



The Unseen Threat of the Synergistic Effects of Microplastics and Heavy Metals in Aquatic Environments: A Critical Review

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Abstract

Purpose of Review The synergistic effects of microplastics (MPs) and heavy metals are becoming major threats to aquatic life and human well-being. Therefore, understanding synergistic interactions between MPs and heavy metals is crucial to comprehend their environmental impacts.

Recent Findings The mechanisms such as electrostatic attraction, surface interactions, ion exchange, hydrogen bonding, hydrophobic forces, and π - π interactions behind the synergistic effects of MPs and heavy metals were critically reviewed and justified. In addition, the roles of surface chemistry in these interactions were also emphasized. Finally, efficient remediation techniques aligning with a circular economy-based initiative to promote sustainable solutions were recommended to mitigate plastic-heavy metal pollution to achieve a cleaner environment.

Summary This review examines the combined impact of MPs and heavy metals in aquatic ecosystems, detailing their mechanistic interactions, and consequences with proposed sustainable solutions. Additionally, this review highlights the MP-heavy metal contamination risks and emphasizes the need for further research to safeguard aquatic life and human health.

Keywords Microplastics · Heavy metals · Adsorption · Contamination · Synergistic effects · Mechanistic interactions

Abbreviations

ABS	Acrylonitrile butadiene styrene
MPs/NPs	Micro/nanoplastics
AOPs	Advanced oxidation processes
WWTPs	Wastewater treatment plants
SDGs	Sustainable development goals
PE	Polyethylene
PS	Polystyrene
PET	Polyethylene terephthalate
PSMP	Polystyrene-microplastics
PMMA	Polymethylmethacrylate
PEI	Polyethyleneimine
PVC	Polyvinylchloride
PA	Polyamide

PHAs	Polyhydroxyalkanoates
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
PU	Polyurethane
PP	Polypropylene
PCBs	Polychlorinated biphenyls
DDT	Dichlorodiphenyltrichloroethane
POPs	Persistent organic pollutants
DOM	Dissolved organic matter
HA	Humic acid
FA	Fulvic acid
PTFE	Polytetrafluoroethylene
CA	Cellulose acetate

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Introduction

Plastic has been used globally for decades, and in 2019, 400 million tonnes of plastic were produced worldwide, a quantity that continues to rise [1, 2, 3, 4]. The volume of plastic-derived products has grown rapidly due to their widespread usage. However, their interactions with other emerging contaminants are poorly understood. Since plastic

garbage takes a long time to disintegrate, improper management and disposal can affect the ecological sphere [5, 6]. A 2021 study projected that 307 to 925 million pieces of garbage, 82% of which were plastic-derived, are dumped into the ocean [7]. The breakdown of plastic wastes in the environment results in pollution and produces smaller plastic particles via disintegration [5, 8]. Therefore, their various sizes determine the category of these resulting small plastic particles [9, 10].

Nanoplastics (NPs) (< 100 nm), microplastics (MPs) (< 5 mm), mesoplastics (5–25 mm), and macroplastics (> 25 mm) make up environmental plastic refuse [11, 12]. These plastics degrade chemically, biologically, or physically into MPs and NPs [5, 13, 14]. Depending on their source, MPs can be categorized into primary (manufactured products) and secondary (degradation of products) types [10, 15]. Thus, waterbodies can get contaminated, and MPs can accumulate in marine habitats, endangering aquatic ecosystems and species [15, 16]. The implications of MPs as vectors for transporting harmful substances across environmental matrices have been explored in recent years [17]. The adverse effects of MPs on the environment and living organisms, ultimately affecting human health, have been well-documented (see Fig. 1).

There are two major types of chemicals associated with MPs, such as polymeric components and additives. Additives in plastic materials serve various purposes, such as flame retardancy, plasticization, antioxidant effects, UV stabilization, and reinforcement [13, 18, 19]. However, studies

have indicated that these additives have adverse health risks on both organisms and the ecological sphere [13, 18]. The resulting environmental risks and potential health effects of MPs are summarized in Table 1.

The interplay between MPs and other chemical contaminants, including heavy metal ions and organic contaminants, has raised significant health concerns for both humans and aquatic life [13, 15, 20]. The rough surfaces and numerous functional groups of MPs enable the attachment of heavy metals and organic contaminants, influencing their environmental behaviour [8, 17]. Heavy metals are hazardous contaminants and can persist with threatening impacts on ecosystems, food quality, and human health safety [21].

Recent studies have revealed the adsorption capacity of both new and aged MPs with heavy metals like Pb, Cr, Fe, Zn, Sn, Ti, Mn, Al, Cu, and Ni, in aqueous environments [15, 20, 22••, 23••, 24•, 25, 26]. However, there exists a remarkable scarcity of research concerning the adsorption of metals. In particular, minimal effort has been made to comprehend the mechanisms governing the sorption interactions between MPs and heavy metals. Addressing this research gap is crucial in this emerging field of study. Hence, this review presents an overview of the escalating environmental challenges from the synergistic effects of microplastics (MPs) and heavy metals, stressing their substantial threats to aquatic ecosystems and human well-being. By examining recent findings, this review elucidates the complex mechanisms that orchestrate these synergies, including electrostatic attraction, surface interactions, ion exchange, hydrogen

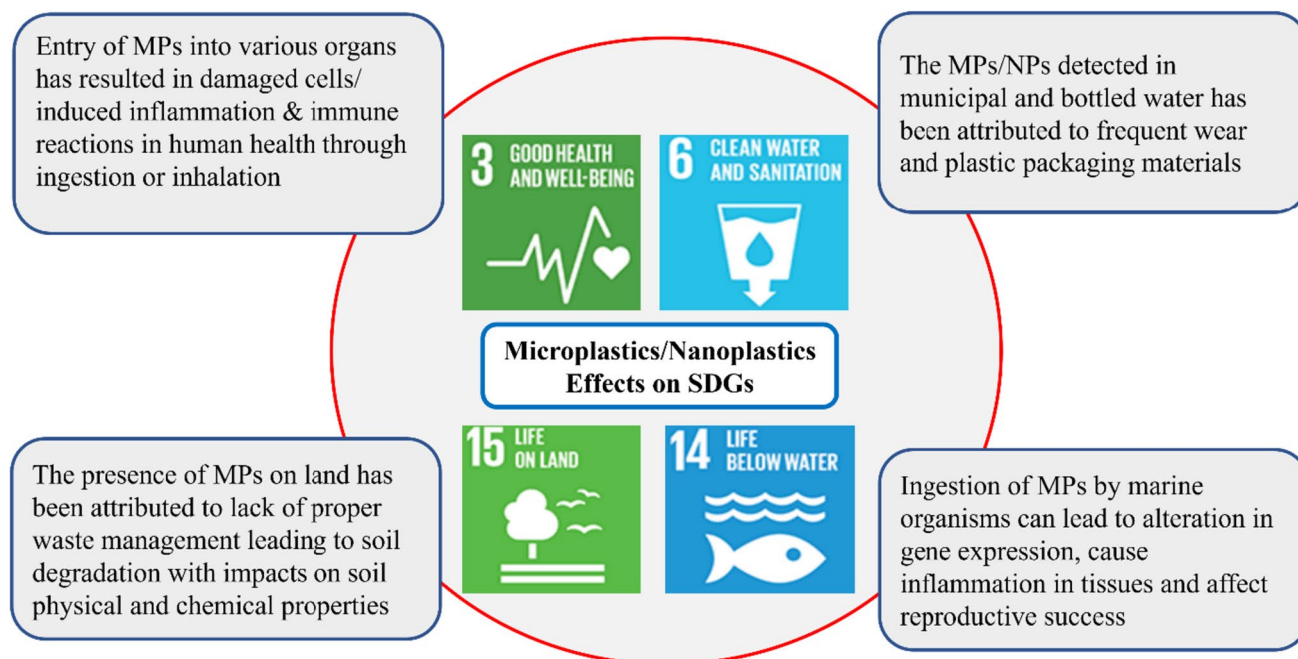


Fig. 1 Effects of ubiquitous MPs/NPs on SDGs with direct/indirect influence on human health

Table 1 Environmental, economic, and potential health risks of MP pollution

Environmental risks of MPs	Study highlights	Potential health hazards	References
Marine pollution	MPs can contaminate the oceans and cause harm to marine life, due to ingestion and entanglement	Inflammation, oxidative stress, and possible interference with the endocrine system	[27, 71]
Water contamination	MPs can accumulate in freshwater sources, including rivers, lakes, and streams, which can cause harm to aquatic life and eventually end up in potable drinking water	Oxidative stress, endocrine disruption, intestinal damage, immunotoxicity	[126, 127]
Soil pollution	MPs can accumulate in the soil, which can impact soil health and fertility, leading to long-term damage to the environment	Contamination of crops and food chain, ingestion and accumulation in the human body, negative impact on soil health, and microbial activity, which can indirectly affect human health	[15, 128]
Air pollution/climate change	Burning of plastic waste, including MPs, releases toxic fumes into the air, leading to air pollution. Plastic production and disposal, including MPs, contribute to greenhouse gas emissions and climate change	Respiratory problems from inhalation of MPs, cardiovascular problems, damage to lung tissue, inflammation of airways, and endocrine disruption	[76, 120]
Ingestion by animals	MPs can be accidentally ingested by animal through food or mistaken for food, which can cause blockages in the digestive system or transfer toxins into the food chain	Damage to digestive organs, internal blockages and obstructions, accumulation of toxins from plastic additives, hormonal disruption, and reproductive problems, weakened immune systems	[105••]
Ecosystem disruption	The accumulation of MPs in the environment can disrupt the balance of ecosystems, leading to negative impacts on biodiversity	Contamination of food sources, leading to ingestion of MPs increased exposure to harmful chemicals that can accumulate in the food chain. Impacts: MPs can also cause genetic and reproductive impacts on organisms, potentially leading to lower reproductive success and long-term population declines	[2••]
Economic losses	The impact of MPs on ecosystems can lead to economic losses, particularly in industries that rely on fisheries, tourism, and recreation. For example, beaches and tourist destinations affected by microplastic pollution may lose visitors and revenue, and fishing communities may experience reduced catches due to the impact on marine ecosystems	Environmental clean-up costs incurred may harm other capital projects including the health sector and thereby impede the smooth running of healthcare facilities and services to the citizens. Furthermore, MPs pollution can also reduce the quality of life as it can lead to decreased mental health and reduced social participation, which can further reduce productivity and increase medical costs	[87, 120]

bonding, hydrophobic forces, and π - π interactions. Furthermore, the role of surface chemistry in these interactions is briefly clarified. To address these concerns, the review also introduces efficient and low-cost remediation techniques with a circular economy approach, indicating sustainable pathways to address issues related to plastic-heavy metal pollution. In conclusion, the study identifies contamination risks, stressing the priority for further research to safeguard the environment, aquatic life, and human health in the face of these complex environmental issues.

Interface Behaviour of MPs with Heavy Metals

MPs Interaction with Heavy Metals

Due to the advancement of metal-derived industries and inappropriate waste disposal, heavy metal pollution in the environment is becoming a major issue [27]. Several research works have highlighted the capacity of MPs to bind to chemical substances typically present in seawater or wastewater treatment plants [18, 28, 29]. Additionally, MPs have the ability to carry heavy metals to different parts of the environment, contributing to the spread of heavy metal pollution due to their strong binding capacity [17, 30]. However, the full extent of these effects is not yet fully understood, underscoring the need for more in-depth studies to thoroughly evaluate the influence of MPs and heavy metals on both the environment and living organisms [17, 31].

Cadmium (Cd) is recognized as one of the most common and hazardous metal contaminants in our environment. While Cd is naturally present, its release into the environment is often amplified by human activities, including mining, smelting, and various industrial operations. Once introduced into the environment, Cd tends to linger, accumulating in both soil and water bodies [32]. The interaction between MPs and Cd may lead to changes in the toxicity, bioavailability, and build-up of Cd within organisms [17]. A recent research revealed that when zebrafish were exposed to both MPs (specifically polystyrene) and Cd, they experienced oxidative harm and inflammation. Moreover, there was a heightened accumulation of Cd in their liver, intestines, and gills. This combined exposure amplified the detrimental effects of Cd on the fish's tissues [30]. Another investigation analyzed plastic pellets from four distinct coastal locations, assessing the accumulation of primary metals like Al, Fe, and Mn and trace metals including Cu, Zn, Pb, Ag, Co, Cr, Mo, Sb, and Sn. However, the exact mechanism by which these pellets enriched metals remained unclear [33]. A study recently demonstrated that certain MPs, notably PE, PP, PS, and PVC, possess a pronounced capacity to bind quickly and store metals like Cr, Cu, Co, and Pb in water environments, reaching an equilibrium in merely 5 days [34]. Another study

with pellet samples from 19 different beaches found that the absorbed metal quantities in these pellets exceeded those of the original particles. Additionally, the concentrations of Fe and Al in the pellets were measured at 0.23 mg g^{-1} and 0.04 mg g^{-1} , respectively [20]. Furthermore, a study explored the adsorption of trace metals like Cd, Co, Cr, Cu, Ni, and Pb on both 'virgin' and 'beached' polyethylene pellets with the 'virgin' pellets obtained from a local moulding facility, while the 'beached' pellets were collected from a nearby sandy beach. The study found that metals mainly adhered to the surface of the plastic pellets as metal cations or oxyanions. Thus, it was affirmed that the adsorption of metals on beached (aged) PE pellets was more pronounced than that observed for virgin pellets in seawater [35].

Effects of Surface Chemistry on Interface Behaviour of MPs and Heavy Metals

The fate and behaviour of MPs in the environment are significantly governed by their surface chemistry, and understanding these properties is important for developing effective strategies to mitigate the environmental impact of MPs [2••, 8, 24•, 35, 36••, 37••, 38]. These inherent attributes of MPs are central to the adsorption and interaction processes with pollutants, offering active sites where these reactions occur [35, 39•, 40]. The microplastic surfaces may become contaminated with contaminants, harming marine life. MPs have the ability to accumulate toxic metals in the marine environment due to their hydrophobic characteristics and large specific surface area [41••]. Adsorption of heavy metals onto MPs involves a complex mechanism. Therefore, the surface characteristics of plastic particles are modified, and a variety of active binding sites for metal ions are generated due to the precipitation of inorganic minerals [35, 42]. Various functional groups like aliphatic, aromatic, hydroxyl, carboxyl, and carbonyl mark the surface chemistry of MPs [8, 43, 44]. For instance, oxygen-containing functional groups on the surface, such as -COO and -OH, significantly impact the adsorption process [22••]. These functional groups tend to influence the synergistic interactions between metal ions and MPs, subsequently forming hydrogen bonds [38]. A study of the interaction of heavy metals with both pristine and aged MPs revealed that in contrast to the pristine MPs, the surfaces of aged MPs became more hydrophilic and exhibited a greater surface area. In addition, there was an increase in the presence of oxygen-containing functional groups, accompanied by a reduction in the point of zero charge (pH_{PZC}) of the MPs [45]. Concurrently, the decrease in the pH_{PZC} observed on the surface of MPs promotes electrostatic attraction between the MPs and heavy metal cations by facilitating the generation of a negative charge on the surface [22••]. Furthermore, when Cu^{2+} and Cd^{2+} were investigated using pristine and aged MPs, the adsorption capacity of aged MPs for the investigated heavy metals was significantly greater

than that of pristine MPs. This phenomenon was attributed to the surface structure of aged MPs becoming rougher during the aging process, accompanied by a proportional increase in both specific surface area and the quantity of oxygen-containing surface functional groups. Therefore, these alterations collectively enhance the MPs' affinity for pollutants [46]. Analytical techniques such as Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance (NMR) spectroscopy can identify and quantify these groups, as evidenced in recent studies [22••, 24•, 36••, 40, 47, 48]. Certain studies have examined the presence of surface functional groups present in MPs, including ester, carboxyl, hydroxyl (-OH), and carbonyl groups [8, 22••, 38, 39•, 44, 49]. A recent study has also shown that MPs demonstrated higher Pb and Cu concentrations than surface water. This phenomenon was attributed to their potential affinity for heavy metals from the aquatic surroundings. Therefore, Pb and Cu tend to form weak bonds with MPs, resulting in the subsequent formation of a thin layer on the surface of the MPs [50]. This accumulation is due to biofilm on the surface of MPs and synergistic interactions with heavy metal-complex organic materials [51, 52]. Thus, the capacity of MPs binding to both organic and inorganic contaminants is attributed to the presence of potential hydrophobic surface [41••, 53]. Key aspects of surface chemistry influencing the behaviour of MPs and heavy metals at their interface are summarized in Table 2.

Factors Governing the Interface Behaviour of MPs with Heavy Metals

pH

The pH level of a solution, indicating its acidity or alkalinity, is understood to be a key determinant in shaping the surface charge of MPs and the form of metal ions [2••, 17, 36••, 54••, 55]. Changes in pH can modify the zeta potential of

MPs, subsequently affecting the precipitation of heavy metals and the degree to which metals are taken up by MPs [2••, 17, 55]. Typically, an increase in pH results in a reduction in the zeta potentials of MPs. However, when the pH level of the water surpasses the point of zero charges of MPs, they acquire a negative charge [2••, 17]. This enhances the electrostatic pull between MPs and metals, especially cations [17, 56]. A study recently investigated the effect of pH on the adsorption of Cd, Cu, Pb, and Zn to virgin plastic pellets (PE and PP) within the usual pH range of natural water (6 to 8) over a span of 4 h. The results revealed that a higher pH generally increased the adsorption rates for most metals, except for lead, which remained unchanged across the pH spectrum according to recent findings by Ahechti et al. [54••].

Another study also examined the adsorption behaviour of various metals with MPs; it was found that the adsorption rates of Pb, Ni, Cd, Pb, and Co rose as the pH of river water increased. However, the adsorption capacity for Cr decreased, while that of Cu remained relatively constant [35]. A separate study examining the effect of metal (Fe and Cu) nanoparticles on three different types of MPs (PS, PP, and PVC) showed a similar pattern. The study found that with a rise in pH, the MP's capacity to adsorb Cu and Fe also increased, with the lowest adsorption observed at pH 3 [36••]. These observations were attributed to changes in the surface charge of MPs and the state of metal ions, both of which are affected by the pH of the solution [57]. The adsorption rate and amount on MPs are significantly impacted by H⁺ and OH⁻ ions, which can modify the MPs' surface charge. Thus, in an acidic environment, the concentration of H⁺ ions induces a positive charge on the MP surface, resulting in electrostatic repulsion between the positively charged microplastic surface and metal cations [36••]. A recent study investigated the effects of solution pH on the adsorption of Cr(VI) by three different types of MPs. The adsorption of Cr(VI) on PE and PS showed a slight decrease

Table 2 Characteristic features of surface chemistry influencing the interface behaviour of MPs and heavy metals

Characteristic features	Study findings	References
Surface charge	Surface charge of heavy metals and MPs can affect their interaction with ions and particles at the interface, altering aggregation and transport	[129, 130]
Surface area	MPs and heavy metals' surface area affects their interactions with other species. Larger surface area facilitates more interactions and can change adsorption behaviour and transport	[31, 48]
Surface functional groups	Functional groups on MPs and heavy metals affect their interactions with other species. For instance, carboxylic acid or amine groups increase heavy metal adsorption	[38, 86]
Surface roughness	A rough surface of MPs and heavy metals enhances their interactions by providing more surface area for adsorption	[31, 35]
Surface coating	The presence of coatings or organic substances on the surface of MPs and heavy metals can influence their interactions with different species at the interface. Coatings can enhance or inhibit adsorption behaviour and affect the transport of MPs and heavy metals. It has been demonstrated that humic acid (HA) has the ability to facilitate the adsorption of Cd(II) on PVC and PS, while simultaneously reducing its adsorption on PET and PA	[89]

with increasing pH. However, the adsorption of Cr(VI) on the original PA demonstrated a positive-negative pattern, culminating in its peak at pH 4 (958.54 ± 102.33 $\mu\text{g/g}$). While aged PE and PS showed a further decrease in adsorption as pH increased from 2 to 7, aged PA reached its maximum at pH 3. This phenomenon was attributed to OH^- competition impeding Cr(VI) adsorption, as indicated by the authors [58]. Thus, the adsorption of Cr(VI) on MPs was found to be influenced by pH-dependent electrostatic interactions, consistent with previous reports [59••, 60]. In a related study, Holmes and colleagues [61] reported that an increase in pH led to a decrease in Cr adsorption onto HDPE, emphasizing the importance of electrostatic interactions. In contrast, another study conducted by different researchers noted that an increase in pH resulted in higher efficiency of Cu and Zn adsorption but not Pb adsorption on beach MPs [35].

Salinity

The impact of salinity on the adsorption of metal ions to MPs depends on both the nature of the polymer and the particular form of the metal [34, 35]. At elevated salinity levels, there is a high tendency for an increase in the competition for adsorption sites between salt ions and heavy metal ions. As a result, there will be fewer available adsorption sites for heavy metals. For instance, in trace metal solutions containing Pb, Cd, Cu, and Zn, elevated salinity levels led to a longer adsorption time on polystyrene microplastics (PSMPs) and a decreased adsorption of trace metals [62]. This can be attributed to the ability of cations to compete for adsorption onto the surface of MPs [35, 53]. In addition, high salinities increase the negative charge on MPs, leading to more significant repulsive forces between MPs and heavy metal ions [35]. This, in turn, tends to induce a reduction in adsorption potential. Conversely, low salinity levels decrease the competition for adsorption sites and weaken the repulsive forces, resulting in an increase in the adsorption of heavy metals onto MPs [62]. For instance, a specific study that explored the adsorption of metals such as Cu, Pb, Cd, Ni, Co, and Cr onto MPs demonstrated that the adsorption ability of Co, Ni, and Cd waned with rising salinity, while that of Cr increased. The adsorption patterns of Cu and Pb in saline water were found to be analogous to those in freshwater. The researchers concluded that the main interaction with the pellet surface was the free ion, and the growing competition for binding sites on the pellet surface was a major key determinant [35].

Ionic Strength

The ionic strength of a solution plays a pivotal role in the adsorption process, determining its specificity [41••]. The

type of adsorption, whether specific or non-specific, is determined by the interaction between the adsorbent and the adsorbate [41••]. Specific adsorption is characterized by the attraction of the adsorbate molecule to the adsorbent through stronger chemical interactions. These can include hydrogen bonding or covalent bonding [63]. In contrast, non-specific adsorption arises from weaker forces, such as electrostatic interactions or van der Waals forces [64, 65]. Specific adsorption is usually more selective and stronger, while non-specific adsorption is less selective and weaker [41••]. The presence of ions in the solution impacts how heavy metals adsorb onto MPs. For example, a study was conducted to explore the effects of ionic strength and the presence of competitive ions on the adsorption of As(III) by polytetrafluoroethylene (PTFE)-based MPs. The findings indicated that the presence of ions such as NO_3^- and PO_4^{3-} in the solution hindered the adsorption of As(III) by PTFE, which caused a reduction in the adsorption amount of As(III) onto PTFE as the concentrations of NO_3^- and PO_4^{3-} increased. However, the introduction of NO_3^- from an external source equally reduced the adsorption of As(III) by PTFE, but the effect was less significant with increasing NO_3^- concentration. Therefore, the authors proposed that the adsorption of As(III) by PTFE is likely the result of a combination of specific adsorption and electrosorption [65]. For instance, the decline in Pb(II) adsorption under varying environmental conditions emphasized the critical significance of ionic strength in regulating the adsorption capacity of MPs [66].

In the study conducted by Lin et al. [66], elevated ionic strength levels diminish the adsorption of Pb(II) onto MPs. The authors hypothesized that this reduction might be attributed to the presence of salt ions. These ions could create an electrostatic barrier between the negatively charged surface of MPs and the positively charged Pb(II) ions, thereby affecting the adsorption process. Similarly, Zou et al. [55] also observed a decline in Pb(II) adsorption onto MPs under high ionic strength conditions. Another study that explored the adsorption of lead on virgin MPs and other solid substrates found that as the ionic strength increased from 0.01 to 0.10, there was a uniform decrease in lead adsorption by the MPs. On the other hand, for the other solid substrates, there was an initial reduction in Pb(II) adsorption, which was then followed by a stabilization phase. Therefore, the authors confirmed that the decrease in adsorption identified might be triggered by the presence of electrostatic interactions, while the remaining portion might have been connected to irreversible chemical adsorption [51]. The efficiency of Pb(II) ion adsorption onto aged nylon MPs is heavily influenced by the ionic strength. In a study that used NaCl to mimic oceanic conditions, it was found that the presence of electrolyte cations (Na^+) notably heightened the competition for the adsorption sites on nylon MPs. This increased competition,

in turn, had an impact on the adsorption of Pb^{2+} ions [56]. The findings underscore the intricate interplay between ionic strength and adsorption behaviour, particularly in conditions that simulate natural marine environments.

According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, an increase in the ionic strength of a solution leads to the compression of the electrical double layer and a decrease in repulsive forces, ultimately causing an increase in aggregation [12]. For example, a study by Wegner et al. [67] observed that carboxylated polystyrene MPs sized 30 nm in seawater quickly aggregated and formed aggregates exceeding 1000 nm within 30 min. As a result, this would decrease their surface area and adsorption capacity. Furthermore, the aggregation caused by electrolytes can explain why the introduction of NaCl resulted in a reduction in Cd adsorption onto MP in the study recently reported by Wang et al. [17].

Dissolved Organic Matter (DOM)

DOM has the ability to bind to both MPs and heavy metals, creating complexes that modify their physicochemical properties [56, 68]. The presence of DOM can lead to competition with metals for binding sites on MPs, reducing the available sites for heavy metal sorption and causing the desorption of these metals [68]. Fulvic acid (FA), a significant component of DOM prevalent in water, soil, and sediment environments, plays a key role in this process [69]. A recent study explored the impact of FA on the adsorption of Pb(II) and nylon MPs. The research revealed that the adsorption process was strongly affected by the FA concentration, especially at high levels. Specifically, an increase in FA concentration led to the inhibition of Pb(II) adsorption, suggesting potential complexation interactions between FA and Pb^{2+} ions. As a result, a considerable number of Pb(II) ions are first attached to FA and then bound to the aged nylon MPs [56].

DOM can increase the hydrophilicity of MPs by coating their surfaces with polar functional groups. This hydrophilic coating increases the surface area of MPs, enabling them to adsorb heavy metals and form metal-DOM-MP complexes, which enhances their likelihood of adsorbing heavy metals [1, 2, 56], possibly due to the hydrophilic properties of FA, as reported in another study [70]. Moreover, the competitive dynamics between DOM and MPs for binding sites can also influence the adsorption of heavy metals onto MPs [1, 71].

The coexistence of MPs and DOM has been reported to trigger high levels of bioaccumulation and toxicity of Cu in fish. The underlying reasons for this phenomenon were linked to the inhibition of Cu-ion transport in liver cells (hepatocytes) and a surge in oxidative stress [71]. Humic acid (HA), another component of DOM, is rich in oxygenated functional groups, including carboxylic and hydroxyl groups. HA can impact the colloidal stability of microplastics in aquatic settings [1, 2]

Another study showed that humus, mainly composed of HA and FA, enhanced the adsorption of As(III) by PSMPs. The phenolichydroxyl groups present in HA facilitated the transport of As(III), and the interaction HA and PSMPs formed a π complex, generating additional adsorption sites on the MPs and decreasing the time required to reach adsorption equilibrium. When both HA and FA were present, the adsorption of As(III) on MPs significantly increased, reaching as high as 81.83% and 80.83%, respectively [72]. Other factors influencing the sorption interaction of MPs with heavy metals can be found in the “Other Factors Influencing the Sorption Interaction of MPs with Heavy Metals” section.

Other Factors Influencing the Sorption Interaction of MPs with Heavy Metals

The sorption of metals by MPs is particularly influenced by the aging process, leading to changes in crystallinity and the formation of oxygen-containing groups [2, 56, 73, 74, 75]. This concept was further elaborated by Maity et al. [76] and [5], Lambert et al. [8], who emphasized that the state of crystallinity of MPs is an essential factor to consider. Low crystallinity or high amorphous characteristics of MPs result in rough surfaces, which tend to facilitate the sorption of other emerging contaminants and potentially increase their toxicity in the environment [55].

MPs persist in the environment for extended periods and undergo aging due to various factors [48]. As plastics enter the environment, they undergo degradation and come into contact with pollutants. During their migration, MPs tend to absorb pollutants to a greater extent. Therefore, aging is another factor that can influence the adsorption capacity of MPs [31, 48, 73] found that Cu and Zn were more likely to bind with aged PVC. This increased binding affinity could be attributed to the enhanced polarity and surface area of the aged PVC, offering more sites for metal ion adsorption. Another research effort revealed that the adsorption capacity of various metal ions by PS grew with the degree of aging. This increase was likely due to the augmented surface roughness and the presence of oxygen-containing functional groups. The aging and biofouling of MPs also led to the accumulation of more substantial amounts of trace metals [35].

Functional groups on the surface of MPs, including $-\text{NH}_2$, phenyl-OH, and $-\text{COOH}$, can facilitate metal binding via a complexation mechanism [77]. Biodegradable MPs such as polycaprolactone (PCL), polybutylene adipate terephthalate (PBAT), and polylactic acid (PLA), which contain a high density of oxygen-containing groups, exhibit enhanced adsorption of heavy metals [78]. Oxygen-containing functional groups on the surface, like $-\text{COO}$ and $-\text{OH}$ groups, can modify the surface interactions between MPs and metal ions, often leading to hydrogen bonding [2, 73, 79].

Particle size is another crucial factor influencing the interaction between MPs and heavy metals. It is a primary factor affecting adsorption and shaping the adsorption capacity of MPs [62]. In the natural environment, MPs are subject to fragmentation due to environmental factors, resulting in smaller particles. This fragmentation notably affects the adsorption potential of heavy metals onto MPs [8]. Generally, MP particles with smaller dimensions exhibit greater efficacy in adsorbing and retaining trace amounts of metals than larger particles, predominantly due to their increased surface-to-volume ratio [15, 17]. This observation was supported by a study where the metal adsorption capabilities of PE, PET, and PP towards Cu(II), Cr(III), and Pb(II) were found to increase with decreasing particle size [80]. However, a recent study contradicted this trend and found that larger particles of PSMPs showed higher adsorption levels for Pb, Cd, Cu, and Zn. This discrepancy was attributed to the larger particle size of PS [81]. The type of polymer also plays a role in determining the adsorption capacity of MPs with heavy metals [82]. The adsorption capacity varies based on the specific type of MP and metal, given their unique physicochemical properties. For instance, PS and film MPs have a higher adsorption capacity for Cu(II) compared to PVC, PE, bottle cap particles, and fishing line fibres, primarily due to the favourable physicochemical properties of film MPs [46, 82].

The initial concentration of heavy metals can also influence the adsorption capacity. While higher initial concentrations lead to increased adsorption capacity, they can also decelerate the adsorption rate [62]. For example, Hodson and colleagues [83••] demonstrated in their study that the adsorption capacity of Zn increased substantially at higher initial concentrations (0.1–100 mg L⁻¹), reaching values between 236 and 7171 mg g⁻¹, which were significantly greater than those at lower initial concentrations [35, 61]. Overall, aging, crystallinity, functional groups, and particle size are other factors that determine the adsorption capacity of MPs with heavy metals and chemical contaminants [17, 48, 55, 76, 78].

Insights into Adsorption Mechanisms Between MPs and Heavy Metals

The adsorption mechanisms between MPs and heavy metals involve various processes, including ion exchange [84], hydrogen bonding [63, 85], electrostatic interactions [2••, 86], hydrophobic surface [41••, 87], pore-filling [88], precipitation, surface sorption, and complexation [55, 84].

Electrostatic Interaction

Electrostatic interaction refers to the attractive or repulsive force between electrically charged particles [64]. When MP particles have a net negative charge and heavy metal ions have a

net positive charge, they can interact electrostatically [59••]. Electrostatic sorption occurs when a plastic polymer and heavy metal come into contact, resulting in the attraction of molecules that have an opposite electric charge to that of the plastic polymer [86]. Conversely, electrostatic repulsion arises when both the plastic polymer and the heavy metal share the same charge. Factors such as the pH of the medium and the pH at the point of zero charge (pHpzc) influence electrostatic interactions. Typically, when the pH of the medium exceeds the pHpzc, the adsorbent generally acquires a negative charge [22••].

According to the studies by Guo et al. [60] and Liu et al. [84], the zeta potential is related to the propensities of chemicals to bind to MPs through electrostatic interactions. It has been hypothesized that the zeta potential represents the surface electrical potential of MP particles. The latest study examined how Pb(II) adsorbs onto virgin and natural-aged MPs in various electrolyte solutions. According to the authors, the adsorption process was significantly influenced by the presence of salt ions, despite the crucial role played by the electrostatic interaction [84]. The pH of 6.0 yielded the maximum adsorption capacity for Pb(II). The researchers demonstrated that the surfaces of aged-PE and virgin-PE had a negative charge between pH 3 and 7, which decreased as the pH increased. This electronegativity enhanced the binding process of Pb(II) to the MPs via electrostatic interaction. Nevertheless, when the pH increased to 7, Pb(II) was present in the forms of Pb²⁺, Pb(OH)⁺, and Pb(OH)₂, resulting in a reduction in Pb(II) adsorption [84].

Electrostatic interaction has also been identified as a crucial mechanism in the adsorption of divalent metal ions (such as Cu, Zn, and Ni) onto MPs. The extent of this interaction was found to be notably dependent on the salinity of the solution, and its efficacy subsequently diminished as the concentration of NaCl increased [59••]. In the case of Cd adsorption onto MPs, electrostatic interaction was found to be the major governing mechanism. When the pH of the solution is above 7, the negatively charged surface of MPs favours the adsorption of positively charged Cd²⁺ ions. However, under acidic conditions, the decrease in adsorption primarily resulted from the electrostatic repulsion between the positively charged MP surfaces and the cationic Cd²⁺ ions. Furthermore, a higher concentration of H₃O⁺ ions in the solution can reduce Cd adsorption as they compete with Cd²⁺ ions for available binding sites. Electrostatic attraction and ionic exchange were concluded to be the key mechanisms for Cd sorption by MPs [17].

Surface Complexation

Surface complexation has also been reported as one of the major mechanisms influencing the interface behaviour of MPs and heavy metals [55, 84, 89]. Surface complexation is a significant mechanism that influences the fate and transport of pollutants in the environment [90]. The mechanism operates by attracting ions or molecules onto the surface of solid materials,

such as minerals or soil particles, by forming a bond between the surface of the solid and the charged species in the solution [91]. This bonding process is referred to as surface complexation, and the end product is called a surface complex [90, 91].

In a study conducted by Liu et al. [84] on the interaction of Pb with naturally aged MPs, it was observed that introducing NaCl and CaCl₂ led to a decline in Pb²⁺ ions and an uptick in the formation of ion pairs such as PbCl⁺ and PbCl₂. This shift resulted in a reduced activity coefficient for Pb(II) ions. Notably, CaCl₂ formed more robust ion pairs with metal ions compared to NaCl, which hindered the movement of Pb(II) ions towards the MPs' surface. The addition of these salts influenced both the adsorption kinetics and the isotherms. These effects were interconnected with other solution factors, such as pH and DOM, which could further alter the adsorption dynamics. When higher concentrations of FA were introduced, varying inhibition levels were observed in the presence of Na⁺ and Ca²⁺, suggesting a significant impact of surface complexation and aggregation on the interaction between MPs and metal ions. The study also emphasized that variations in environmental conditions, particularly pH and ionic strength, played a crucial role in shaping the adsorption capacity of MPs for Pb(II) ions.

In a separate investigation by Zou et al. [55], surface complexation was identified as a crucial mechanism for the adsorption of three separate different divalent metals onto four distinct virgin MPs. The behaviour of this adsorption was found to vary widely, influenced by the surface physicochemical characteristics of the MPs and further modulated by various environmental factors. At a pH of 6, all the MPs investigated in their study had negative zeta potentials, which implied that the three types of metals investigated were drawn to the MPs through electrostatic forces. The study determined that chlorinated polyethylene (CPE) had a negative and polar nature due to its chlorine content, which led to a significant difference in the sorption affinity observed among the three metals. Despite having similar hydrated ionic radii, Cu²⁺ exhibited stronger sorption than Cd²⁺, indicating that stronger complexation was responsible for the sorption behaviour of Cu²⁺ onto the MPs. Thus, the adsorption of Cu²⁺ onto the plastic surface was found to be largely influenced by the surface complexation [55]. In a related study by Tang et al. [59••], the focus was on the adsorption of Cu(II), Ni(II), and Zn(II) onto nylon MPs found on beaches. The study emphasized the importance of oxygen-containing groups on the MPs' surface for the adsorption process. Surface complexation was again behind the adsorption process, highlighting its central role in the interaction between MPs and heavy metals.

Hydrogen Bond Interaction

The process of sorption on polymers can be influenced by the formation of hydrogen bonds which are relatively weak

interactions involving the hydrogen ion, H⁺. The presence of proton donor and acceptor groups on the polymer surface can further modulate these interactions, emphasizing their role in the overall sorption mechanism [92]. Hydrogen bonds are comparatively weaker than covalent and ionic bonds as they result from the partial charge attraction, not the exchange or sharing of electrons. However, they are stronger than van der Waals forces, which are the least strong kind of intermolecular forces occurring between non-polar molecules [64]. A recent study in which the maximum adsorption of As(III) obtained was attributed to the involvement of hydrogen bonding [63]. The investigated PSMPs were prepared using a ball milling technique, endowing the plastic particles with a distinct porous surface structure and specialized surface attributes. A significant portion of the PSMP surface exhibited a positive electrostatic potential. Notably, the hydrogen atom within the carboxyl group showcased an exceptionally high positive potential, measured at +56.6 kcal/mol. This resulted in the attraction of arsenic oxyanions towards the carboxyl group, demonstrating that As(III) was adsorbed onto the PSMP surface via hydrogen bonding with this specific group. When exposed to higher temperatures, the hydrogen bonds between As(III) and PSMPs weakened, causing a decrease in the attachment of As(III) to the PSMP. This behaviour indicated that the adsorption process was exothermic in nature [63].

In the case of PTFE interacting with As(III), hydrogen bonding has been predicted to be responsible for the interaction of As(III) with the existing hydroxyl functional group on the surface of PTFE. The rise in binding energy was linked to the interaction, suggesting that the electron density of the hydroxyl group's oxygen atom decreased and resulted in a higher proton dissociation. It was observed that As(III) undergoes chemisorption on the PTFE surface, and the structure surrounding the hydroxyl group was subsequently affected significantly. In the case of the hydroxyl group present on the surface of PTFE, the hydrogen atom forms a covalent bond with the electronegative oxygen atom. This interaction results in the establishment of hydrogen bonds, facilitating the adsorption of the oxy-arsenic anion onto the PTFE surface [65]. Furthermore, in a more recent investigation, the primary mechanism for Pb ions adsorbing onto polyethylene microplastics (PE MPs) was identified as chemical adsorption. This process is driven by hydrogen bonding and surface complexation. Notably, the introduction of humic acid (HA) amplified the adsorption of Pb onto PE MPs. This enhancement is likely attributed to HA's ability to act as a bridge, connecting the Pb species to the PEMP. HA facilitated the formation of complexes between Pb ions and itself via cation exchange and hydrogen bonding, which then attached to the surface of PE MPs. In contrast, FA, which had a strong negative charge across a broad range of pH range, hindered the binding of Pb ions to the PE MPs

when in association with FA [85]. Other possible mechanistic interactions, such as van der Waals forces and π - π interactions, and interaction of the hydrophobic surfaces of MPs with chemical contaminants together with their implications on health and environment, are detailed in the “[Other Possible Mechanistic Interactions Between MPs and Heavy Metals](#)” section.

Other Possible Mechanistic Interactions Between MPs and Heavy Metals

Given the aliphatic (e.g. PE) and aromatic (e.g. PS) properties of many plastic polymers, the sorption of heavy metals can be driven by the van der Waals forces and π - π interactions. Guo et al. [1•] identified these forces as key components in the sorption of Cd with four different MPs, emphasizing the dominant role of van der Waals forces due to the nonspecific functional groups of PE and PP. Conversely, given the presence of benzene rings, π - π interactions may be significant in PS polymers. The adsorption capacity of the MPs was strongly correlated with their specific surface area and total pore volume. Key mechanisms driving Cd (II) adsorption on MPs encompass π - π interactions, electrostatic interactions, and the presence of oxygen-containing functional groups [1•, 35]. Previous research has depicted major mechanistic pathways for interactions between various types of MPs and heavy metals, emphasizing the vector role of MPs in environmental contamination and associated ecotoxicological risks [77].

Holmes et al. [35, 61] stressed the importance of oxygen-containing functional groups and π - π interactions in metal adsorption onto MPs. Subsequent analyses of the C 1 s XPS spectra of various polymers, before and after Cd(II) sorption, aimed to unveil the underlying mechanism. Notably, increased proportions of the C=O band on most MPs post-Cd(II) adsorption (Fig. 2) suggest reactions leading to the formation of more C=O bonds. Conversely, the rise in the C=C/C-C band proportions for PA and ABS post-Cd(II) sorption affirms the significant role of π - π interactions in the metal ion adsorption process for certain MPs. Zhou et al. [2••] concluded that the main mechanisms of Cd(II) adsorption onto MPs are electrostatic and π - π interactions, with oxygen-containing functional groups also playing pivotal roles. Desorption hysteresis was observed in both simulated gut and sediment environments, with a notably higher degree of Cd(II) desorption from MPs in the gut environment. This emphasizes potential ecological risks associated with the adsorption–desorption behaviour of MPs in plastic-enriched environments [1•, 2••].

Overall, the adsorption of heavy metals by MPs, particularly those with simple structures and polymer types, has always relied heavily on physical adsorption, which includes

electrostatic interaction. In physical adsorption, water molecules move onto the absorbent surface or interior through simple diffusion without creating new substances or altering chemical bonds. The mechanisms governing the adsorption of each heavy metal differ depending on the characteristic features of the MPs (See Fig. 3) [93].

Synergistic Hazards of the Hydrophobic Surfaces of MPs with Heavy Metals

The presence of MPs in aquatic environments can have implications for the transport and fate of environmental pollutants, leading to their diffusion and accumulation within organisms and subsequent bio-enrichment [2••]. Research has shown that heavy metals, discharged into aquatic ecosystems through various industrial effluents, can accumulate in different parts of aquatic life, including fish, through processes such as dissolution in water and subsequent accumulation in the organisms [35, 62]. This bioaccumulation of heavy metals in fish can have toxic effects and pose potential health risks to humans, especially through consuming contaminated fish [31, 62]. Similarly, studies have demonstrated the bioaccumulation of heavy metals in water, sediment, and organisms in various aquatic environments, highlighting the potential threat posed by the accumulation of these toxic substances [94]. Moreover, over 8 million tons of plastic debris are discharged annually in both global freshwater and marine ecosystems [95]. The interactions between MPs and heavy metals in the ecological sphere are inevitable and can lead to adverse effects. These interactions can alter the environmental behaviours, bioavailability, and potential toxicity of both MPs and heavy metals, leading to ecological risks [63]. The exposure routes to MPs include ingestion, inhalation, and dermal contact [96]. These routes can lead to potential ecosystem toxicity and human health risks [35]. The ingestion of MPs has been a significant concern, with studies reporting an increase in MPs ingested by humans [97]. Understanding these exposure routes is important for assessing the potential risks associated with microplastic contamination [19]. Therefore, these routes can lead to health issues. For instance, ingested MPs can accumulate in the digestive tract, potentially causing inflammation and other health problems (see Fig. 4) [98]. Inhaled MPs can also accumulate in the lungs, potentially causing respiratory issues. MPs that come into contact with the skin can also cause skin irritation [38].

One of the factors influencing the concentration of heavy metals in MPs is their availability in the environment [56, 94]. For instance, a study recently examined environmental effects on the adsorption of Pb and Cu in water and MPs. With low pH and salinity, the Musi River was freshwater-dominated (pH 6.2–6.6). PP > PE > PES > PVC and nylon

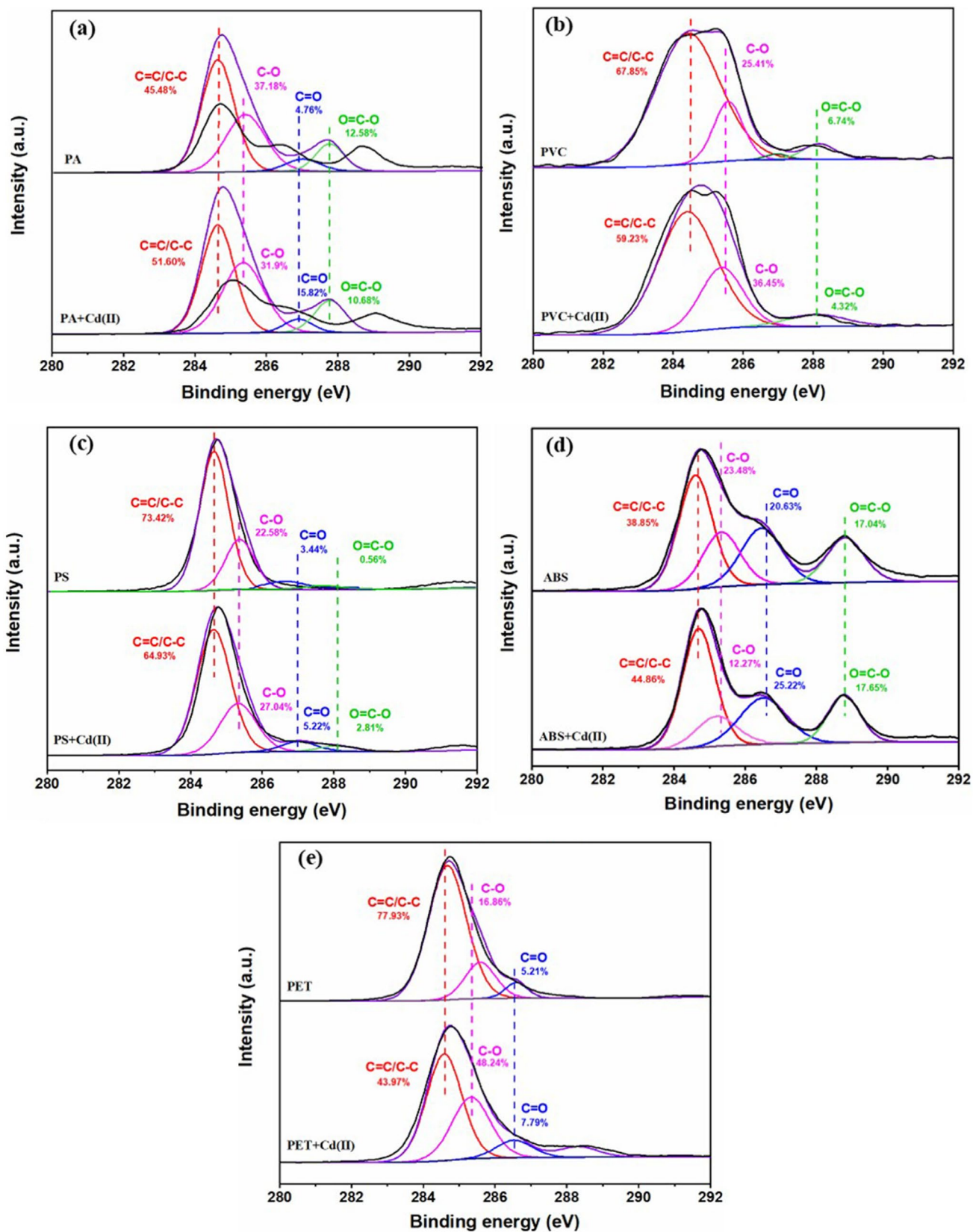


Fig. 2 XPS C 1s spectra for PA (a), PVC (b), PS (c), ABS (d), and PET (e), both before and following cadmium adsorption at a concentration of 80 mg/L [20] with permission. Copyright 2020 Elsevier

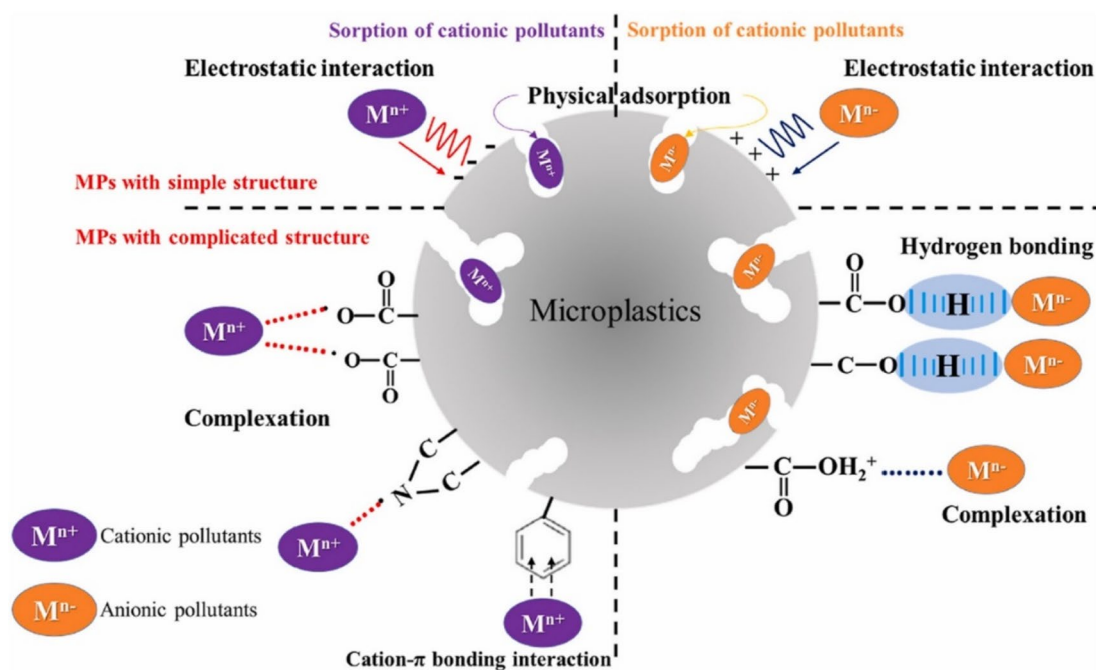


Fig. 3 Various mechanisms that govern the adsorption of heavy metals by the MPs [93] with permission. Copyright 2022 Elsevier

polymers were randomly selected as MPs samples. Their findings showed increased concentrations of Pb and Cu in the river towards the estuary, ranging from 0.0245 to 0.0711 mg L⁻¹ and 0.0099 to 0.0173 mg L⁻¹, while higher Pb and Cu concentrations (0.152–2.218 mg kg⁻¹ for Pb,

0.017–0.371 mg kg⁻¹ for Cu) were noticed in MPs exceeded river values, with Pb outweighing Cu. The authors affirmed the dominance of the Freundlich model with weak bonds facilitating the easy release of MPs-laden heavy metals into the aquatic ecosystem due to environmental influences [50].

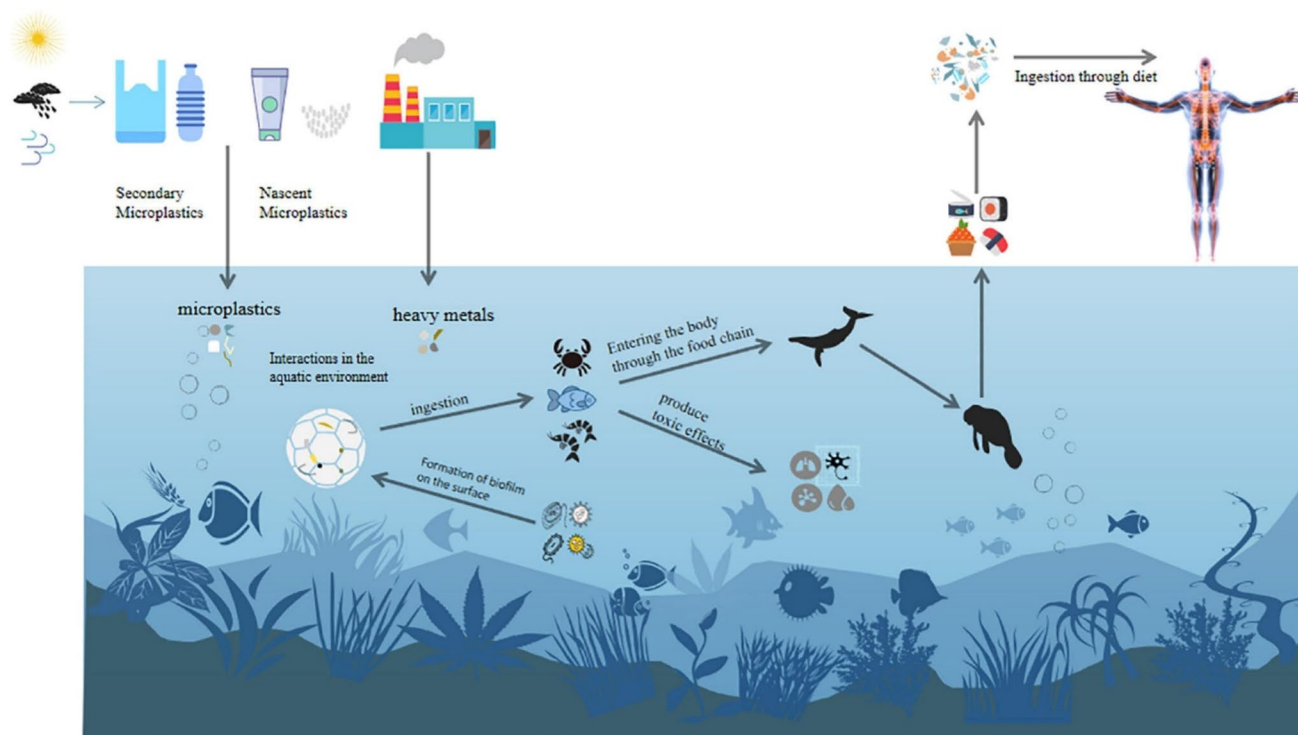


Fig. 4 Interaction of MPs and heavy metals in aquatic environments [98] with permission. Copyright 2020 Elsevier

The hydrophobic nature of MPs can be attributed to their non-polar polymer chains, which result in a hydrophobic surface that can attract contaminants such as heavy metals, pharmaceuticals, or dyes [41••, 64, 99]. This interaction may cause the build-up of heavy metals on MPs, posing a potential risk to the environment and human health [29, 41••, 100•]. MPs have been detected in different tissues of marine fish, such as their brains, muscles, gills, and gastrointestinal tracts [101••]. Furthermore, the presence of MPs in the human gastrointestinal tract has also been confirmed [97]. The interaction between MPs' hydrophobic surfaces and various chemicals is a significant concern, as it could potentially increase the risk. A recent study demonstrated that when mussels are exposed to MPs loaded with fluoranthene, the substance is transferred from the MPs to the mussels' bodies [100•].

Moreover, Hildebrandt et al. [102] have reported that in a physiologically based extraction test (PBET) solution, metals can be significantly desorbed from MPs, and the 'Trojan horse' effect is stronger in smaller particles. The results imply that the adsorption of pollutants onto MPs may result in their leaching out of the plastic particles and penetrating the tissues of organisms, leading to harmful effects. Thus, the 'Trojan horse' effect is a significant concern in the context of microplastic pollution [102]. Various studies have documented the adsorption of different pollutants onto MPs [2••, 72, 103], highlighting the need to evaluate the desorption kinetics of these pollutants from MPs [2••].

Studies have also shown that the complexes of cadmium (Cd) and lead (Pb) can adsorb onto MPs, altering their environmental behaviours, bioavailability, and potential toxicity. For instance, a recent study examined the adsorption of Pb(II) and Cd(II) ions onto PP and PS in water and their desorption in a simulated gastrointestinal environment. It revealed that within this simulated environment, the desorption rates of these metal ions from MPs were high and

correlated with the MP particle size [2••]. Both MPs and heavy metals can accumulate at high levels in the environment and consequently contaminate the food chains, leading to significant ecological risks. Thus, ingesting MP-laden heavy metals can cause direct harm to the digestive system, potentially leading to fatal blockages in the gastrointestinal tract [104, 105••, 106]. These reports indicate a potential toxicological hazard for organisms that ingest metal-contaminated microplastics [2••]. Overall, the adsorption of heavy metals by MPs may induce toxic effects on aquatic biota, affecting processes such as photosynthesis, growth, and reproduction of organisms [107]. The synergistic hazards of MPs with chemical contaminants can result in various environmental concerns (see Fig. 5). Therefore, the synergistic interaction between MPs and heavy metals in aquatic environments presents a significant concern for the health of marine ecosystems and human populations.

Systematic and Effective Strategies for the Mitigation of MPs Triggered Pollution

Sustainable Remediation Strategies for the Clean-up of MPs from an Aqueous Environment

Strategies aimed at removing MPs are critical for mitigating plastic pollution. Therefore, this necessitates their clean-up to avoid further environmental degradation towards achieving a sustainable and habitable environment [19]. Thus, different removal strategies such as coagulation [108], photocatalysis [19], advanced oxidation processes [19, 109], filtration [110], and adsorption [10, 111] have been employed to mitigate their prevalence in various media.

Coagulation has also been reported for the mitigation of MP. According to the previous study, iron or aluminium-derived salts were employed through a coagulation

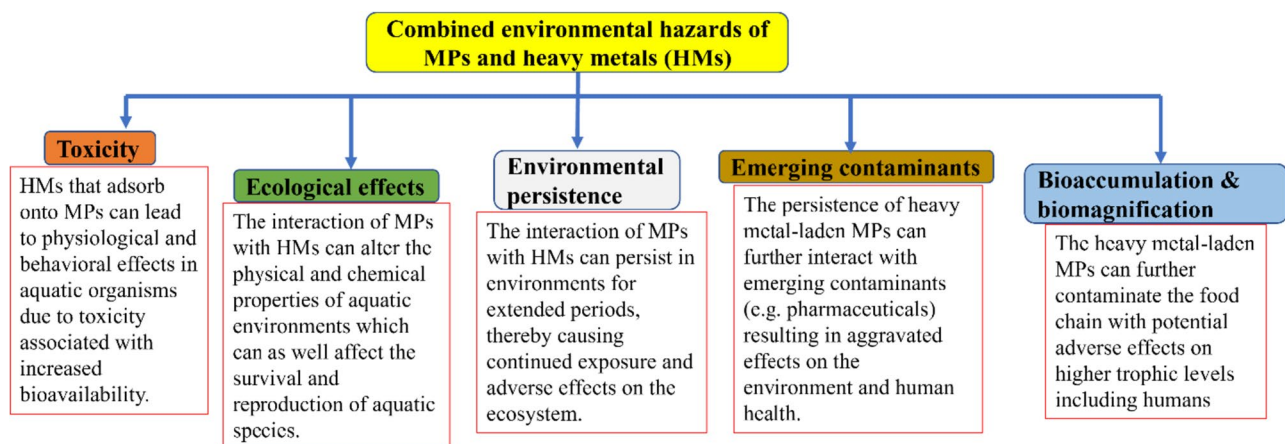


Fig. 5 Synergistic environmental hazards of MPs and heavy metals

technique involving a mechanistic approach of electrostatic interactions between MP (PE or PS) and the existing metal ion. However, the reported removal efficiency was <40%. When the authors improved the coagulant using plant-produced tannic acid, >95% of the MP-PS beads were reportedly removed through filtration compared to when ordinary coagulants were applied [108].

Advanced oxidation techniques are efficient and eco-friendly strategies for removing environmental pollutants. The application of homogeneous advanced oxidation processes (AOPs) has been extensively utilized in treating industrial wastewater. However, this technique is associated with noteworthy limitations such as a restricted pH range, production of sludge, and catalyst inactivation. To mitigate these challenges, scientists have directed their attention towards developing heterogeneous AOPs, featuring heterogeneous catalysts for efficient clean-up [19].

Kang et al. [112] recently demonstrated the degradation of cosmetic MPs by applying a combined approach encompassing carbon catalytic oxidation and hydrothermal hydrolysis [112]. A wide variety of air and water contaminants have been reportedly degraded through photocatalysis with the aid of semiconductor-derived materials as photocatalysts [19]. Photocatalysis allows light to be used as a source of energy supply, and frequently, non-toxic byproducts are produced [113, 114]. Photodegradation is a promising technique, but it produces toxic by-products that enter aquatic systems, and the removal rate is lower. For example, zinc oxide nanorods took 456 h to achieve 65% removal of a 150 µm polypropylene particle, rendering it impractical for industrial usage [115]. While smaller plastic particles can reduce the photodegradation time, they also emit hazardous carbon emissions like CO, which restricts their application [19].

Recent studies have explored using N-TiO₂ powders as catalysts in the photocatalytic degradation of PE. These studies demonstrated efficient degradation of the MP through active involvement of photogenerated e⁻ in the process leading to the production of free OH[•] [116]. Additionally, the synergistic effect of ozonation and H₂O₂ on the degradation of PE MPs was observed. Changes in the structure of MP, including increased intensity of O–H and C = O bands and a decrease in the intensity of the C–H groups, were observed. These findings suggest that the presence of hydrophilic features could enhance the performance of microorganisms to facilitate the degradation of polymers later, and the approach was recommended as a pre-treatment before the biodegradation [109].

Filtration has also been applied using biochar to enhance the efficient performance of sand filters for removing MP spheres (microbeads) in wastewater. In the process, MP spheres stuck, trapped, and entangled in the biochar were employed to improve the sand filter, which accounted for over 90% of removal using biochar [110].

Another removal technology that has also been employed for the remediation of contaminants is adsorption [10, 117, 118]. The recent work reported biochar synthesized using agro-wastes as precursors (rice husks) and magnetically modified was employed as efficient and low-cost adsorbent for removing MPs from aqueous solution. The magnetic biochar showed 99.96% removal efficiency. The adsorbent's performance was attributed to electrostatic attraction and surface complexation in the adsorption process [111]. The performance of various removal techniques for removing MPs is presented in Table 3. Replacing plastic polymers with sustainable alternatives derived from natural sources and implementing environmental policy, regulation, and circular

Table 3 Various remediation techniques for the removal of MPs

Remediation approach	MP type	MP size (µm)	Time	Removal/degradation efficiency (%)	References
Photocatalytic degradation (TiO ₂ nanoparticle film)	PS	1 and 5	24 h	93.49 and 99.9	[131]
Photocatalytic degradation (catalyst: C. N-TiO ₂ powder)	HDPE	725 ± 108	50 h	71.77 ± 1.88	[132]
Biodegradation (<i>Bacillus sp.</i> and <i>Paenibacillus sp.</i>)	PE	40–600	60 days	14.7	[133]
Biodegradation (<i>Shewanella</i> , <i>Rheinheimera</i> , and <i>Bacillus</i>)	LDPE	-	120 days	47.07 ± 6.67	[134]
Adsorption (adsorbent: magPOMSILPs)	PS	1000	24 h	90–100	[135]
Adsorption (adsorbent: ZIF-67)	PS	1	20 min	92.1	[136]
Coagulation	PE	140	-	99	[137]
Electrocoagulation	Microbeads	-	60 min	90	[138]
Electrocoagulation	PP, CA, PE, PMMA	1–2 mm (for PP & CA), 286.7 µm (for PE), 6.3 µm (for PMMA)	-	98.4, 98.2, 93.2, 91.7	[139]

economy practice are other sustainable solutions to MP pollution (see “[Replacing Plastic Polymers with Sustainable Alternatives Derived from Natural Sources](#)” and “[Implementation of Environmental Policy, Regulation, and Circular Economy Practice: A Key Solution to MP Pollution](#)” sections).

Replacing Plastic Polymers with Sustainable Alternatives Derived from Natural Sources

The environmental impact of synthetic plastics has highlighted the need for sustainable alternatives. Synthetic plastics, derived from petroleum, have desirable physical and chemical properties but are non-biodegradable, leading to environmental pollution and the release of hazardous substances [3]. Plastic pollution is an imminent environmental challenge, largely due to the widespread use and non-biodegradable nature of plastic products that eventually accumulate in natural habitats, including landfills and oceans. Consequently, the quest for sustainable alternatives to plastic polymers that can mitigate their harmful effects on the environment has become increasingly popular [119]. A promising solution is the substitution of plastic polymers with natural materials derived from renewable sources such as corn starch, cellulose, chitosan, or natural fibres like cotton, hemp, and bamboo [3, 120]. These materials possess numerous benefits as alternatives to plastic since they are biodegradable, thus facilitating their degradation by microorganisms in the environment, which helps minimize the accumulation in oceans and landfills [119].

Additionally, natural materials are renewable and can be obtained through sustainable harvesting methods that limit the environmental impact of their production. Biopolymers, derived from plant, animal, or microbial sources, offer a sustainable alternative, with some being naturally biodegradable, such as polylactic acid [3]. Biopolymers have been successfully used in various fields, including packaging, disposable goods, and medicine. Using biopolymers can help preserve natural ecosystems and prevent further environmental damage [120]. Nevertheless, some challenges exist in substituting polymers with natural materials, such as the limited mechanical properties of natural materials compared to plastic, which could restrict their applicability in certain products [3, 119, 120]. Furthermore, producing natural materials may require additional resources, including land, water, and energy, that may also contribute to environmental degradation. Despite these challenges, continued research and innovation in this area hold the promise of achieving a sustainable and eco-friendly future by substituting plastic polymers with natural materials [3, 120].

Implementation of Environmental Policy, Regulation, and Circular Economy Practice: A Key Solution to MP Pollution

The issue of MP pollution poses a growing threat to both aquatic ecosystems and human well-being. Therefore, implementing policies and regulations to encourage the adoption of sustainable practices that minimize plastic production and use is critical [43]. In addition, a circular economy approach that prioritizes reducing, reusing, and recycling plastic waste can effectively address microplastic pollution [10, 18, 121]. Policies promoting biodegradable materials and sustainable waste management practices can help reduce the amount of plastic waste in water bodies [32, 119, 120]. Regulations requiring manufacturers to adopt sustainable production processes can prevent the creation of MPs [43]. Rather than imposing taxes and levies on plastic bag users, some countries have incentivized plastic household consumers to return used plastic materials to regulate and reduce plastic litter in the environment [43, 121].

Several countries have advocated for legislation to exclude MPs and microbeads from cosmetic products and other consumables. By implementing policy, regulation, and meticulous utilization of circular economy strategy, we can mitigate the further accumulation of MPs in the environment and its harmful impacts on protecting the planet [121, 122]. In response, there has been growing interest in transitioning towards a circular economy to mitigate plastic pollution and promote sustainable production and consumption practices, according to SDG-12 [119, 123, 124]. Therefore, engaging a circular economy in managing plastic pollution is inevitable, considering the recent high plastic and plastic-related material consumption [10, 119, 123]. A circular economy is a systemic approach that seeks to minimize waste, conserve resources, and enhance environmental sustainability by promoting a closed-loop system of production, consumption, and disposal [123, 124]. Within this framework, the value of materials and products can be productively maintained for as long as possible, and waste is minimized through innovative recycling and recovery processes [121, 124, 125].

Conclusion, Perspective, and Future Outlook

Over the decades, plastic and plastic-related products have offered beneficial applications in various aspects, with humans enjoying a greater share of their benefits. This overview provides crucial perspectives on the intricate relationships between MPs and heavy metals in aquatic environments. The increasing combined effect of MPs and heavy

metals presents substantial risks to both aquatic organisms and human health. Therefore, to manage the environment effectively, it is essential to have a thorough understanding of synergistic interactions between MPs and heavy metals. Thus, this review has identified and emphasized mechanistic processes such as electrostatic attraction, surface interactions, ion exchange, hydrogen bonding, hydrophobic forces, and π - π interactions as possible key players involved in such interactions. Furthermore, the review has also critically justified the influence of surface chemistry on these interactions. In addition, the review supports effective remediation techniques that align with the principles of a circular economy, promoting sustainable solutions to address this menace.

Nevertheless, several research gaps persist and are identified below:

Gap 1. Limited studies on metal desorption from MPs: Despite extensive research on heavy metal adsorption onto MPs, a significant gap exists in comprehending the desorption of metals from MPs.

Gap 2. Limited studies on desorption phenomenon: This research gap left a vacuum in the understanding of the broader consequences, including heavy metal-MPs pollution, bioaccumulation, and human exposure.

Gap 3. Lack of studies on heavy metal-biodegradable MPs interaction: The recommendation of biodegradable plastics as an alternative to conventional plastics sounds interesting. However, there is a need to explore the potential ecological consequences and underlying mechanisms of biodegradable MPs, representing a significant research gap.

Gap 4. Lack of effective remediation strategies: Research gaps persist in developing effective remediation strategies for the removal of both MPs and heavy metals from aqueous media.

In addition, to be able to critically address MPs-heavy metal pollution successfully, we identify research priorities for future focus as below:

- Future studies should investigate the persistence of these pollutants in the environment and their long-term impacts in the field.
- As plastic products persist over time, they degrade, leading to the discharge of their inherent chemicals into the surroundings. Therefore, dedicated studies are required to investigate the combined effects of plastic leachates/additives and heavy metals released into the environment.
- Future research should evaluate the long-term effects of exposure to combined plastic leachates/additives and heavy metals on various ecosystems, including aquatic and terrestrial environments.
- Despite the growing body of research on the adsorption of heavy metals onto MPs, there remains a substantial

need for a better understanding concerning the desorption of metals from MPs. Among various articles reported in this study, only five studies reported the desorption of heavy metals from MPs [20, 15, 17, 68, 72]. Therefore, studying this phenomenon would facilitate our understanding of the consequences of heavy metals-MP pollution, bioaccumulation, and human exposure to them.

- Furthermore, extensive investigations are needed to explore the potential ecological consequences and mechanisms of biodegradable MPs-heavy metal pollution.
- In addition, there is a need to develop effective remediation strategies to remove MPs and heavy metals from aqueous media.
- Therefore, collective efforts are required. Given this, we envisage that environmental laws should prioritize the reduction of single-use plastics and promote sustainable alternatives. Workable procedures/blueprints and action plans to achieve the enforcement of environmental laws require efficient study.

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