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Understanding Interface Exchanges for Assessing Environmental Sorption of Additives from Microplastics: Current Knowledge and Perspectives

João Pinto da Costa, Astrid Avellan, Aleksandra Tubić, Armando Duarte, Teresa Rocha-Santos

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Understanding Interface Exchanges for Assessing Environmental Sorption of Additives from Microplastics: Current Knowledge and Perspectives.

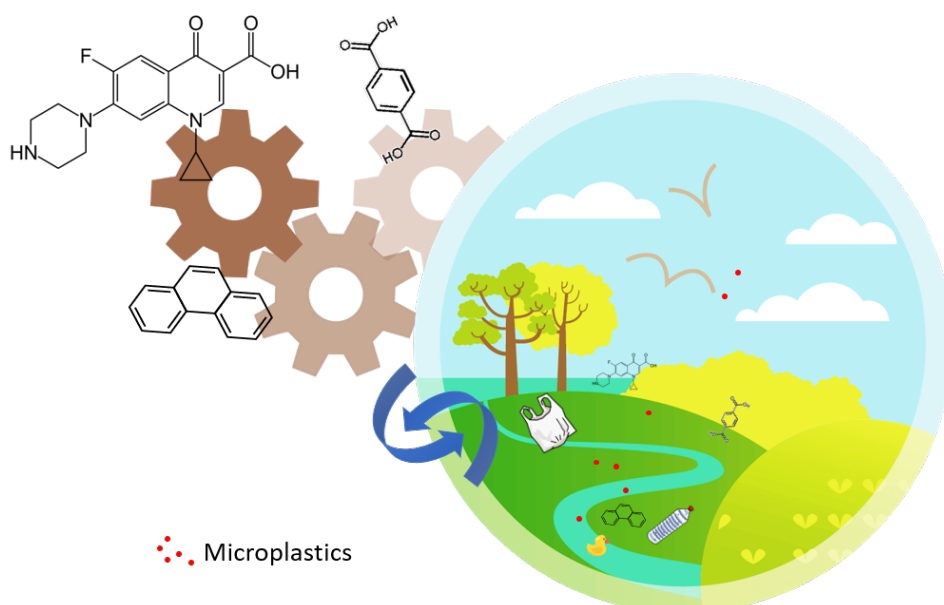
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Abstract: Though the impacts of plastic pollution have long been recognized, the presence, pervasiveness and ecotoxicological consequences of microplastic – i.e., plastic particles <5mm – contamination have only been explored over the last decade. Far less focus has been attributed to the role of these materials, and, particularly, microplastics, as vectors for a multitude of chemicals, including those (un)intentionally added to plastic products, but also organic pollutants already present in the environment. Owing to the ubiquitous presence of microplastics in all environmental matrices and to the diverse nature of their chemical and physical characteristics, thoroughly understanding the mechanistic uptake/release of these compounds is inherently complex, but necessary in order to better assess the potential impact of both microplastics and associated chemicals to and in the environment. Herein, we delve into the known processes and factors affecting these mechanisms. We center the discussion on microplastics and discuss some of the most prominent ecological implications of the sorption of this multitude of chemicals. Moreover, the key limitations on the currently available literature are described and a prospective outlook for the future research on the topic is presented.



Keywords: microplastics; additives; environment; sorption mechanisms

1. Introduction

Owing to their plasticity, plastics may be molded, extruded or pressed into solid objects of an endless multitude of shapes. They are most commonly derived from petrochemicals and, due to their inherent characteristics, such as low cost, imperviousness to water, and chemical, temperature and light resistance, plastics are used in an ever-increasing range of products, and, particularly, packaging and single-use plastics. After use, plastic waste may, for example, be collected and sorted through formal or informal waste management schemes or by manufacturers. Subsequently, they may be transformed into plastic pellets or flakes, and thus re-enter the production and use phases. However, most of these plastics are incinerated or openly burned, with severe environmental and health impacts [1], disposed of in landfills/dumpsites, or escape into the environment [2]. Indeed, concurring estimates highlight that, considering all plastic products manufactured since the 1950s, less than 10% has been recycled or re-used, with concomitant economic and environmental impacts. However, environmental contamination with plastics occurs not only at the end-of-life of these materials, but throughout their life-cycle. For example, virgin plastic resin pellets, commonly referred to as “nurdles”, disc-shaped plastic particles which are typically 3–5 mm in diameter and used as the raw material for the production of most thermally molded plastic products [3], are frequently lost during transport and are considered the second-largest source of ocean microplastics [4]. These are particles smaller than 5mm, and, in the marine environment, although only accounting for 8% of the total mass of the estimated plastic waste, microplastics correspond to over 94% of the estimated 1.8 (1.1–3.6) trillion pieces floating in the area [5], and have been found to be ubiquitous in all spheres of the environment, namely, soil, water and air, as well as in food [6].

However, plastics do not consist only of polymers. They also include additives that contribute to improved plastic functions by modulating chemical and physical properties. Every plastic item contains additives that determine the properties of the material and influence their cost of production [7], and, according to an estimate by van Oers and colleagues, any random piece of plastic collected in environmental samples will contain at least 20 different additives [8]. The Global plastic additives market, in 2020, was valued at USD 48.41 billion, and, at an estimated average annual growth rate of 5.7%, it is projected to surpass the USD 75 billion mark in 2028 [9].

Plastics are composed of chains of polymers and these different additives may be weakly bound to the polymers or mixed within the polymer matrix. And, because of this weak linkage, additives may leach during use or when disposed of. Additionally, additives themselves, still associated to the plastic materials or following their leaching, could degrade and form other toxic compounds, and may persist and bioaccumulate in biota (e.g., [10]). Even when plastic waste is recycled, plastic additives are difficult to remove during the recycling process, due to their inherent chemical characteristics, and it is therefore highly likely that these compounds will be integrated into the new manufactured products [11]. This is aggravated by the fact that many industrial manufacturers are not fully transparent regarding the used additives and their concentrations and, consequently, a detailed view across the value chain of the chemical profile of the final products is not available, with concomitant health risks [7]. For example, brominated flame retardants have been inadvertently incorporated into recycled products, including household items [12] and toys [13], posing a significant health risk [14].

These health risks are not minimized when plastic waste is burned, which is particularly problematic when in low-technology incinerators or under uncontrolled conditions. When combustion is incomplete, the process causes the emission of hazardous compounds, including persistent organic pollutants (POPs), namely, dioxins, as well as acid gases and ash [5].

Plastic additives, which are usually of low molecular weight and not bound to the polymers, may in fact elicit biochemical responses and effects. It should also be noted that, to a lower extent, residual monomers, that may be present due to incomplete polymerization reactions, can also migrate, similarly to other adsorbed organic pollutants, and these frequently exhibit a considerable degree of toxicity [15]. As most of these substances are lipophilic, they have an inherent affinity for cell membranes, rendering them potentially hazardous, as they may transverse membranes and then actively participate or interfere in biochemical reactions [16].

The risks of these substances become of even greater concern when associated with increasingly smaller particles, such as microplastics, owing to their high surface area-to-volume ratios. As such, microplastics containing additives and/or residual non-polymerized monomers may constitute new sources of exposure to chemicals, particularly when ingested. However, this will depend on the physical-chemical properties matrix and the ecosystem compartments they will be present in. In fact, some studies have highlighted that the observed ecotoxicity of microplastics in water was mainly due to the release of additives, rather than to the ingestion of the particles themselves (e.g, [17]), and additive release might have a bigger impact on plastic ecotoxicity than initially thought [18]. Contrarily, nonetheless, it has also been stated that the characteristics of both plastics and additives may render the former *de facto* sinks for not only additives, but also other organic pollutants present in the environment and subsequently adsorbed by these particles [19]. These issues highlight the intrinsic difficulties in assessing the risk linked to the presence of additives into environmentally-contaminating polymers, also due to the fact that a large part of the used additives have unknown hazardous effects. Further, many additives are not solely used for polymeric functions enhancement, but in other engineering and industrial processes as well, and the source of origin of a given pollutant in ecosystem remains difficult to assess. Finally, additives released in various environmental/biological compartments will be dictated by their migration and desorption from the polymers, which would be dependent on the additive, polymer, and the matrix physical-chemical conditions [20], as described below.

Hence, the risk for the ecosystems and their biota linked to the presence of additives in microplastics is linked to their hazard and the exposure of the ecosystem. Therefore, to assess the environmental exposure to this new class of contaminants and to ascertain the risks to organisms and human health, an in-depth comprehension of the mechanisms happening at the plastic-environment interface-biota driving additives released is needed.

2. Migration and Sorption

When present in plastics, chemicals added – whether intentionally or unintentionally – have the potential to migrate to the surrounding matrix, namely, food, water, sediments or others, as well as across the material itself, to its surface [21]. This migration may be intentional: for example, some mold release agents are added to be gradually and continuously released to the surface of numerous plastic products, which results in improved antistatic, mechanical or optical properties (e.g., [22, 23]) or that prevent the oxidation of silver, yielding a longer shelf-life for foodstuff [24]. This is also the case in some medical applications, as the precise controlled release of drug dosages may greatly improve the quality of life of patients. In most cases, however, and particularly in environmental settings, this observed release is uncontrolled and unplanned, potentially resulting in serious environmental consequences. The overall process of migration can be divided into four essential steps [21]:

- (1) diffusion through the polymer;
- (2) desorption (from the polymer surface);
- (3) sorption at the plastic-matrix interface and;
- (4) absorption/dispersion in the matrix.

Broadly, these steps are governed by Fick's Law, which postulates that the "rate of diffusion of a substance across unit area (such as a surface) is proportional to the concentration gradient" [25]. In simpler terms, Fick's Law states that the flux of a given compound takes place from areas or regions of higher concentrations to those of lower concentrations. The scale of said migration is proportional to the concentration gradient (spatial derivative) [26]. This may assume many forms, but the most common version is based on the molarity of the chemical substance in question (Equation 1):

$$J = -D \frac{d\varphi}{dx} \quad (\text{Equation 1})$$

where:

- J is the diffusion flux. It refers to the amount of substance per unit area per unit time. This parameter measures the amount of substance that flowing through a unit area during a unit time interval.

- D is the diffusion coefficient. It is expressed in area per unit time. 130
- ϕ is concentration, expressed as the amount of substance per unit volume. 131
- x is position, the dimension of which is length. 132

For organic chemicals, as plastic additives, the rate of migration is molecular weight-dependent, meaning that smaller molecules, typically exhibiting lower boiling points, will migrate faster, even at ambient temperatures, as is the case for monomers such as ethylene or butadiene; conversely, larger molecules will migrate more slowly [21]. 133-136

On the other hand, sorption describes the transfer of chemicals between phases, typically, a solid phase, as plastic materials, and a fluid phase, such as air or water. The term *sorption* thus describes both *absorption* and *adsorption*. In adsorption, the molecules of the chemical remain on the interface between the fluid and the solid phases [27], whilst, in absorption, the molecules of the chemical penetrate and become embedded in the matrix of the solid phase. Typically, adsorption involves bonding interactions such as van der Waals, ionic or covalent bonds; absorption takes place through the partitioning of the sorbate molecules into the sorbent matrix and are subsequently held by weak van der Waals forces [28]. This process is highly dependent on the properties of the sorbate chemical, in particular, its hydrophobic characteristics, but also on the properties of the solid phase and on the surface area-to-volume ratio, which increases exponentially with decreasing particle size, as is the case for microplastics [5]. Especially at this scale, the surface polarity of these materials will play a key role in determining the interaction with organic contaminants. For example, contaminants exhibiting hydrophobic characteristics will have a higher likelihood of adhering to non-polar surfaces [29]. Indeed, the identified environmental hazards posed by these additives when associated to microplastics result from the fact that many of these chemicals, as PAHs, are apolar planar molecules. These molecules commonly possess adsorption coefficients higher than those of non-planar molecules of identical hydrophobicity [28]. 137-153

In general, lower concentrations of sorbate favor adsorption and higher concentrations favor absorption [30]. This is because, when concentrations of the chemical (sorbate) are sufficiently low, a higher degree of partitioning of the sorbate between both solid and fluid phases will be observed, due to stronger forces of interaction at the surface. Broadly, sorption processes may be categorized as either physisorption (physical adsorption) or chemisorption (chemical adsorption). In the case of the former, molecular interactions between the adsorbate molecules and the adsorbent (solid phase) are primarily governed by van der Waals forces [31]. In the case of the latter, a chemical reaction between the surface and the adsorbate takes place, during which new chemical bonds are generated at the surface of the adsorbent [32]. Hence, chemisorption processes are sometimes irreversible, except when the covalent bonds are broken, thus making desorption of the chemicals from the solid phase an inherently difficult process. Physisorption, on the other hand, is non-specific in nature and it is mostly regarded as a weak and reversible process. In the following section, some of the most pertinent properties affecting the sorption – absorption, adsorption and desorption – of organic contaminants by microplastics are discussed. 154-167

| | |
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| 2.3. Factors affecting sorption | 169 |
| 2.3.1. Particle size of (micro)plastics | 170 |
| The reduction in size of polymeric particles, as well as their irregularity in shape, is accompanied by an increase in surface area-to-volume ration which, commonly, results in an enhanced sorption capacity [33]. By determining the specific surface area through the Brunauer–Emmett–Teller (BET) method, these authors found that the BET area of three polymers – PE, PS and PVC – showed a positive correlation with the sorption of pyrene. However, though shape and size may play a role in the adsorption process, these factors will likely have a less important role in absorption, as the latter does not depend on the availability of sorption sites on the surface [34]. It should also be noted that, particularly for smaller particles, as those commonly referred to nanoplastics (<1 μm in size) [35], aggregation phenomena could occur that may result in the effective reduction of the available surface area, as reported by [36], whom noted that sorption behaviors altered when microplastics were reduced to the nanoscale and attributed this lower sorption capacity was due to the aggregation of nano-sized microplastics. Moreover, the presence and size of pores on the surface of microplastics is of the utmost importance, as smaller pores will enhance the interaction of the sorbate with the surface of the sorbent, leading to the formation of monolayer adsorption, while larger pores will result in both mono- and multilayer adsorption [37]. | 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 |
| 2.3.2. Crystallinity of (micro)plastics | 186 |
| Plastics, and, therefore, microplastics, are made up of amorphous and crystalline regions. Based on the extent of molecular chain alignment, these materials may be classified as either amorphous, semi-crystalline and crystalline [29]. Therefore, the degree of crystallinity of a given polymer expresses the fraction of crystalline regions, or, in other words, the fraction in which the polymer chains are aligned with each other, and this parameter varies greatly among different polymers, ranging from just over 0% (e.g., atactic PS) to over 90% (e.g., some commercial PE microspheres [38]), though no polymer is 100% crystalline. A higher prevalence of amorphous regions will result in higher mobility and polymer accessibility, thus favoring the diffusion of the chemical's molecules, as opposed to crystalline regions, which require higher energies for their uptake [34]. For example, Yao and colleagues studied the sorption of dibutyl phthalate, a member of the phthalate acid esters (PAE) family, commonly used in plastics to impart flexibility in a wide variety of plastic products [39] onto PE microplastics of different morphological characteristics and degrees of crystallinity [38]. Not only did they conclude that size was not a decisive factor, they also established a significant decrease in adsorption with increasing crystallinity ($r^2 = 0.98$). | 187 188 189 190 191 192 193 194 195 196 197 198 199 200 |
| 2.3.3. Glass transition temperature of (micro)plastics | 201 |
| Closely associated to crystallinity, glass transition temperature (T_g) also affects MPs and chemical sorption processes. Simply put, T_g is the temperature value at which there is a transition of the amorphous region of a polymer, when heated, from a “glassy” to a “rubbery” state [33]. It is, in other words, “the macro-manifestation of polymer chain's flexibility” [40]. At lower temperatures, the amorphous regions of the polymer are in the so-called “glassy” state, and, as such, they are more rigid and only vibrate; but, when heated, some regions will transition to the noted “rubbery” state, and these segments will show higher flexibility, as molecules will have a greater degree of freedom to move and, therefore, absorption of chemicals in these regions will be enhanced [34], owing to higher accessibility to hydrophobic organic compounds. As noted in the previous section, the crystalline regions of the polymer will not favor sorption, owing to the necessary high energy needed to destabilize the strongly ordered polymer chains. Hence, it is possible to postulate that the effect of T_g will thus be mostly felt within the amorphous regions, which will be more susceptible to sorption processes, though this requires more detailed research. | 202 203 204 205 206 207 208 209 210 211 212 213 214 |
| 2.3.4. Functionalization and cross-linkage of (micro)plastics | 215 |
| Polymers exhibiting higher degrees of cross-linking, i.e., presence of strong covalent bonds amongst polymeric chains, commonly show higher structural rigidity, and, therefore, do not favor the internal diffusion of contaminants [29]. A typically cited example is that of vulcanized rubber with sulfur; the cross-linking results in an increased T_g , thus increasing the range of temperatures associated to the “glassy” state of the polymer [41], ultimately influencing the sorption process as discussed above. | 216 217 218 219 220 |
| Similarly, the presence of functional groups may also affect their sorption behavior. For example, it has been demonstrated that highly aromatic PS exhibited a higher sorption affinity to polychlorinated | 221 222 |

biphenyl compounds, likely attributable to the hydrophobicity and π - π interactions when compared with PE [42]. Conversely, functional groups containing oxygen could also act as H-bond acceptors, thus interacting with water molecules, leading to the formation of water clusters on the surface of the polymeric materials. These three-dimensional water clusters may reduce the accessibility of contaminants to the sorption domains of plastics, due to competition, yielding a *de facto* reduction in sorption affinities [33, 43]. Hence, the type and extent of functionalization will affect the sorption process, though this will not, by itself, enhance or negatively affect the sorption behavior, and attention should be paid to these specific characteristics of the polymers.

2.3.5. Surface polarity of (micro)plastics

Carbon is the key constituent of the most commonly used plastics. Having four valence electrons, it achieves stability through sharing four more electrons, allowing it to form a wide range of covalent bonds. Carbon also catenates, forming strong bonds with itself [44]. In polymers, the existing functional groups, hydrophobicity and presence of unsaturated bonds all contribute to the type and strength of the formed secondary bonds [28] and these parameters are essential for ascertaining and determining the interactions of the polymers with chemical compounds. Velzeboer and colleagues, for example, showed that planar PCBs exhibited show stronger surface adsorption due to their supposed ability to move closer to the sorption surface than the more bulky nonplanar congeners [45], though their findings were not consistent between the two studied matrices, fresh and saltwater (in freshwater, effects of planarity were inconsistently or not significantly different).

2.3.6. Age and degree of weathering of (micro)plastics

When exposed to the elements, plastics undergo degradation and structural alterations that may lead not only to morphological changes, but also modifications at the level of surface area and polarity [29]. These alterations have been demonstrated to enhance the sorption of different compounds, including metals and organic contaminants. For example, Liu and colleagues showed that ciprofloxacin had elevated sorption capacity towards UV-aged PS when compared to the virgin plastic [46]. An identical observation was made for the adsorption of oxytetracycline on weathered PS by Zhang and colleagues [47]. The authors suggested that these effects may be due to the formation of oxygen-containing groups at the surface of these materials [48], as well as to the light-induced surface oxidation of plastics [28]. Aging may also result in reduction of hydrophobicity of plastics, thereby favoring the sorption of hydrophilic contaminants. In fact, it has been shown that non-polar compounds were more likely to sorb onto weathered microplastics than those of polar nature, thus suggesting that weathered or aged plastics may exert a more toxic effect than virgin or pristine plastics, due to the higher sorption potential of contaminants [49].

2.3.7. **Color** of (micro)plastics

Though severely understudied, color constitutes a parameter that may also play a role in the sorption of contaminants by plastics. Frias and colleagues, for example, collected microplastics from two beaches and showed that black pellets had the highest concentrations of POPs, except for PAHs [50]. This could be due to the fact that colored and darker plastics typically contain more additives, which may enhance their sorption capacity [29]. Fisner and colleagues [51] also concluded that darker colors mirrored a higher concentration of PAHs, though the degree or darkness was associated to weathering. As such, the enhanced sorption capacity could be reflective of weathering and not color itself. This limited set of results highlight the current need to further explore this parameter and how it affects – if at all – sorption capacity.

2.3.8. Hydrophobicity and planarity of the sorbate

The properties of the sorbate (contaminant) also constitute a key factor in its uptake and release by microplastics, reflected upon the accumulation capacity and the equilibrium state. Though not thoroughly studied, it has been demonstrated that hydrophobicity/hydrophilicity, surface charge and the presence of functional groups in the sorbate do exert an effect over the overall sorption behavior. Among these, however, hydrophobicity is considered to be the most important, as the hydrophobic nature of most MPs' surfaces renders these interactions the main driving of the sorption mechanism of numerous chemicals [28, 29, 52]. Accordingly, organic contaminants with high hydrophobicity tend to be more readily adsorbed on (micro)plastics [33]. In cases in which diffusion is the rate-limiting step of the sorption process, the molecular weight of the molecule should also be considered, as the lower both the molecular weight and the hydrophobicity of the compound (higher hydrophilicity), the faster

the diffusion mass transfer until reaching equilibrium or steady-state conditions. This is because, in such cases – diffusion as the rate-limiting process – the molecular weight of the sorbate becomes more relevant than hydrophobicity, as diffusion is more prominently hindered by the increase of molecular size [34].

Planarity also plays a role in the kinetics of the sorption process. In fact, planar molecules, as PAHs, show higher sorption coefficients when directly compared with other non-planar molecules, as PAHs, of identical hydrophobicity. This is due to the fact that higher degrees of planarity will result in higher proximities towards the surface of the plastics, facilitating non-covalent π - π interactions between sorbent and sorbate [30].

2.3.9. Speciation/ionization and functionalization of the sorbate

Chemical speciation is also a noteworthy aspect. Simply put, speciation depends on the acid dissociation constant (pK_a) of the contaminant and the pH of the solution (pH_{sol}), as these will determine the isoelectric charge of the chemical. If $pH_{sol} > pK_a$, the contaminant will predominantly be in an ionized form [53]. For organic contaminants, namely, ionic compounds, different ionization states under different conditions, could affect the sorption mechanism due to electrostatic interaction [33]. For example, when studying the partition behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA) on commercial microplastics, Wang and co-workers showed that FOSA was adsorbed on PS, but PFOS was not, due to the electrostatic repulsion observed between PS and PFOS, as both were negatively charged [54]. Similarly, for metals, chemical speciation could be an important parameter for predicting their sorption behavior, as the process is partly driven by the formation of free cationic species and coordination complexes within the matrix [34]. Free cations subsequently have a higher likelihood of interacting with the negatively charged regions of microplastics, which can be generated through the adsorption of organic molecules [55] or even due to the presence of other plastic additives. The organo-metallic complexes, however can interact with areas of the surface of the plastics showing a neutral charge, due to hydrophobic interactions.

The presence of functional groups in the contaminant/sorbate could also impact the degree and extent of sorption. For example, in an already mentioned study, Wang and colleagues described a higher sorption of FOSA than that of PFOS on PE, which could, at least partially, be ascribed to the presence of a sulfonamide group on FOSA [54]. Similarly, when assessing the sorption of three anti-inflammatory drugs to microplastics, Elizalde-Velázquez and colleagues showed that some exhibited an enhanced sorption, likely due to the presence of amino groups in their structure [56]. This likely stems from the fact that functional groups may attract the π electron(s) on the surface of plastics and therefore enhancing π - π electrostatic interactions between polymers and chemicals.

2.3.10. pH of the medium

External factors of the surrounding milieu will play an active role in the sorption of processes and numerous characteristics and parameters will be of relevance. By far, however, the most studied of these is pH. As previously noted, the pH of the solution will contribute in determining the charged state of the contaminants, this affecting the sorption affinity through electrostatic interaction. For example, it has been described that the degree of sorption by commercially acquired virgin PS particles increased with increasing pH value when this was kept under the 5. The authors suggested that this was likely due to the fact that, within the studied range of pH values, PS was negatively charged and the sorbent was positively charged; however, the high concentration of H^+ inhibited the sorption of the positively charged chemical, and, as such, sorption increased with a decrease in H^+ concentration [46]. Subsequently, when the pH value was further increased, sorption quickly decreased as the positively charged chemical became negatively charged, resulting in an electrostatic repulsion between sorbate and sorbent. Fred-Ahmadu and colleagues [28] summarized the role of pH as follows:

- (i). electrostatic repulsion will increase with an increase in the solution's pH, suppressing electrostatic interaction between differently charged sorbate and sorbent;
- (ii). an increase in pH may favor the dissociation of the hydrophobic neutral sorbate molecules into negatively charged, hydrophilic species, resulting in a diminished hydrophobic interaction;
- (iii). high pH may increase the π donor ability of sorbate, thus enhancing π - π interactions.

The role of pH may be of paramount importance when assessing potential ecotoxicological consequences, especially at the level of human health, as it has been shown that, for metals, for example, high desorption rates from contaminated plastics can be observed under particularly low pH environments, as is the case when these materials are exposed to gastric fluid [57].

2.3.11. Salinity of the medium

Salinity plays an especially important role in marine environments. Salts, and, particularly, NaCl, promote a “salting-out” effect, that increases with molecular weight and decreases with compound polarity [29]. This results in a shift of equilibrium towards the organic/polymeric phase. In other words, the presence of salts in a solution where sorption may occur will induce alterations in the partition equilibrium of natural organic solutes towards non-aqueous phases and may end up increasing sorption to microplastics by decreasing the solubility of the chemical contaminant [34]. The effects of salinity can also manifest through the rate or extent of agglomeration of sorbent, namely, microplastics, inducing changes at the level of size and available surface area, causing a reduction in the sorption of contaminant ions. In cases in which electrostatic interactions are the predominant driving force, there can also take place a competition ion-exchangeable sites, thus, again, yielding a *de facto* decrease in sorption of chemical compounds [58]. However, other authors have found that a wide range of levels of salinity exerted little to no effect on the rate of sorption of different chemicals on a variety of plastics, such as polybrominated diphenyl ethers to four microplastics (PE, PP, PA and PS) [59], suggesting that the sorption mechanisms by microplastics may indeed be contaminant-specific, resulting in sorption processes that are not dependent on the salinity of the surrounding environment.

On the other hand, ions available in the surrounding medium may compete with organic compounds for sorption sites on the surface of plastics, thus negatively affecting the sorption process by these materials. This has been confirmed by Zhang and colleagues, whom showed that increasing concentrations of CaCl₂ or Na₂SO₄, for example, decreased the sorption of oxytetracycline in both virgin and weathered plastics [47], which was ascribed to the strong competition of Ca²⁺ and Na⁺ for cationic exchange sites at the surface of the tested microplastics. Similarly, by directly comparing the sorption affinity of PFAs on microplastics in both fresh and seawater, Llorca and co-workers [60] found this to be weaker in the latter, thus confirming the expected behaviors for these cases. These findings showcase the need to further expand research on the topic, as contamination of the environment and subsequent ecotoxicological implications will likely vary depending on the environmental compartment such contamination refers to. This is especially relevant for metals, namely, copper, lead and cadmium [61], as the sorption mechanisms for these will more directly vary depending upon the existing competition for binding sites between ions in solution and contaminants. Indeed, this appears to be the determinant factor for the observed effects of ionic strength during sorption [28].

2.3.12. (Dissolved) organic matter in the medium

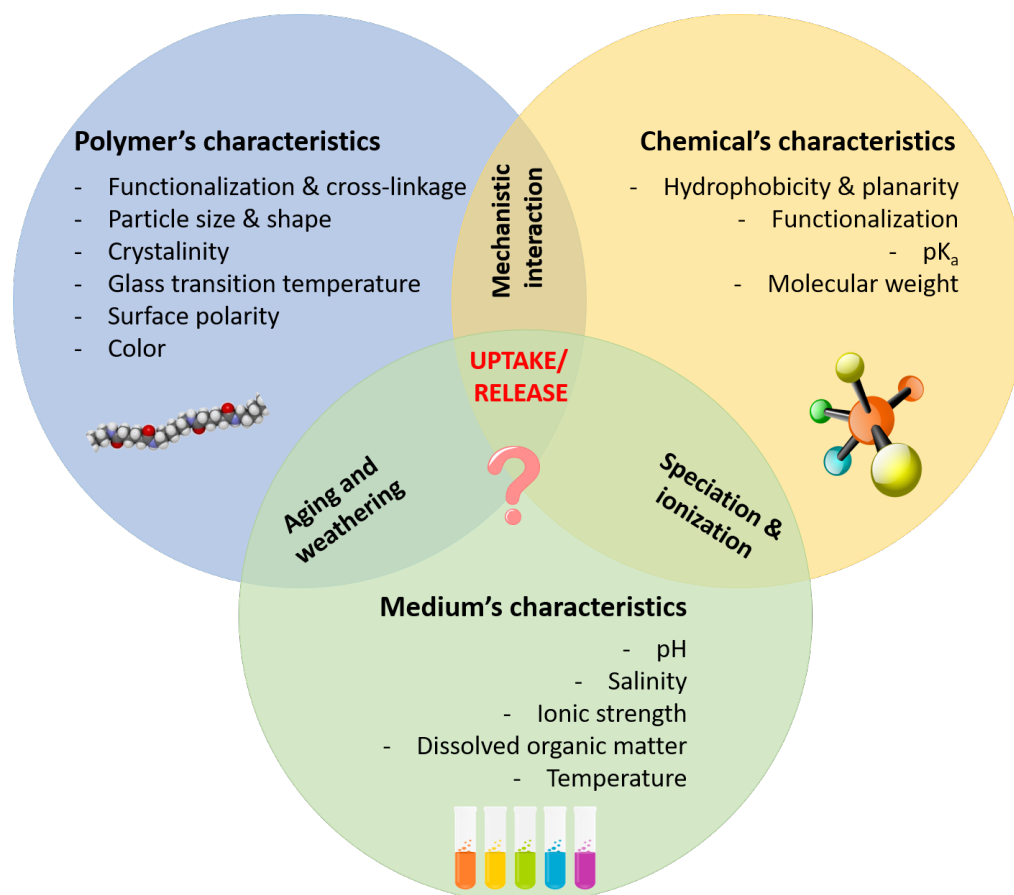
Organic matter (OM) is of special importance for metals, as it can react with these and affecting the sorption process. Generally, this interaction yields neutral organo-metallic complexes, which display higher degrees of hydrophobicity, when compared to that of the free ions. Consequently, this favors the sorption to the hydrophobic microplastics [33]. On the other hand, this complexation also contributes to a decrease in the concentration of the free ions in solution, which may result in a lower degree of sorption. As such, the overall process should be analyzed on a case-by-case basis, as it will depend on the specificity of the (dissolved) organic matter, ions and their concentrations, making difficult determining or assuming a “general” behavior of the sorption process when (D)OM is present [34]. Nonetheless, the size of the plastics will also likely play a role. In fact, Chen and colleagues demonstrated that the interactions of DOM and plastics depended, among other factors, on the size of the particles [62], due to effects over the stability of the dispersions.

For organic chemicals, the presence of dissolved organic matter probably results in a decrease in their sorption to microplastics, as it will likely bind the chemicals and compete with microplastics [60]. However, these effects will possibly vary with the polarity of the chemicals: non-polar chemicals have a higher affinity towards organic matter, resulting in a decreased sorption to plastics, but this influence will likely be reduced in the case of polar chemicals. For cases in which absorption is the dominant process, the presence of DOM has been demonstrated to be of less significance, owing to the fact that its effects are more preeminent at the surface of polymeric materials, especially non-porous ones, as there is no blockage of pores by the organic matter [63].

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| 2.3.13. Co-existing pollutants in the medium | 382 |
| It is known that multiple contaminants and pollutants are found in the environment and, especially, in the aquatic environment. As such, their co-existence could lead to competition for sorption sites on microplastics. Though not many studies have focused on the subject, Bakir and colleagues, for example, studied the sorption of DDT and phenanthrene on unplasticized PVC and ultra-high molecular weight polyethylene in seawater [64]. They found that DDT outcompeted phenanthrene for sorption onto plastic, thus illustrating an antagonistic effect. However, as noted by the authors, their work depicted a binary component process, and that, in the environment, a multitude of such contaminants exist. As such, it is necessary to further study these interactions, focusing on an ever-increasing degree of complexity. | 383 384 385 386 387 388 389 390 391 |
| 2.3.14. Temperature of the medium | 392 |
| The temperature of the medium can induce modifications of the polymers at the structural level, as higher temperatures may result in larger motions of segments of the polymer, thus favoring lower crystallinity, whose effects on the sorption process have been previously described. In spite of the expected role of this parameter in the uptake/release of contaminants by plastics, most of the sorption studies have been conducted at room temperature, except when the experimental design is specifically tailored to determine said effects [28]. Some studies have demonstrated that, generally, higher temperatures result in higher sorption rates, which could imply an increase in the number of active sites at the surface of the (micro)plastics [31]. For example, Lin and colleagues demonstrated that a slight increase in temperature translated into a small increase in the sorption of tetracycline by PS microplastics [65]; similarly, desorption of different bisphenols has been shown to increase with increasing temperatures [66]. However, broadly speaking, the effects of temperature of the matrix will depend on the chemical's microstructure, meaning that the sorption process will vary depending on the degree of crystallinity (as discussed above) and that this will, in turn, depend on the temperature. In other words, the sorption rates may increase with increasing temperature, but will decrease with increasing degree of crystallinity, which increases with increasing temperature. Again, it is therefore likely that the behavior of sorbate-sorbent interactions will have to undergo analysis on a case-by-case basis, owing to the inherently different characteristics of contaminant and polymer and their interaction with the environment. | 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 |
| 2.3.15. Confounding factors | 411 |
| Multiple factors affect the uptake/release of chemical compounds by polymeric materials, as illustrated in Figure 2. However, how these affect the sorption behavior is, in some cases, insufficiently described and, even for those whose effects are understood, as is the case for weathering, often divergent and contrasting findings are reported, and predictive modelling becomes extremely difficult. For example, some authors have described microplastics found in riverine systems to be less susceptible to weathering phenomena than those found in marine systems [67], as the former are less subject to tidal flows and are beached less frequently and for shorter periods of time. Others, though, have claimed that microplastics found in rivers are more exposed to UV radiation, and, therefore, undergo more intense weathering [68]. | 412 413 414 415 416 417 418 419 420 |
| Soil and sediment matrices are highly complex media, and most studies focusing on assessing the sorption behavior of chemicals onto (micro)plastics have been performed in aquatic environments. Nonetheless, both matrices are key reservoirs of chemical contaminants and microplastics [34]. Chen and colleagues studied the uptake and release of triclosan, a bacteriostatic agent widely used in numerous consumer products intended to reduce or prevent bacterial contamination, by soil and PS and PE particles [69]. Interestingly, these authors described different patterns of release of triclosan, which was highest for soil, followed PE and PS microparticles. This suggests that the typical high rate of uptake of chemicals by plastics [29], subsequently accompanied by this lower rate of desorption, could constitute a potential risk for the transfer of pollutants from loaded microplastics to the surrounding environment, whether sediments, water or even biota. | 421 422 423 424 425 426 427 428 429 430 |
| Another potentially confounding factor is microbial activity. In fact, most plastics, and particularly microplastics, are prone to microbial colonization [70]. These include bacteria, algae and fungi, which may form a biofilm on the surface of these materials. As discussed by Rodrigues and colleagues [71], the presence of biofilms could result in a two-tiered effect on the sorption of contaminants: it may prevent the penetration of UV radiation, and, consequently, actively reduce the weathering of | 431 432 433 434 435 |

microplastics, with concomitant decrease in sorption rates, as previously discussed, but it may also induce higher rates of sorption through modifications of the plastics' surface morphology. Hence, the overall effect of biofilm formation might depend upon the protective role it confers to the microplastics against weathering, which, in turn, may depend on the type of organism, as well as on the putative alterations these materials will undergo in response to the presence of said biofilm.

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Figure 2. General overview of the key factors affecting the uptake and release of contaminants by (micro)plastics. The question mark represents the potentially still undetermined factors as well as the unpredictable contribution of confounding factors, such as matrix complexity. Adapted from [29].

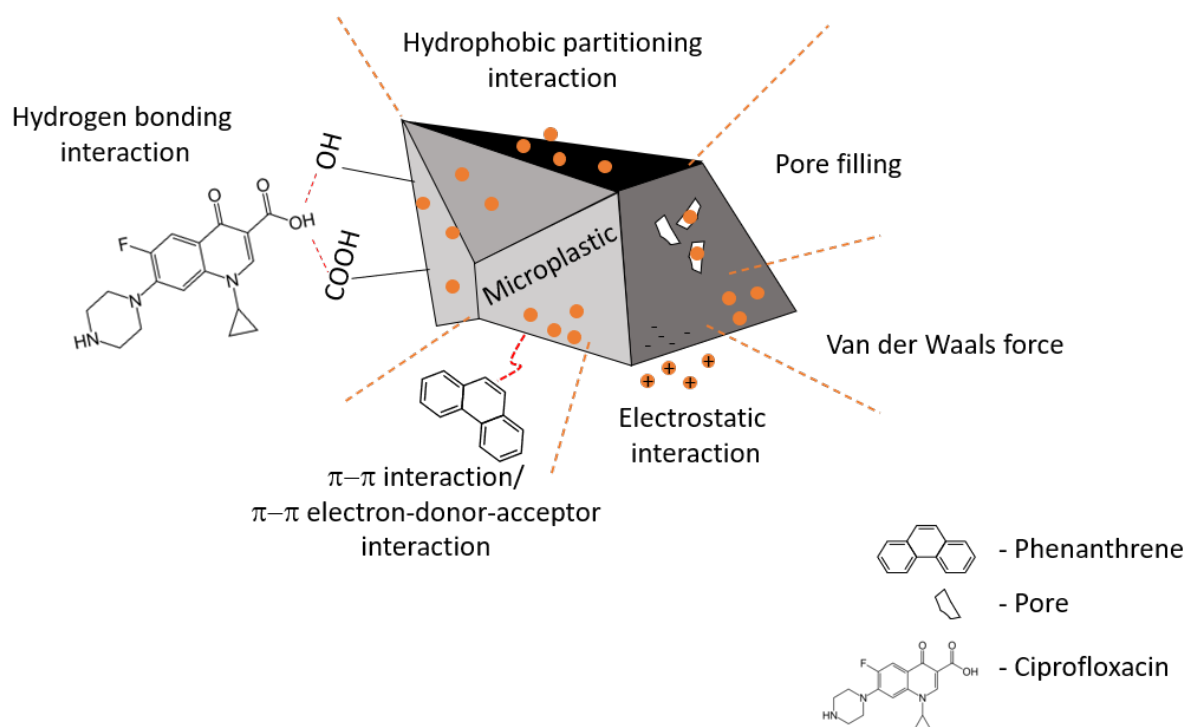
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2.4. Sorption mechanisms

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The mechanisms involved in the sorption of contaminants onto (micro)plastics are overviewed in Figure 3, and are discussed below.

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Figure 3. Overview of the sorption mechanisms of organic contaminants onto microplastics. Research suggests that these phenomena may lead to microplastics acting as vectors for these contaminants [30]. Phenanthrene and ciprofloxacin are used merely as examples. Adapted from [33].

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2.4.1. Hydrophobic partitioning interaction

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This mechanism refers to the partition of organic compounds between the matrix, usually, an aqueous phase, and the particles. It is widely regarded as one of the predominant sorption mechanisms affecting the sorption of pollutants, particularly hydrophobic organic contaminants to (micro)plastics [31]. This mechanism is mostly driven by the hydrophobic nature of plastics, and Raza-najatovo, for example, found that the main sorption mechanism for three drugs on PE was hydrophobic partitioning interaction [72]. These authors also found that compounds with higher degrees of hydrophobicity were more easily adsorbed onto microplastics.

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2.4.2. Pore filling

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Plastics, and, particularly, microplastics that have undergone weathering processes, usually display morphological surface alterations, including the formation or increase in pore number and size [48]. As such, contaminants can be trapped in said pores, thus affecting the rate of sorption of such compounds onto (micro)plastics. When studying the adsorption of oxytetracycline to both virgin and weathered microplastic PS, Zhang and colleagues found that the process included the pore-filling mechanism [47]. In their observations, the authors concluded that the increased rates of adsorption noted for beached PS foam when compared to that of virgin foam were likely attributable to the higher total area of micropores determined for the former. On the other hand, Guo and co-workers experimentally determined the average size of pores occurring at the surface of PE, PS, PP and PVC and found that these were smaller than that of Tylenol, resulting in an inability of pollutants to enter the pore interior.

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2.4.3. Surface sorption – hydrogen bonding interaction

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This interaction involves the hydrogen atoms located at the surface of (micro)plastics and the organic compounds. These are, indeed, specific electrostatic interactions [34], weaker than a covalent or ionic bond, but stronger than van der Waals forces, and may affect the sorption when proton donor and proton acceptor groups are involved. For instance, the amide group (proton donor group) of polyamide and the carbonyl group (proton donor group) of three different antibiotics – amoxicillin, tetracycline and ciprofloxacin – were found to form hydrogen bonds, resulting in an enhanced sorption affinity [73]. Similarly, as described by [33], [74] also found that polyamide had a stronger sorption affinity for different hydrogen bond donor compounds of different natures, including biocides, hormones and

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pharmaceuticals, than PE, which was ascribed to the formation of H-bonds between PA and the different tested organic compound. 480
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2.4.4. Surface sorption – electrostatic interactions 482

When both the sorbent and sorbate have electric charges, electrostatic interactions may occur. Electrostatic sorption occurs when these have opposite charges, as identical charges will lead to repulsion. The mechanism is extensively affected by pH and point of zero charge (pH_{pzc}), i.e., the pH value for which “the surface density of positive charges (contribution of cations) equals that of negative charges (anions)” [75]. The adsorbent shows a net positive charge when the pH is lower than the adsorbent’s pH_{pzc} and, conversely, it exhibits a global negative charge when the pH is higher than its pH_{pzc} . As reported by Razanajatovo and colleagues, when evaluating the sorption and desorption of three pharmaceuticals on PE microplastics in an aqueous system, the pH_{pzc} of PE was lower than the pH of the aqueous medium; this suggested an overall negatively charged surface of the microplastics and, consequently, there was an increased electrical attraction towards the positively charged pharmaceuticals, with a concomitant increase in the rate of sorption. Though for other contaminants and plastics, the same behaviors were reported in aqueous systems by other authors (e.g., [73]). Generally, therefore, electrostatic repulsion or attraction (sorption) between charged polymers and contaminants is primarily governed by the medium’s pH, the pH of point of zero charge of the microplastics and the acid dissociation constant associated with the pollutant [33]. 483
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2.4.5. Surface sorption – π - π interaction/ π - π electron-donor-acceptor (EDA) interaction 498

This type of interaction is especially relevant for benzene ring-containing materials. The sorption affinity of four types of microplastics – PA, PS, PE and PVC – towards seven aliphatic and aromatic organic compounds (benzene, chlorobenzene, cyclohexane, ethyl benzoate, *n*-hexane, naphthalene and toluene) were evaluated by [43]. These authors reported affinity of PS was the highest, and suggested that this could be due to the π - π interaction between the aromatic phenyl group of PS and the aromatic organic compounds. Similarly, [45] observed that PS particles exhibited a stronger sorption affinity towards PCBs when compared to PE, concluding that, at least partly, this was consequence of the presence of the benzene ring in the structure of PS. Such interactions have been demonstrated to be of key importance in other numerous processes, including the sorption of ibuprofen, diclofenac and naproxen on PS microplastics [56] or in the sorption of pyrene and phenanthrene on polyurethane (PU) microplastics [76]. 499
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The π - π EDA interaction is a particular non-covalent interaction between the electron donor and electron acceptor [77]. When studying the sorption mechanisms between PS and nitrobenzene, Wang and colleagues concluded that the π - π EDA interaction played a pivotal role in the process, as PS could act as an π -electron donor, whilst nitrobenzene behaved as a stronger π -electron acceptor [36], owing to the electron-depleted benzene ring and strong electron-withdrawing nitro group [33]. 510
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2.4.6. Surface sorption – Van der Waals Force 515

These forces are relatively weak and, basically, describe the attraction of intermolecular forces between different molecules and do not involve the formation of covalent or ionic bonds. Xu and colleagues described a linear sorption of sulfamethoxazole on polyethylene microplastics, though both were negatively charged under the specific experimental conditions tested (pH 6.8) [78]. Therefore, hydrophobic nor electrostatic interactions could explain the observed sorption process, which was subsequently attributed to a Van der Waals interaction. In fact, it is generally considered that the sorption of chemicals by aliphatic polymers, as PE, takes place *via* Van der Waals interactions, whilst aromatic polymers, such as PS, undergo π - π interactions [34]. 516
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2.5. Mechanistic modelling 524

Generally, the uptake process of a solute onto a solid particle involves 4 distinct steps [79]: 525

- (1) transport of the solute within the bulk solution/matrix; 526
- (2) diffusion of the solute through the boundary layer around the sorbent; 527
- (3) diffusion of the solute inside the solid sorbent and; 528

(4) sorption on the active sites on the solid surface.

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The release process, in turn, results from the reverse sequence of steps, beginning with the desorption from active sites [29]. The overall rate of the process is determined by the slowest of these steps, though it should be noted that the contribution of each individual step depends on the properties of the chemicals and the particles themselves, as well as on the environmental characteristics, as discussed in the previous section. Most studies, however, focus on the kinetics of the sole sorption process, and, as such, very few works have delved into the identification of the rate limiting step. One frequently – and understandably – ignored step is the initial step, as the solute transport through the solution may be considerable negligible, due to the often powerful mechanical stirring used in laboratorial studies [80]. Generally, step 4 is considered the one controlling the overall sorption process, and, therefore, is the step modeled through simplified empirical equations [29], such as pseudo-first and second order kinetics equations.

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The overall retention (or release) of a fluid on a solid and their thermodynamic equilibrium are defined as “sorption isotherm” [81], a term that accounts for the fact that these equilibria must be determined for a constant temperature, which should be should be specified. Sorption isotherms are, therefore, a graphical representation of the interactions between sorbent and sorbate per unit weight of the former, whilst also allowing the determination of the remainder of the latter when equilibrium is reached. As such, sorption isotherms can be used to predict the total amount of sorbate that can sorb on onto the solid surface of the sorbent, and the kinetic models developed estimate the efficiency of the sorption process [28]. Experimental data on equilibria usually fit well into one parameter linear model, also known as Henry’s Law, or two-parameter linear or non-linear Langmuir or Freundlich isotherms [28].

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In essence, and simply put, kinetic models serve the purpose of estimating the efficiency of the sorption process, whilst sorption isotherms can be used to predict the amount of sorbate that can sorb onto a solid matrix.

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Hence, determining the kinetics and the isotherm models will allow a better understanding of the sorption behavior of different chemicals onto plastics, and multiple studies have focused on this aspect, mostly, by modelling such sorption mechanisms based on empirical equations, primarily Table 1 details some of the most commonly used kinetic and isothermal models for describing the sorption mechanisms of chemicals on/by plastics.

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Table 1. – Common kinetic and isothermal models described in sorption/desorption interactions between contaminants and (micro)plastics. Adapted from [28] and [31].

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| Type | Model | Equation | Ref. |
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| Kinetic models | Pseudo first-order | $\log (q_m - q_t) = \log q_m - K_1/2.303.t$ | [72] |
| | Pseudo second-order | $1/q_t = 1/K_2q_m^2 + 1/q_m.t$ | [82] |
| | Intra-particle diffusion | $q_t = K_{id} \times t^{1/2} + C_i$ | [83] |
| | Intra-particle diffusion (desorption) | $f_{desorbed} (t) = 1 - M_t/M_o = 1 - 6/\pi^2 \cdot \sum(1/n^2) \cdot \exp(-n^2 \pi^2 t D_P/r^2)$ | [84] |
| | Aqueous boundary layer diffusion (desorption) | $f_{desorbed} (t) = 1 - M_t/M_o = 1 - \exp(D_w S A_{P/t} / \delta V_P K_{P/W}) = 1 - \exp(-3 D_w t / r \delta K_{P/W})$ | |

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|-----------------|---------------------------|--|------|
| | Film diffusion | $B_t = -\ln(1 - q_t/q_e) - 0.4977$ | [85] |
| Isotherm models | Henry's isotherm (linear) | $q_e = K_d \times C_e$ | [61] |
| | Langmuir (linear) | $C_e/q_e = 1/q_m K_L + C_e/q_m$ $q_e/C_e = K_L q_m - K_L q_e$ $1/q_e = [1/q_m K_L]1/C_e + 1/q_m$ | [86] |
| | Langmuir (nonlinear) | $q_e = Q_{\max} \times K_L \times C_e / 1 + K_L \times C_e$ | [87] |
| | Freundlich (linear) | $\log q_e = \log K_f + 1/n \log C_e$ | [38] |
| | Freundlich (nonlinear) | $q_e = K_f \times C_e^{1/n}$ | [47] |

q_m and q_e are the amount of adsorbate at equilibrium or adsorption capacity (mg/g), q_t is the adsorbed amount at time t ; K_{id} and C_i are intra-particle diffusion constants, K_1 and K_2 are the rate constants; B_t is the Boyd constant, K_d is the partition coefficient between the sorbent and the solution at equilibrium; C_e is the sorbate concentration at equilibrium; Q_{\max} is the maximum adsorption capacity; K_L is the Langmuir constant (mg/g), K_f is the sorption affinity coefficient (L/mg) and $1/n$ is the adsorption intensity (Freundlich constants), f_{sorbed} is the cumulative fraction of desorbed contaminant between time 0 and t ; M_0 and M_t are the initial mass and mass of sorbate remaining at time t , respectively; D_p is the diffusion coefficient in plastic; r is the radius of plastic, D_w is the diffusion coefficient in water, S_{ap} is the surface area of plastic, δ is the thickness of the aqueous boundary layer; V_p is the volume of the plastic, $K_{P/W}$ is the partition coefficient between water and plastic.

2.5.1. Kinetic models

Typically, the acquired or experimental data is fitted into a pseudo-first and pseudo-second order model, though other kinetic models have been shown to accurately depict the sorption process of some chemicals onto plastic materials, such as intraparticle diffusion model (e.g., [61]) and the film diffusion model (e.g., [47]). Frequently, pseudo second-order kinetic models correlate better with experimental data, likely due to ability of accounting for other processes other than sorption. Overall, however, pseudo-first order and pseudo second-order models, owing to their empirical nature, do not adequately describe the entire uptake/release process [29]. Indeed, models are recurrently considered as valid through a simplified analysis of correlation/determination factors, though this is an insufficient parameter for model validation. In fact, in most cases, the hypothesis that step 4 was the rate-limiting step was not supported – and validated – with real data [88]. These observations led to the consideration of alternative models that driven by diffusion-based equations, thus considering steps 2 and/or 3 – diffusion of the solute through the boundary layer and diffusion of the solute inside the solid sorbent, respectively – as the controlling step(s). Therefore, these models consider the external and internal resistances to the mass transfer of the sorbate, assuming, nevertheless, an equilibrium at the surface of the particles. Hence, external and internal mass transfers (IMT/EMT) are evaluated by considering numerous parameters (see Table 1), such as partition coefficient of the solute in the particles ($K_{P/W}$), diffusivities of the solute in water and the polymer/particle (D_w and D_p , respectively), as well as the radius (r) and the thickness of the boundary layer that surrounds the particle (\square).

Yet, as described in detail by [29], different mass transfer models have been validated for different experimental conditions, highlighting the need to further investigate these processes considering an extensive and thorough analysis of the external factors that may play a role in these mechanisms. For example, when evaluating the uptake of several PAHs and PCBs on PS particles, Liu and colleagues found that IMT was the rate-limiting step of the general process [46]. Oppositely, [84] researched the desorption mechanism of PCBs from PE particles and found that step 2 was the governing mechanism, as the aqueous boundary layer diffusion model (Table 1) was a better fit to the obtained experimental data. Their findings confirmed that experimental or environmental conditions can significantly affect the release process of the sorbate by the sorbent. In turn, when evaluating the adsorption of oxytetracycline to both virgin and weathered microplastic polystyrene particles, Zhang and colleagues

found that the intrinsic characteristics of the particles played a role, as IMT was the rate-limiting step of the sorption process for both types of particles, but EMT was especially relevant for virgin polymers, which the authors related to the porosity of the two sets of particles [47]. Lastly, other researchers have set out to determine the release of pollutants from microplastics and whether this was governed by the mass transfer in an aqueous boundary layer or by intraparticle diffusion. Seidensticker and colleagues, for example, found that these mechanisms depended on multiple factors, including partition coefficients, particle size, boundary conditions, and time [53]. The authors concluded that desorption exhibited distinct behaviors depending on whether this was performed under batch (finite bath) conditions or field conditions (infinite bath); in the case of the former, desorption accelerated with increasing partition coefficients for intraparticle diffusion, becoming independent of the partition coefficients if film diffusion prevailed. In the case of the latter, release controlled by intraparticle diffusion was not affected by partitioning of the compound, and external mass transfer slowed down with increasing sorption [53]. Hence, it becomes clear that mass transfer phenomena have been studied for a relatively limited number of contaminants-(micro)plastics sets and that further research into other contaminants and polymeric materials is needed. Additionally, as evidenced in some of the aforementioned studies, results observed and kinetic models developed for batch experiments may not necessarily translate into real-world settings, as the mass transfer mechanisms involved may differ.

2.5.2. Equilibrium models

The condition of equilibrium is frequently considered as a tool to estimate the potential of different particles, including microplastics, to act as vectors for chemical contaminants [29]. For this, it is necessary to characterize the equilibrium, which is done through the partition coefficient ($K_{P/W}$), which is the ratio between solid and liquid phases. To model this equilibrium state and estimate $K_{P/W}$, several sorption isotherms have been developed, of which the most commonly mentioned in the literature are the linear, Freundlich and Langmuir isotherms. Nonetheless, other sorption isotherms have been described to correlate the concentrations of chemicals in aqueous and solid phases, including the Temkin, Dubinin-Radushkevich, Redlich-Petersen and Polanyi sorption isotherms [29], though these are considerably less common.

The linear isothermal model is also referred to Henry's Law. It represents the most fundamental adsorbent-adsorbate isotherm, and reflects a linear relation between sorbed amount at equilibrium and the equilibrium concentration of the adsorbate in the adsorbent [88]. This linear model is an empirically determined equation that describes a suitable fitting of the sorption capacity in cases in which the adsorbate concentration is relatively low [31] and is a widely used model for ascertaining the partitioning of chemical contaminants between liquid and solid phases. Generally, it has been noted that the linear sorption isotherm provides good levels of correlation when the surface adsorption is of limited relevance when compared to that of the step of diffusion into the bulk polymer. Conversely, non-linear isotherms appear to provide better predictive attributes in cases of hydrophobic interactions and non-covalent π - π -interactions [89].

The Freundlich isotherm model can be used to describe both linear and non-linear sorption processes. Similarly to the linear model, it is an empirical adsorption model that may be used to describe the adsorption or equilibria data into heterogeneous surfaces (i.e., adsorbing particles having variable adsorption affinities), and it is applicable to mono- and multilayer sorption and relates, first, to the occupation of high-energy sites, followed by the occupancy of low energy sites [34]. The model's equation (see Table 1) contains the factor n , the Freundlich isotherm exponent (dimensionless), which determines the degree or extent of nonlinearity [90]. As summarized by [31], the Freundlich isotherm model can be basically used in describing the non-linear sorption between adsorbates and adsorbents and has been successfully used in describing the sorption process of, for example, some antibiotics by PE microplastics [72]. The authors added that, broadly, higher concentrations of adsorbates will translate to higher affinities of the adsorbates on the surface of the adsorbents.

Postulated by Langmuir in 1916, the Langmuir sorption model relates to the sorption process on homogeneous surfaces on which sorbents will exhibit high sorption affinities and form monolayers with specific finite sorption sites on the surface of the adsorbent [91]. It was originally developed for gaseous systems and balances the relative adsorption and desorption by considering that the surface coverage of the adsorbent is such that adsorption is as directly proportional to the open adsorbent surface as desorption is to the covered adsorbent surface [28]. It is based on a series of assumptions, namely [88, 92]:

- (1) A dynamic equilibrium exists between adsorbed and free sorbate molecules; 652
- (2) The surface of the adsorbent is uniform; 653
- (3) The adsorbed molecules have no form of interaction with each other; 654
- (4) The mechanism is identical for all adsorptions and; 655
- (5) At maximum adsorption, molecules only deposit on the adsorbent surface, not on each other (monolayer adsorption). 656
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The Langmuir model, however, is amenable to extensions ((Extended Langmuir isotherm and Interaction Factor Model), which can be used to study the sorption process of more than one sorbate, as performed by Bakir and colleagues, whom studies the competitive sorption of phenanthrene and DDT to PVC [64] and found that, although an extended Langmuir model allowed for an accurate fitting of the data, alternative models, such as an extended Freundlich model, did not. However, the authors also reported that the developed model showed a good agreement with the experimental data only for lower concentrations, fitting poorly for higher concentrations. The Langmuir model may also allow for taking into account other phases. This has been done, for example, for organic matter [53]. Such approaches should be further pursued and considered in future works, as the inclusion of distinct equilibrium constants into a single general equation may yield more realistic and robust models. 658
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Some authors have attempted to develop such generalized models for any isotherms. For example, Hinz proposed Equation 2 as potentially being able to describe any type of isotherm [93]: 668
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$$Q = Q_{max} \sum_{i=1}^{\omega} f_i \prod_{j=1}^{\tau_i} \left(\frac{A_{i,j} C^{p_{i,j}}}{1 + B_{i,j} C^{q_{i,j}}} \right)^{r_{i,j}} \quad (\text{Equation 2}) \quad 670$$

where Q_{max} denotes the asymptotic amount of adsorption at high concentrations, ω is the total number of different types of site, f_i is the fraction of sites of type i , and τ_i gives the number of interaction terms between the different types of sites. The $A_{i,j}$ and $B_{i,j}$ terms denote empirical affinity constants; $p_{i,j}$, $q_{i,j}$ and $r_{i,j}$ are dimensionless empirical parameters. 671
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As noted by the description of the different parameters considered, Equation 2 is fully empirical, with numerous fitting parameters. However, this same empiricism allows for decomposing any isotherm for different types of sites [81]. 675
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2.5.3. Thermodynamic models 678

Classical mechanistic approaches can be complemented with the application of predictive thermodynamic models, which are used to assess the equilibrium of microplastics and contaminants [29]. Such predictive approaches may be used independently, or they may be accompanied by experimental work. In the latter case, if used before acquiring experimental data, these methodologies may provide clues to the most significant parameters to be investigated and provide an idea of the results to be obtained. Different predictive models have been devised, and, broadly, these may be classified based on thermodynamic affinity, fugacity and free energy. These have been extensively reviewed by [29] and are only briefly overviewed herein. 679
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The affinity between contaminant and polymer is a key determinant in the uptake/release process. Bacon and colleagues, for example, proposed a framework to evaluate and predict polymer-solute thermodynamic affinity *via* the polymer-phase activity coefficient [94]; they found that the model was effective at very dilute concentrations, conditions under which the partition coefficients can be estimated using infinite dilution activity coefficients. However, for non-dilute systems, the models failed to consider the full effects of concentration on partition coefficient, and were thus inadequate. It should be emphasized, nonetheless, that no works describing such a predictive strategy for microplastics and environmental micropollutants are not currently available, meaning that the potential of this methodology is yet to be ascertained. 687
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In chemical thermodynamics, fugacity is an effective partial pressure which replaces the mechanical partial pressure in an accurate computation of the chemical equilibrium constant [95]. Mathematically, 696
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it equates to the ratio of the pressure of an ideal fluid, i.e., a fluid in which there are no microscopic processes of energy dissipation from internal friction (viscosity), or of energy transport from one set of particles to another (thermal conduction), with the same temperature and molar free Gibbs energy as the real fluid [96]. Because fugacity is known to be linearly related to the concentration in dilute systems, representative of the prevalence of contaminants found in environmental matrices, Mackay and Paterson proposed a simple methodology based on the evaluation of fugacity to assess the behavior of chemicals in the environment, as well as their distribution in different phases [97, 98]. Depending on the conditions of steady-state and equilibrium, these authors defined different systems describing the reference environment:

- (i). Level I: equilibrium, steady-state, no-flow system;
- (ii). Level II: equilibrium, steady-state, flow system;
- (iii). Level III: steady-state, non-equilibrium, flow system;
- (iv). Level IV: unsteady-state, non-equilibrium, flow system

This approach, applied at different levels of complexity, can be directly applied to predict the partitioning of chemical contaminants between microplastics and other environmental phases, including biota, as exemplified by the study performed by [99], whom assessed the environmental exposure of persistent bioaccumulative toxic compounds absorbed to microplastics and, therefore, amenable to ingestion by numerous organisms. Therefore, such tools could be promising instruments in predicting the role of (micro)plastics as vectors for contaminants in the environment.

Based both on fugacity and free energy, models dubbed Single Parameter Linear Free Energy Relationships (SP-LFERs) have been developed but, owing to their inherent limitations on describing different various molecular interactions essential for determining environmental partitioning [29], models known as poly-parameter linear free-energy relationships (pp-LFERs), capable of accounting for such various intermolecular interactions, have been developed [28]. In fact, such models have been successfully used to investigate, for example, the influence of an artificial aging procedure on the interaction of organic compounds with polystyrene microplastics [43]. Other authors have reported the utility of such models in exactly predicting different intermolecular interactions to the overall adsorption of organic compounds on different types of microplastics [100]. In principle, pp-LFER models can be used to predict any partitioning equilibrium between different environmental phases, including microplastics, provided the system parameters are available [28, 29]. And in there lies the (current) weakness of these models, as the descriptors for many compounds are available, but, for the most environmentally relevant plastics, regression coefficients are currently still lacking.

3. Knowledge limitations and implications

The ingestion of microplastics has been described across all trophic levels, ranging from zooplankton (e.g., [101]) to whales (e.g., [102]). From a human health perspective, the presence of microplastics has also been regularly described in important commercial aquatic species, including *Scomber japonicus* (Chub mackerel) [103] and bivalves (e.g., [104]) and trophic transfer has been confirmed in multiple studies (e.g., [105]). Tandemly, some key environmental pollutants have been found in plastics ingested by sea animals, namely, polychlorinated biphenyls and organochlorine pesticides (e.g., [106, 107]). Consequently, chemicals found sorbed on/into these materials do, in fact, constitute a threat to biota. Nonetheless, the putative effects of this (co-)contamination remain, largely, undetermined, due to the inherent difficulty in ascertaining the degree and extent of these phenomena in the natural environment. Nonetheless, considering the present estimates of 25 trillion macro- and 51 trillion microplastics littering the aquatic systems worldwide [5], and the increasing number and quantities of plastic additives used by the plastic industry, as well as the described accumulation of organic pollutants in the environment, it is essential to further expand our knowledge in this issue.

Though in recent years research on the topic of microplastics has increased exponentially, including the assessment of the potential ecotoxicological effects of these materials, and, less frequently, associated chemicals, far less attention has been paid to plastic additives and their potential environmental consequences. Additionally, a considerable fraction of this research has been supported or based on knowledge garnered from engineered nanomaterials. Although the general basics and principles may be of assistance, microplastics exhibit inherent characteristics that render direct comparisons

inadequate. Engineered nanomaterials are usually uniform in size, shape and physical and chemical characteristics, which is not the case for plastics: an extensive range of plastic resins exist, and, in turn, each one occurs in numerous variations, each one with distinct physicochemical properties, including porosity and density. These, in turn, will affect, among others, their environmental distribution, owing to differences in properties such as biofilm formation or buoyancy. Hence, establishing clear reference materials for hazard evaluation is extremely difficult [108].

An important and long recognized additional limitation in many laboratorial studies is the use of pristine, often highly homogenous, plastic particles. These differ greatly from microplastics found in the environment, which are estimated to consist of, mostly – at least, two-thirds – secondary microplastics [109], i.e., smaller plastic particles generated by the fragmentation and degradation of larger plastic debris. A less considered aspect regarding the use of such commercially available materials is that these are often available as suspensions that contain numerous agents, such as dispersants, that may impart any subsequently assessed ecotoxicological consequences stemming from their use. Perhaps even less frequently considered is the difference between nominal (i.e., established or pre-determined) and actual (i.e., measured) microplastic concentrations. Although, in many studies, it is assumed that the tested concentrations are those referring to nominal concentrations, actual concentrations have been experimentally vary up to an order of magnitude [110], owing to the experimental conditions and settings used, highlighting the need for a continuous experimental determination of the established concentrations. All of these limitations are compounded by the still existing lack of standardized methodologies to sample, process, characterize and evaluate the impacts of microplastics.

For both microplastic and plastic additives studies, field and laboratory test conditions continue to differ drastically, in spite of the current awareness regarding this issue. Laboratorial settings are determined and tightly controlled, but, in the environment, these may vary considerably, including temperature, media composition and sorbate concentration, which, in laboratorial settings, is often considerably higher than those reported in the environment [34]. When assessing the uptake and release of chemicals, including additives, a key difference between these types of studies is the necessary time for reaching equilibrium [111]; minutes or hours – less frequently, days – suffice for equilibrium to be reached in the laboratory, equilibrium time of sorbate in the environment may take months or years, due to the fact that, in the lab, concentrations are higher, constant agitation is often used and the test media is uniform in composition. Lab tests are also frequently designed to determine the behavior of a limited number of compounds; in the environment, numerous chemicals co-exist and there is potential competition between sorbates and interaction, in addition to other confounding factors, such as microbial activity, biofilm formation and polymer degradation. Still, some examples exist of successful fitting of sorption isotherms and kinetics equations to samples collected from the field [112], suggesting that currently available models may actively contribute towards a realistic prediction of sorbate-microplastic interactions in the environment, even when all variables are not considered.

In spite of the existence of numerous studies centered on the adsorption, absorption and release of different additives by microplastics (e.g., [59, 85, 89]), there is still very limited knowledge on the leaching of such additives from these polymeric materials. As such, there is the need to further explore the leachability and ecotoxicity of additives associated to existing environmental microplastics. This will comprise increasingly complex and iterative studies, as those reported by Jang and colleagues. These authors initially explored the role of Styrofoam as a source of hazardous additives for different marine organisms, and determined that Styrofoam constituted a source of hexabromocyclododecane (HBCD) intake for mussels [113], subsequently, these authors confirmed this assessment and also observed a significant ingestion of these materials and a concomitant bioaccumulation of HBCD [114]. The toxicity of microplastics and their lixiviates needs also to be explored and, for example, [17] noted that different microplastic particles – PA, PE, PVC – were not toxic to these organisms alone, but that chemical compounding with their additives, in the form of lixiviates, rendered them toxic. Observed consequences included reproduction, survival and population growth.

4. Perspectives

In spite of the extensive literature review and of the currently available data on the mechanistic behavior between microplastics and organic contaminants, much remains unknown. The vast majority of the currently available data has been obtained through the study of simplified systems, and a deep understanding of the complex environmental interactions between sorbent and sorbate, as well as of their consequences, remains largely undetermined. Hence, integrated strategies and approaches are

necessary in order to adequately consider all the mass transfer stages and related factors contributing to the rate of sorption – uptake and release. It is also clear that most of these studies have been focused on aquatic systems, and understanding these phenomena in other matrices, such as soils, is essential. This may be of special relevance in areas such as landfills, as the frequently reported leaching processes taking place in these facilities may enhance the overall role of microplastics as vectors for numerous organic contaminants. The same is true for wastewater treatment plants effluents, including the resulting sludge, often used in agricultural practices, and that may contain elevated quantities of microplastics and associated chemicals.

Predictive models, as those based on thermodynamic parameters, are still limited, owing to the lack of detailed descriptors for the most common microplastics and pollutants of interest. Exploring these models could be quite useful for a preliminary determination of the key features to study in experimental works and determining the most relevant ambient conditions to evaluate, which is of special importance given the aforementioned limitations in the classical modelling approaches.

Ecologically, it will also be necessary to establish the accurate bioavailability of organic compounds and the role of microplastics, including the determination of how different morphological and chemical properties, such as polymer type, size, porosity and degree of weathering, may affect the subsequent degree of bioavailability, of both microplastics and associated chemicals. Of immediate importance is the need to perform such assessments by resorting to environmentally relevant concentrations of sorbate and sorbent, as most available data pertains to experimental conditions that do not mimic, in any way, real-world conditions. Lastly, often foreshadowed as a “magic solution” that could solve the global plastic pollution, bioplastics have been described as a promising alternative that overcome most, if not all, of the environmental issues that “traditional” synthetic plastics hold. However, not only is the literature is confusing in the definition of bioplastics – that may refer to bio-based or partially bio-based materials, as bio-PE, biodegradable fossil-based plastics, such as PBAT, or bio-based and biodegradable plastics, as PLA [5] – but recent studies have also shown that these materials may exacerbate the uptake/release of organic pollutants. For example, Zuo and colleagues demonstrated that biodegradable microplastics sorbed/desorbed more phenanthrene than conventional plastics [115], a behavior that has also been demonstrated for metals (e.g., [116]). As such, it will be necessary to determine whether, even for truly bio-based and biodegradable plastics, increased renewability and biodegradability are, indeed, proof of lower environmental impact.

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