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Adsorption of benzophenone-3 and octocrylene UV filters on polyethylene: analysis by HPLC-MS/MS and voltammetry with screen-printed electrodes

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ARTICLE INFO

Keywords: Marine environment Microplastics Environmental risk Seawater Sunscreens voltammetry Screen-printed electrodes

ABSTRACT

Microplastics (MPs) are persistent pollutants that can adsorb contaminants, facilitating their accumulation in aquatic ecosystems. The presence of UV filters (UVFs) such as benzophenone-3 (BP3) and octocrylene (OC), exacerbates this issue, particularly in coastal areas. This study presents an innovative dual-method approach combining high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) and differential pulse adsorptive stripping voltammetry (DPAdSV) to assess the adsorption of UVFs on polyethylene (PE), a widely found polymer in aquatic environments. Adsorption kinetics were analysed using pseudo-first-order (PFOM) and pseudo-second-order (PSOM) models, revealing a higher equilibrium sorption capacity for OC due to its stronger hydrophobic interactions with PE. A central composite design (CCD) was employed to enhance resources efficiency in experimentation and controlled experiments exposed the materials to both pure fresh water and synthetic seawater. The results indicate a higher adsorption affinity of OC on PE than BP3, attributed to its high octanol-water partition coefficient (log Kow 6.88) and stronger hydrophobic interactions. Exposure time was the most influential variable across both media, while pH and temperature had a significant effect on BP3 adsorption in synthetic seawater. Hydrophobic partitioning, aided by van der Waals forces, was identified as the dominant interaction mechanism for both UVFs, with π - π and electrostatic interactions playing minimal roles due to the nature of the polymer. The study provides new insights into how polymer-pollutant interactions vary across environmental conditions and offers a novel voltammetric alternative for in-situ UVFs monitoring.

1. Introduction

Plastics are pollutants that have been accumulating in the aquatic environment on a large scale for decades. Their difficult elimination and low degradation rates further increase their presence in the environment, persisting for long time periods. Microplastics (MPs) originate from the breakdown of larger plastics and direct sources such as synthetic fibres, cosmetics, and industrial products (Atugoda et al., 2021; Auta et al., 2017). MPs from these sources often enter aquatic environments through the release of effluents from wastewater treatment plants (WWTPs), which do not effectively eliminate them (Auta et al., 2017; Contreras–Llin and Diaz-Cruz, 2024).

Research on MPs provides evidence of their bioaccumulation and biomagnification (Browne et al., 2008; Cole and Galloway, 2015), and

the adverse effects they cause, particularly to aquatic organisms. These effects include harmful damage when they are accidently ingested during feeding, causing intestinal blockage (Duan et al., 2022); decreased food intake due to satiety and reduced growth (Cole et al., 2015; Watts et al., 2015); and metabolic alterations (Wan et al., 2019).

MPs interact with the environment due to their hydrophobic nature (Gouin et al., 2011; Takada, 2006), and high volume-to-surface ratio, enabling them to adsorb and transport pollutants (Atugoda et al., 2021; O'Donovan et al., 2020; Wang et al., 2015), as evidenced by studies summarized in Table S1, which examine the adsorption of various contaminants, onto plastic materials. Therefore, intrinsic factors of the polymer, such as polarity, size, and weathering, are crucial in the adsorption process. The main interactions between MPs and organic compounds include hydrophobic, electrostatic, partition, and π - π

https://doi.org/10.1016/j.envpol.2025.126468

Received 26 March 2025; Received in revised form 12 May 2025; Accepted 15 May 2025 Available online 15 May 2025

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interactions, van der Waals forces, and pore filling (Menéndez-Pedriza and Jaumot, 2020; Wang et al., 2020). For instance, MPs in marine environments have been shown to act as significant carriers of various pollutants, including persistent organic pollutants (POPs). A recent study by Wang et al. (2024) demonstrated that MPs have a higher capacity for concentrating POPs compared to suspended particulate matter (SPM) in coastal waters (Wang et al., 2024).

UV filters (UVFs) are chemicals used to protect against UV radiation (Hanun et al., 2023). These compounds are commonly found in sunscreens, cosmetics, and skin care products but also can be present in plastics, paints, and textiles to increase resistance to photodegradation (O'Donovan et al., 2020). UVFs enter the aquatic environment through direct pathways, such as recreational water activities and indirect pathways, such as discharges from WWTPs, as well as urban and industrial runoff (Díaz-Cruz and Barceló, 2015), leading to their release into rivers, seas, and oceans.

UVFs, bioaccumulate and biomagnify through the food chain (Díaz-Cruz et al., 2019), posing toxicity risks to aquatic organisms. OC induces sublethal toxic effects in blue mussels (M. edulis) (Falfushynska et al., 2021), and it has been recently demonstrated that OC degrades into the carcinogenic compound benzophenone. In response, The European Chemical Agency called for OC-related data in 2023, while France proposed marketing restrictions (European Commission, 2018), and Hawaii banned BP3 and octinoxate due to its observed endocrine-disrupting activity (Downs et al., 2022). Benzophenone-3 (BP3) can alter endocrine or reproductive parameters (Coronado et al., 2008; Downs et al., 2021; Fent et al., 2008), and promote viral infections leading to coral bleaching (Danovaro et al., 2008). Exposure to MPs can also enhance the toxicity of pollutants. O'Donovan et al. (2020) demonstrated that MPs contaminated with BP3 induce greater oxidative stress, lipid peroxidation, and neurotoxic effects in clams (Scrobicularia plana) compared to virgin MPs (O'Donovan et al., 2020). These findings suggest that the observed toxicity is mainly driven by BP3 rather than MPs alone, reinforcing concerns about MPs as carriers of harmful pollutants, emphasizing the importance of evaluating the adsorption capacity of these contaminants onto MPs and their potential effect on aquatic ecosystems (Haque and Fan, 2023).

It is important to integrate climate change-related variables into the study of MPs in aquatic environments. Climate change alters environmental conditions such as temperature and pH, directly influencing the behaviour and impact of MPs and associated pollutants (Wei et al., 2024). The ongoing acidification of water bodies due to atmospheric CO_2 absorption leads to changes in chemical equilibria, including the formation of carbonic acid, affecting the adsorption and transport of pollutants. Moreover, rising temperatures accelerate the degradation and fragmentation of plastics (Haque and Fan, 2023). Given the need to understand how climate change affects aquatic ecosystems, research that incorporates these aspects is essential for a more accurate assessment of the ecological effects of MPs.

This study evaluates the adsorption of BP3 and OC onto polyethylene (PE), one of the most frequently found plastic polymers in ecosystems (Fig. S1) considering MPs' role in pollutant transport and bioaccumulation. A central composite design (CCD) was developed for this study to assess key variables—temperature, exposure time, pH, and salinity—affecting adsorption dynamics. High-Performance Liquid Chromatography-Tandem Mass Spectrometry (HPLC-MS/MS) ensured precise quantification of the selected UVFs, while Differential Pulse Adsorptive Stripping Voltammetry (DPAdSV) with screen-printed electrodes (SPE) provided a cost-effective, portable method for in-situ analysis of BP3 and OC, and other UVFs in water samples (Muschietti et al., 2020; Sunyer et al., 2019).

2. Materials and methods

2.1. Experimental materials

BP3 (2-hydroxy-4-methoxybenzophenone, oxybenzone), OC (2-ethylhexyl-2-cyano-3,3-diphenylacrylate, octocrylene), both >98 % purity, and PE in pellets with an average particle size of 4 mm were purchased from Sigma-Aldrich (Darmstadt, Germany). Water and Methanol (MeOH) used for chromatographic analysis (LiChrosolv®, LC-MS Grade), were supplied by Merck KGaA (Darmstadt, Germany). The isotopically labelled internal standards (IS, >98 % purity) used were benzophenone-2,3,4,5,6-d5 (BP3-d5) purchased from Isotopes CDN octocrylene-(2-ethyl-d5-hexyl-(Ouebec. Canada). and 2,3,3,4,4,5,5,6,6,6-d10) (OC-d10), purchased from Toronto Research Chemicals (Toronto, Canada). Hydrochloric acid fuming 37 % (HCl) supplied by Merck KGaA and sodium hydroxide (NaOH) purchased from Sigma-Aldrich were used to adjust the pH. For the DPAdSV analysis of OC, hexadecyl-trimethylammonium bromide (CTAB) from Sigma-Aldrich, and formic-formate buffer solution 0.1 mol/L at pH 4.25 were used. Synthetic seawater was made from the water dilution of a sea salt mix (ASTM D1141-98, Lake Products Company, USA). Stock solutions of individual standards (1000 mg/L) and intermediate mix standards solutions containing all analytes were prepared in MeOH. Water samples were collected in amber glass bottles to avoid photodegradation. All prepared solutions were stored at -20 °C in the dark.

2.2. Characterization of MPs

PE pellets were examined under a Stereoblue SB.1903-U stereomicroscope by Euromex (Duiven, The Netherlands) to assess their surface morphology and uniformity. Pictures were taken with a VC.3031 HD Lite camera (Euromex), attached to the stereomicroscope. Pellets' diameters were measured with a digital caliper. Additionally, their structure and microstructure were characterized by field-emission scanning electron microscopy (SEM), while also determining their chemical composition by X-ray microanalysis (SEM, JSM-7100F, JEOL, BV, Europe).

2.3. Methodology

2.3.1. Adsorption experiments & factors selection

The three variables that most significantly affect plastic polymers and organic contaminants were selected according to the literature review conducted, temperature, exposure time, and pH. Salinity is another important factor affecting the adsorption of these contaminants in plastic particles, thus its influence in the adsorption dynamics has also been assessed. Our selected response variable is the concentration of each contaminant in the exposition solution. Experiments were conducted in pure water, and in synthetic seawater, which simulates a natural environment, providing a more realistic evaluation of the adsorption process without other natural interferences.

We performed preliminary batch adsorption tests by exposing PE beads to 15 mg/L BP3 and OC solutions, monitoring contaminant concentration decreases over time (aliquots were collected at 0, 1, 2, 4, 8, 24, 48, 72, 96, and 120 h). These results helped define the appropriate exposition time range for further experiments. For sample preparation, 25 mL of a solution of 15 mg/L of BP3 and OC prepared with aqueous solution (pure water/synthetic seawater) were added to a suit of glass beakers. The pH of the solution was adjusted with NaOH and HCl using a pH-meter (Thermo scientific, Orion Star A215). Seven PE pellets (\sim 210 mg total) were weighed and added to the aqueous solution, which was then stirred at 350 rpm. This number was determined based on the results of preliminary tests designed to prevent interference with UVF detection caused by excessive plastic mass and to ensure reproducibility under all experimental conditions. The glass beaker was covered with aluminum foil to prevent photodegradation of the compounds. After

each experimental run, a 100 μ L aliquot of the sample was collected and transferred to an amber LC-vial containing the IS and MeOH, then analysed by HPLC-MS/MS. Another 3 mL aliquot was collected and preserved for further DPAdSV measurements. To ensure reproducibility, three aliquots were taken at each sampling time point for both HPLC-MS/MS and DPAdSV analyses.

2.3.2. Data analysis

The sorption kinetics were analysed using both the pseudo-firstorder (PFOM) and pseudo-second-order (PSOM) models (Wang et al., 2015), using OriginPro 10.2 (OriginLab Corporation). These models are mathematically expressed as follows:

$$Q_t = Q_e \times (1 - e^{-k_1 t}) \tag{Eq. 1}$$

For PFOM, where Q_t (mg/L) is the adsorbed concentration of the UVF at a time *t* (h), Q_e (mg/L) is the equilibrium concentration, and k_1 (h^{-1}) is the rate constant. In the case of PSOM it is expressed as:

$$Q_t = k_2 Q_e^2 t / (1 + k_2 Q_e t)$$
 (Eq. 2)

where k_2 (g/(mg·h)) is the rate constant.

2.3.3. Experimental design

Since temperature, exposure time, and pH were identified as key factors influencing PE interaction with BP3 and OC in aquatic environments, an experimental design was developed for multi-stressor testing. A central composite design (CCD), one of the most widely used response surface design experiments, was chosen for this purpose. The application of the CCD allowed us to evaluate the behaviour for each analyte where three variables and five levels are applied for the optimization of the adsorption experiments. For CCD experiments, samples were collected at specific time points defined by the design matrix (Table S2).

Data of the selected design and the levels considered were processed using STATGRAPHICS Centurion XVIII (v 18.1.16). Respective experiments were carried out by spiking the exposition beaker solution (HPLC grade water/synthetic seawater) with BP3 or OC at 15 mg/L.

2.4. HPLC-MS/MS analysis

The separation and quantification of the two UVFs and corresponding isotopically labelled IS were performed using a Transcend TLX-1 liquid chromatography system coupled to a TSQ triple quadrupole mass spectrometer (Thermo Fisher Scientific, San José, CA, USA). The LC system was equipped with a PUROSPHER® STAR RP-18 ec column (Merck, New Jersey, USA) and a precolumn of the same material. The samples were assessed using positive ionization mode with electrospray ionization (ESI+), and a binary gradient was applied. The chromatographic mobile phase used consisted of water and MeOH, both containing 0.1 % formic acid. An injection volume of 20 μ L and flow rate of 0.3 mL/min were used.

Selected reaction monitoring (SRM) mode was used for the operation of the MS detector. The two most characteristic fragments of the precursor molecular ion were monitored for each analyte, as shown in Table S3. The most intense fragment was used for quantification (SRM1). Acquisition and processing of data were performed with Thermo Xcalibur software (v 3.1.66.7). The quantification of the samples was carried out using an eight-point calibration curve in MeOH. Deuterated IS (BP3-d5 and OC-d10) were added to the samples and the calibration curve standards to guarantee the quantification accuracy. Additionally, MeOH was used as blank to evaluate any possible contamination.

2.4.1. Method validation

Quality parameters (Table S4) were studied and validated using a blank of HPLC grade water. Several tests were carried out to determine

method limits of detection and quantification (mLOD and mLOQ) and linearity. In addition, precision and trueness were subsequently studied by spiking the blank sample at two concentrations. mLODs were 3 ng/L and 1 ng/L for BP3 and OC, respectively, while mLOQs were 11 ng/L and 3 ng/L for BP3 and OC, respectively. The calibration curves for UVFs quantification were linear for both compounds, with correlation coefficients (R^2) ranging from 0.9997 to 0.9999, over a wide concentration range (from 0.1 to 1000 µg/L). The validated method demonstrated its suitability for the determination of BP3 and OC in water samples and an optimal separation of the target compounds were achieved (Fig. S2).

2.5. Voltammetric analysis

DPAdSV was performed using screen-printed carbon electrodes (SPCE) to evaluate the concentration of BP3 and OC in water. The voltammetric measurements were conducted using a μ Autolab Type III potentiostat (EcoChemie, The Netherlands) connected to a 663 VA Stand Metrohm (Herisau, Switzerland) and to a PC equipped with the GPES (v 4.9) software (EcoChemie). SPCE (reference DRP-110) were purchased from Metrohm DropSens (Oviedo, Spain) and connected to the potentiostat by means of flexible cable (ref. CAC) (Metrohm DropSens). All electrochemical measurements were performed applying a deposition potential of -0.6 V during a deposition time of 240 s, and a differential pulse scan from -0.5 V to -1.6 V, using pulse heights of 50 mV, pulse times of 50 ms, and scan rates of 20 mV/s. Additionally, a conditioning oxidative potential of -0.2 V was applied for 60 s before each new measurement.

The DPAdSV measurements were applied to the samples obtained after the experimental runs of the BP3 and OC CCDs prepared in synthetic seawater. Before analysis, 800 μ L of a 0.1 mol/L formic-formate buffer solution at pH 4.25 were added to each BP3 and OC sample, which were then placed in a glass cell. In the case of OC, it also required the addition of the surfactant CTAB (100 mg/L) to prevent precipitation. Next, the sensing part of the SPCE was immersed in the solution under magnetic stirring conditions among measurements.

2.5.1. Method validation

In the DPAdSV method, six calibration solutions were prepared in synthetic seawater, with concentrations ranging from 0.1 to 15 mg/L, for both BP3 and OC. In both cases, well-defined voltammetric peaks were obtained. Fig. S3 shows the DPAdS voltammograms of BP3 and its calibration plot, respectively. Good regressions were obtained with R^2 greater than 0.997 for both compounds. The mLOD was 0.1 and 1 mg/L for BP3 and OC, respectively.

3. Results and discussion

3.1. Characterization of PE pellets

Stereomicroscopy was used to verify the dimensions of the pellets supplied by the manufacturer. An image of one pellet obtained by the stereomicroscope is shown in Fig. 1a. It exhibits a rounded, nearly spherical morphology with slight irregularities. The surface appears smooth overall but contains noticeable striations that run across its exterior. The transparency and glossy appearance are consistent with the properties of PE materials. A recorded X-ray spectrum is shown in Fig. 1b. The primary peak, labelled "C," corresponds to carbon, which is consistent with the major elemental composition of PE, a polymer composed primarily of carbon and hydrogen ((C₂H₄)_n). Most of the signal is concentrated at low energy values near the carbon peak, with no significant additional peaks detected within the resolution of the analysis. This aligns with the expected composition of pure PE material. The diameter measurements revealed a relatively narrow distribution, as illustrated by the radar plot (Fig. 1c), with a diameter of 4.2 ± 0.3 mm. This characterization serves as a baseline for understanding the physical properties of the PE pellets, which is critical for evaluating their



Fig. 1. PE pellet structure (a), X-ray microanalysis of a PE pellet (b), 81 pellet diameter distribution (c), SEM image magnification of $250 \times$ (d), and SEM image magnification of $5500 \times$ (e).

response to UVFs exposure.

As shown in Fig. 1d and e, the surface of PE pellets observed in more detail with SEM shows a combination of rough and smooth regions, with cracks and fissures, likely caused by stress during fabrication, particularly due to the cutting of the pellets.

3.2. Sorption kinetics

Fig. 2 illustrates the kinetics of BP3 and OC sorption onto PE. The concentration decay over time was well captured by both PFOM and PSOM, with the latter providing a slightly closer match to the experimental data. Each data point represents the mean of three independent aliquot analyses.

The equilibrium sorption capacity was higher for OC compared to BP3 in both models, suggesting a stronger interaction of OC with PE. The superior performance of PSOM for both compounds imply a chemically controlled sorption mechanism dominated by hydrophobic interactions, consistent with the nature of the compounds and their affinity for the PE surface.

The adsorption kinetic analysis of BP3 and OC onto PE reveals that both PFOM and PSOM models provide good fits to the experimental data, evidenced by $R^2 \sim 1$ (Table 1). Correlation coefficients for PFOM $(R^2 = 0.963-0.933)$ were lower compared to those of PSOM $(R^2 =$ 0.989-0.947) under the experimental conditions. This suggests that PSOM better describes their adsorption kinetics. Furthermore, the equilibrium adsorption quantity of BP3 and OC calculated with PSOM was closer to the experimental value than with PFOM, confirming PSOM model's applicability. The calculated Q_{e} , (Table 1), align well with the observed data, while the rate constants $(k_1 \text{ and } k_2)$ fall within ranges typically observed for adsorption processes. Different adsorption behaviours have been reported in literature for pollutants onto PE. For instance, Xu et al. (2018) studied the sorption kinetics of sulfamethoxazole onto PE, reporting lower Q_e values (0.10 mg/g for PFOM and 0.11 mg/g for PSOM) and rate constants ($k_1 = 0.619 \ h^{-1}$ and $k_2 = 7.9$ g/(mg·h)) (Xu et al., 2018). Similarly, Guo et al. (2018) evaluated the sorption of tylosin onto PE, obtaining Q_e values of 0.32 mg/g (PFOM) and 0.67 mg/g (PSOM) with rate constants of 0.084 h^{-1} and 0.94 g/(mg·h) for k_1 and k_2 , respectively (Guo et al., 2018). In comparison,



Fig. 2. Experimental adsorption kinetics and model fits for BP3 and OC.

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Regression parameters of	sorption 1	kinetics of	BP3 and	OC on PE pellets.	
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Model	Compound	Parameters			
Pseudo-first-order Model (PFOM)		Q _{e,exp} (mg/g)	Q _{e,cal} (mg/g)	$k_1 (h^{-1})$	R ²
	BP3	0.89	$\begin{array}{c} \textbf{0.83} \pm \\ \textbf{0.03} \end{array}$	0.25 ± 0.04	0.963
	OC	2.03	$\begin{array}{c} 1.91 \pm \\ 0.09 \end{array}$	$\begin{array}{c} 0.33 \pm \\ 0.07 \end{array}$	0.933
Pseudo-second- order Model (PSOM)		Q _{e,exp} (mg/g)	Q _{e,cal} (mg/g)	k₂ (g∕ (mg·h))	<i>R</i> ²
	BP3	0.89	$\begin{array}{c} \textbf{0.89} \pm \\ \textbf{0.02} \end{array}$	$0.32~\pm$ 0.05	0.989
	OC	2.03	$\begin{array}{c} \textbf{2.01} \pm \\ \textbf{0.11} \end{array}$	$0.20~\pm$ 0.06	0.947

OC and BP3 exhibit significantly higher adsorption capacities onto PE, with OC reaching the highest Q_e .

Our findings suggest that PSOM is more suitable for describing the adsorption kinetics of BP3 and OC onto PE beads, although both models provide valuable insights into the adsorption behaviour of these contaminants. This indicates that hydrophobic interactions primarily drive their adsorption onto PE, with other interactions also playing a significant role.

3.3. Adsorption experiments

To ensure an adequate exposure time range for the CCD, a preliminary study was conducted in HPLC-grade water. Fig. 3 shows the adsorption dynamics of the two UVFs used. HPLC-MS/MS was applied in these analyses to quantify the UVFs concentrations. Each data point represents the mean of three independent aliquot analyses.

The concentration of BP3 and OC decreases over time, as expected, due to their adsorption onto the PE beads present in the solution. OC exhibited a sharper decline in concentration over the first 24 h, indicating faster initial adsorption, but it reached lower equilibrium levels, with its concentration continuing to decrease until nearly complete adsorption. The concentration of BP3 stabilizes after approximately 50 h, indicating that adsorption has reached equilibrium (Fig. 3). The difference in the adsorption dynamics of BP3 and OC can be attributed to their distinct physicochemical properties. Medium to high hydrophobic compounds (log $K_{ow} > 3.5$) like BP3 and OC tend to interact more strongly with hydrophobic and inert surfaces like PE, leading to a higher affinity for adsorption. OC has a very high octanol-water partition constant (log Kow of 6.88) indicating strong affinity for apolar environments. BP3, however, exhibits a much lower affinity (log Kow of 3.79) for the hydrophobic surface of PE compared to OC. This leads to a slower and less extensive adsorption process, resulting in BP3 reaching equilibrium but not being adsorbed totally onto the plastic. Therefore, we considered extending exposure time for OC in the CCD experimental runs (Table S2). These preliminary results also suggest that hydrophobic interactions are the primary mechanism driving the adsorption of both OC and BP3 onto PE.

3.3.1. CCD experimental model

The number of controlled experiments for each compound was 17. The ranges for each factor were selected according to general parameters found for seawater in the literature (Table S2), with temperature varying from 3 to 37 °C and pH from 5.3 to 8.7. Regarding exposure time and based on the previous adsorption study (Fig. 3), the time range selected was from 0 to 32 h for BP3 and from 0 to 64 h for OC. PE beads were exposed to BP3 and OC (15 mg/L) at a temperature of 20 °C with constant agitation at 350 rpm for 120 h, with samples collected at scheduled exposure times.



As shown in Table S5, exposure time was statistically significant for both BP3 and OC in HPLC water (p = 0.0002 and 0.001, respectively) and synthetic seawater (p = 0.002 for both analytes) at the 95 % confidence level. Temperature was only significant for BP3 in synthetic seawater (p = 0.04). Concerning second order factors, no interaction between two factors resulted significant, meaning the combined influence of factors is not substantial.

To support the given data, Pareto charts and main effect plots of BP3 and OC are displayed in Fig. 4, clearly indicating that exposure time is the most significant factor for the adsorption of both UVFs onto the PE in HPLC water. It exhibits a negative effect since the concentration of the exposition solution decreases as time increases. Both temperature and pH had no significant influence in the adsorption dynamics in HPLC water medium. It is worth noting that temperature had a slightly negative effect on the adsorption process for OC, meaning that as temperature increases, the concentration of the exposure solution decreases as the UVF is being adsorbed onto the PE particles. In contrast, the opposite effect was observed for BP3. However, this difference is minimal, as the variations in the main effects plots are very small. Concerning second order factors, no interaction among the factors resulted significant.

Focusing on the main effects plots and Pareto charts, it is clear that exposure time is the most significant variable, exhibiting a very steep response in concentration over time. This is consistent with the adsorption kinetics, where the rate of adsorption is influenced by the concentration gradient between the adsorbate and the adsorbent. For BP3 in pure water, pH did not have a significant influence, whereas lower temperatures resulted in higher adsorption. For OC, pH is more significant compared to temperature. At low pH levels, there is less concentration of OC in the solution, indicating that more OC is being adsorbed onto the PE. Meanwhile, temperature has a slight effect; as the temperature increases, more OC is adsorbed onto the PE. Surface response plots, shows that as time increases both BP3 and OC are adsorbed.

The statistical results obtained in synthetic seawater medium represented in Fig. 5 shows that exposure time remains the most significant factor, as expected. However, it is notable that temperature also plays a significant role in this case. In Table S5 we can observe that temperature statistically influences the adsorption of BP3 (F = 5.5, p = 0.04), whereas its effect on OC adsorption is statistically not significant (F =3.0, p = 0.1). This disparity can be attributed to the distinct physicochemical properties of BP3 and OC, which govern their interactions with PE and their behaviour in aqueous environments. OC's adsorption appears less sensitive to temperature variations, possibly due to its hydrophobic nature and the dominance of van der Waals interactions, which are relatively unaffected by temperature changes. Additionally, the complex ionic composition of synthetic seawater can influence adsorption dynamics. Ions present in the medium may interact with BP3 and OC differently, altering their availability and affinity for the PE surface.

3.3.2. Determination of BP3 and OC by DPAdSV

BP3 and OC concentrations derived from the voltammetry analysis ranged from 2.46 to 9.34 mg/L, and from 0.48 to 15.21 mg/L, respectively. These findings were consistent with the expected outcomes based on the experimental design and also validated the effectiveness of the CCD approach in determining UVF levels in synthetic seawater. Voltammograms of BP3 and OC in synthetic seawater are shown in Fig. S4.

Electrochemical analysis provided concentration values similar to HPLC-MS/MS, though slightly lower (Fig. S5), since sensitivity and specificity of HPLC-MS/MS often exceed those of electrochemical methods. DPAdSV, while highly reproducible and linear, may slightly underestimate concentrations due to adsorption losses or incomplete electrochemical reactions at the electrode's surface. Despite these, the strong correlation between both methods confirms DPAdSV (Table S6) as a reliable complementary screening technique for BP3 and OC



Fig. 4. Pareto charts, main effects, and surface response plots for BP3 (a) and OC (b) in HPLC water. (+ and – indicate whether the given factor has a positive or negative effect, where a positive effect means the response increases as the factor variable increases, and a negative effect means the response decreases as the factor variable increases; the red line represents the significance threshold with a 95 % confidence level). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

determination at relatively high concentrations. Its rapid, straightforward nature allows fast, real-time UVFs monitoring. The ability to quickly and accurately assess their levels without the need for extensive sample preparation or complex instrumentation makes it a valuable tool for environmental monitoring and iterative adjustments in experimental protocols. This advantage is particularly beneficial in dynamic environments where timely data acquisition is critical for decision-making and process optimization.

3.4. Physicochemical properties of BP3, OC, and PE and their role in adsorption

The physicochemical properties of organic compounds are among the main factors that influence their adsorption onto MPs. These properties include molecular size and shape, hydrophobicity (log K_{ow}), polarity, solubility, functional groups, ionization (pK_a), and specific interactions such as π - π and van der Waals forces (Menéndez-Pedriza and Jaumot, 2020). Additionally, MPs characteristics, such as surface area, porosity, degree of crystallinity, and chemical composition, play an important role.

Plastics are predominantly semicrystalline polymers, consisting of both crystalline and amorphous regions. PE is semicrystalline, with high-density PE being more crystalline (70–80 %), making it more rigid and less permeable, whereas low-density PE is less crystalline (40–50 %), providing greater flexibility and transparency. Hydrophobic contaminants preferentially adsorb onto amorphous regions due to the greater free volume among polymer chains (Hartmann et al., 2017; Martín et al., 2022).

Significant differences were observed in the adsorption behaviour of BP3 onto PE pellets between experiments using synthetic seawater and HPLC grade water. These differences can be attributed to variation in water chemistry, particularly ionic strength of the medium. In synthetic seawater, BP3 interacts via hydrophobic, electrostatic, and hydrogen bonding interactions, which are sensitive to changes in pH and



Fig. 5. Pareto chart and main effects plot for BP3 (a) and OC (b) in synthetic seawater.

temperature. The solubility in water of BP3 and the ionization of salts present in the medium vary with these factors, affecting its availability for adsorption. In this medium, BP3 can interact with ions in the solution, with pH influencing the charge of ionic species and temperature affecting solubility and molecular dynamics (atomic interactions).

3.4.1. Hydrophobic interactions

PE is a non-polar and hydrophobic polymer with a high affinity for organic contaminants. Its rubbery nature, combined with its flexibility and mobility, enhances diffusivity by increasing free volume, thereby facilitating the absorption of organic contaminants (Menéndez-Pedriza and Jaumot, 2020). The C-C and C-H covalent bonds in PE confer high structural and chemical resistance. Since it is a saturated hydrocarbon polymer lacking functional groups, it promotes the sorption of hydrophobic organic contaminants (Atugoda et al., 2021; Wang et al., 2015). On a molecular level, the adsorption of BP3 and OC onto PE surfaces is primarily governed by hydrophobic ($3.5 \le \log K_{ow} \le 5$), while OC (log $K_{ow} = 6.88$) is strongly hydrophobic (Kapelewska et al., 2021). In fact, many studies find a linear relationship between a contaminant's log K_{ow} and its sorption affinity for PE, indicating partition-like adsorption dominated by hydrophobic forces (Cui et al., 2023).

3.4.2. $\pi - \pi$ interactions

BP3, characterized by two benzene rings and a moderate hydrophobicity, is likely to interact with PE surfaces primarily through hydrophobic partitioning into the non-polar domains of the polymer (Wang et al., 2020). π – π stacking interactions driven by the overlap of aromatic π -electron clouds are a common mechanism for the adsorption of aromatic compounds. Both BP3 and OC contain aromatic rings, which could theoretically engage in π – π interactions if the surface also has aromatic character. However, pristine PE lacks aromatic moieties, making direct π – π stacking with the polymer unlikely. In contrast, aromatic polymers such as polystyrene, which possess aromatic phenyl groups, has been shown to adsorb aromatic pollutants more effectively via π – π interactions (Chen et al., 2023; Hüffer and Hofmann, 2016). In our case, while π – π interactions are expected to be negligible, it is possible that under real environmental conditions, surface associated

aromatic additives or surface attached contaminants could facilitate this kind of interaction. Additionally, weak self-association of BP3 or OC via π - π interactions in a surface layer cannot be ruled out entirely though it is likely a minor contribution compared to dominant hydrophobic dispersion forces.

3.4.3. van der Waals forces

van der Waals forces are likely to play a significant role in the stabilization of BP3 and OC adsorption onto PE surfaces. (Wang et al., 2020). The sorption of chemical contaminants onto aliphatic polymers such as PE and polyvinyl chloride (PVC) takes place through van der Waals forces (Hüffer and Hofmann, 2016; Torres et al., 2021). Pristine PE (assuming no surface oxidation or presence of additives), lacks polar functional groups, therefore does not readily participate in specific interactions such as hydrogen bonding or ionic interactions (Yari et al., 2024). OC with its high hydrophobicity, driven by its long aliphatic 2-ethylhexyl chain and low polarity, exhibits strong affinity for PE through hydrophobic partitioning and dispersion-type van der Waals forces (Osman et al., 2023). These interactions are expected to dominate the sorption behaviour of both BP3 and OC in the absence of surface modifications on the polymer.

3.4.4. Hydrogen bonding

BP3 contains functional groups capable of hydrogen bonding, including a phenolic hydroxyl group (H-bond donor) and carbonyl and ether oxygens (H-bond acceptors). However, PE, composed by chemically inert C–H chains, lacks functional groups capable of acting as hydrogen bond donors or acceptors groups. As a result, direct hydrogen bonding between BP3 and PE is not expected. In aqueous environments, it may form H-bonds with water molecules or other solutes at the waterpolymer interface, but these interactions do not contribute significantly to its retention on PE. In contrast, hydrogen bonding becomes highly relevant for polar polymers such as polyamide; where this mechanism can dominate sorption behaviour as observed on certain pharmaceuticals onto nylon (Osman et al., 2023). For OC, which lacks polar functional groups, hydrogen bonding is inherently irrelevant. Overall, in the case of pristine PE, hydrogen bonding is expected to play a minimal role in adsorption unless the surface is oxidized or coated with polar

substances.

3.4.5. Electrostatic interactions

The adsorption behaviour of BP3 and OC on PE surfaces in aquatic environments may also be modulated by pH-dependent electrostatic interactions. Although pristine PE is non polar, its surface can acquire a slight negative charge in natural waters, especially seawater, due to the adsorption of anions such as hydroxide or chloride (Osman et al., 2023). Nonetheless, electrostatic interactions are not expected to be a dominant mechanism under the environmental conditions tested, as both PE and the studied UVFs (BP3 and OC) are generally neutral across the typical aquatic pH range. BP3 remains neutral in its protonated form and electrostatic effects are minimal, but deprotonates at pH values equal or above 7, acquiring a negative charge. Under such alkaline conditions (towards the upper end of the environmental pH range, typically pH 5-9), BP3 is in its anionic form, with negative charge. This leads to electrostatic repulsion, reducing adsorption. OC, which lacks ionizable groups, remains neutral across environmental pH values, and given that PE surfaces do not carry positive charges, electrostatic attraction is not expected to contribute to OC sorption. While the overall contribution of electrostatics is likely minor, localized polarization effects or donor-acceptor interactions at the polymer interface cannot be entirely excluded.

3.5. Media characteristics and adsorption processes

3.5.1. Temperature

Temperature influences molecular kinetic energy, affecting adsorption dynamics. In HPLC grade water, BP3 adsorption is slightly higher at lower temperatures whereas at higher temperatures desorption can exceed adsorption. Bakir et al. (2014) demonstrated that increased temperatures weaken the binding of organic compounds to MPs, promoting desorption (Bakir et al., 2014). However, for OC, moderately high temperatures enhance molecular mobility, facilitating its adsorption onto PE. Furthermore, an increase in temperature typically enhances the water solubility of compounds. OC is significantly less soluble in water (log S = -7.18) compared to BP3 (log S = -3.37), which helps explain why OC does not readily desorb with rising temperatures, whereas BP3 exhibits slight desorption. In synthetic seawater, ionic strength further influences BP3 adsorption. Higher temperatures increase BP3's kinetic energy, reducing its affinity for PE by weakening the effective electric field between them. Additionally, ions in solution interfere with electrostatic interactions, further diminishing BP3's attachment to the polymer surface.

3.5.2. pH

In HPLC water, pH has little effect on BP3 and OC adsorption onto PE, likely because PE lacks ionizable functional groups. Therefore, its charge density remains unaffected by pH variations. Some UVFs form cationic species at low pH (Atugoda et al., 2021), enhancing their adsorption.

BP3 is a weak acid with a pK_a of 7.6. At higher pH values, BP3 deprotonates becoming more hydrophilic in its anionic form and less likely to adsorb onto the hydrophobic PE surface (Charaabi et al., 2019). However, OC is a highly lipophilic and neutral compound, lacking ionizable acidic protons or functional groups that accept protons, meaning its adsorption onto PE is primarily driven by hydrophobic interactions and van der Waals forces (Llorca et al., 2018).

In synthetic seawater, pH has a more pronounced, though not statistically significant, effect on BP3 adsorption compared to HPLC water. As shown in Fig. 5, at higher pH values (7–9), BP3 predominantly remains in the aqueous phase, due to its deprotonation. The resulting increase in polarity, combined with electrostatic repulsion from the negatively charged PE surface, leads to a significant reduction in adsorption In HPLC water, with very low ionic strength, pH has minimal influence. Hydrophobic interactions contribute to the high adsorption of BP3 across different pH levels (Kapelewska et al., 2021). As expected in this medium, OC's adsorption is barely affected by pH, since it is an apolar hydrophobic compound with low water solubility and no ionizable groups.

3.5.3. Exposure time

Exposure time is a key factor influencing the adsorption of the two UVFs onto PE. Longer contact times allow adsorption equilibrium to be reached, maximizing compound retention on the PE surface. In HPLC water, BP3 reaches equilibrium after 50 h of exposure, although not all BP3 in solution is adsorbed onto the PE surface. In contrast, nearly all OC is adsorbed onto the plastic.

3.5.4. Ionic strength

The presence of salts influences the adsorption behaviour of both BP3 and OC BP3 and OC adsorption (Brewer et al., 2021). At higher ionic strength, deprotonated BP3 becomes more soluble in water, reducing its affinity for PE and thus lowering its adsorption. In contrast, the salting-out effect, where high concentrations of dissolved salts decrease the solubility of hydrophobic compounds (Atugoda et al., 2021), enhances OC adsorption by promoting hydrophobic interactions (Gezahegn et al., 2019; Moringo et al., 2019). Indeed, the elevated ion concentrations typical of seawater have been shown to reduce the solubility of certain organic pollutants, thereby favoring their adsorption onto MP surfaces (Joo et al., 2021).

These experimental findings can be interpreted through theoretical frameworks such as the Debye–Hückel theory, which explains how increasing ionic strength compresses the electrical double layer surrounding charged species. In systems where electrostatic interactions play a role, this compression reduces long-range repulsive forces and can, in some contexts, enhance adsorption by enabling closer approach of ions or ionizable molecules to surfaces. However, in our study, at alkaline pH where BP3 exists predominantly in its deprotonated form and negatively charged (anionic), the increase in ionic strength does not enhance adsorption. Instead, it appears to diminish it, likely by weakening long-range electrostatic attractions and facilitating solubilization of BP3 in the aqueous phase.

Additionally, competitive adsorption effects may be relevant. Cations such as Na^+ , Ca^{2+} , and Mg^{2+} present in seawater could occupy potential binding sites or alter the surface charge properties of PE, indirectly affecting the adsorption behaviour of BP3. These mechanisms are especially relevant for BP3, whose adsorption is more sensitive to ionic strength variations compared to OC. In contrast, OC remains neutral and highly hydrophobic across the pH range studied. Its adsorption is enhanced under saline conditions due to the salting-out effect, which reduces its aqueous solubility and promotes partitioning into the hydrophobic PE matrix.

3.5.5. Environmental complexity and co-contaminants

Although this study evaluated UVFs adsorption onto PE under controlled conditions, natural aquatic environments are significantly more complex. MPs in environmental ecosystems co-exist with a matrix of dissolved organic matter (DOM), heavy metals, contaminants of emerging concern (CECs; ex. pharmaceuticals and pesticides) and POPs, all of which can alter their adsorption behaviour (Frère et al., 2016; Hermabessiere et al., 2017; Joo et al., 2021; Menéndez-Pedriza and Jaumot, 2020; Wang et al., 2020). Firstly, competitive adsorption may occur when multiple contaminants compete for the same adsorption sites on the plastic's surface, potentially reducing the adsorption capacity for UVFs. Secondly, surface fouling by DOM and other organics can change hydrophobicity, charge, and roughness, either blocking adsorption sites or promoting co-adsorption (Bhagwat et al., 2021; Gao et al., 2025). Finally, aging processes such as sunlight exposure, oxidation, and mechanical abrasion, modify the surface morphology and chemical functionality of MPs, increasing the number of polar functional groups available, which can enhance uptake of hydrophilic pollutants

and modify hydrophobic interactions (Fotopoulou and Karapanagioti, 2017; Liu et al., 2020).

Thus, while this study provides valuable insights into UVF-PE interactions under controlled salinity and environmental conditions, future research should investigate the combined effects of multiple pollutants and MP aging to better mimic environmental scenarios. Integrating these complexities would provide a more comprehensive understanding of the pollutant-MP interactions and the associated ecological risks. Additionally, while our experiments were conducted at higher UVF concentrations (15 mg/L) to enable robust kinetic modeling and analytical detection, we recognize that environmental concentrations are typically in the low μ g/L range. The mechanisms observed here—particularly hydrophobic partitioning and electrostatic modulation—remain relevant at trace levels, and predictive extrapolation models (e.g., log K_d and K_{ow}-based approaches) can help estimate behaviour at environmentally realistic concentrations.

4. Conclusions

The impact of MPs-UVFs adsorption differs between freshwater and marine ecosystems due to their distinct physicochemical properties. In marine environments, BP3 adsorption is affected by ionic strength, reducing its affinity for MPs, whereas OC, being highly hydrophobic, exhibits stronger adsorption in both fresh and marine waters. This increase in BP3 bioavailability has real-world implications, as marine organisms, including filter feeders such as mussels and corals, are directly impacted by these contaminants. OC, while adsorbed onto MPs, can still pose risks through ingestion by marine organisms, leading to indirect toxicity and pollutant transfer via trophic interactions. This distinction highlights the dual threats of UVFs in marine systems: BP3's immediate bioavailability and OC's potential for delayed toxicity through MP ingestion. The results also demonstrate the effectiveness of combining HPLC-MS/MS and DPAdSV for assessing UVF adsorption, providing both high sensitivity and field-deployable capability. Hydrophobic interactions were found to be the most relevant, while electrostatic and π - π interactions played a minimal role due to the chemical nature of both the UVFs and PE. Overall, this study contributes new insights into how UVF-polymer interactions vary across environmental conditions and emphasizes the importance of integrating salinity, pH, and temperature into MP pollution assessments.

CRediT authorship contribution statement

Albert Contreras–Llin: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization. Mariana Palape Oxa: Writing – original draft, Validation, Methodology, Investigation, Data curation. José Manuel Díaz-Cruz: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. Núria Serrano: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. M. Silvia Diaz-Cruz: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. M. Silvia Diaz-Cruz: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Acknowledgments

The authors acknowledge the financial support of the Generalitat de Catalunya (projects 2021 SGR 00753 and 2021 SGR 00006), the Spanish State Research Agency (AEI) through project PID2022-136709OB-C22, co-funded by the European Union NextGenerationEU/PRTR, and the

Ministry of Science, Innovation, and Universities through project PID2023-151815OB-I00.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2025.126468.

Data availability

Data will be made available on request.

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