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Review

Sorption of chemical contaminants on degradable and non-degradable microplastics: Recent progress and research trends

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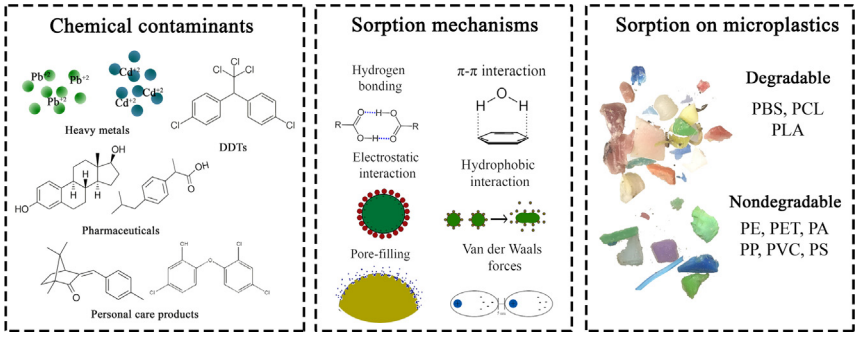
HIGHLIGHTS

- Microplastics (MPs) serve as vectors of chemical contaminants.
- The sorption capacity of MPs depends on mechanisms and factors.
- The sorption capacity of degradable MPs is similar or higher than nondegradable MPs.
- Future research must focus on elucidating the full potential of degradable MPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Microplastics (<5 mm) are ubiquitous contaminants of growing concern. These have been found in multiple environmental compartments, including remote sites where anthropogenic activity is null. Once released, microplastics interact with multiple chemicals in the environment, many of which are classified as organic contaminants or heavy metals. Some contaminants have an affinity for microplastics, attributed to certain sorption mechanisms, and thus become vectors of hazardous chemicals. Here, we focused on the sorption behavior of degradable and non-degradable microplastics, including field and laboratory experiments. We reviewed the sorption mechanisms, namely hydrophobic interactions, electrostatic interactions, pore-filling, Van der Waals forces, hydrogen bonding, and π-π interactions, and the factors strengthening or weakening these mechanisms. Then, we analyzed the literature investigating the sorption behavior of a wide range of chemicals contaminants on microplastics, and the current knowledge regarding the occurrence of organic contaminants and heavy metals on microplastics extracted from the environment. The future perspectives and research priorities were discussed. It is apparent that degradable microplastics, such as polylactic acid or polybutylene succinate, have a greater affinity for hydrophobic contaminants than conventional synthetic non-degradable microplastics according to recent studies. However, studies assessing degradable microplastics are scarce and much research is required to further prove this point. We stated several knowledge gaps in this new line of research and suggest the future studies to follow an integrative approach, allowing to comprehend the multiple factors involved, such as ecotoxicity, bioaccumulation, and fate of the chemical contaminants.

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Contents

1. Introduction

Since their development, plastics have become an essential element in modern society due to their versatility, durability, strength, and lightweight (Andrady, 2011). Commercial plastics are mostly composed of synthetic polymers derived from fossil-based sources, such as polystyrene (PS), polyethylene (PE), polyvinyl chloride (PVC), among others (Crawford and Crawford and Quinn, 2017). The widespread use and incorrect disposal of plastic items resulted in worldwide pollution of terrestrial and aquatic environments (de Souza Machado et al., 2018; Derraik, 2002). In 2018, global plastic production reached 359 million tons (PlasticsEurope, 2019), and around 10% of the plastic produced end up in the ocean (Avio et al., 2017). Their persistence, durability, and massive production have turned plastics into one of the major environmental challenges in the Anthropocene (De-la-Torre et al., 2021).

Microplastics (plastic particles smaller than 5 mm in size) gained increasing attention since they were first described by Thompson et al. (2004). These are classified into two categories: (1) Primary microplastics, which are plastics manufactured of microscopic size, and (2) secondary microplastics, which are microscopic plastics derived from the breakdown of larger plastics after being degraded in the environment (Cole et al., 2011). The main sources of primary microplastics are industrial and domestic products, including cosmetics, personal care products, coatings, and pre-production pellets. Regarding secondary microplastics, these are produced from larger plastics that undergo physical (e.g., wave action and mechanical abrasion), chemical (e.g., photodegradation), and biological degradation after disposal (Wang et al., 2018a, 2018b). Microplastics are ubiquitous in the environment, being found in marine sediments (De-la-Torre et al., 2020; Hidalgo-Ruz and Thiel, 2013), marine and continental waters (Mao et al., 2020; Sun et al., 2018), terrestrial and agricultural environments (Dioses-Salinas et al., 2020; Piehl et al., 2018). The widespread distribution and small size of microplastics make them readily bioavailable to marine biota (De-la-Torre, 2020). Thus, ingestion of microplastics has been reported in organisms across different trophic levels (e.g., zooplankton, mollusks, and fish), up to apex predators, such as marine mammals and seabirds (Bessa et al., 2019; Desforges et al., 2015; Garcés-Ordóñez et al., 2020; Gedik and Eryaşar, 2020; Ory et al., 2017; Santillán et al., 2020).

Although multiple ecotoxicological studies suggest that realistic environmental concentrations of microplastics may not induce significant detrimental effects on marine biota nor compromise their survival (Canniff and Hoang, 2018; Rist et al., 2016), co-exposure of microplastics and other associated contaminants could exacerbate their effects. For instance, Webb et al. (2020) reported no alterations on biochemical biomarkers in mussel *Perna canaliculus* exposed to microplastics alone. However, the combined effects of microplastics and triclosan (TCS), a common anti-microbial agent, increased the superoxide dismutase activity and lipid peroxidation, which are indicators of oxidative stress. Moreover, the presence of microplastics enhanced the uptake of TCS in mussel tissue (Webb et al., 2020), potentially serving as a pathway of exposure to other contaminants (Scopetani et al., 2018).

Microplastics are known to interact with a variety of chemicals in the environment. These may be categorized into heavy metals and organic pollutants. Among the organic pollutants, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and pharmaceuticals are generally found (Brennecke et al., 2016; Camacho et al., 2019; Li et al., 2018; Wang and Wang, 2018a). Heavy metals mostly refer to metals and metalloids with high atomic weights. Some heavy metals, such as Cu, Pb, Hg, Cd, and Cr, can seriously affect the wellbeing organisms (Duan et al., 2020; Mahfooz et al., 2020). Many of these contaminants are able to sorb onto microplastics. Hence, owing to their ability to sorb xenobiotic chemicals, microplastics are regarded as vectors of hazardous contaminants. This phenomenon occurs due to one or many sorption mechanisms, such as hydrophobic interactions, hydrogen bonding, or electrostatic interactions, between the sorbent and sorbate (Yu et al., 2019). Stronger sorption mechanisms will result in a higher sorption capacity of certain contaminant onto microplastics. However, the strength and number mechanisms that take place will depend on the physical and chemical properties of the microplastics, pollutant and the medium where the sorption occurs (Fred-Ahmadu et al., 2020).

Until recent years, researches have concentrated on synthetic oil-based microplastics and discriminating bio-based and degradable microplastics by chemical-analytical means. Despite conventional plastics being gradually replaced by bio-based degradable plastics, it is still uncertain whether biodegradable plastics are an encouraging solution to the plastic crisis (Fojt et al., 2020; Shen et al., 2020). Furthermore, bio-based and biodegradable plastics have been reported to be a source of microplastics (Weinstein et al., 2020) and adsorb chemical contaminants (Gong et al., 2019). This review focuses on the sorption behavior of degradable and non-degradable microplastics, and the occurrence of chemical contaminants sorbed to microplastics extracted from the environment. First, we summarized the sorption mechanisms of chemical contaminants on microplastics and the factors that influence those mechanisms. Then, we reviewed and analyzed the available literature regarding the sorption behavior of a wide range of chemical

contaminants and studies reporting sorbed contaminants on microplastics from the environment. Lastly, we discussed the future perspectives and research priorities in the emerging area of research that are degradable microplastics. We aimed to provide a reference frame of the interaction of microplastics with other contaminants with special focus on degradable microplastics.

2. Sorbed contaminants in MPs from the environment

2.1. Organic compounds

Persistent organic pollutants (POPs) are synthetic chemicals characterized for being resistant to multiple environmental degradation processes, allowing them to accumulate in different environments for very long periods (Kodavanti et al., 2014). POPs also tend to be transported through large distances and are able to bioaccumulate and cause adverse effects in biota (Miniero and Iamiceli, 2008). In the beginning, the Stockholm convention identified 12 POPs which were organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polychlorinated dioxins, and furans (PCDFs) (Miniero et al., 2015). Subsequently, the list was expanded to add brominated flame retardants (BFR). Among them, polybrominated diphenyl ethers (PBDEs) are the most detected in the environment and commercially produced POP. Likewise, it was included to reduce the emissions of polysaccharide aromatic hydrocarbons (PAHs) (Miniero et al., 2015). Table S2 describes the literature reporting POPs sorbed to microplastics extracted from the environment.

The presence of POPs sorbed to microplastics from 3 environmental matrices have been reported, namely beach sediment, seawater, and freshwater. The common method was gas chromatography–mass spectrometry (GC–MS) to identify PAHs, OCPs, DDT, hexachlorocyclohexane (HCHs), hexachlorobenzene (HCB), PCBs, and PBDEs; while gas chromatography-electron capture detector (GC-ECD) was used to detect higher-brominated PBDEs. Polypropylene (PP) microplastics are the most widely studied polymers, being present in all studies, followed by PE, PS, polyethylene terephthalate (PET), and other less detected synthetic polymers. None of the retrieved studies reported degradable microplastics in the samples extracted from the environment.

PCBs are a series of organochlorine compounds, used as dielectrics, cooling liquids in electrical appliances, transformers, switches, capacitors, and thermostats (Weber et al., 2018). Lo et al. (2019) determined the concentration of PCBs sorbed to microplastics from beach sediments in Hong Kong, reaching up to 159.67 ng/g, by considering the sum of all the congeners of PCBs. These concentrations are probably associated with the incorrect disposal of electronic wastes in recycling sites in Hong Kong (Man et al., 2011). The concentrations of PCBs reported in microplastics from Japan, specifically in Tokyo Bay (126.13 ng/g) and Sagami Bay (52.12 ng/g), were in similar orders of magnitude (Yeo et al., 2020). Overall, Asian countries showed the highest concentrations of PCBs. In Chile, for instance, an average concentration of 39.90 ng/g was reported in the bay of San Vicente (Pozo et al., 2020), and in the Easter Islands, the concentration was <5 ng/g (Pannetier et al., 2019). In Portugal, it can be observed that the mean PCBs concentrations in beach sediments from Fonte de Telha (14.52 ng/g) and Cresmina (13.05 ng/g) are very similar, although they are not geographically close (Frias et al., 2010). This can be attributed to the ability to travel long distances through the absorption onto microplastics, although transport depends on many factors, such as type of microplastics or concentration of PCBs in the medium (Ravit et al., 2019). Higher concentrations were observed in the isomers CB 138 and CB 153 (Frias et al., 2010; Lo et al., 2019), showing that high molecular weight PCBs are more prevalent.

Polybrominated Diphenyl Ethers (PBDEs) are organobrominated compounds used as flame retardants, electronics, plastics, textiles, and PU foam (ATSDR, 2015). The concentration of PBDEs sorbed to microplastics from the seawater of Tokyo Bay showed that these were mostly composed of lower-brominated PBDEs (125.79 ng/g) (Yeo et al., 2020). Similar concentrations were found in Sagami bay (89.9 ng/g) and Choshi (86.79 ng/g). It should be noted that PBDEs with lower numbers of bromine atoms have a higher affinity for lipids (ATSDR, 2015), which enhances their bioaccumulation in adipose tissues. On the other hand, the presence of decaBDE was reported in Sagami bay (636.87 ng/g), Tokyo bay (111.42 ng/g), and Choshi (97.29 ng/g) (Yeo et al., 2020). Deca-BDE is commonly added as an auxiliary substance to a great variety of polymers used in electronic equipment, one of them being PE (Mei et al., 2020). Due to the differences in the way decaBDE is absorbed and stored in the body, it probably presents less toxicity than PBDEs with low bromine content (ATSDR, 2015).

PAHs are a group of more than 100 different chemicals, some of which are compiled by the Environmental Protection Agency (EPA) as priority PAHs (ATSDR, 2015). Frias et al. (2010) reported the highest total concentration of 16 PAHs, expressed as the sum of the mean concentrations (Σ16PAH) in beach sediments from Fonte de Telha (599 ng/g). Within these, the most abundant PAHs were chrysene (59.43 ng/g), pyrene (109.57 ng/g), benzo(*e*)pyrene (99.97 ng/g). Likewise, in beach sediments from Hong Kong, the abundance of individual PAHs ranged from 0.13 ng/g to 121.35 ng/g (Lo et al., 2019). The three PAHs with the highest concentrations were phenanthrene (121.5 ng/g), pyrene (93.7 ng/g), and fluoranthene (55.05 ng/g). The presence of fluoranthene and pyrene are associated with the incomplete combustion of organic fuels, such as coal (Budzinski et al., 1997).

Regarding pesticides, DDTs turned out to have the highest concentration (156.01 ng/g) in microplastic samples collected in beach sediments from Hong Kong, China (Lo et al., 2019). In this study, it was identified that the main polymers harboring concentrations of DDTs were PE and PVC. This may be associated with the sorption affinity of DDTs for PVC and PE microplastics (Bakir et al., 2014a, 2014b). Camacho et al. (2019) found that the concentration of organochlorine pesticides (except for DDTs) sorbed to microplastics and pellets from Las Canteras beach, Canary Islands, was in the range of 21–13,523 ng/g with a median of 1059.3 ng/g. However, in a less tourist beach named Lambra, the concentration ranged from 0.9 to 43 ng/g.

The results on the concentrations of organic pollutants in microplastics based on each polymer type are not presented in the studies consulted. However, some studies mention that PE and PP have a greater capacity to absorb hydrophobic organic pollutants than other polymers (Fotopoulou and Karapanagioti, 2012; Yamashita et al., 2019). Several studies consulted, PE and PP were reported as one of the predominant polymers in samples of seawater, freshwater, and sediments (Chen et al., 2020; Frias et al., 2010; Lo et al., 2019; Pannetier et al., 2019; Ta and Babel, 2020). Thus, the bioavailability of the pollutants sorbed onto PE and PP microplastics may be of public concern. In the same way, environmental conditions such as weathering processes possibly increase the sorption capacity of microplastics due to the erosion the surfaces, turning them rougher and/or creating cracks, increasing the porosity, specific surface area, and alterations in the functional groups (Fotopoulou and Karapanagioti, 2012; Yamashita et al., 2019).

2.2. Heavy metals

The term “heavy metal” has been widely used for decades, usually to refers to metals and metalloids with an atomic weight in the range of 64.5–200.6 g/mol and densities greater than 5 g/cm (Duffus, 2002; Srivastava and Majumder, 2008). Some studies include lightweight metals as aluminum and no metals as selenium under the term “heavy metals” (Srivastava and Majumder, 2008; Zhou et al., 2020a). Currently, there is no standardized definition for the term and therefore there is not a defined list of the elements included in the heavy metal classification, being the usage of this term of high controversy among the scientific community (Pourret and Hursthouse, 2019). Nevertheless, in this study, we used this classification as it is the most commonly used on the studies retrieved, and the discussion on whether this term should

or should not be used and what other alternatives of classification do we have is beyond the scope of this study. Still, we suggest that a more precise and well-defined classification should be used, for example, a classification by groups (metals, metalloids, and no metals) (Pourret and Hursthouse, 2019).

After a review of the literature, nine studies reporting heavy metals in microplastics from the environment were retrieved for further analysis of their results. Some other studies that reported metals on microplastic were separated, as they did not apply any polymer identification method, thus it was not confirmed that the debris was in fact microplastics. The studies retrieved encompass five different countries from Europe and Asia and five environmental matrices that included: Beach sand, freshwater, mangrove sediment, river sediment, and soil. In the studies, the presence and quantity of Ag, Al, As, Ba, Cd, Co, Cr, Cu. Fe, Hg, Mn, Mo, Ni, Pb, Sb, Sn Ti, U, and Zn on environmental microplastics were reported. For this, three analytical methods were used. Inductively coupled plasma-mass spectrometry (ICP-MS) was the most common method for the quantification of Ag, Cd, Co, Cr, Cu, Mo, Ni, Sb, Sn, U, and Zn., while inductively coupled plasma-optical emission spectrometry (ICP-OES) and x-ray fluorescence (XRF) spectrometry were more commonly used for the quantification of Al, Fe, Mn, and Ba, Ti; respectively. The most studied plastic polymer was PE, followed by PP. All the studies reported the presence of PE, being in some of them the only polymer analyzed, whereas PP was reported and analyzed in 7 of the 9 studies. No studies analyzing metals sorbed to degradable microplastics from the environment were found.

From all the literature consulted, Ti registered the highest mean concentrations of all metals (22,841.05 μg/g) (Wang et al., 2017a, 2017b). This concentration was present on microplastic samples taken from sediments of the Beijian river littoral zone, in China. Similarly, the third (5200 μg/g) and fourth (4600 μg/g) highest mean concentrations from all metals were from Ti presented on beach sand microplastic samples from England, France, and the Netherlands (Turner et al., 2019). Prunier et al. (2019) reported similar results of Ti concentration on plastic debris sampled on the North Atlantic subtropical gyre. These results suggest that Ti concentration on microplastic and larger plastic debris from the marine environment may be in an order of magnitude of thousands μg/g, even in remote areas such as the North Atlantic subtropical gyre. The high concentration of Ti on microplastic samples may be due to the sorption from the environment or the constitution of the plastic of origin (Prunier et al., 2019). Ti may be added to the plastic during its manufacture as TiO_2 to function as a white pigment or a UV blocker and later be released during the degradation of the material (Wang et al., 2017a, 2017b). In 2007, the plastic industry in the US had a market share of 26% of TiO_2 pigments, which is approximately 288,600 metric tons (Varner et al., 2010).

The heavy metal with the lowest concentration reported was Cd on microplastic sampled on beach sand from Honk Kong (<0.00063 μg/g) (Li et al., 2020a, 2020b). Cd, unlike Ti, presented a high variability on its concentration on microplastics having a difference of six orders of magnitude between the mentioned lowest mean concentration and the highest mean concentration (651 μg/g), reported on the county of Devon in England (Massos and Turner, 2017). Likewise, levels of Zn, Sb, Pb, Cu, and Cr on microplastics varied greatly among studies. For example, the range of mean concentrations of Zn varied between 1.06 and 8242.52 μg/g (Ashton et al., 2010; Wang et al., 2017a, 2017b). Similarly, mean concentrations of Sb varied between 0.011 μg/g to 621 μg/g (Ashton et al., 2010; Turner et al., 2019). The highest mean concentrations of the rest of the elements named were between 3 and 5 orders of magnitude higher than the lowest. On the other hand, the concentration levels of Ni, Mn, Hg, Fe, Co, Ba, Al, and Ag were more consistent, with differences up to two orders of magnitude between the highest and lowest mean concentration.

In geographical terms, the microplastics from the Beijian River littoral zone in China presented the maximum levels of Ti, Zn, and Cu, with a difference of one order of magnitude compared to the second-highest concentration. Asian countries present the highest concentration of Ni, with similarities between their results, especially for the Beijian River littoral zone and Jinjiang in China and downtown Bangkok in Thailand. Microplastics sampled in the Celtic Sea, the North Sea, and the English Channel presented the highest concentrations of Sb, Hg, and Cr, with differences of at least 2 orders of magnitude with concentrations of Sb and Hg from the rest of the sites. In the same area microplastics with high concentrations of Zn, Ti, Pb, Fe, Cu, and Ba were found. No evident big scale regional trend was observed between the results of the different studies.

On a smaller regional scale level, concentrations of Cd and Pb in microplastic from beaches from the same bay on the Cornwall county in England were different by several orders of magnitude in different years (Holmes et al., 2012; Massos and Turner, 2017). These results may suggest a recent dramatic increase of metal pollution in the area. Similarly, other studies have reported a high variability of concentrations or presence of metals within samples, thus no geographical pattern was identified (Deng et al., 2020; Holmes et al., 2012; Turner et al., 2019; Zhou et al., 2019). The variability may suggest that the content of heavy metals in microplastics may be driven by local factors rather than regional ones. Some suggested factors are the local environmental conditions, the concentration of metals in the surrounding environment, and the proximity to sources of contamination (Holmes et al., 2014; Turner et al., 2019; Zhou et al., 2019). For instance, increasing the pH of the river and estuarine waters seems to increase the Cd, Co, Ni, and Pb adsorption capacity from microplastics while decreasing the adsorption of Cr (Holmes et al., 2014; Turner and Holmes, 2015). In addition, salinity may increase the adsorption of Cr on microplastics, while decreasing the adsorption of Cd, Co, and Ni (Holmes et al., 2014). Concentrations of Hg ions on microplastics were positively correlated with the concentrations of Hg in sediments from Jinjiang, China (Deng et al., 2020). Likewise, the concentration of Cd, Pb, Hg, and Mn were strongly correlated with the content of those metals in the soils of the surroundings of Wuhan city (Zhou et al., 2019). In Hong Kong and the Devon county of England, metals concentrations in microplastic increased with the proximity to pollution sources such as urban areas or polluted rivers (Li et al., 2020; Turner et al., 2019).

Results on the metal concentrations of microplastics based on their polymers were not present in the consulted studies. It is unclear how much influence the polymer type of microplastics has in its capacity to adsorb heavy metals. Even though some laboratory experiments have found differences in the accumulation of heavy metals between plastic types (Fischer et al., 2007; Holmes et al., 2012) their representativeness is limited for the environmental microplastics as microplastics and the surrounding environment are in a dynamic exchange of metals ions (Gao et al., 2019; Rochman et al., 2014). Hence, field studies may be more accurate to describe this issue. The results of the long-term field study developed by Rochman et al. (2014) suggest that PET, HDPE, PVC, LDPE, and PP tend to accumulate similar concentrations of metals. In a similar study, Gao et al. (2019) found that PP had a higher adsorption capacity than PVC. Both studies suggest that the presence of biofilms may have influenced their results either by prompting the adsorbance of heavy metals or neutralizing the differences for metal accumulation between the types of plastics (Gao et al., 2019; Rochman et al., 2014).

3. Determinants of the sorption of chemicals on microplastics

3.1. Mechanisms of sorption

There are mainly six sorption mechanisms that describe the interaction, forces, and bonding involved between microplastics and chemical contaminants: hydrophobic interaction, electrostatic interaction, pore-filling, Van der Waals forces, hydrogen bonding, and π-π interaction (Fig. 1). The actuation of one or several mechanisms depend on the

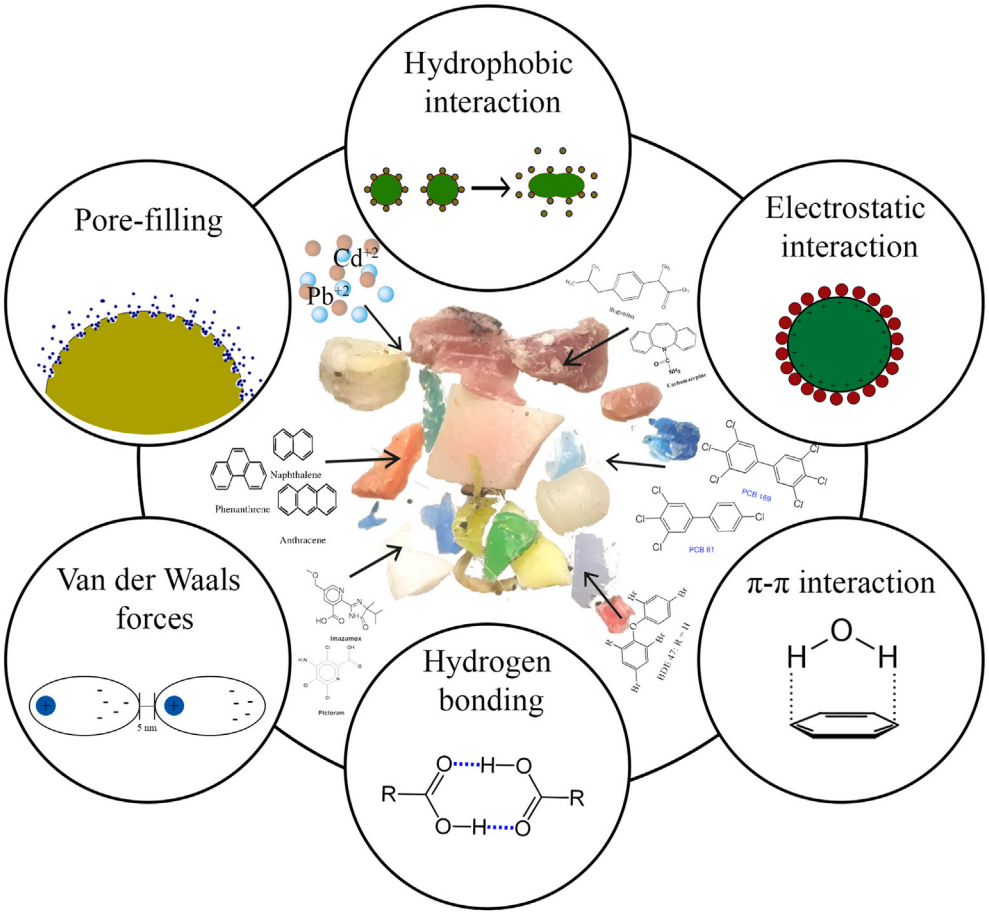

Fig. 1. Schematic representation of the six sorption mechanisms.

physical and chemical characteristics of the sorbent (microplastic polymer) and sorbate (chemical contaminant).

Hydrophobic interactions describe the attraction between two non-polar substances causing them to aggregate or cluster (Meyer et al., 2006); in this case, hydrophobic contaminants are adsorbed to the surface of microplastics. Since most microplastic polymers found in the environment are hydrophobic, such as PS, PE, PP, or PET, the hydrophobic interactions are one of the dominant mechanisms of sorption (Tourinho et al., 2019), especially for hydrophobic organic pollutants (Wang et al., 2016). Wu et al. (2016) investigated the sorption behavior of four pharmaceuticals and personal care products (PPCP), carbamazepine (CBZ), 17α-ethinyl estradiol (EE2), 4-methybenzylidene camphor (4MBC), and TCS, on PE microplastics. The linear sorption coefficients (K_d) were 191.4, 311.5, 5.14×10^3, and 53.2×10^3 L/kg for CBZ, EE2, TCS, and 4MBC, respectively. It was noted that the K_d was conditioned by the hydrophobicity of each PPCP. The octanol/water partition coefficient (K_{ow}) was 2.45, 3.67, 4.76, and 5.10 for CBZ, EE2, TCS, and 4MBC, respectively. In other organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), perfluoroalkyl substances (PFASs), and phenols, hydrophobic interaction have been suggested as the predominant sorption mechanisms in different microplastic polymers (Wang et al., 2015; Wang and Wang, 2018b; Wu et al., 2019). Moreover, Wu et al. (2019) conducted a correlation analysis of the K_{ow} of several bisphenols and their adsorption efficiency to PVC microplastics. The analysis indicated a very strong correlation, with a coefficient of determination (R^2) of 0.999.

In electrostatic interactions, attraction between particles occurs by means of oppositely charged molecules or repulsion by molecules with the same charge (Tourinho et al., 2019). The increasing pH of the solution is generally associated with stronger electrostatic attractions, thus increasing the sorption capacity (Padilla-Ortega et al., 2014). This is due to the zeta potential, which describes the surface electric potential and is influenced by the pH (Xu et al., 2018a). When the pH of point of zero charge (pH_{pzc}) of a material is lower than the pH of the medium, their surfaces become negatively charged and prone to attract positively charged chemicals (Liu et al., 2018). Most plastics, such as PP, PS, and PE, have a lower pH_{pzc} than the pH of most aquatic mediums (4.26, 3.96, 4.30, respectively; Xu et al., 2018a), which enhances the adsorption of positively charged chemicals. Razanajatovo et al. (2018) researched the sorption of two positively charged pharmaceuticals, propranolol (PRP) and sertraline (SER), and one negatively charged, sulfamethoxazole (SMX), on PE microplastics under freshwater conditions (pH 6.85). The pH_{pzc} of PE microplastics is 4.30 (Xu et al., 2018a), which makes them negatively charged. The K_d values in the isotherm linear models were 3.33×10^3, 2.30×10^3, and 0.70×10^3 L/kg for SER, PRP, and SMX, respectively. The low K_d of SMX was attributed to the repulsion force between the negatively charged sorbate and the sorbent (Razanajatovo et al., 2018). As reported in previous studies, electrostatic interactions have a significant influence on the sorption of polyfluoroalkyl substances (PFASs) and bisphenols (Llorca et al., 2018; Wang et al., 2015; Wu et al., 2019). Although it is generally assumed that plastics are relatively inert, the sorption of metals has been observed in previous studies. Holmes et al. (2012) suggests that bivalent cations, like Cu^{2+}, Pb^{2+}, and Cd^{2+}, interact with the polar regions of the plastic surface, which can be altered by other contaminants and plastic additives. Thus, electrostatic interactions are one of the main sorption mechanisms for metal ions (Liao and Yang, 2020).

The pore-filling mechanism consists of contaminants entering and remaining trapped in the nano-scale pores of microplastics (Wang et al., 2020a, 2020b). Bakir et al. (2012) indicate that the pore-filling

mechanism may apply for glassy polymers (amorphous polymers with high glass transition temperature, T_g). This mechanism has been observed in pesticide DDT and phenanthrene with PVC and PE microplastics (Bakir et al., 2014a, 2014b; Obst et al., 2011). Zhang et al. (2018a, 2018b) investigated the sorption behavior of the broad-spectrum antibiotic oxytetracycline (OTC) on virgin and weathered PS microplastics. It was observed that the best fitting model was the Freundlich model, which describes a nonlinear sorption behavior. This behavior is due to a heterogeneous distribution of sorption sites, attributed to specific interactions between sorbate and sorbent (Sun et al., 2010) and pore-filling mechanism (Zhang et al., 2018a, 2018b). Similarly, Seidensticker et al. (2018) report pore-filling mechanism results in a slightly non-linear sorption isotherm of phenanthrene and two heterocyclic compounds on PS. The N_2-BET surface areas of PS revealed a mesoporous network with a pore size of around 195 Å, while PE is non-porous. This characteristic of PS allowed the pore-filling mechanism to take place, increasing the sorption capacity.

Hydrogen bonding can be involved in the sorption of chemical contaminants when proton donor and acceptor groups are present (Tourinho et al., 2019). Although the participation of this mechanism is fairly limited for a wide range of polymers, some may significantly enhance the sorption capacity. Liu et al. (2019a, 2019b, 2019c) investigated the sorption behavior of 17β-Estradiol on many microplastic polymer types. Polar polymers, such as PA, polycarbonate (PC), and poly(methyl methacrylate) (PMMA), and the presence of hydrophilic groups was associated with a lower hydrophobicity, thus limiting the enrichment of 17β-Estradiol by means of hydrophobic interactions. However, PA showed the highest sorption capacity due to the presence of hydrogen bonding. The presence of hydrogen-donor chemicals forms hydrogen bonds with the amide groups of PA (Endo et al., 2011; Nghiem et al., 2002, 2004), significantly enhancing the sorption capacity.

Additionally, Van der Waals forces and π-π interactions may take place and promote the sorption of chemical contaminants depending on the polymer type. Aliphatic polymers, like PE and PVC, exhibit Van der Waals interactions, while aromatic polymers, such as PS, exhibit π-π interactions (Guo et al., 2012; Hüffer et al., 2018; Hüffer and Hofmann, 2016). These interactions play a minor role compared to the ones described before but can further enhance the sorption capacity. For instance, Velzeboer et al. (2014) reported that the high aromaticity of PS microplastics significantly increases the sorption of PCBs, where the π-π and hydrophobic interactions mechanisms take place simultaneously.

3.2. Factors that influence the sorption mechanisms

3.2.1. Physical and chemical characteristics of the sorbent

The characteristics of microplastics have been found to affect the sorption of chemical pollutants in multiple ways. The polymer type plays a major role in determining several factors, such as polarity, crystallinity, and functional groups. Others, such as microplastic size and weathering, are subject to environmental stressors that act on microplastics, changing their physical and chemical characteristics. Depending on these characteristics, one or multiple sorption mechanisms may take place.

Polymers are determined as crystalline, semi-crystalline, or amorphous depending on the alignment of their molecular chains (Fred-Ahmadu et al., 2020). Crystalline domains are characterized for having molecular chains arranged straight, while the amorphous parts do not form a specific arrangement (Fig. 2). The degree of crystallinity and specific characteristics of the crystalline domains are key to determine morphological properties, such as mechanical strength, density, permeability, among others (Murthy, 2018). Zhao et al. (2020) investigated the sorption behaviors of organic chemicals (phenanthrene, pyrene, 1-nitronaphthalene, 1-naphthylamine, and atrazine) on polar (PBS, PCL, and PU) and nonpolar (PS) microplastics. The linear isotherm model showed that the five organic contaminants had a higher K_d in

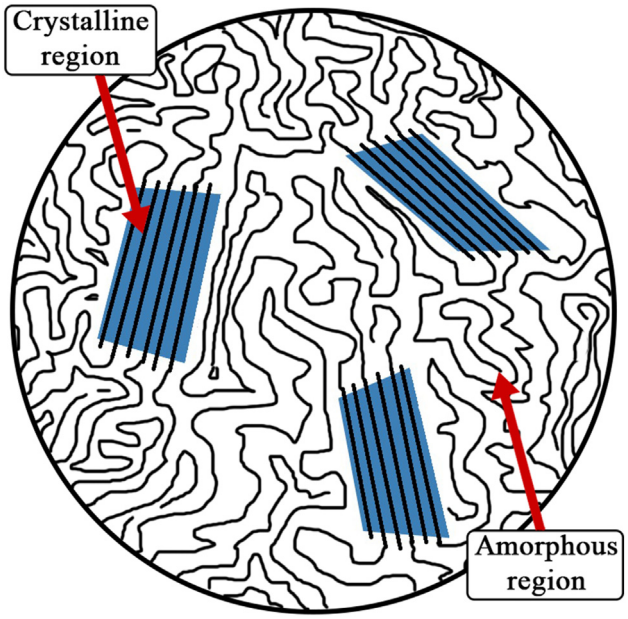

Fig. 2. Schematic representation of the crystalline and amorphous regions of a polymer.

polar microplastics and PS. For instance, for pyrene highest K_d decreased in the order of PCL (1.42×10^5 L/kg) > PBS (1.21×10^5 L/kg) > PS (1.78×10^3 L/kg); and for atrazine in the order of PU (76.1 L/kg) > PBS (68.8 L/kg) > PCL (58.1 L/kg) > PS (not detected). As ported by Zhao et al. (2020), the higher proportion of rubbery domains (crystalline domains) was associated with a higher K_d. The temperature at which the glassy domains change to a rubbery is determined by T_g. The T_g values of PU, PCL, PBS, and PS have been reported to be −61.8, −60.2, −33.8, and 95.8 °C, respectively (Fanovich and Jaeger, 2012; Jin et al., 2016; Qiu et al., 2003), hence, PU, PCL, and PBS are regarded as rubbery polymers at room temperature. (See Fig. 3.)

The functional groups in microplastics may also influence the sorption capacity. Specific functional groups are related to additional sorption mechanisms described previously. Notably, Van der Waals forces are weak interactions among particles separated by a medium that easily disappear when separated from each other. They are associated with aliphatic and aromatic groups. Aromatic groups are generally related to π-π interactions. In the case of hydrogen bonding, this mechanism is associated with the presence of functional groups with hydrogen donor/receptor properties in the sorbent and sorbate. Li et al. (2018) investigated the sorption behavior of five antibiotics, sulfadiazine (SDZ), amoxicillin (AMX), tetracycline (TC), ciprofloxacin (CIP), and trimethoprim (TMP), on five types of microplastics, PE, PS, PP, PA, and PVC. Overall, PA had the strongest sorption capacities and K_d values, ranging from 7.36 to 756 L/kg. These results are related to hydrogen bonding as an additional mechanism due to the amide groups (which are proton donor groups) in PA and carbonyl groups (proton acceptor) in AMX, TC, and CIP (Antony et al., 2010). However, in the absence of a chemical with proton acceptor groups, hydrogen bonding is not observed in PA microplastic-chemical systems. For example, Guo et al. (2019a) reported that hydrogen bond energy was zero in sulfamethazine (SMT)-microplastics (PA, PS, PVC, and PP) interactions. However, polar groups (amide in PA, aromatic ring in PS, —Cl and aliphatic groups in PVC) may promote electrostatic reaction energies between the sorbate and sorbents (Kotdawala et al., 2005). Thus, Van der Waals and electrostatic interactions dominated the sorption behavior of SMT to different microplastics (Guo et al., 2019a). Most biodegradable plastics are distinguished for having oxygen-containing functional groups that allows them to degrade easier than conventional plastics (Zhao et al., 2020). Some of the most commercially available biodegradable plastics, such as polycaprolactone (PCL), polybutylene succinate (PBS), and polylactic

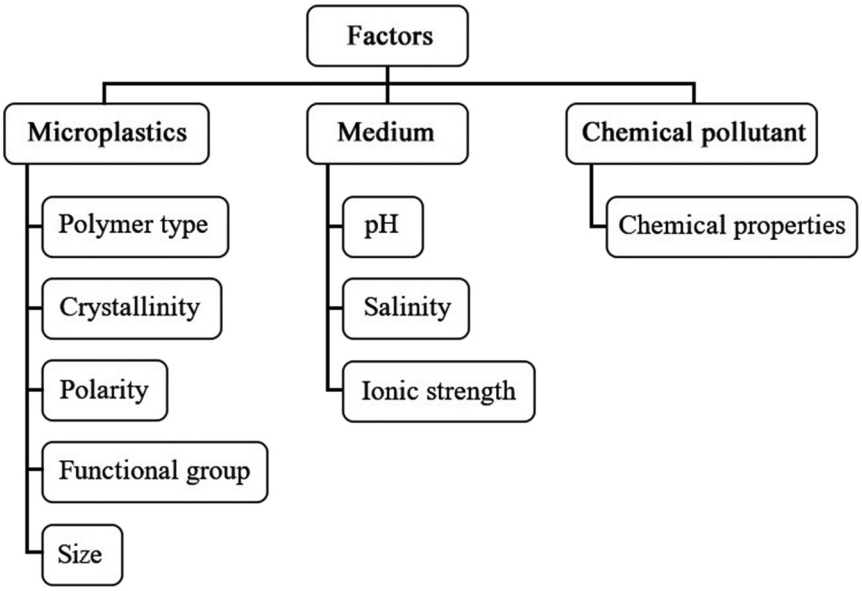

Fig. 3. Factors that influence the sorption of chemical contaminants to microplastics.

acid (PLA), have one or more hydroxyl and carbonyl groups in their backbone chain. Hence, biodegradable microplastics are generally of polar nature. Gong et al. (2019) indicated that carboxylate oxygens in PBS and PLA may form hydrogen bonds with polar moieties of the pesticide fipronil, which are stronger than the hydrophobic and π-π interactions between the pesticide and nondegradable microplastics (PE, PS, PVC, and PP).

Microplastics in the environment undergo weathering conditions that may form surface functional groups, decreasing their hydrophobicity, decrease their molecular weight and density through chain scission, become fragile and irregularly shaped (Alimi et al., 2018; Celina, 2013; Hüffer et al., 2018). Fan et al. (2021) researched the effect of UV aging on the sorption of TC and CIP to PLA and PVC microplastics. It was noted that UV aging increased the specific surface area and the surface negative charges. UV also increased the intensity of oxygen-containing functional groups, such as hydroxyl and carbonyl groups in PLA, which enhanced the hydrophilicity of microplastics. For PVC, an absorption peak in 1718 cm^{-1} associated with the carbonyl group was observed in the FTIR spectra, which is caused by the presence of plasticizers. The sorption capacity of UV-aged PLA and PVC was higher than pristine microplastics for both contaminants. Similarly, Liu et al. (2019a, 2019b, 2019c) observed that the sorption capacity of CIP increased in UV-aged PVC and PS microplastics. Zhang et al. (2018a, 2018b) compared the sorption isotherms of OTC in virgin and beached (collected from a local beach) PS microplastics. The K_d was about 10 times higher (from 41.7 to 428.4 L/kg) in beached PS compared to pristine PS.

Mechanical and chemical degradation of microplastics causes them to fragment into even smaller particles. Fragmented microplastics increase their specific surface area, which influences the sorption capacity of chemical pollutants. Wang et al. (2019) investigated the sorption behavior of phenanthrene and nitrobenzene to PS microplastic of different sizes, ranging from 50 nm to 170 μm. The results indicated that the K_d was inversely related to the particle size, except for 50 nm particles (Fig. 4). This relation was attributed to the drastic increase in the specific surface area (from 0.4 m^2/g in 170 μm microplastics to 63.4 m^2/g in 50 nm microplastics) in smaller microplastics. Particles of 50 nm formed aggregates about seven times their size after sorption equilibrium, which limited the sorption capacity. Li et al. (2019) also concluded that K_d values of TCS sorbed to PS microplastics increased at smaller particle sizes due to larger specific surface areas.

3.2.2. Chemical characteristics of the medium

Changes in pH conditions of the medium could potentially alter the fate and behavior of certain contaminants, such as some pharmaceuticals and personal care products (PPCPs) (Bundschuh et al., 2016; Karlsson et al., 2017). For the sorption of OTC to beached PS microplastics, for example, pH is crucial (Zhang et al., 2018a, 2018b). The cationic, zwitterion and anionic forms of OTC are present in pH <3.27, 3.27–3.32, and > 7.32, respectively. Moreover, the pH_{pzc} of beached PS was 4.96, which means that higher or lower pH will increase the electrostatic repulsion created by equal charges. Zhou et al. (2020b) determined that the adsorption of Cd(II) to microplastics (PA, PVC, PS, acrylonitrile butadiene styrene [ABS], and PET) first increased and then gradually decreased with increasing pH in the medium (ranging from 2 to 9), reaching peak adsorption capabilities at pH 7 for PA and pH 6 for the rest. This behavior was associated with the pH_{pzc} values of the microplastic polymers, which ranged from 5.42 to 5.97. For Cd (II), electrostatic interactions are strengthened by reaching pH values around the pH_{pzc} of the sorbent. However, if the pH continues increasing, electrostatic repulsions are expected to occur as it becomes further

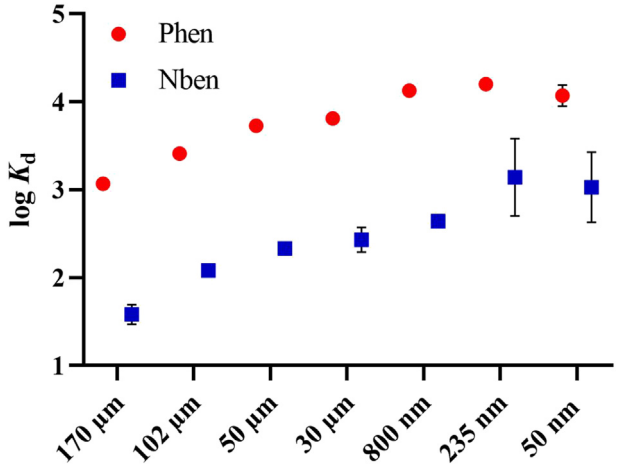

Fig. 4. The relation between K_d of phenanthrene (Phen) and nitrobenzene (Nben) and microplastic size. Error bars indicate SD. Data obtained from Wang et al. (2019).

from the pH_{pzc} owed to the enhanced anionic surface at pH values near the pH_{pzc} (Wang et al., 2020a, 2020b).

Apart from electrostatic charges, Elizalde-Velázquez et al. (2020) reported that the pH dependency of non-steroidal anti-inflammatory drugs (ibuprofen, naproxen, and diclofenac) sorption to microplastics was related to the speciation of the compounds.

The contribution of salinity on the sorption capacity will vary depending on the chemical pollutant and mechanisms that take place. High salinity may alter the aqueous solubility of organic compounds, encouraging their addition to solid phases (Turner, 2003). However, multiple studies suggest that salinity has little effect on the sorption of different contaminants on microplastics. Wu et al. (2020) found a slight decrease but no significant differences in the equilibrium sorption capacity of BDE-47 to PS at 0, 5, 10, 20, and 35% salinity. Comparably, Wang et al. (2015) reported that increasing concentrations of $CaCl_2$ and NaCl in the medium had a limited effect on the sorption of perfluorooctanesulfonic acid (PFOS) and perfluorooctanesulfonamide (FOSA) to PE microplastics. Additionally, Qiu et al. (2019) reported that the sorption of polyhalogenated carbazoles (PHCs) to PP and PE was not significantly altered by the addition of NaCl in concentrations ranging from 0.05 to 3.5%. However, a notorious decrease was observed on PVC, probably due to ionic competition. The ions in the aqueous medium may compete with other compounds for sorption areas on microplastics (Wang et al., 2020a, 2020b). This is also applied to realistic aquatic scenarios. For example, Llorca et al. (2018) compared the sorption behavior of perfluoroalkyl substances (PFASs) to microplastics in a realistic freshwater and seawater medium. Higher sorption affinity was found in seawater, mainly attributed to the presence of salts dissolved in seawater. The same behavior was observed by Vockenberg et al. (2020), where diphenylamine (DPA) showed stronger sorption affinity to microplastics under high NaCl concentrations. Puckowski et al. (2021) reported that ionic strength also affected the sorption of multiple pharmaceuticals, resulting in reduced interactions in environmental conditions.

Dissolved organic matter (DOM) are water-soluble compounds consisting of reduced organic carbon from various biotic and abiotic sources (Findlay and Findlay and Parr, 2017) that could influence on the sorption of chemical pollutants. Wu et al. (2016) applied humic acid in different concentrations as a proxy of DOM to understand its influence in the sorption of pharmaceuticals on microplastics. DOM was measured in dissolved organic carbon and the pharmaceuticals CBZ, EE2, 4MBC, and TCS were evaluated. Higher DOM significantly reduced the sorption of all the test chemicals except for CBZ. This behavior could be attributed to the interaction of DOM with the test chemicals by means of hydrophobic interaction of complexation (Ilani et al., 2005), or competition for sorption areas on the sorbate (Cox et al., 2007). However, Xu et al. (2018b) indicated that DOM had negligible effects on the sorption capacity of SMX on PE microplastics. Whether DOM influences on the sorption capacity will vary depending on the sorbate and sorbent. Wu et al. (2016) suggests that the polarity of the sorbent plays an important role in this behavior.

3.2.3. Chemical characteristics of the sorbate

The properties and behavior of the sorbate also influence the sorption capacity. These characteristics are mainly hydrophobicity, ionic property, and functional groups (Mei et al., 2020; Wang et al., 2020a, 2020b). Yu et al. (2020a, 2020b) investigated the sorption capacities and intramolecular interactions of naphthalene (NAP) derivatives (NAP-NH_2, NAP-CH_3, NAP-COOH, and NAP-OH) to PS with and without surface modification of -COOH (PS-COOH). Computational modeling was conducted to investigate the intramolecular interactions. Overall, NAP with uncharged functional groups (NAP-CH_3) exhibited the highest sorption capacity to both PS and PS-COOH. These results are owed to NAP derivatives with charged functional groups becoming more hydrophilic due to alterations in their polarity, ultimately weakening hydrophobic interactions. The computational modeling revealed that π-π interactions were influenced by the presence of certain functional groups. High δg values at lower Sign(λ_2)ρ(a.u.) in the computational modeling indicated stronger π-π interactions in NAP, NAP-CH_3, and NAP-COOH. On the other hand, δg peaks at higher Sign(λ_2)ρ(a.u.) indicated stronger repulsions between benzene rings or benzene rings and another functional group. This behavior induced minute sorption capacities in NAP-NH_3, NAP-COOH, and NAP-OH to PS-COOH. For further detail on the computational modeling results are displayed in Yu et al. (2020). The hydrophobicity of the chemical pollutants is also an important characteristic influencing on the sorption capacity (Mei et al., 2020). Hüffer and Hofmann (2016) found a positive and significant correlation between the distribution coefficient and octanol/water partition coefficient of various sorbates (n-hexane, cyclohexane, benzene, toluene, chlorobenzene, ethylbenzoate, and naphthalene) adhering to PE, PS, PA, and PVC microplastics. A similar correlation was reported by Li et al. (2018) with the antibiotics sulfadiazine, amoxicillin, tetracycline, ciprofloxacin, and trimethoprim adsorbed to PS, PE, PP, and PVC. In general terms, the chemical properties of test contaminants affect their sorption capacity through stronger or weaker mechanisms, similar to the properties of the sorbent.

4. Sorption properties

4.1. Non-degradable microplastics

Early works by Teuten et al. (2007) and Adams et al. (2007) pioneered this line of research by investigating the sorption capacity of hydrophobic organic compounds, such as PAHs, and PCBs, to small plastic particles. This line of research has come a long way, focusing on chemical pollutants from a wide range of sources. We have divided the recent progress of the interaction of chemical pollutants and microplastics based on the type of chemical, source or commercial use: Flame retardants (Chen et al., 2019; Xu et al., 2018a; Seidensticker et al., 2018), metals (Besson et al., 2020; Guo et al., 2020a, 2020b; Wang et al., 2020a, 2020b; Wang et al., 2021; Zhou et al., 2020b; Zon et al., 2020; Zou et al., 2020), PAHs (Li et al., 2020; Lin et al., 2019; Wang et al., 2019; Wang and Wang, 2018b; Wang et al., 2018a, 2018b; Zhao et al., 2020), PBDEs (Wu et al., 2020a, 2020b; Xu et al., 2019), PCBs (Lin et al., 2019; Zhan et al., 2016), PHCs (Qiu et al., 2019; Zhang et al., 2019), Phthalate esters (Liu et al., 2019a, 2019b, 2019c), personal care products (Dong et al., 2019; Ho and Leung, 2019; Li et al., 2019; Wu et al., 2020a, 2020b; Zhang et al., 2018a, 2018b), pesticides (Gong et al., 2019; Šunta et al., 2020; Tubić et al., 2019), pharmaceuticals (Guo et al., 2018, 2019a, 2019b; Liu et al., 2019a, 2019b, 2019c; Zhang et al., 2018a, 2018b), radioactive elements (Guo et al., 2020a, 2020b; Guo and Wang, 2019), and other organic contaminants (Hu et al., 2017; Müller et al., 2018; Shan et al., 2020). Table S1 summarizes the sorbate, sorbent, sorption capacity, and sorption coefficient in multiple studies within these categories.

PAHs are organic compounds composed of two or more benzene rings bonded in multiple arrangements, released to the environment by natural or anthropogenic means, such as fossil fuel or wood burning, and automobile emissions (Mukhopadhyay et al., 2020). Their presence is commonly identified in multiple environmental compartments and poses a risk to the wellbeing of aquatic organisms (Ofori et al., 2020). Hence, multiple studies under different conditions studied the sorption behaviors of these types of compounds onto microplastics. Wang and Wang (2018b) reported that the K_d values of pyrene ranged from 3.4×10^3 to 9.8×10^3 in PE, PS, and PVC. Rather than purchasing pristine plastic particles for experimentation, Wang et al. (2018a, 2018b) extracted microplastic fibers (PE and nylon) from a mariculture farm in Xiangshan Bay, China. The K_d values of phenanthrene ranged from 2.76×10^3 to 8.84×10^3 in PE, and from 2.09×10^3 to 2.24×10^3 in nylon. The Langmuir isotherm model showed very low correlation coefficients (R^2), in the range of 0.04–0.82, thus the maximum sorption capacity values were not reliable. Since chemical contaminants sorbed to

microplastics are readily bioavailable to aquatic biota (Fig. 5), an interesting approach was conducted by Sørensen et al. (2020) consisting of evaluating the sorption behavior of PAHs and their co-exposure toxicity to marine copepods. The K_d values of phenanthrene and fluoranthene onto PE were 2.7×10^2, and 7.0×10^2 L/kg, respectively. Marine copepods *Calanus finmarchicus* and *Acartia tonsa* were exposed to microplastics sorbed with phenanthrene or fluoranthene in a medium with these contaminants present in the dissolved phase. The presence of microplastics reduced the concentration of PAHs in the dissolved phase. However, the co-exposure bioassays indicated that, although the ingestion of microplastic-sorbed PAHs occurred, no mortality was observed. Also, the PAH body burden was higher in the medium with no microplastics added, which indicates that the dissolved parts of PAHs are more bioavailable than microplastic-sorbed parts.

Pharmaceuticals and personal care products (PPCPs) are a group of many chemical compounds produced to prevent human and animal disease and are part of the chemical composition of many products used in daily life (Boxall et al., 2012). These contaminants have been on the scope of many recent studies as they are considered as contaminants of emerging concern. Other than the studies summarized in the previous section and Table S1, some researchers opted for different approaches, including in situ experiments and sorption interactions with multiple contaminants simultaneously. Magadini et al. (2020) investigated the sorption of three pharmaceuticals, atenolol, ibuprofen, and sulfamethoxazole, onto microplastics in NYC waterways. The K_d values of the plastic bags-derived microplastics were the largest (~0.2 L/kg), while most of the other microplastic pellets (HDPE, PVC, LDPE, and PP) were about ~0.005 L/kg. The rapid growth of biofilms was identified to positively affect the sorption of pharmaceuticals onto microplastics. Yu et al. (2020) evaluated the combined sorption of levofloxacin and heavy metals to PVC microplastics. The sorption capacity of levofloxacin alone was 2.32 mg/g. The addition of Zn^{2+}, Cu^{2+}, and Cr^{3+} enhanced the sorption capacity of levofloxacin, while Pb^{2+} and Cd^{2+} weaken the sorption. The presence of metals in the sorbate solution competes with levofloxacin for active adsorption sites on microplastics due to electrostatic interactions, thus weakening the maximum sorption capacity (Wang et al., 2017a, 2017b). Simultaneously, the complexation of heavy metal ions is carried out by hydroxyl groups and specifically chloride groups in PVC complex with Pb^{2+} ions (Lee and Choi, 2018; Yu et al., 2020a, 2020b).

4.2. Degradable microplastics

Contrary to nondegradable microplastics, studies investigating the sorption behavior of pollutants onto degradable plastics are very recent and limited. Only eight articles were found in this line of research, encompassing metals (Li et al., 2020; Liao and Yang, 2020), PAHs (Zhao et al., 2020; Zuo et al., 2019), PFASs (Ateia et al., 2020), pesticides (Gong et al., 2019; Tubić et al., 2019), and pharmaceuticals (Fan et al., 2021). Table 1 summarizes sorption capacity and coefficient in degradable polymers. Some researchers made comparative analyses between the sorption behavior of certain pollutants onto degradable or nondegradable microplastics (Fan et al., 2021; Gong et al., 2019) while highlighting the necessity for extensive research of the sorption of contaminants onto degradable microplastics.

Regarding pharmaceuticals, it was observed that the PLA's sorption capacity of tetracycline (2.51 mg/g) and ciprofloxacin (3.19 mg/g) was significantly higher than PVC's (Fan et al., 2021). A simulated aging process of PLA and PVC microplastics by UV light increased their sorption capacity. The original sorption capacity of tetracycline increased from 2.51 to 5.49 mg/g, while in PVC went from 0.96 to 1.57 mg/g. It was noted that PLA was more susceptible to UV radiation, which increased the intensity of oxygen-containing functional groups and thus becoming more hydrophilic. The highest sorption capacities of tetracycline and ciprofloxacin were reported by Li et al. (2018), being 3.84 and 2.20 mg/g in PA, respectively. The results by Fan et al. (2021) show that the sorption capacity of PLA to antibiotics is among the highest in contrast with nondegradable microplastics. Additionally, Ateia et al. (2020) found that PLA originated from biodegradable plastic cups had the highest adsorption of acetamidophenol when compared to a wide range of microplastic polymers (HDPE, PE, PP, PET; EPS, PA66, among others).

The sorption of fipronil, a broad-spectrum insecticide, to six microplastic polymers, including PLA and PBS, was investigated by

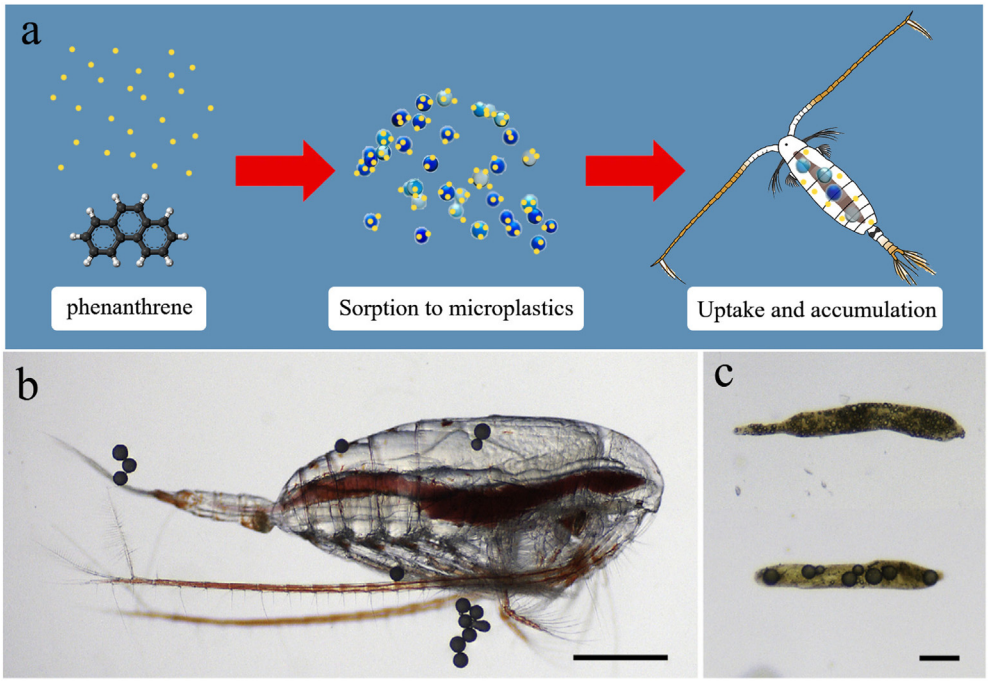

Fig. 5. Sorption of chemical contaminants to microplastics as a pathway to marine organisms. (a) A representation of the three steps for bioavailability of sorbed contaminants. (b) *Calanus finmarchicus* surrounded by 90–106 μm PE microplastics (non-ingestible). (c) Feces of *C. finmarchicus* showing encapsulates PE microplastics of different sizes. Scale bar (a) indicates 500 μm and (b) 100 μm. Reprinted from (Sørensen et al., 2020). Copyright (2020) with permission from Elsevier.

Table 1
Sorption properties of various chemical pollutants on degradable microplastics. 4-CP: 4-chlorophenol. 2,4-DCP: 2,4-dichlorophenol- 2,4,6-TCP: 2,4,6-trichlorophenol. PCP: pentachlorophenol.

Compound		Plastic polymer	Sorption capacity (mg/g)[a]	Sorption coefficient (L/kg)[a]	Reference
Pharmaceuticals	Tetracycline	PLA	2.51	–	(Fan et al., 2021)
	Ciprofloxacin	PLA	3.19	–	
PAHs	Phenanthrene	PBAT	–	5.48×10^4	(Zuo et al., 2019)
		PBS	–	2.50×10^4	
		PCL	–	3.18×10^4	
	Pyrene	PBS	–	1.21×10^5	(Zhao et al., 2020)
		PCL	–	1.42×10^5	
	1-nitronaphthalene	PBS	–	7.14×10^2	
		PCL	–	9.31×10^2	
	1-napthylamine	PBS	–	5.07×10^2	
		PCL	–	5.18×10^2	
Pesticides	Atrazine	PBS	–	68.8	(Zhao et al., 2020)
		PCL	–	58.1	
	Fipronil	PBS	0.23	3.26×10^3	(Gong et al., 2019)
		PLA	0.72	0.42×10^3	
	4-CP	PLA	3.27×10^{-2}	2.52×10^4	(Tubić et al., 2019)
	2,4-DCP	PLA	4.55×10^{-2}	1.52×10^4	
	2,4,6-TCP	PLA	8.22×10^{-2}	1.18×10^4	
	PCP	PLA	6.27×10^{-2}	9.40×10^4	

[a] Data was obtained from the best-fitted model.

Gong et al. (2019). The highest sorption capacities decreased in the order of PBS (0.72 mg/g) > PLA (0.23 mg/g) > PP (62.7×10^{-3} mg/g) > PE (57.5×10^{-3} mg/g) > PS (50.8×10^{-3} mg/g) > PVC (38.3×10^{-3} mg/g). The high sorption capacities of the degradable microplastics were many times higher than conventional ones, probably attributed to the presence of oxygen-containing functional groups (carbonyl oxygens), and the sorption rates were faster. Tubić et al. (2019) investigated the sorption behavior of four chlorinated phenols, compounds commonly used in multiple pesticides, onto PE, PP, and PLA. In none of the four compounds, PLA exhibited the highest sorption capacity. However, little variability was observed for this parameter among polymers except for pentachlorophenol. For instance, the sorption capacity of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol were in the ranges 2.46×10^{-2}–3.27×10^{-2} mg/g, 4.55×10^{-2}–6.90×10^{-2} mg/g, and 3.75×10^{-2}–8.71×10^{-2}, respectively.

Ateia et al. (2020) also investigated the sorption of two PFASs: Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). Although isotherm models were not conducted, chromatographic methods were applied to quantify the percentage of contaminants uptaken by the microplastics from the aqueous medium. Results indicated that the maximum adsorption of PFOS was achieved by several polymers: PE, ABS, PA, PMMA, and PLA. For PFOA, PE, Nylon, and PLA were among the microplastic polymers with the highest adsorptions.

The sorption of PAHs was investigated encompassing four compounds in two different studies. Zuo et al. (2019) compared the sorption of phenanthrene to PBAT, PS, and PE in the form of microplastics or powder. The sorption coefficient in PBAT was many times higher than in the other polymers, with a mean K_d value of 5.48×10^4 L/kg, compared to 15.6×10^3, 14.1×10^3, and 1.34×10^3 L/kg in PE microplastics, PE powder, and PS, respectively. The K_d values of phenanthrene in PBS and PCL were reported to reach similar quantities, specifically 2.50×10^4 and 3.18×10^4 L/kg, respectively (Zhao et al., 2020). For pyrene, the K_d value was also higher in degradable plastics. However, for 1-nitronaphthalene and 1-napthylamine PU exhibited the highest K_d values. Contrary to previous studies, PLA was not assessed for PAHs.

In the studies focusing on the sorption of metals, kinetic or isotherm models were not conducted to estimate the sorption capacity and coefficient. However, the available literature may present insights into the sorption behavior of metals onto degradable microplastics. Liao and Yang (2020) simulated the adsorption of Cr onto five microplastic polymers and determined the concentrations by spectrophotometric methods. Results indicated that the sorption process reached equilibrium after about 48 h; the concentration of Cr in PLA was the lowest with 2.88 μm/g, while the concentrations in PE, PP, PVC, and PS ranged from 3.50 to 5.07 μm/g. Lastly, Li et al. (2020) quantified the adsorption of heavy metals during the degradation of PE and PBAT in soil. It was observed that after six weeks of degradation, PBAT microplastics had adsorbed significantly higher concentrations of mainly Cr, Ba, As, and Pb.

5. Future perspectives

For over a decade, extensive research efforts have been devoted to sorption studies with nondegradable microplastics and a wide range of environmental contaminants. Despite the increasing use of degradable plastics in many markets and industries, such as packaging, catering products, electronics, toys, agriculture, among others (Shruti and Kutralam-Muniasamy, 2019), it is evident that biodegradable microplastics have been overlooked within this line of research. Hence, it is necessary to conduct new studies aiming to fill in the knowledge gaps regarding the sorption and desorption behavior of chemical contaminants onto degradable microplastics. The eight studies previously described may give baseline insights into the potential that degradable microplastics may pose as carriers of chemical contaminants. Future studies are required to approach the sorption behavior under both simulated and natural aquatic mediums and assess the multiple interactions of two or more contaminants simultaneously under realistic scenarios. Furthermore, sorption studies must be accompanied by ecotoxicological assays to determine (1) the lethal and sublethal effects of degradable microplastics and other contaminants in co-exposure experiments, and (2) the bioavailability of the sorbed contaminants to aquatic biota of different taxa. We believe that mass-produced polymers that are proven to form microplastics during degradation, such as PLA (Lambert and Wagner, 2016), are of special interest in sorption behavior studies.

Few studies have addressed the problem of heavy metals and organic pollutants associated with environmental microplastics, and the study sites are mainly concentrated in European and Asian countries. No studies were found that evaluated or discussed the issue of metals and organic pollutants associated with degradable microplastics from the environment. Therefore, although the ability of degradable and non-degradable plastics to sorb heavy metals and organic contaminants has been demonstrated in laboratory and field experiments (Ateia et al., 2020; Gao et al., 2019; Holmes et al., 2014; Liao and Yang, 2020;

Rochman et al., 2014; Zhao et al., 2020), the interaction between the different chemical compounds that make up PAHs and microplastics is not well understood and therefore should be investigated further. On the other hand, we still know little about the actual fate in the environment or sorbed contaminants and the magnitude of this problem. Furthermore, most of the studies have focused on analyzing the content of heavy metals and organic pollutants in microplastics in coastal areas. Other ecosystems, such as terrestrial and continental water, need to be studied further, paying particular attention to fragile ecosystems. These issues must be addressed to develop a more realistic assessment of the risk posed by heavy metals and organic contaminants associated with microplastics to humans and the environment.

6. Conclusions

This review analyzed the recent progress in the sorption of chemical contaminants onto microplastics, focusing on experimental studies reporting kinetic and isotherm models, and field studies identifying the contaminants sorbed to microplastics from the environment. Most studies focused on typical nondegradable microplastics, such as PE, PP, PS, among others, which leaves an important knowledge gap regarding degradable microplastics. Very few studies aimed to determine the sorption behavior of chemical contaminants onto degradable microplastics and none of the field studies reported their occurrence. Hence, we encourage future research to address these uncertainties by conducting integrative approaches, allowing to not only determine the sorption capacities of certain contaminants, but to understand their toxicity, interaction, bioavailability, and fate in the environment.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.143875.

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