Adsorption of PAHs and PCDD/Fs in Microplastics

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Plastics are synthetic organic polymers that are malleable and can be molded into solid objects of various kinds. Furthermore, they are strong, light, durable and inexpensive, properties that make them suitable for the manufacture of a wide range of products. Polyaromatic hydrocarbons (PAHs), dioxins, and furans (PCDD/Fs), these compounds have also been detected in products made from plastics and in recycled plastics by different procedures.

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1. Microplastics (MPs) as Input Vector of Polycyclic Aromatic Hydrocarbons (PAHs) and Persistent Organic Pollutants (POPs) in the Food Chain

Chua et al. [1] were the first scholars to reveal the role that MPs play as a vector for the assimilation of POPs in organisms. It was showed that the polybrominated diphenyl ethers (PBDEs) present in MPs are assimilated by living organisms, especially the more brominated congeners, while the particles are eliminated through the intestinal tract.

Kleinteich et al. [2] studied the toxicity of PAHs in contact with polyethylene microplastics in tests with bacteria. It was showed that that MPs are an efficient transport vehicle for hydrophobic contaminants, but at the same time, the bioavailability of these contaminants in the environment is decreased, because of the adsorption that occurs quite rapidly. For example, it was showed that that the presence of phenanthrene and anthracene has less effect when they are loaded on microplastics than without them.

Sorensen et al. [3] studied the kinetics of the adsorption process at 10 and 20 °C of fluorene and phenanthrene in polyethylene (PE) and polystyrene (PS) microbeads. It was distinguished the ingestible (10 µm) and non-ingestible (200 µm) fraction by copepods. They show that MP-adsorbed PAHs do not accumulate in crustaceans, since only dissolved free PAHs are available to copepods. They also show that salinity is a very important point in the process. Similarly, Zhang et al. [4] indicated that an increase in the salinity of the water increases the zeta potential of the surface of MPs, and this produces an increase in the adsorption capacity of phenanthrene on polyurethane, polyurea, and urea-formaldehyde resin particles.

Zhu et al. [5] also showed that the presence of MPs delays the leaching of phenanthrene in the soil and decreases the bioavailability of this noxious. Additionally, Bartonitz et al. [6] discovered that the toxicity of phenanthrene is much lower in the presence of microplastics, and the presence of sediments is much more dangerous.

Hanslik et al. [7] evaluated the toxicity of PE and polymethyl metacrilate (PMMA) microplastics (less than 100 μm) and insist on the reduced bioavailability of contaminants in the presence of microplastics, which means that the potential of MPs as vectors is limited. Liu et al. [8] also showed that the accumulation of phenanthrene in crops is lower if a certain amount of microplastics is present together with the contaminant.

It is also important to note that not only are the number of contaminants adsorbed on the surface of the polymer but also those that are in the central part. Wang et al. [9] proposed a method to distinguish the surface and total concentration, which consists of the ultrasonic extraction of the compounds on the surface, and the total dissolution of the particles prior to determining the total concentration. The main focuses are on dioxins and related compounds, including brominated congeners. The total concentration is shown to be approx. 355 times higher than the surface for dioxins and chlorinated furans, and this ratio increases to ca. 8100 in the case of brominated congeners. Compounds with a higher number of chlorine or bromine are more abundant, and in most cases, they are concentrated in the central part of the microplastic.

2. Kinetics of the Adsorption and Desorption Process

Microplastics (MPs) uptake different potentially toxic elements. According to Igalavithana et al. [10], different mechanisms are present, such as physical adsorption, pore filling, surface complexation, and electrostatic attraction. The presence of UV radiation, microbes, and humidity can influence the pollutant uptake, as well as different environment conditions.

Many studies have been carried out showing that the kinetics of the adsorption process follows a pseudo-second-order equation. A pseudo-first-order model would represent that the rate-limiting step is a physical process affecting analyte concentrations. On the contrary, the pseudo-second-order model suggests the adsorption process involving the (chemical) interaction affinity between adsorbents and adsorbates [11].

For example, Zhao et al. [12] mentioned such kinetics for the adsorption of phenanthrene, pyrene, and some derivatives on the surface of different microplastics. Additionally, Bao et al. [13] reached this conclusion when studying the adsorption of phenanthrene and its hydroxy-derivatives in polyvinyl chloride (PVC) particles of 134 μm. This would indicate that the kinetics are dominated by the hydrophobic interaction. Yang et al. [14] used micro PS to determine the adsorption kinetics of pyrene and its substituted derivatives, also concluding that the rate is of second order with respect to the amount of contaminant.

It has also been observed that the presence of some adsorbed compounds interferes with the kinetics of the process for other compounds. Thus, Bakir et al. [15] showed, using isotopically labeled phenanthrene and dichlorodiphenyltrichloroethane (DDT), that phenanthrene adsorption is modified by the presence of DDT on the particle surface. In another work, Bakir et al. [16] carried out a similar study but with perfluorooctanoic acid (PFOA) and di(2-etilhexil) phthalate (DEHP), also showing interference. In the same work, it was measured the kinetics of the desorption of these contaminants in the intestinal tract, compared to that which occurs in seawater, the former being much faster. This indicates that the desorption that would occur after the ingestion of microparticles by different animals would be very fast. Cormier et al. [17] also showed a rapid desorption of other contaminants (PFOS) under conditions similar to those existing in the stomach. Comier et al. insisted that the diameter of the particles plays a key role, with smaller particles' desorption being much faster. The same is also indicated in the study by Zhang et al. [18]. Additionally, values of distribution coefficient were much higher (62.6 L/kg) for small particles of PE (4–6 μm) than for bigger particles (20.9 L/kg for 125–500 μm particles) [19].

Li et al. [20] mentioned that the desorption is dominated by the diffusion steps in the outer layer. Lin et al. [21] concluded that the external diffusion is fast and it is the diffusion in the pores that controls the speed, both for PAHs and for PCBs when studying the phenomenon in PS particles of 100 nanometers.

Gao et al. [22] studied the adsorption of compounds from oil (structurally similar to PAHs) in PE particles between 165 and 500 μm. They carried out a study of the kinetics, arriving at a pseudo-second-order adsorption model in which diffusion in the pores is the rate-controlling step. Adsorption at 25 °C and at neutral pH was the fastest when they studied the variation between 4 and 65 °C and at pHs between 2 and 12. The presence of an alkaline environment and the increase in ionic strength (presence of salts) also decreased adsorption of nitro-anthracene in various MPs, including PS, PP, and PE [23].

387 Končarsk et al. [24] used the second-order model to estimate the kinetics of the adsorption process of PAHs on poly lactic acid (PLA), which implies that chemisorption is the adsorption mechanism involved.

3. Effect of Aging

Abaroa et al. [25] showed an increase in adsorption with aging, and proposed that the use of an indicator, the yellowness index (YI), related to the color change that microplastics present over time. This YI is estimated visually based on the color of the MPs and is related to the speed at which the POPs are adsorbed on the particles.

Likewise, Chen et al. [26] showed that the aging of MPs increased the presence of compounds related to dioxins in a very original study.

The presence of oxygenated groups on the surface increases its hydrophilicity, causing a reduction in the adsorption of organic compounds such as PAHs and other hydrophobic organic compounds (HOCs) [27]. Li et al. [28] showed that aging and etching (artificial weathering (etching)) of PE particles produces surface oxygenation, but also an increase in the specific surface area of the plastics, which ultimately translates into an increase in the adsorption of PAHs on polymers that have been subjected to aging and, particularly those that have been etched. Zhang et al. [4] indicated that aging decreases the affinity of MPs with organic pollutants, by increasing the amount of oxygenated functional groups.

Other authors, such as Cerná et al. [29] did not show significant differences in the adsorption capacity of MPs of polyurethane that had been subjected to aging. This may be because polyurethane is already a good adsorbent for PAHs, as will be discussed later. It was indicated that the main driving factor is the flexibility of the polymer.

Aging is also responsible for the increase in the adsorption capacity of PS particles in water, air, and seawater, according to Ding et al. [30].

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