenanthrene on plastic decreases in the order of PE > PP > PVC (Alimi et al., 2018). Such an observation may affect the transport of hydrophobic chemical contaminants in biota and their bioaccumulation and eco-toxicity (Koelmans et al., 2016). A total of 16 PAHs were also detected in plastic debris (within 0.33–5 mm sized fractions) in marine ecosystems in China (Mai et al., 2018). The subsequent desorption of PAHs is considered hazardous due to their carcinogenic, mutagenic, and teratogenic nature (Yu et al., 2020a, 2020b). Likewise, polymeric materials such as PS MPs can adsorb diethylhexyl phthalate, diisobutyl phthalate, dibutyl phthalate, 2,4-di-tert-butyl phenol, and dimethyl phthalate benzaldehyde in ocean basins (Zhang et al., 2019a). In addition, a good number of chemical components in plastic debris (e.g., PCB congeners, PAH isomers, dichlorodiphenyltrichloroethane (DDT) metabolites, and hexachlorocyclohexane (HCH) isomers) have also been reported to interact with MPs and NPs (F. Wang et al., 2018; Z. Wang et al., 2018). In another study, three types of MPs (PE, PS, and PVC) were tested for the sorption of tetracycline (Yu et al., 2020a, 2020b). Among them, PE was superior for tetracycline adsorption relative to PS and PVC, in view of its non-planar structure and van der Waals interactions (Yu et al., 2020a, 2020b). Unlike non-planar PE MPs, PS MPs obtained higher planarity with an affinity for hydrophobic and π–π interactions with tetracycline. Moreover, as the adsorption of tetracycline on PE MPs depends on the coexisting metallic contents in the solutions, their sorption capacity can be reduced by competitive sorption on the available sorption sites (Yu et al., 2019). Such a decrease in the sorption capacity was also attributed to the effect of biofilms on the adsorption process of tetracycline on PE MPs surface. Also, the adsorption of tetracycline on PE MPs was impacted by alterations in salinity and pH, which influenced sorption conditions by changing the chemical state of adsorbate and adsorbent (Yu et al., 2019). In another study, dissolved organic matter (DOM) was found to negatively impact the adsorption process of tetracycline on MPs surfaces (Xu et al., 2018a, 2018b). In this context, the sorption of tetracycline on MPs (PE, PP, and PS) decreased in the presence of DOM (as 90% fulvic acid at 20 mg L^{-1}) (Xu et al., 2018a, 2018b). This is due to the greater affinity of DOM for taking up fulvic acid (rather than being adsorbed on the MPs surfaces). Thus, the MPs played a minor role in determining the environmental fate and transport of tetracycline in the presence of DOM (Xu et al., 2018a, 2018b). On this basis, it can be concluded that the sorption process of chemical contaminants on MPs surface is highly dependent on the weathering driven alterations in physicochemical properties of the environment (in terms of coexisting metallic ions, pH, DOM, etc.).

The polar MPs (e.g., polybutylene succinate (PBS), polycaprolactone (PCL), and polyurethane (PU)) also exhibited a higher affinity to absorb polar organics (e.g., PAH derivatives, phenanthrene, and pyrene) (Zhao et al., 2020). In this context, the sorption of polar phenanthrene and pyrene derivatives on PU MPs (capacity of 1.06×10^4 and 5.87×10^3 mg/kg, respectively) fit well with the Langmuir model to support the interactions between π (n) - π electron donor-acceptors (Zhao et al., 2020). Further, a high adsorption capacity for pharmaceutical (nonsteroidal anti-inflammatory drugs (NSAIDs)) contaminants was noted on the PE/PP MP surface in relevant field conditions (Elizalde-Velázquez et al., 2020). Herein, NSAID adsorption on MPs was ranked in the order of diclofenac (DCF) (K_d-4.51 L kg^{-1}) > ibuprofen (IBU) (K_d-3.97 L kg^{-1}) > naproxen (NPX) (K_d-3.18 L kg^{-1}) (Fig. 5 and Table 3). In this respect, the K_d values of PE/PS/PP MPs for these NSAIDs were in the order DCF (K_d:10.9) > NPX(K_d:6.5) > IBU(K_d:3.4). Similarly, in soil samples irrigated with wastewater, the sorptive potential of NPX (K_d:2.39) on plastic particles was noted to be higher than IBU (K_d:1,05–2.26), as shown in Fig. 5. A similar sorption trend on MPs (DCF (K_d:4.66) > IBU (K_d:1.69)) was noted in a natural aquifer and sandy sediments (Fig. 5) (Elizalde-Velázquez et al., 2020). Elizalde-Velázquez et al. (2020) attributed the varying extent of NSAID sorption on various MPs to the roles of pH and hydrophobic interactions. In other studies, the chemical configuration of hydrophobic contaminants also influenced the sorption efficiency of plastic particles. For example, planar PAHs (e.g., phenanthrene and heterocyclic atrazine) had higher sorption coefficients on nonpolar PS MPs than their non-planar counterparts (e.g., 1-nitronapthalene and 1- napthylamine) (Velzeboer et al., 2014). In addition, the K_d (Lkg^{-1}) values of the PAHs and their derivatives (e.g., phenanthrene, pyrene, 1-nitronapthalene, 1-napthylamine, and atrazine) ranged from 29.6 to 1.42×10^5 on diverse MP plastic polymers (e.g., PS, PU, PCL, and PBS MPs) (Zhao et al., 2020). It was also noted that the adsorption affinities of PS, PU, PCL, and PBS MPs toward different organic aromatic contaminants decreased in the order of PAHs > derivates of PAHs > atrazine (Zhao et al., 2020). This adsorption trend was attributed to variable polarity, chemical kinetics, hydrophobic interaction, and hydrogen bonding. In this respect, the calculated log K_{OC}/log K_{OW} values of PAHs and its derivatives on polar MPs (e.g., PU, PCL, and PBS) were higher than unity, indicating the vital role of hydrogen bonding during the adsorption process (Zhao et al., 2020). The sorption coefficient of PAHs (10^{-5} to 1 μg L^{-1}) was also observed to be independent of the aggregation state of PS NPs (70 nm) due to π–π interactions between planar PAHs and the aromatic PS polymeric surface (Liu et al., 2016). In this case, the higher hydrophobicity of aromatic chemicals facilitates the adsorption process onto non-polar MPs via a hydrophobic interaction mechanism.

The PS-COOH NPs also showed higher adsorption of fluoroquinolone (norfloxacin and levofloxacin) chemicals than virgin PS NPs (Zhang et al., 2020b, 2020b; Zhang et al., 2020; Zhang et al., 2020; Zhang et al., 2020). This was as a result of improved polar/ electrostatic interactions and hydrogen bonding adsorption mechanisms between fluoroquinolones and PS-COOH NPs. Such chemical changes alter the surface charge, significantly influencing their adsorption behavior, fate, transport, and aggregation processes in the relevant environment. For instance, positively charged NPs exhibited more harmful effects on biota health than negatively charged NPs, given their greater efficiency to penetrate the cell membrane (Shen et al., 2019). It was reported that 17 PCBs on PS NP (70 nm) surfaces recorded a K_{pw} (denotes sorption coefficient of the chemical from water to plastic) value of 10^9 L kg^{-1} (Velzeboer et al., 2014). Further, the K_{pw} observed for PCBs adsorption on PS NP was higher than those of PS MPs, nanoscale fullerenes, and multiwalled carbon nanotubes. This observation was attributed to the increased surface contact area of PS NPs and the enhanced chemical interactions (hydrophobic and π-π), as the adsorption of PCBs onto PS NPs surfaces can be promoted by such factors (Velzeboer et al., 2014). Despite the progress in NP chemistry research, there is still a knowledge gap in the contaminant release or desorption mechanism and influence of weathering (Shen et al., 2019). Knowing that weathering and physical-chemical attributes in tandem affect the sorption of chemicals on NPs, the significance of those factors needs to be evaluated further through in-depth holistic analyses.

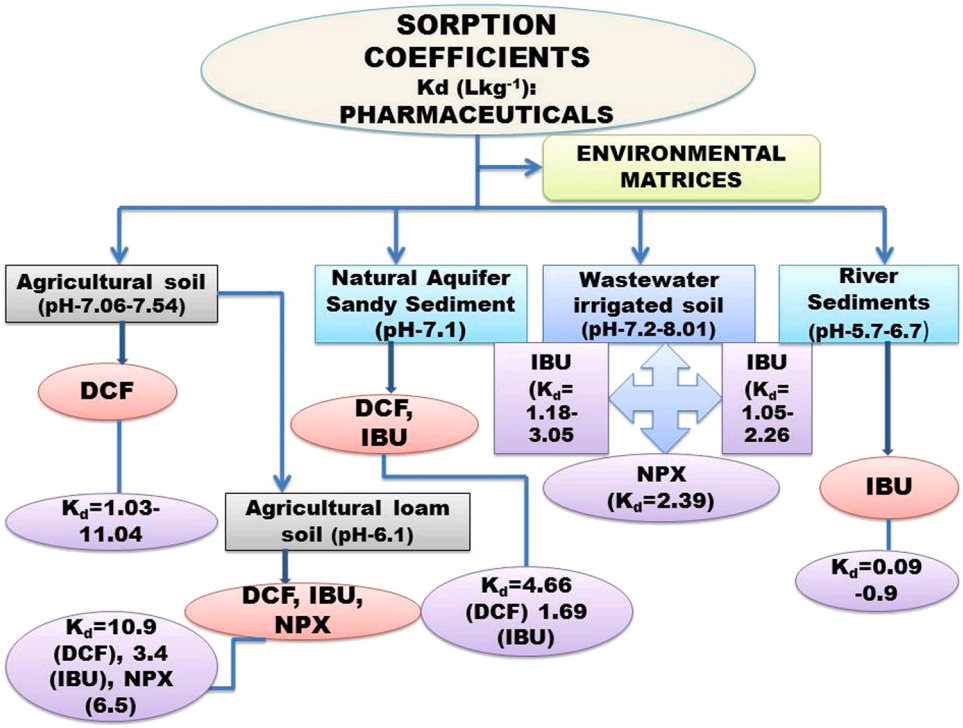

Fig. 5. Sorption coefficients, Kd (L kg^{-1}) of nonsteroidal anti-inflammatory drugs (NSAIDs) [diclofenac (DCF), ibuprofen (IBU), and naproxen (NPX)] in different environmental matrices.
Source ref. Scheytt et al. (2005); Yamamoto et al. (2009); Durán-Álvarez et al. (2012); González-Naranjo et al. (2013); Durán, Álvarez et al. (2014); Zhang et al. (2017); Elizalde-Velázquez et al. (2020).

Table 3
The specific adsorption and mechanisms of inorganic, organic, and emerging environmental contaminants on weathered plastic surfaces.

S. No.	MP/NP polymeric type	Adsorbed contaminant	Adsorption capacity & chemistry/ kinetics	Main environmental /chemical factor (s)	Reference
1.	Natural NP at North Atlantic Gyre	Pb (II)	78.5–97% Pb adsorption on NP; Pseudo-first-order; Freundlich model	pH 7 showed maximum adsorption	Davranche et al. (2019)
2.	PE beads (dose-2–14 g L^{-1})	Cr(VI)	Adsorption capacity of Cr (VI)– 0.39 to 1.36 mg g^{-1};	pH and SDBS concentrations	Zhang et al. (2020b, 2020b), H. Zhang et al. (2020), J. Zhang et al. (2020), and W. Zhang et al. (2020)
3.	PE, PP, PVC and PS MPs	Cd (II)	–Adsorption capacity on PVC MPs (151.4 mgKg^{-1}) > PS (134.1 mg Kg^{-1}) > PP (123.6 mg Kg^{-1}) > PE (113.5 mg Kg^{-1}); Freundlich isotherm non-linear model better suited than Langmuir model	pH, humic acid, polymeric types and ionic strength of solution	Guo et al. (2020)
4.	PE, PP and PS MPs	9-Nitroanthracene (9-NAnt)	9-NAnt adsorption was maximized on PE MPs (734 μg g^{-1}); adsorption mechanism better described with linear isothermal model	Hydrophobic and electrostatic processes	J. Zhang et al. (2020)
5.	PE MPs and PP MPs	Pharmaceuticals (three Nonsteroidal anti-inflammatory drugs i.e., ibuprofen, naproxen, diclofenac)	Highest adsorption capacity noted for Diclofenac	Highest sorption noted at lower pH (2)	Elizalde-Velázquez et al. (2020)
6.	PS NPs and caboxylated (PS-COOH) NPs	Fluoroquinolones	Langmuir model was the best fit model for adsorption isotherms	pH (sorption of fluoroquinolones on PS NPs were higher at pH 5 while pH 6 facilitated their sorption PS-COOH NPs)	H. Zhang et al. (2020)
7.	PS NPs	PAHs (conc. 10–5 μg L^{-1} to 1 μg L^{-1})	log K_f varied from 5.7 to 6.0, adsorption isotherms-nonlinear with π–π interactions; distribution coefficients at lower end of isotherm-109 L kg^{-1}	Pre-extraction with C_{18} polydimethyl-siloxane reduced the sorption of PAHs	Liu et al. (2016)

3.3. Kinetic and isotherm modeling of plastic sorption mechanism

Adsorption and desorption are known to be weathering and time dependent processes in which two basic phenomena should be described: equilibria and kinetics. With regards to sorption kinetics, the phenomenological coefficients characterizing the transfer of substances

from a mobile phase (liquid or gaseous) to a solid phase can be determined. As these phenomenological coefficients are sometimes strongly kinetically controlled, sorption isotherms must be specified to describe the how the sorption mechanism depends on the equilibrium concentration of sorbate and the change of sorbent surface chemistry through time. Accordingly, the kinetic and isotherm coefficient constants can provide information to understand the final state of the sorption system and the changes in the chemical properties of both adsorbates and adsorbents based on adsorption/desorption mechanisms. Various kinetic and isotherm models have been recommended to determine the rate-governing adsorption of chemical contaminants on the plastic adsorbents and their sorption mechanisms under various environmental conditions (Razanajatovo et al., 2018; Mammo et al., 2020; Yu et al., 2020a, 2020b; Vieira et al., 2021).

Among kinetic models (Fig. 6), pseudo-first-order (PFO) and pseudo-second-order (PSO) adsorption models are commonly used to determine the rate-governing adsorption process of chemical contaminants on MP/NP plastic surfaces (Yu et al., 2020a, 2020b). Further, many isotherm models can be used to analyze the equilibria of retention/release processes of a solute on solid plastic particles under various environmental conditions including the Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models (Fig. 6). These isotherm models have also been frequently applied to predict and simulate the sorption mechanism of diverse contaminants on various plastic polymers. The suitability of the Langmuir model was confirmed in the prediction of the sorption of different chemical contaminants onto localized MP/NP sorption sites (Chen, 2015; Tran et al., 2017). This indicates that many chemical contaminants followed a linear, reversible sorption/desorption process onto MPs and NPs surfaces. In some cases, kinetic models can also be used to investigate the effect of weathering and ageing conditions on adsorption capability and mechanism of plastic waste (P. Liu et al., 2019; Z. Liu et al., 2019; G. Liu et al., 2019).

For instance, the adsorption of ciprofloxacin on pristine PVC/PS MPs was well-fitted by PFO rather than PSO kinetics (P. Liu et al., 2019; Z. Liu et al., 2019; G. Liu et al., 2019). Such fitting adequacy was however reversed when tested against aged PVC and PS MPs as adsorbents. Likewise, adsorption of phenanthrene on PE and poly-butylene adipate co-terephthalate (PBAT) MPs can be suitably explained using the Freundlich isotherm and PSO kinetics models (Liu et al., 2016; Zuo et al., 2019). In this context, the linear PFO equation is only appropriate to simulate the initial 20–30 min of the adsorption process rather than the whole sorption range (Tran et al., 2017). Also, kinetic (or isotherm) models on a linear basis are less accurate with several errors and thus are not ideal for elucidating weathering mechanisms (Zhang et al., 2020b, 2020b; Zhang et al., 2020; Zhang et al., 2020; Zhang et al., 2020). As such, a non-linear PSO model was used effectively to address the effect of weathering on chemical adsorption (e.g., pristine and weathered MPs) (P. Liu et al., 2019; Z. Liu et al., 2019; G. Liu et al., 2019). Herein, adsorption on pristine and weathered MPs occurred mainly via complex physicochemical adsorption mechanisms. In addition, other studies on chemical sorption also demonstrated that the non-linear isotherms should establish a better link between experimental and simulated data (Tran et al., 2017). Henceforth, it should be noted that in studying the adsorption kinetics of chemical contaminants on the sorbent (plastic) surface, a nonlinear kinetic (or isotherm) model should be used (Tran et al., 2017; G. Liu et al., 2019; Seidensticker et al., 2019; Lima et al., 2020; Zhang et al., 2020b, 2020b; Zhang et al., 2020; Zhang et al., 2020; Zhang et al., 2020). Furthermore, Zhang et al. (2020b, 2020b), Zhang et al. (2020), Zhang et al. (2020), and Zhang et al. (2020) also used a non-linear Langmuir model to estimate the adsorption potential of norfloxacin and levofloxacin on PS NPs (Table 4). Likewise, Liu et al. (2016) used a non-linear adsorption isotherm to study the sorption of PAHs on the PS NPs. In this case, adsorption of PAHs on PS NP surfaces was controlled by π–π interactions between planar PAHs and the aromatic PS polymeric surface. Similarly, the interactions of PS MPs (0.047 μm) with five soil types was best explained by the non-linear PFO model ($R^2 = 0.998$) (H. Luo et al., 2020; H. Luo et al., 2020; Y. Luo et al., 2020). Here, the sorption efficiency of PS MPs on soil types decreased with increased pH. Notably, the sorption coefficient (K_d) of PS MPs within the soil matrix was positively correlated with soil organic carbon content ($R^2 = 0.999$) and Fe_2O_3 content ($R^2 = 0.967$). On the other hand, the clay content showed an inverse correlation ($R^2 = 0.952$) with the K_d of PS MPs (H. Luo et al., 2020; H. Luo et al., 2020; Y. Luo et al., 2020). This observation indicates that the sorption mechanisms of MPs

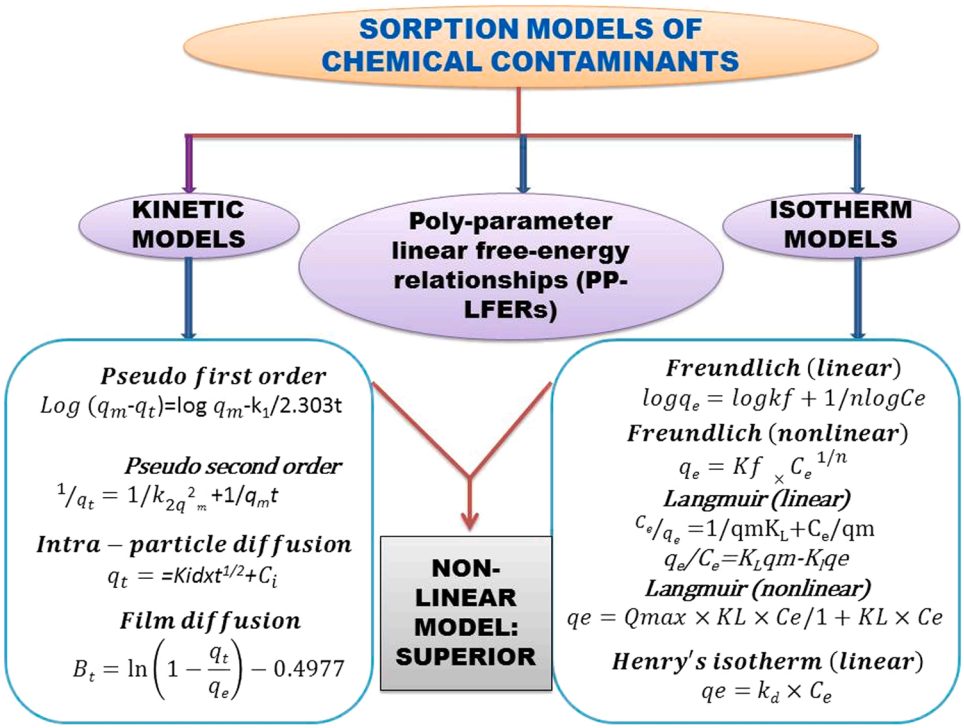

Fig. 6. Sorption models (kinetic and isotherm) used to study the interactions of chemical contaminants on plastic surfaces. Here, q_m and q_e are the amount of adsorbate at equilibrium or adsorption capacity (mg/g), q_t is the adsorbed amount at time t, K_{id} and C_i are intra-particle diffusion constants, B_t is the Boyd constant, K_d is the partition coefficient between the sorbent and the solution at equilibrium, C_e is the sorbate concentration at equilibrium, Q_{max} is the maximum adsorption capacity, K_L is the Langmuir constant (mg/g), K_f is the sorption affinity coefficient (L/mg), and 1/n is adsorption intensity (Freundlich constants).

Table 4
Concentrations of organic, inorganic, and emerging contaminants (sorbate) on plastic polymers (sorbent) and their eco-toxic cellular responses on exposure to biota.

S. No.	Adsorbed Chemical contaminants (Sorbent)	Microplastic (MP) polymeric types (Sorbate)	Adsorption capacity (ng g^{-1})	Eco-toxic responses	Reference
ORGANIC CONTAMINANTS					
1.	PAH derivatives	PE, PP	24,400–164,900	Through covalent bonding to DNA, RNA, proteins & other biomolecules have cytotoxic, mutagenic, teratogenic & carcinogenic effects on biota	Mammo et al. (2020)
2.	PCBs (18 congeners)	PE, PP	5–18,700	Endocrine disrupting chemicals (EDCs) perturbing gap junctional intercellular communication	Endo et al. (2005)
3.	DDTs	PE, PP	1.69–276	Cytotoxic effects & DNA damage	Ogata et al. (2009)
INORGANIC CONTAMINANTS					
4.	Cd	PE, PP, & PS	38–1980	Perturbs cellular proliferation & differentiation leading to cell death or apoptosis	Massos and Turner (2017)
5.	Halogens (Bromine)	PE, PP, & PS	4–13,300	Perturbs hepatic metabolism & gene expression	Massos and Turner (2017)
6.	Pb	PE, PP, & PS	12–4820	Binds calmodulin by replacing calcium and disturbs protein confirmation & enzyme regulation	Massos and Turner (2017)
7.	Metalloid (As)	PE, PP, cellophane, & polyester	0.35–2.89	Enzyme inhibition by binding through sulfhydryl (-SH) groups and adversely influencing the cellular respiration	Mohsen et al. (2019)
8.	Cu	PE, PP	80.9–500.60	Inducts oxygen species (ROS) by binding to the thiol group	Wang et al. (2017)
9.	Cr	PE	44–430	Perturbs cellular energy metabolism	Holmes et al. (2012)
EMERGING CONTAMINANTS (microcosm/lab based observation on contaminant's concentrations)					
10.	Sertraline; Propranolol	PE	0–80,000 Sertraline; 0–60,000 Propranolol	Antioxidative & cytotoxic responses, DNA damage	Mamitiana et al. (2018)
11.	DEP (Diethyl phthalate)	PE, PS, PVC	10,000–30,000	Binds & forms DEP-haemoglobin complexes thereby perturbing the normal physiology	P. Liu et al. (2019)
12.	Sulfamethoxazole	PE, PP, PS, PET, PVC.	660–96,400	Perturbs cell development by blocking nucleic acids and proteins synthesis	Guo et al. (2019)
13.	Triclosan	PS	720,000–1,000,000	Hazardous chemical inhibiting lipid synthesis & cell membrane disruption leading to apoptosis	Li et al. (2019)
14.	17b-Estradiol (E2)	PA, PE, PP, PS, PC, PVC	2500–20,000	E2 binds with DNA and forms complex that can lead to mutation by inhibiting other biomolecules	G. Liu et al. (2019)
15.	DBP (Dibutyl phthalate)	PS, PE, PVC	1,100,000–2,400,000	Like DEP, forms DBP- haemoglobin complexes adversely impacting normal physiology	P. Liu et al. (2019); Mammo et al. (2020)

within soils are mainly guided by electrostatic and hydrophobic interactions (H. Luo et al., 2020; H. Luo et al., 2020; Y. Luo et al., 2020).

Besides kinetic and isotherm modeling, many partition coefficient terms are utilized to assess the sorption potential of emergent chemicals onto plastic polymers and their sorption mechanisms in different environmental streams (air, water, and soil). In this regard, K_{pw} metric is a vital parameter that defines the ratio of C_p (mg $kg^{-1}{}_{plastic}$ adsorbed fractions of chemicals in plastic) and C_w (mg $L^{-1}{}_{water}$ free residual chemical in water) at equilibrium. The K_{pw} metric can be estimated based on another partition coefficient (octanol-water coefficient (K_{ow})) term, which is often applied to investigate the equilibrium ratio of target contaminant between two liquid phases (organic solvent (octanol) and water) (Mammo et al., 2020). Using the logarithmic equation (Eq. 12), the K_{pw} can easily be estimated based on K_{ow} values. The K_{pw} value is mainly dependent on the types of MPs and the pollutants (Endo and Koelmans, 2016).

$$\log K_{pw} = \alpha log K_{ow} \quad + \beta \tag{12}$$

Here, the α and β are the coefficient terms calculated using experimental data for K_{pw} and K_{ow} values.

Notably, if the ratio $C_p/C_w < K_{pw}$, the sorption process of chemical contaminants only occurs via the mass transfer/diffusion from water to the plastisphere. In contrast, the desorption process is possible when $C_p/C_w > K_{pw}$ (Endo and Koelmans, 2016). Under the conditions of $C_p/C_w \approx K_{pw}$, sorption equilibrium is reached (e.g., neither adsorption nor desorption). It has been shown that an usually low concentration of sorbate generally encourages the adsorption process, while the high concentration of the sorbate facilitates the absorption process due to the increase in volume (Hartmann et al., 2017; Fred-Ahmadu et al., 2020). Additionally, linear sorption is more favorable if K_{pw} is constant and independent of the type of environmental contaminants such as heavy metals, PCBs, and nano-materials (Endo and Koelmans, 2016). However, if the K_{pw} is dependent on the concentration of contaminants, non-linear sorption could occur in a more preferable mechanism.

Another partition coefficient (K_d) based on a linear sorption model (Eq. 13) can elucidate the sorption mechanism occurring on the MPs surfaces because the K_d defines the relative movement of target contaminants from one environmental system to MPs/NPs solid particle (F. Wang et al., 2018; Z. Wang et al., 2018).

$$K_d = [q_e]_{solid} / [C_e]_{LM} \tag{13}$$

In Eq. 13, K_d denotes partition coefficient (L kg^{-1}), q_e is the mass of chemicals adsorbed on the plastic surface at equilibrium (μg chemical. kg^{-1} of plastic), and C_e (μg L^{-1}) represents the concentration of a chemical in the liquid phase at the equilibrium stage (F. Wang et al., 2018; Z. Wang et al., 2018).

The K_f term is another partition coefficient that denotes the sorption capacity, and it can be computed using the Freundlich model shown in Eq. 14.

$$Log q_e = log K_f + 1/n_f log \lceil C_e \rceil_{LM} \tag{14}$$

Here, $1/n_f$ represents the Freundlich exponent for modeling the energy distribution and sorbent heterogeneity at adsorption sites (Mammo et al., 2020). K_f represents the non-linearity of how low hydrophobic chemical contaminants behave. Generally, the values of $1/n_f$ range between 0.7 and 1 reflect the relative decrease in adsorption with an increase in sorbate concentrations. It is also linked with the availability of adsorption sites (Endo and Koelmans, 2016; Fred-Ahmadu et al., 2020).

For example, PE MPs were found to have a higher partition coefficient for DDT (log K_{ow}: 6.79 and log K_f: 5.9) than that of phenol (log K_{ow}: 4.5 and log K_f: 4.9), DEHP (log K_f 2.4), and perfluorooctanesulfonic acid (PFOS; log K_f 1.25) adsorption (Teuten et al., 2007; Velzeboer et al., 2014). In this respect, the units of log K_{ow} and log K_f are variable and may be denoted as $L_{chemical}/L_{plastic}$ or $L_{chemical}/Kg_{plastic}$, depending on

the concentrations/medium of sorbate and sorbent (Endo and Koelmans, 2016). The decreasing trend in values of sorption coefficients (DDT > phenol> DEHP > PFOS) can be attributed to a decrease in planarity of a molecule (Velzeboer et al., 2014). In this respect, the high planarity of a molecule (e.g., DDT and phenol) encourages the proximity and movement of chemicals close to the plastic particle surface, thereby facilitating the adsorption process.

In terms of partition coefficient terms, the one-parameter linear free energy relationship (OP-LFERs) is one of the less frequently used models to describe the sorption of chemical contaminants on MPs/NPs in various environments. This model is inadequate to study chemical-MP complexes associated with multiple chemical interactions, such as H-bonding, hydrophobic, and electrostatic interactions (Nguyen et al., 2005; Endo and Koelmans, 2016). Instead, poly-parameter, linear free-energy relationships (PP-LFERs) have proven to be useful for predicting and characterizing the equilibrium partitioning of most chemical contaminants on MPs/NPs in various environments and for predicting their respective partition coefficients (Stenzel et al., 2013; Fred-Ahmadu et al., 2020). In this context, the Abraham Linear Solvation Energy Relationships (LSERs) for K_{pw} may be used to assess partition coefficients of a wide range of chemical contaminants on plastics, as per Eq. (15):

$$logK_{pw} = c + eE + sS + aA + bB + vV \quad (15)$$

Here, E denotes excess molar fraction, S is the solute dipolarity/polarizability, A is the solute H-bond donor property (acidity), B represents the solute H-bond acceptor property (basicity), and V is the molar volume. Solute descriptors (denoted by E, S, A, B, and V), and the regression coefficients (represented by c, e, s, a, b and v) can be studied using Eq. (15).

Therefore, in the LSERs model, both the potential of chemical contaminants to undergo molecular interactions (as defined by solute descriptors) and the variances in interface/phase attributes between MPs and aqueous media (as defined by regression coefficients) are taken into consideration (Endo and Koelmans, 2016; Hüffer et al., 2018; Fred-Ahmadu et al., 2020). The PP-LFERs model (with $R^2 > 0.84$; RMSE (root mean square error) −0.27) performed better when compared with the Freundlich isotherm with $R^2 > 0.5$ and a RMSE of 0.27 (Uber et al., 2019). Likewise, adsorption studies of hydrophobic chemical contaminants on MPs using Abraham LSERs further revealed that the non-linear Freundlich isotherm ($R^2 > 0.75$) was even more efficient than the linear isotherm form (with $R^2 > 0.5$), suggesting the preferable use of nonlinear models in sorption studies.

Information on the adsorption kinetics of various chemical contaminants on plastic polymers is summarized under different physical, chemical, and environmental factors (Table 3 and Fig. 5). Tables 3 and 4 also list the measured concentrations of organic, inorganic, and emerging contaminants on plastic polymers in the literature and their eco-toxic cellular responses upon exposure to biota. Although hydrophobic surfaces of MPs and NPs are favorable to facilitate the adsorption of most organic chemical contaminants (Gu et al., 2020), the adsorption of 9-nitroanthrene on PE, PP, and PS MPs was controlled by both hydrophobic and electrostatic interactions (J. Zhang et al., 2020). Among those MPs, PE was superior for 9-nitroanthrene (734 μg g^{-1}) adsorption, and its performance was independent of pH and ionic strength due to the role of hydrophobic interactions as the main adsorption mechanism. In another study, a non-linear Langmuir model was useful to estimate the adsorption mechanism of fluoroquinolone pharmaceuticals (such as norfloxacin and levofloxacin) on PS NPs and PS NP-COOH surfaces (Zhang et al., 2020b, 2020b; Zhang et al., 2020; Zhang et al., 2020; Zhang et al., 2020). The data revealed that the adsorption potential of PSNP-COOH for those pharmaceuticals is larger than that of PS NPs due to the polar surface, which facilitated electrostatic interactions and H-bonding. On the other hand, hydrophobic interactions provoked high sorption of these pharmaceutical drugs on PS/PE NPs under acidic (at pH 2) conditions, although adsorption was significantly suppressed under environmentally realistic chemical conditions (Elizalde-Velázquez et al., 2020).

The eco-toxic impacts of chemically adsorbed PAHs onto PS NPs and humic acid-PS MPs were also investigated on *Daphnia magna* using a biodynamic kinetic model (Lin et al., 2020). The reported data confirmed that the PS NPs delayed the intestinal bioaccumulation of less hydrophobic PAHs in *D. magna*, while the humic acid complexed PS NPs facilitated the allocation of PAHs to the gut. Fisner et al. (2013) emphasized that the sorption interrelationship of MPs with hazardous organic chemicals can vary in vertical aquatic sediment strata. Therefore, characterization at each sediment level is required for explicit elucidation of MP-chemical interactions.

Different organochlorine pesticides (e.g., DDT (dichlorodiphenyltrichloroethane) and HCHs (hexachlorocyclohexane) isomers) can also be adsorbed on MP and NP surfaces in various environments (Rai et al., 2021a). In addition to organic chemicals, inorganic contaminants such as heavy metals (e.g., Cd, Pb, and Cr) and metalloids (e.g., As) can also be adsorbed to the surface of MPs (Holmes et al., 2012; Mohsen et al., 2019). In this case, it was found that the adsorption of Cr (VI) on PE MPs was promoted by the addition of sodium dodecylbenzene sulfonate (SDBS) at pH < 6 (i.e., capacity increased from 0.39 to 1.36 mg g^{-1}), while the capacity decreased at pH > 6 (Zhang et al., 2020b, 2020b; Zhang et al., 2020; Zhang et al., 2020; Zhang et al., 2020). This is due to the higher inhibitory competition between SDBS and CrO^{2-}_4 for binding at the PE adsorption sites in an alkali pH solution. During photo-oxidative weathering, the increased availability of oxygenated binding sites greatly improved the Pb adsorption on NPs (150–450 nm) surfaces via chemical electrostatic interactions (PSO model fit) as the main rate-limiting adsorption step (Davranche et al., 2019). The adsorption of Cu ion on modified or fractured plastic pellets in conjunction with DOM was 180.64 ng g^{-1}, which was greater than other heavy metals (Zn (178.03 ng g^{-1}), Ni (12.69 ng g^{-1}) and Pb (1.17 ng g^{-1})) (Wijesekara et al., 2018). This is attributed to the enhanced surface complexation resulting from oxygen-mediated functional groups introduced after the interaction with DOM. Hence, the sorptive potential of chemical contaminants (e.g., heavy metals, pharmaceuticals, hydrocarbons, and organic pesticides) on plastic surfaces can be varied in multiple environmental matrices. Therefore, multiple hazardous contaminants (organic, inorganic, and emerging) can be concentrated on MPs/NPs via the absorption or adsorption process to be subsequently released into environmental matrices (via desorption). Such release from plastisphere can threaten the biota and human-well-being. Plastic particles therefore act as both sources and a sink of environmental contaminants (i.e., increase their toxicity levels) which should be explicitly unveiled in future studies toward pollutant adsorption on MPs/NPs surface.

3.4. Adsorption chemistry of pollutants between plastics and non-plastic environmental matrices

The recent advances in comparative adsorption chemistry of pollutants and ENPs on plastisphere or weathered plastic particles and other environmental matrices have helped us expand our understanding of plastic polymer science (Roes et al., 2012; Lambert et al., 2017). These chemically synthesized ENPs display colloidal attributes that are similar to NPs that are omnipresent in diverse environmental settings in terms of their shape, surface charge, and highly poly-disperse attributes (Praetorius et al., 2014; Besseling et al., 2017; Rai et al., 2018a, 2018b; Hadri et al., 2020). Under weathering effects, ENPs (e.g., AgO/CuO ENPs and TiO_2/CeO_2 ENPs) usually undergo surface-based dissolution reactions depending on their chemical composition (Kaegi et al., 2013; Conway et al., 2015; Vencalek et al., 2016; OECD, 2016). Nonetheless, non-engineered MPs/NPs do not undergo dissolution; instead, they can undergo fragmentation to be subject to weathering effects (Hüffer et al., 2017). Therefore, synthetic or engineered nano-scale particles display colloidal behavior while their adsorption mechanisms are also different from MPs (Hadri et al., 2020).

Adsorption science on weathered plastic particles is different from other solid waste pollutants and biochar in terms of their small sized colloidal attributes and physical-chemical attributes (Zhou et al., 2007; Vikrant et al., 2020). Their chemical interactions with adsorbates (both biological and chemical) can thus be distinguished during adsorption on plastisphere (Fu et al., 2021). Hydrophobic interaction is the main mechanism of adsorption of organic pollutants on MPs surface along with other ones like hydrogen bonds, π–π interactions, and halogen bonds (Agboola, and Benson, 2021; Fu et al., 2021).

Like emerging contaminants, certain ENPs can act as adsorbates to be adsorbed to surfaces of weathered plastic particles (Li et al., 2020a, 2020b). For instance, Li et al. (2020a, 2020b) recognized that Ag-ENPs could be adsorbed on PS MP surfaces via a monolayer adsorption mechanism (Langmuir fit), depending on the mass ratio of NPs to ENPs and π-π interactions. However, it should be noted that the adsorbed ENPs can also act as adsorbents to chemical contaminants in line with plastic particles. For example, the sorption of 17 PCB congeners on multi-walled carbon nanotubes (MWCNT), fullerene-C_{60}, and PS NPs adsorbents was reported to be influenced greatly by the presence of organic matter (Velzeboer et al., 2014). Notably, the adsorption affinity of MWCNTs and C_{60} was 3–4 times higher for PCBs than that of PS MPs (Velzeboer et al., 2014). The encapsulation of ENPs (TiO_2-ENPs) to plastic polymers (PS MPs) also enhanced their transport in quartz sand hetero-aggregates to influence their environmental fate and ecotoxicity (Cai et al., 2019). Therefore, ENPs can either act as the adsorbate on MPs/NPs or as adsorbents (like plastic particles) to emerging chemical contaminants. Also, ENPs can be additives to plastic particles and influence their environmental transport and fate pathways (Cai et al., 2019).

The studies on colloidal and interfacial attributes of MPs/NPs can remarkably facilitate in decoupling of their weathering and physico-chemical interrelationship while concomitantly help couple their potential effects and remediation technologies (Harraq and Bharti, 2021). Adsorption of certain emerging (pharmaceutical) contaminants such as tetracyclin on organic montmorillonite fitted well with non-linear Freundlich model, in accord with sorption chemistry on plastic surface (Liu et al., 2012; Yu et al., 2020a, 2020b). Further, the supplementation of plastics in several carbon based nano-adsorbents was reported to augment the efficiency of environmental remediation (Zhou et al., 2007). In this respect, further studies are warranted to explicitly differentiate the adsorption mechanisms of pollutant between MPs/NPs surface and other non-plastic environmental matrices (e.g., ENPs, biochar, and other engineered adsorbents). Interestingly, such comparative studies between plastic and non-plastic surfaces can help broaden the factors and processes governing the sorption chemistry of pollutants to implement the sustainable environmental remediation.

4. COVID-19 pandemic: challenge and opportunity for plastic weathering driven adsorption studies

The recent upsurge of COVID-19 pandemic has significantly disrupted the planetary health, environmental quality, and sustainability (Rai, 2021). The emergence of the COVID-19 pandemic has remarkably increased the consumption and disposal rates of plastic products to strengthen their environmental footprint (Silva et al., 2020; Patrício Silva et al., 2021). An increase in plastic footprint which may reflect global environmental burdens of plastic products can be exemplified through the projection of the growing global need for personal protective equipment (PPE) such as 129 billion face masks (e.g., N95) and 65 billion gloves during this pandemic along with an upsurge in other commodities (e.g., packaged meals, plastic cups, and home-delivered groceries) (Adyel, 2020; Patrício Silva et al., 2021). Note that the poor management on PPE plastic waste can be a serious issue because of its subsequent deleterious implications on natural ecosystems and public health. This is because most PPE waste products are composed of polyethylene terephthalate (PET), polypropylene (PP), and nonwoven materials that are weathered into smaller MPs/NPs to enhance the adsorption propensity of hazardous chemicals on plastisphere.

The weathered plastic waste, in addition to chemicals adsorption, can indeed act as a medium for coronavirus contamination, as the COVID-19 virus was demonstrated to survive on polypropylene plastic for two to three days (van Doremalen et al., 2020; Wu et al., 2020a, 2020b, 2020c, 2020d; Wang et al., 2021). Accordingly, the adsorption-desorption of hazardous chemicals or pathogens (like SARS-CoV-2) within these 'plastispheres' can create multiple ecological challenges (Lehner et al., 2019; Rubio et al., 2020). In this sense, plastic-microbe interactions are also found to influence the fate of pathogens by inducing genomic changes such as horizontal gene transfer and promotion of antibiotic-resistant genes (Cole, 2016; McCormick et al., 2016; Rai et al., 2021b). Besides adsorption, the weathered plastics can also influence the fate of specific hazardous chemicals (like PAHs, nonylphenol (NP), PCBs, and heavy metals) through their involvement in metabolomics, biodegradative metabolic pathways, pathogenicity determinants, and evolution of microbiomes (Oliveira et al., 2019; Rogers et al., 2020; Rai et al., 2021b; Luo et al., 2022).

The enormous increase in quantity of disposed plastic products during coronavirus outbreak further exacerbated the challenges to elucidate the influence of weathering on plastisphere adsorptive attributes. In addition, the increased use and disposal of plastics during COVID-19 pandemic strained the sustainable management prospects. Nevertheless, the coronavirus pandemic can be considered as an opportunity to better unveil the interactive roles between weathering and physico-chemical adsorption on plastisphere. Concomitantly, the pragmatic future studies on plastic waste management can explicitly help us minimize the plastic waste footprint and to effectively sustain the planetary public and environmental health.

5. Conclusions

As the adsorption of pollutants on plastic particles is remarkably influenced by weathering, the mechanisms governing such interaction is important enough to govern the potential risks associated with plastic pollution. The use of plastic products and their release into environmental systems increased drastically during the COVID-19 pandemic. Micro- and nano-scale plastic polymers (MPs/ NPs) can serve as the potential vectors of inorganic, organic, and emerging environmental contaminants. These hazardous contaminants can be associated with MPs/NPs via the absorption or adsorption process to be subsequently released into environmental matrices. Weathering of plastic polymers under the effects of both abiotic and biotic environmental stressors can induce significant alterations in the physical-chemical processes and properties of plastics to affect the pollutant adsorption on plastisphere significantly. Concomitantly, adsorption dynamics for different contaminants can also vary due to their interactions with diverse factors (e.g., surface chemistry, size, shape, and crystallinity of MPs particles) during weathering process. Furthermore, the factors governing the changes in physicochemical attributes can be evaluated to learn more about the adsorption/desorption mechanisms in relation to the fate, behavior, transport, and eco-toxicity of MPs/NPs. The adsorption kinetics and isotherm models of environmental pollutants on the plastisphere can also be used to expand our knowledge toward the most effective remediation technologies for target pollutants. In this sense, an assessment of interactive relationship between pollutant adsorption on plastic/other non-plastic substrata (e.g., ENPs and biochar) and weathering induced alterations in physical-chemical/environmental factors may help us better understand the detailed mechanisms of plastisphere sorption so as to achieve an optimized remediation/sustainable management approach to effectively resolve plastic pollution.

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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