PRELIMINARY ASSESSMENT OF BISPHENOL A ADSORPTION ON MICROPLASTICS: CAPACITY, EFFICIENCY AND CONTROL FACTORS

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In this study, the main focus is on how microplastics (MPs) interact with bisphenol A (BPA) and how this interaction indicates that this is correlated with the polymer and environmental conditions. Each material tested showed a distinct adsorption pattern. Polyethylene (PE) exhibited the highest adsorption capacity at equilibrium. Polystyrene (PS) achieved the highest removal efficiency, while polypropylene (PP) obtained the lowest removal efficiency. BPA binding to MPs may be influenced by hydrophobic interactions, which are accentuated in acidic environments, and contact time, both of that can affect the attainment of equilibrium. Lastly, this study provided precious insights into the environmental impact of microplastics, which can serve as both a vector for organic compounds, and as a source of pollution.

Keywords: microplastics characterization, bisphenol A, environmental factors, adsorption capacity, removal efficiency

1. Introduction

One of the biggest challenges to ecological protection because of the excessive accumulation of waste is represented by plastics. It affects both terrestrial and aquatic ecosystems, even though it is considered a massive achievement of 20th century. At the same time, microplastics (MPs), which are particles that measure less than 5 mm, have attracted substantial interest, by proving their capability to bioaccumulate throughout the food chain [1]. MPs have various uses and although they do not cost much, their recycling rates remain very low, resulting in big amounts of waste that either end up in the environment, or undergo degradation processes through exposure to ultraviolet radiation or climatic factors (UV) [2].

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Microplastics have been found in various compartments of the environment, such as sediments, soils, atmosphere or surface water [3,4]. In order to calculate the contamination levels, many researchers reported that it depends on one environment to another, with amounts varying from a few to large particles per kilogram of soil/sediment: per cubic meter of water/air [5]. There are a multitude of ways from which MPs can enter aquatic and terrestrial ecosystems, such as wastewater treatment plants [6], transport through drainage networks and waterways [7], and littering from maritime and recreational activities [8]. The use of fertilizers obtained from tainted sludge from wastewater treatment, tire wear and the release of synthetic fibers during textile washing and drying processes [9], also represents major sources.

From an environmental standpoint, microplastics raise serious concerns as they can act as carriers for toxic chemicals and pathogens. Accumulating in living organisms, it can be transported along the food chain, with possibly damaging impacts on the ecosystem [10,11]. Polystyrene (PS), polyvinyl chloride (PVC), polypropylene (PP), along with polyethylene (PE) are few of the numerous microplastics that can be identified among the environment [12]. They are the most widely used because of their properties, which allow them to be used in building isolation, freight transport and food packaging. Similarly, they can act as vectors for organic and inorganic contaminants by multiple transfer mechanisms in the environment, because of their high porous structure and large surface-to-volume ratio, that facilitate the retention of a various range of substances [13].

It is widely known that, for the manufacture of plastics, a various number as additives are used, including bisphenols (BPs) [14]. Studies have shown that although they are frequently detected on the surface of MPs, the concentrations identified exceed those in plastics, highlighting their high adsorption capacity [15]. This study concentrates on bisphenol A (BPA), which demonstrates its usefulness in a large range of consumer products, such as food packaging, medical devices, toys and plastics containers. Even though its effects are toxic and well known, its relationship with MPs is the one that raises alarming signals, due to the ecological and biological risks. There are numerous studies that concentrate on this relationship, but there are inconsistent. Some of them showed that MPs can retain BPA from the environment, amplifying toxic effects by increasing oxidative stress and organ damage in aquatic organisms [16,17]. Contrarily, other studies suggest that BPA could decrease the bioaccumulation and toxicity of PS particles in marine species [18], or microplastics may restrict the bioavailability of BPA reducing its effect [19], while some studies indicate that there is no evidence of an interaction between the two components [20].

BPA has been found in a variety of human biological fluids and tissues, such as breast milk, urine and blood [21], reinforcing concerns about its potential role as an endocrine disruptor. Exposure to this compound has been linked to several adverse health effects, including kidney and cardiovascular disease, reproductive disorders, immune system dysfunction, and neurological development disorders [22]. In addition, BPA has been associated with metabolic disorders such as non-alcoholic fatty liver disease, obesity, and insulin resistance, and is classified as a substance that affects metabolism [23].

Although the presence of BP residues on the surface of MPs has been confirmed in natural environments [24], studies on the interfacial processes between BPs and MPs remain insufficient. There are still significant gaps in our understanding of how different types of microplastics retain these contaminants and of the physicochemical mechanisms underlying these interactions. Additionally, further research is needed to clarify the influence of MPs' physicochemical properties and environmental parameters on their interfacial behavior [25]. In this context, the present study aims to systematically analyze the adsorption of bisphenols onto microplastics and to highlight the roles of microplastic characteristics and hydrochemical factors in the underlying adsorption mechanisms. Thus, in order to highlight the role of MPs characteristics and hydrochemical factors in the adsorption mechanisms involved, this study aims to systematically analyze the adsorption of bisphenols (BP) on microplastics (MPs).

2. MATERIALS AND METHODS

2.1 Reagents

Analytical standards of BPA, along with pure microplastic standards – polystyrene (PS, <100 µm), polyethylene (PE, $\rho = 0.94$ g/mL at 25°C, 40-48 µm), and polypropylene (PP, 300 µm) – were purchased from Sigma-Aldrich (St. Louis and Darmstadt, Germany). HPLC-grade methanol and analytical-grade glacial acetic acid were sourced from Merck (Darmstadt, Germany) and Sigma-Aldrich, respectively. At the same time, ultrapure water was produced in-house using a Milli-Q system (Merk Millipore, USA). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) from Sigma-Aldrich were used to adjust the pH.

2.2 Analytical procedure

BPA quantification was performed on an Agilent 1260 HPLC coupled with an Agilent 6410B triple-quadrupole MS (LC-MS/MS) using a Luna C18 column (150 x 2.0 mm, 3 µm), at 35 °C. The mobile phase consisted of 0.01% acetic acid in water and methanol (30:70 v/v) at 0.15 mL/min, with 1 µL injection volume. Detection was carried out in multiple reaction monitoring (MRM) mode (mass transitions: 227 → 212, 227 → 133), under optimized MS conditions (1V cell accelerator, 150 V fragmentor, 15 V collision energy, 250 ms dwell time). BPA eluted within 6 min under ESI conditions of 6000 V capillary voltage, 300 °C drying gas temperature, 7L/min gas flow, and 40 psi nebulizer pressure.

2.3 MPs characterization

In order to identify the functional groups on the surface of MPs, an FTIR Spectrum BX II spectrophotometer (Waltham, USA) was used. The measurement range for this study was between 4000 and 500 cm^{-1}.

2.4. Adsorption of BPA onto microplastics (MPs)

To assess a preliminary assessment of BPA adsorption on MPs, this study was designed to evaluate: the effect of pH on BPA adsorption, the influence of contact time on adsorption dynamics, and also the relative adsorption capacity and the removal efficiency under optimized conditions. The experiments were performed to identify general adsorption trends and favorable conditions for BPA retention on different MPs.

Bach adsorption experiments were performed in series using 50 mL of ultrapure water containing an initial concentration of 2.5 mg/L bisphenol A at 25 °C. In each test, 0.5 g of microplastics was added to the BPA solution, and the suspensions were continuously agitated at 100 rpm using an IKA KS 501 digital stirrer (Germany). The solid-to-liquid ratio (0.5g of MPs in 50 mL aqueous solution) was selected to ensure sufficient contact between the MPs' surface and BPA. To evaluate the influence of contact time on BPA adsorption, experiments were performed with contact times ranging from 0 to 30 minutes and from 1 to 6 hours. For each experimental condition, independent batch adsorption systems ere prepared using 50 mL of BPA solution. At each selecting time point, 1 mL aliquots were collected and analyzed using LC-MS/MS. These experiments were used to describe the adsorption behavior over time and to identify the time range required to approach adsorption equilibrium, without applying kinetic models.

The effect of pH variations on BPA adsorption was investigated by adjusting the pH of 50 mL BPA aqueous solutions to in range of 3.00 and 11.00 using 0.01 M HCl or 0.01 M NaOH. After pH adjustment, 0.5g MPs were added to each solution and maintained at 25 °C under constant agitation for 24 hours to ensure sufficient contact for equilibrium conditions. All the experiments were performed in duplicate.

After the adsorption experiments, the removal efficiency (%) and the equilibrium adsorption capacity (Qe) were calculated to compare the relative adsorption performance of the tested MPs under similar conditions.

2.5. Evaluation of Removal Efficiency and Adsorption Capacity

The removal efficiency (%) of BPA was calculated by comparing the initial and final concentrations of the contaminant in solution after the adsorption experiment, using Equation (1):

$$R(\%) = \frac{C_0 - C_T}{C_0} \; x \; 100 \qquad (1)$$

, where C_0 is the initial concentration of BPA and C_t is the concentration measured after the defined contact time.

The adsorption capacity of microplastics at equilibrium (Q_e, mg/g) was calculated using equation (2).

$$Qe = \frac{(C0-Ct)\cdot V}{m} \qquad (2)$$

Where Ce (mg/L) is the BPA concentration measured after the predefined contact time corresponding to equilibrium condifitions, V (L) is the solution volume, m (g) is the mass of microplastics.

3. RESULTS AND DISCUSSION

3.1 FTIR characterization of microplastics before and after BPA adsorption

The FTIR spectra obtained for PE, PP, and PS microplastics before and after exposure to BPA (Fig. 1a-c), do not indicate significant changes between the initial and contaminated samples. The spectral profiles of the materials after adsorption almost overlap those of the unexposed polymers entirely, with no new bands or relevant signal shifts observed.

The FTIR spectrum of pure BPA (Fig. 1a-c) is characterized by intense bands corresponding to broad O-H vibrations (~ 3200- 3600 cm^{-1}), aromatic C=C vibrations (~ 1500-1600 cm^{-1}), and C-O/C-O-C vibrations (~ 1200-1300 cm^{-1}). In comparison, polyethylene and polypropylene are predominantly marked by bands associated with aliphatic C-H bonds (~ 2800-3000 cm^{-1}), as well as low-intensity vibrations around 1460-1470 cm^{-1}, which give these polymers simple, relatively uniform spectra. Polystyrene has an aromatic structure that causes the appearance of a distinct band, attributed to the phenyl nucleus, in the range of 1450-1600 cm^{-1}. This could theoretically favor the overlap or intensification of aromatic signals in the presence of BPA.

In the case of PS samples exposed to BPA (Fig. 1c), only slight changes in the aromatic area are observed, without the appearance of new bands that can be clearly attributed to BPA. For PE and PP, the BPA signal is not detectable, with the spectra before and after exposure overlapping completely.

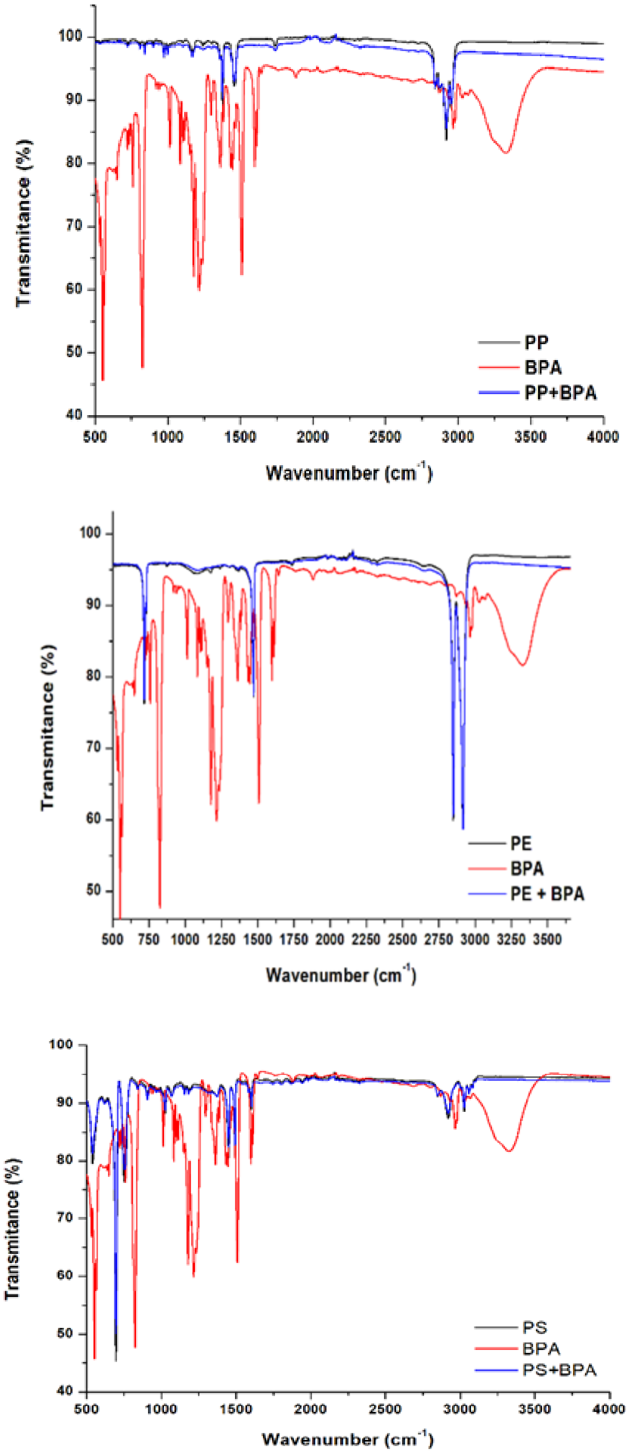

Fig. 1. FTIR spectra of pristine and BPA-exposed microplastics: PE (a), PP (b) and PS (c), compared with pure BPA

The absence of spectral changes correlates with very low adsorption capacity values (Qe = 0.05 – 0.08 mg/g), indicating the presence of only tiny amounts of BPA on the surface of microplastics (<0.01% by mass). For solid samples, the characteristic BPA bands at these levels are well below the detection limit of FTIR, so the spectrum is dominated by the polymer signal. In the case of PE and PP, the adsorption of BPA on microplastics is determined by hydrophobic interactions, and in the case of PP by weak π-π interactions, so the adsorption is physical in nature and does not form chemical bonds that can generate additional bands or serious modifications. From a molecular point of view, the adsorbed BPA layer is thin and discontinuous, which is why it cannot produce significant changes in the FTIR profile of the polymers.Therefore, the absence of FTIR signatures of BPA does not necessarily reflect the absence of adsorbate but rather reflects the analytical limitations and in the presence of unconventional interactions. Quantitative confirmation of BPA retention is thus based on experimental values of removal efficiency and adsorption capacity, not on spectroscopic analysis.

3.2 Influence of contact time on adsorption dynamics

The influence of contact time on BPA adsorption is highlighted by the adsorption profiles of the three polymers (Fig. 2). For all materials an increased adsorption is observed with increasing of contact time, indicating the presence of free active sites to which BPA molecules can easily attach. A fast adsorption occurs during the first 3 minutes, suggesting that BPA uptake is favored at short contact times. Among the three MPs, PE highlights this stage with a much steeper slope than PS and PP, indicating a higher affinity and a larger number of available sites. From 60 to 180 minutes, the sites are gradually occupied and the rate of the process decreases. PE continues to maintain the top growth rate, compared to PP which presents a reduced evolution rate, probably due to its smoother surface with little defects. After 240 minutes, the curves of all materials tend to stabilize, reaching the equilibrium point, which indicate that further increases in contact time result in only minor5 changes in adsorption capacity. The differentiation between polymers can be clearly observed in the plateau area, where polystyrene stands out with the peak adsorption capacity, followed by polyethylene, while polypropylene has the lowest equilibrium value [11, 26].

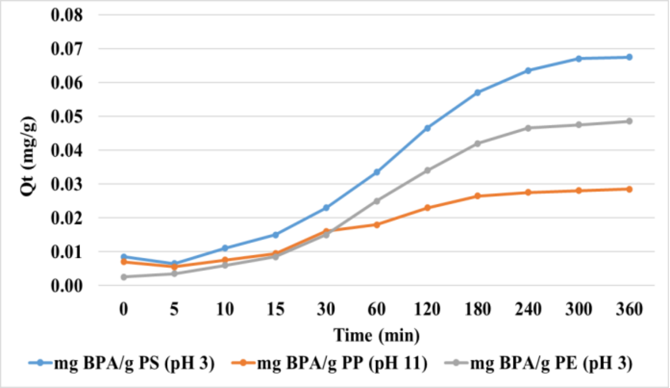

Fig. 2. Effect of contact time on BPA adsorption onto microplastics.

3.3 pH effect on BPA adsorption

Fig. 3 clearly illustrates the considerable influence of pH on the equilibrium adsorption capacity (Qe) of BPA across all three polymer types, with differences in behavior depending on the chemical form of BPA and the surface characteristics of each material. The value at which maximum adsorption was recorded was pH 3, notably because BPA is found in a neutral state under these conditions. The acidic environment favors hydrophobic interactions, helping BPA to attach to the polymer structures. The Qe values reflected the combined effect of surface topography and hydrophobicity. For this pH, the maximum value was recorded for PE, followed by PP and PS. Compared to strongly acidic conditions, at pH 5 a decrease is observed, even though for all polymers the adsorption level remains approximately high. This can be explained by the deprotonation phenomenon of BPA, a phenomenon that leads to an increased solubility in water, therefore a reduced affinity for hydrophobic surfaces. For this range, the best adsorption performance was obtained by PP, suggesting a favorable interaction in a weakly acidic to almost neutral environment. As the pH reached a neutral-slightly alkaline range (pH 7 and 9), all the analyzed materials had a reduced adsorption, the reason being the transition of BPA to the ionized form, which limits its interaction with the non-polar surfaces of the polymer. However, the Qe values remained higher for PE compared to PS and PP, probably due to its more pronounced hydrophobic character and more irregular surface structure.

At pH 11, BPA is entirely in its deprotonated and negatively charged form, yet an increase in adsorption is observed compared to the pH range of 7-9, especially in the case of PE and PP. The occurrence of specific interactions between ionized BPA and oxidized or defective polymer areas, as well as an increase in the number of available binding sites due to changes in microstructure or surface roughness in an alkaline environment, may explain this intensification. In direct proportion to its pronounced hydrophobic character, polyethylene registers the highest values of Qe. In the figure below, it is highlighted that acidic environments, with pH from 3 to 5, favor BPA adsorption, neutral to moderately alkaline ones (pH 7-9) reduce it, and strongly alkaline environments (pH 11) cause a partial recovery of the process. Furthermore, PE maintains the highest adsorption capacity over the entire pH range.

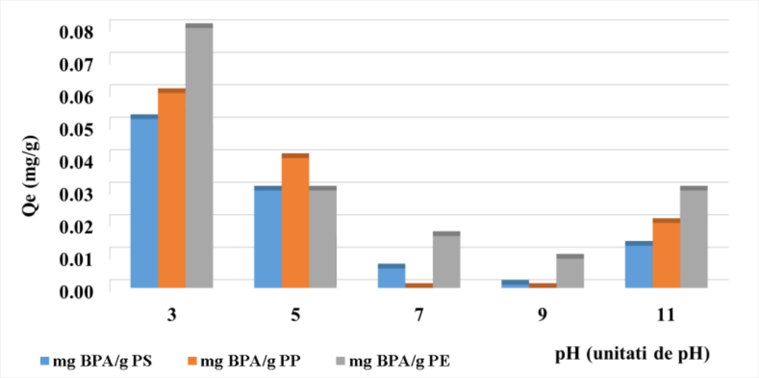

Fig. 3. Influence of pH on BPA adsorption onto MPs

Among the plastics analyzed, PE stood out with the highest adsorption capacity values across the entire pH range analyzed, followed by PP and PS. These results emphasize, once again, that the hydrophobicity and chemical properties of the surface are vital in controlling BPA adsorption onto microplastics. Improved adsorption of organic pollutants has been reported in the literature especially under acidic conditions, due to favorable electrostatic interactions. Thus, the optimal pH value for this study was pH 3 [26,27]. However, it is worth noting that significant adsorption was also observed for the types of MPs studied at pH 11, justifying further analysis of the influence of contact time in this alkaline environment.

3.4. Relative adsorption capacity and removal efficiency

In terms of equilibrium adsorption capacity (Qe) and removal efficiency (R%), the meaningful differences between the three polymers can be seen in Table 1. Consistent with the limited functionality of the pristine microplastice surface, the absolute values remain relatively low. Due to physicochemical properties of each material, they indicate different adsorption mechanisms.

Table 1.

Removal efficiency (RE%) and equilibrium adsorption capacity (Qe) of BPA on the three polymer types

Polymer	Removal Efficiency, RE (%)	Adsorption Capacity, Qe (mg/g)
PS	54	0.05
PP	22.8	0.06
PE	38.8	0.08

The top removal efficiency (54%) indicates that a large amount of BPA is removed from the solution very quikly. This percentile was obtained by PS, even though its Qe value (0.05 mg/g) is lower than the comparable results for PP and PE. This suggests that, although hydrophobic and π–π interactions promote the initial adsorption of BPA, the relatively smooth surface and limited number of binding sites result in a lower total adsorbed amount at equilibrium. In the case of PS, it is observed that the adsorption capacity (Qe = 0.06 mg/g) is a little higher than that of PS, but it exhibited the lowest removal efficiency (22.8%). This behavior can be explained by a lower affinity for BPA or a slower initial process. It can also present a slightly better accumulation capacity at equilibrium, possibly influenced by its partially crystalline structure. The difference between R(%) and Qe is marked by the adsorption regime, which can be controlled either by diffusion or by slow kinetics over time intervals. PE demonstrated the highest adsorption capacity at equilibrium (Qe = 0.08 mg/g) and a significant interaction efficiency (38.8%), otherwise marking it as the superior material in BPA retention.

PE has a pronounced hydrophobic character and a surface rich in defects, making it the most efficient adsorbent, as demonstrated by the results of this study. PE achieved the highest removal rate, but also a loading equilibrium that highlights a favorable connection between initial rapid adsorption and collective aggregation until equilibrium is reached. This study suggested that PS stands out for its ability to remove BPA, PE has the highest affinity and adsorption capacity, and PP has the lowest efficiency under the conditions analyzed. All of these support the use of the Qe parameter as a relevant practical indicator for the comparative evaluation of adsorption capacity in this study.

3.5 Future perspectives and environmental implications

To understand the interactions between bisphenol A and the three types of microplastics studied (PS, PP, and PE), this study emphasized the role of pH, contact time and polymer morphology in controlling adsorption processes. Although the analysis focused mainly on equilibrium behavior and qualitative changes in the surface, many aspects remain open for further investigation of the mechanisms involved. Future research will include modeling adsorption isotherms and kinetic studies to elucidate BPA binding mechanisms, maximum retention capacities, and limiting steps in the process. These approaches will enable more rigorous predictions of MPs' behavior in natural aquatic environments. Microplastics play a dual role that could have a strong impact on bioavailability and trophic transfer, both as persistent pollutants and as mobile vectors for organic contaminants. At the same time, their intrinsic sorption properties suggest a potential application in developing sorbent materials structurally inspired by microplastics, without the disadvantages of persistence in the ecosystem.

4. Conclusions

The study reveals that polymer-specific properties and environmental conditions are both factors that influence the adsorption of BPA on microplastics. Influenced by surface characteristics, BPA speciation and hydrophobicity, PS, PP and PE exhibited different adsorption behaviors. While the PP showed the weakest performance, PE displayed the highest adsorption capacity and PS achieved the greatest removal efficiency. Acidic conditions improved BPA adsorbtion, while at neutral to slightly alkaline pH it was reduced. Adsorption occurred rapidly at first, followed by a slower approach to equilibrium. Overall, these findings highlight the role of microplastics as carriers of organic contaminants and provide a foundation for future studies on adsorption mechanisms and environmentally sustainable sorbent design.

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