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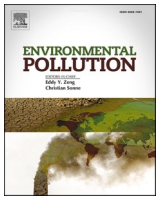

Mechanistic interpretation of the sorption of terbuthylazine pesticide onto aged microplastics☆

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ABSTRACT

Microplastics (MPs) pose a global concern due to their ubiquitous distribution. Once in the environment, they are subject to aging, which changes their chemical-physical properties and ability to interact with organic pollutants, such as pesticides. Therefore, this study investigated the interaction of the hydrophobic herbicide terbuthylazine (TBA), which is widely used in agriculture, with artificially aged polyethylene (PE) MP (PE-MP) to understand how aging affects its sorption. PE was aged by an accelerated weathering process including UV irradiation, hydrogen peroxide, and ultrasonic treatment, and aged particles were characterized in comparison to pristine particles. Sorption kinetics were performed for aged and pristine materials, while further sorption studies with aged PE-MP included determining environmental factors such as pH, temperature, and TBA concentration. Sorption of TBA was found to be significantly lower on aged PE-MP compared to pristine particles because aging led to the formation of oxygen-containing functional groups, resulting in a reduction in hydrophobicity and the formation of negatively charged sites on oxidized surfaces. For pristine PE-MP, sorption kinetics were best described by the pseudo-second-order model, while it was intra-particle diffusion for aged PE-MP as a result of crack and pore formation. Sorption followed a decreasing trend with increasing pH, while it became less favorable at higher temperatures. The isotherm data revealed a complex sorption process on altered, heterogeneous surfaces involving hydrophobic interactions, hydrogen bonding, and π-π interactions, and the process was best described by the Sips adsorption isotherm model. Desorption was found to be low, confirming a strong interaction. However, thermodynamic results imply that increased temperatures, such as those resulting from climate change, could promote the re-release of TBA from aged PE-MP into the environment. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) confirmed TBA sorption onto PE.

1. Introduction

Plastics, versatile and cost-effective, are extensively used worldwide (Andrady and Neal, 2009). In 2022, global plastic production reached 400.3 million tons (PlasticsEurope, 2023) and is estimated to further increase (MacLeod et al., 2021). The widespread use poses disposal challenges, leading to plastic distribution in various environments, such as oceans, lakes, and other water bodies, as well as in soils (Petersen and Hubbart, 2021). As plastics are non-biodegradable and persistent, their presence in the environment is of great concern (Rochman, 2018). Despite their persistence, larger plastic pieces can be weathered and broken down into smaller fragments called microplastics (MPs). MPs raise concerns due to their interactions with aquatic organisms (Ma et al., 2020), potential trophic transfer in aquatic food chains (Nelms et al., 2018), and adverse effects on soil organisms within terrestrial ecosystems (Ji et al., 2021). Their hydrophobic nature makes MPs prone to interact with organic pollutants (Ateia et al., 2020; Guo et al., 2012; Lara et al., 2021; Seidensticker et al., 2018; Zhao et al., 2020), acting as

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adsorbents that can influence the partitioning of contaminants in the environment. This could pose an additional risk to organisms, as pollutants sorbed to MPs may enhance toxicity when ingested (Ma et al., 2020; Wang et al., 2019). Therefore, understanding the interactions of MPs with organic pollutants is crucial for predicting the environmental impact of MPs.

Environmental MPs are not pristine; they are subject to chemical, physical, mechanical, and biological processes (Mosca Angelucci and Tomei, 2020) that cause complex long-term weathering effects and alter surface properties such as surface area (Zhang et al., 2018), crystallinity (Hu et al., 2020), surface charge (Al Harraq et al., 2022) and polarity (Bhagat et al., 2022). These factors are likely to affect sorption of organic contaminants (Liu et al., 2020). Oxidation by UV radiation is one of the main drivers of polymer surface degradation and leads to the introduction of oxygen-containing functional groups, which alter the surface properties (Feldman, 2002). For example, Campanale et al. (2023) detected the presence of oxygen-containing groups on aged MPs exposed to UV radiation in a natural freshwater body in Italy. Another study examined MPs from a total of 47 beaches worldwide and found changes in chemical and morphological properties compared to pristine MPs (Fotopoulou and Karapanagioti, 2012). Examination of experimentally weathered MPs over three years and long-term aged MPs from three Californian ocean sites also revealed major changes in chemical bond structures (Brandon et al., 2016). MPs found in the environment are therefore likely to be different from the MPs commonly used in laboratory studies, which are often pristine particles with uniform shapes and sizes (Ateia et al., 2020; Rubin et al., 2021). Thus, studies that establish laboratory conditions in a simple and rapid procedure to mimic the effects of natural weathering in order to better understand MPs fate in the environment, including the interaction with organic pollutants, are critical (Sun et al., 2020).

Triazines are a class of organic pollutants commonly found in the environment. Triazine herbicides (e.g., atrazine, terbuthylazine, simazine, propazine) are widely used pesticides due to their effectiveness in controlling a broad spectrum of weeds in agriculture. Their environmental relevance stems from their persistence in soil and high potential for leaching into water bodies (Diagboya et al., 2023b; Klementova and Keltnerova, 2015). In 2004, the European Union (EU) banned the use of atrazine, one of the most commonly detected pesticides in surface waters, because its heavy use resulted in high levels of surface and groundwater pollution (Metcalfe et al., 2022). Since then, the more hydrophobic terbuthylazine (TBA) has become the main alternative (Álvarez et al., 2016). As a result, TBA is one of the most frequently detected pesticides in groundwater and surface waters in some EU countries (Bottoni et al., 2013; Köck-Schulmeyer et al., 2014; Silva et al., 2015). Due to its persistence in natural waters (Navarro et al., 2004) and its toxicity to non-target organisms (EFSA, 2011), TBA is considered a pollutant of emerging concern (Tasca et al., 2018), and recent studies have confirmed its diverse ecotoxicity (Khatib et al., 2023; Li et al., 2023; Queirós et al., 2018). Therefore, research on the fate and transport of TBA in the environment is crucial to assess its long-term impact on ecosystems and water resources. Against the background of its hydrophobic properties and abundant MP distribution, the question arises whether the fate of TBA in the environment is also influenced by the presence of MPs.

Polyethylene (PE) was selected as a model substance for this study because it is one of the most commonly produced and abundant polymers in the environment (Hohenblum et al., 2015). Although a few studies to date have addressed the interaction between some triazines and various MPs (Ateia et al., 2020; Hüffer et al., 2019; Seidensticker et al., 2018; Wang et al., 2020; Zhao et al., 2020), only one of these examined the interactions between PE-MP and TBA (Wang et al., 2020). Thus, the objective of the present study was to investigate the sorption of TBA onto aged PE-MP from a surface chemistry perspective to provide a better understanding of the partitioning of TBA in an aqueous environment. To simulate environment-like weathering, the PE-MP particles were aged in a dual-UV light environment in the presence of hydrogen peroxide (H_2O_2) and ultrasonication. Further environmental parameters, including residual time, ambient pH and temperature, as well as TBA concentration, were considered. The sorption data were analyzed using various kinetics and equilibrium adsorption isotherm models. To the best of our knowledge, this is the first study to date that provides an in-depth mechanistic view of the interaction between TBA and aged PE-MP.

2. Material and methods

2.1. Materials, treatments, and characterization

All reagents employed for the study were analytical grade, and Milli-Q water was used. Low-density PE-MP powder (≤500 μm; CAS: 9002-88-4) with a density of 0.945 g/cm^3 and a melting point of 104–138 °C used for the experiments was purchased from Thermo-Fisher Scientific. TBA (purity ≥98%) was obtained from Sigma-Aldrich, and HPLC grade acetonitrile (ACN) was used throughout.

The plastic powder was sieved through a stainless steel 250 μm mesh size sieve to obtain particles ≤250 μm. These dimensions are based on their environmental significance in the low μm range (Bigalke et al., 2022; Uurasjärvi et al., 2020). To obtain weathered (aged) PE-MP, pristine PE-MP was placed in 30% H_2O_2, incubated for 5 d in a shaker at 150 rpm under dual wavelength (366 and 254 nm) UV lamp (220 V, 75 W UVA/C-bulbs) irradiation, and ultrasonicated for 24 h (Fig. S1), a modified protocol of Hüffer et al. (2018). Subsequently, the samples were dried at 30 °C for 72 h.

Pristine and aged PE-MP were characterized (see SI-1) in terms of chemical-physical properties using a scanning electron microscope (SEM, GeminiSEM 560 Zeiss, Germany) with an energy-dispersive X-ray probe (EDX). The Brunauer-Emmett-Teller (BET) specific surface area (SSA) was measured using a QUADRASORBevo analyzer (Quantachrome Instruments, USA), while changes in surface functionalities were observed using an attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, VERTEX70, Bruker Optics, Germany). Changes in crystallinity were recorded by obtaining the X-ray diffraction (XRD) patterns using an Empyrean spectrometer (Malvern Panalytical, Germany). The contact angle was measured on pristine and aged PE films (obtained from the same supplier) by the sessile water drop method using a drop shape analyzer (OCA20, Dataphysics, Germany), while the pH at the point of zero charge (pHpzc) was determined using the pH drift method (Al-Maliky et al., 2021; AttahDaniel et al., 2022).

2.2. Terbuthylazine sorption studies onto pristine and aged polyethylene microplastics

TBA stock solution (500,000 μg/L) stored at 4 °C was prepared in ACN/Milli-Q water (50/50%) for use throughout this study. Working solutions prepared as serial dilutions in 0.01 M $CaCl_2$ (background electrolyte) and 100,000 μg/L NaN_3 (biocide) were made from this stock. To avoid cosolvent effects, the ACN content in the working solutions was kept under 0.1%. Replicate TBA batch sorption studies were carried out using pristine and aged MPs. The experiments were conducted in amber glass vials with 20 mg of PE-MP and a 10 mL volume of the specified TBA working solution, resulting in a solid-to-liquid ratio of 1–500 (0.002 kg/L). The MP-TBA mixtures were incubated in an orbital shaker at 20 °C for a specified time at 200 rpm. The vials were withdrawn at equilibrium or a specific time and filtered through 1 μm syringe filters (glass fiber, MACHEREY-NAGEL, Germany) (other types of filters significantly adsorbed TBA), and the TBA concentrations in the filtrates were read on HPLC equipped with a diode array detector (DAD) (1200 Series, Agilent Technologies Inc., USA). Typically, the TBA concentrations employed in the study were set based on their solubility in water (Ronka, 2016) and the sensitivity of the analytical test method by ensuring a high signal-to-noise ratio (ICH, 2006). The TBA sorption rate

experiments were carried out over 48 h at varying times (1–2880 min) using a TBA concentration of 600 μg/L. The effect of TBA solution pH on sorption was examined at varying pH values (3–11) using 600 μg/L solution, while equilibrium experiments at varying TBA concentrations (100–500 μg/L) were carried out at three different ambient temperatures (20, 30, and 40 °C). These experiments were carried out at pH 6.5 ± 0.2 except for the pH effect experiment, where solution pH was adjusted with 0.2 M NaOH or HCl. The experimental vials were covered in aluminum foil and incubated in the dark to reduce possible losses from photochemical degradation. Preliminary studies without MPs were carried out to predict possible losses of TBA due to adsorption on the walls of the vials as well as volatilization according to OECD (2000). TBA sorption on the vials' walls and caps, as well as volatilization was found to be negligible. Background controls (blank runs) consisting of only MPs and background solution (without TBA) were included in each experiment to check for artifacts or matrix effects in the analytical method. The TBA sorption on PE was further investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) (M6 Plus ToF-SIMS instrument, IONTOF Company, Germany) (see SI-2). Detailed information about the ToF-SIMS technique can be found in Kern et al. (2023).

To ascertain desorption and hysteresis, a TBA desorption study was carried out after equilibrium sorption. This was implemented by carefully removing the solutions at equilibrium from the vials to avoid sorbent loss, refilling the vials containing the residual sorbents with the same background electrolyte/biocide above (without TBA), and incubating in an orbital shaker at 20 °C and 200 rpm as in the equilibrium study. The vials were withdrawn at the equilibrium time (24 h), filtered through 1.0 μm glass fiber syringe filters, and the TBA concentrations in the solutions were determined as above. Pristine and aged PE-MP were employed during the TBA sorption rate experiments, while only aged PE-MP (which is environmentally relevant) was used for the remaining experiments.

2.3. Chemical analysis

The HPLC system used for determining TBA concentrations was fitted with a column oven (G1316A), autosampler (G1329A), quaternary pump (G1311A), and DAD detector (G1315B). The instrument was operated at 35 °C with an injection volume of 40 μL and a flow rate of 0.3 mL/min. A wavelength of 223 nm and a 6 min run time were employed, while the retention time was ≈3.36 min. The mobile phase was 60:40 ACN (0.5% H_2O):H_2O (H_2O containing 10% ACN). To ensure integrity of the readings during determination, the column was cleaned using a 100% ACN gradient for 10 min after each set of samples and subsequently, the initial gradient was re-established within 20 min. The TBA calibration curve exhibited a linear range with $r^2 = 0.99$ using TBA concentrations between 75 and 2000 μg/L in 0.01 M $CaCl_2$ and 100,000 μg/L biocide (NaN_3).

2.4. Data analysis

The amount (μg/g) of TBA sorbed (q_e) onto the MP was evaluated from Eq. (1) where C_o, C_e, m, and v are the TBA concentrations (μg/L) at start and equilibrium, PE-MP mass (mg) and experimental solution volume (mL), respectively.

$$q_e = (C_0 - C_e)v / m \quad (1)$$

To investigate the controlling factors involved in TBA sorption on PE-MP, the sorption kinetics data were fitted to nonlinear pseudo-first-order (PSO), pseudo-second-order (PFO) and intra-particle diffusion (IPD) models. Equilibrium sorption data were fitted to the Freundlich and Langmuir isotherm models and a combined form of the two isotherms, the Sips model. The equations of these models are provided in Table S1.

The equilibrium sorption data were used to calculate the thermodynamic parameters (Diagboya et al., 2023a), namely, the equilibrium constant K_d (L/g) (Eq. (2)), enthalpy change: ΔH° (kJ/mol) (Eq. (3)), entropy change: ΔS° (J/mol/K) (Eq. (3)), and Gibbs free energy: ΔG° (kJ/mol) (Eq. (4)) where R is the universal gas constant and T is the temperature (K).

$$K_d = \frac{q_e}{C_e} \quad (2)$$

$$Ln\ K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

$$\Delta G^\circ = -RTLnK_d \quad (4)$$

Data were analyzed using the software OriginPro 2022 (OriginLab Corporation, Northampton, MA, USA.). The quality of curve fit for sorption kinetics and isotherm models was evaluated based on the coefficient of determination (r^2), chi-square (χ^2), and the Akaike's Information Criterion (AIC). The AIC can be used for non-nested models and takes into account the number of parameters of each model. In this case, the model with the lowest AIC value is most likely to be correct and provides a better fit (Motulsky and Christopoulos, 2004).

3. Results and discussion

3.1. Characterization of pristine and aged polyethylene microplastics

Photo-oxidation of MPs occurs when UV irradiation is absorbed. This leads to the dissociation of C–H bonds and the formation of free radicals (Feldman, 2002). Upon the formation of free radicals, hydro-peroxides result from reactions with oxygen (Al Harraq et al., 2022; Bhagat et al., 2022), which decompose to form oxygen-containing functional groups such as carbonyl (C═O), carboxyl (COOH) and hydroxyl (OH) groups associated mainly with aldehydes and ketones. The addition of H_2O_2 enhances this process, as its reaction with UV radiation provides an additional source of free radicals (Hüffer et al., 2018; Liu et al., 2019; Zha et al., 2022). These changes due to aging are usually observed in the FTIR spectrum at regions depicting oxygen-containing functionalities. A comparison of pristine and aged PE-MP (Fig. 1a) showed that the hydroxyl group was expressed between 3600 and 3000/cm, while the carbonyl group was observed around 1640/cm (Akpotu et al., 2022; Binda et al., 2023). These regions showed the formation of new characteristic peaks in aged PE-MP which were absent in pristine PE-MP. This stands in accordance with previous studies (Bhagat et al., 2022; Binda et al., 2023; Brandon et al., 2016; Campanale et al., 2023; Guo and Wang, 2019; Zvekic et al., 2022). The formation of hydroxyl groups was confirmed by the calculation of the hydroxyl index (H_i), which is the ratio between the detected absorbance in the 3600-3000/cm window and the absorbance of the CH_2 band at 1472/cm (Binda et al., 2023). This CH_2 band is characteristic of PE and remains mostly unaffected during the aging process (Fairbrother et al., 2019). The calculated H_i increased from 0.45 for pristine PE-MP to 3.38 for aged PE-MP, confirming the presence of hydroxyl. Similarly, the calculation of the carbonyl index (C_i), which is the ratio of the absorbance of the C═O and the reference absorbance for CH_2 at 1472/cm (Brandon et al., 2016; Mylläri et al., 2015) confirmed the presence of carbonyl group on the aged PE-MP; the C_i increased from 0.07 for pristine PE-MP to 0.25 for aged PE-MP. In addition to –OH and C═O peaks, a new peak was observed for C–O stretching around 1300/cm on the aged MPs (Fig. 1a), suggestive of the formation of esters (Binda et al., 2023). The presence of oxygen groups on aged PE spectra was also supported by SEM-EDX analysis (Fig. 1b) which showed a non-significant trend for an increase in oxygen content of 4.4 ± 0.9% on aged PE-MP compared to pristine PE-MP (3.7 ± 0.5%) when measurement was carried out on randomly selected regions of individual particles. Using a more liberal threshold ($p < 0.1$), the increase in oxygen content was significant.

One effect of the addition of oxygen groups to the PE surface is the noticeable decrease in surface hydrophobicity, which is caused by the

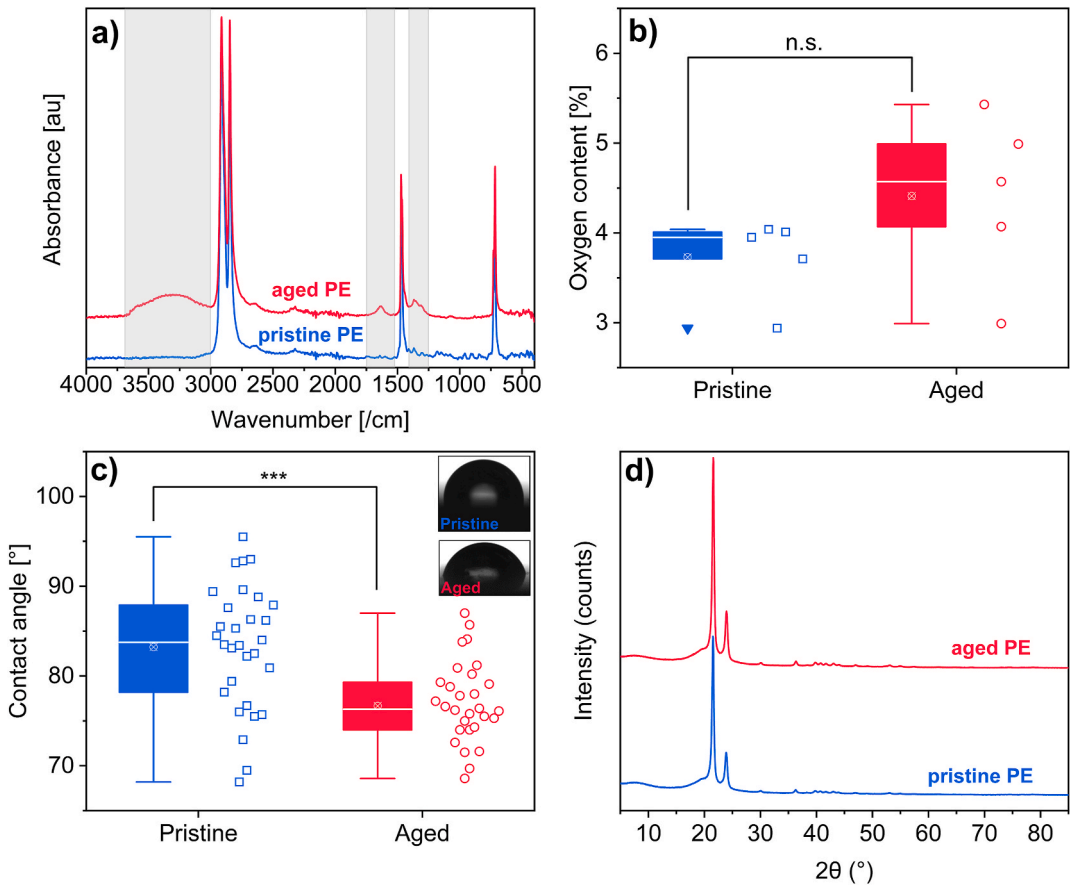

Fig. 1. Comparisons of the pristine and aged PE-MP (a) FTIR spectra; (b) SEM-EDX oxygen content; (c) contact angle, and (d) XRD pattern.

polar nature of attached oxygen-containing functional groups (Bhagat et al., 2022). The reduction in surface hydrophobicity can be determined by measuring the contact angle (Al Harraq et al., 2022; Binda et al., 2023; Lara et al., 2021). The measured contact angles (Fig. 1c) confirmed a significant ($p < 0.001$) reduction in hydrophobicity from $83.2 \pm 6.9°$ in the pristine PE to $76.7 \pm 5.1°$ in the aged PE, consistent with reports for aged polymers (Al Harraq et al., 2022; Binda et al., 2023; Liu et al., 2019; Salehi et al., 2018).

Aging by UV radiation promotes surface embrittlement, leading to changes in surface morphology (cracking and fractures) (Feldman, 2002), which could affect the MPs SSA. Examination of the SEM images for pristine and aged PE-MP showed particle types of both flakes and fibrous particles with irregular shapes (Figs. S2a and d). The individual particles showed heterogeneous surface texture for both pristine and aged samples (Figs. S2b and e) with small cracks on the surfaces (Figs. S2c and f). In contrast to pristine PE-MP, larger cracks and small holes were detected on the aged surfaces (Fig. S2f), which may reflect artificial aging. Similarly, Binda et al. (2023) reported formation of small holes on aged PE surfaces after artificial aging under UV irradiation and H_2O_2 treatment for 10 days, Hüffer et al. (2018) observed the formation of surface cracks under similar conditions for polystyrene MPs for 4 days.

Investigation of SSA by BET measurement showed slight differences between pristine (0.129 m^2/g) and aged (0.107 m^2/g) PE-MP. Although a slightly higher SSA of the aged PE-MP was expected based on the SEM results above, the results of this study showed an opposite trend, although the values were not significantly different. However, some authors have observed decreasing SSA after aging of PE, polypropylene (Bhagat et al., 2022), and polystyrene particles (Sarkar et al., 2021). Sarkar et al. (2021) attributed the lower SSA of UV-aged MPs to the formation of carbonyl groups, which may occupy available sites for krypton adsorption during BET measurement.

Photo-oxidation may alter the crystallinity of the polymer (Halle et al., 2017); thus, XRD, which is used to determine the degree of crystallinity of polymers, was employed to ascertain this. Crystalline regions appear in the XRD diffractogram as sharp diffraction lines, implying an ordered polymer chain (Lara et al., 2021). Low crystallinity or amorphous regions where atoms can move more freely (Tourinho et al., 2019) appear as noisy peaks. Such regions are oxidation-sensitive and may be affected by aging (Müller et al., 2018). Fig. 1d shows the XRD patterns of pristine and aged PE-MP. Characteristic diffraction peaks for PE were found at 2θ angles of 21.4° and 23.6°, indicating nearly identical crystallinity of 70.1% for pristine PE-MP and 69.4% for aged PE-MP, implying that the aging process did not cause any significant changes in crystallinity.

The data in Fig. 1a–c shows that the PE surface was altered by aging, implying that the surface charge could have been affected as well. The surface charge of an adsorbent is a function of the charge density around it, and it influences the adsorption performance (Akpotu et al., 2022; Diagboya et al., 2022). Hence, this was examined by determining the pHpzc, the pH at which the net charge of the adsorbent surface is zero. The pHpzc values for pristine and aged PE-MP were 7.3 and 6.9, respectively (Fig. S3). Interestingly, these values are similar to other studies that determined pHpzc for PE-MP in the range of 6 and 7 (Li et al., 2018; Wu et al., 2016) and show that aging of PE-MP results in a reduction of pHpzc, possibly facilitating the formation of negative charges on the MP surfaces (Fu et al., 2021).

3.2. Sorption studies on polyethylene microplastics

3.2.1. Preliminary sorption experiments onto pristine and aged polyethylene microplastics

Following characterizations, preliminary sorption experiments were carried out to ascertain the difference in TBA sorption between pristine and aged PE-MP. The experimental conditions were 20 mg mass of MPs each, 10 mL of 600 μg/L TBA solutions in 0.01 M $CaCl_2$ background electrolyte, 100,000 μg/L biocide, and incubation time of 1440 min in a shaker at 200 rpm. It was observed that pristine PE-MP exhibited ≈245% more TBA sorption than aged PE-MP ($p < 0.05$) (Fig. 2a). Reduced TBA sorption on aged MPs could be attributed to degradation and reduced hydrophobicity due to oxidation of the MP surfaces and presence of negatively charged sites resulting from formation of functional groups such as aldehydes, ketones and carboxylic acids (Al Harraq et al., 2022; Bhagat et al., 2022; Feldman, 2002; Tourinho et al., 2019). Photo-oxidation by UV light is one of the predominant degradation processes of polymers, which can increase the polarity of the surfaces (Tourinho et al., 2019) and reduce the attractiveness of the surfaces to non-polar organic compounds such as TBA. TBA molecules have low solubility and high affinity toward non-polar surfaces such as those of pristine MPs. Following this, the sorption of a positively charged substance on both the pristine and aged MPs would exhibit an opposite effect. Thus, Pb(II) sorption on both adsorbents was carried out in 10 mL of 5000 μg/L Pb(II) solution for 1440 min under incubation in a shaker at 200 rpm. Results (Fig. 2b) show that, unlike the TBA sorption data (Fig. 2a), the charged Pb(II) sorption followed the opposite trend; sorption on the aged MPs was significantly (≈300%) higher ($p < 0.01$) than for pristine PE-MP. Thus, sorption followed the assumption above and proved that the surfaces of PE-MP became more negatively charged (less hydrophobic) upon aging. This result suggests that cationic species such as Pb(II) are adsorbed mainly by electrostatic interactions, while non-polar organic species such as TBA are adsorbed mainly by hydrophobic interactions, which is in line with literature reports (Al Harraq et al., 2022; Beneš and Paulenová, 1973; Fu et al., 2021; Guo et al., 2018).

3.2.2. Terbuthylazine sorption rates onto pristine and aged polyethylene microplastics

The sorption rate trends of TBA pesticide on pristine and aged PE-MP are shown in Fig. 3a. It was observed that sorption of TBA on pristine PE-MP increased sharply in the early stages (180 min) and slowed down until sorption equilibrium was reached after 12 h (720 min). Compared to pristine PE-MP, aged PE-MP showed a small increase in TBA sorption over time but also reached sorption equilibrium after 12 h (720 min) (Fig. 3a). Accordingly, the sorbed amount of TBA at equilibrium (q_e) was 68.0 ± 3.3 μg/g for pristine PE-MP and 29.0 ± 3.7 μg/g for aged PE-MP (Table 1), thus accounting for a total sorption of 21.6% and 9.2%, respectively. The results are consistent with ToF-SIMS studies of the PE surfaces that are shown in Fig. S4. Pristine PE shows in contrast to aged PE the highest TBA surface concentration. The reasons for this difference in sorption are described above. The rate trend of high sorption, especially for pristine PE-MP, in the initial 720 min may be ascribed to the high affinity of TBA to numerous vacant non-polar or hydrophobic sites on the MP surfaces. After these sites were filled, the initial rapid rate slowed to almost equal sorption and desorption rates called equilibrium (Fig. 3a) (Olu-Owolabi et al., 2022).

To better understand the influencing factors involved in TBA sorption on PE-MP, the kinetic data were fitted by PFO, PSO, and IPD models. The curves of the kinetic models are presented in Fig. 3b and c, while the key model parameters are listed in Table 1. Evaluating model fits is usually assessed based on the following criteria: r^2 value closer unity, lowest χ^2, and AIC values, and sometimes the closeness of the calculated q_e value to the experimental q_e. PFO is usually employed to explain sorption processes that are fast and completed within a short time compared to the full duration of the process (Olu-Owolabi et al., 2018; Olu-Owolabi et al., 2022). This seemed to be the case for TBA sorption on pristine PE-MP, where the PFO described the experimental data in the early stage (Fig. 3b), but significantly deviated from it at equilibrium (12 h) ($r^2 = 0.91$). On the other hand, the fitting was poor for aged PE-MP throughout the data points (Fig. 3c–Table 1). Thus, PFO could not be used to describe the sorption processes on either MP.

A comparison of parameters from all three sorption models for pristine PE-MP showed that the PSO model fits the data best (Table 1) and may be used to explain the sorption process. The PSO model r^2 value is closer to unity (0.95) with the lowest χ^2 (26.5) and AIC (40.6) values, and the calculated q_e (69.5 μg/g) value is closer to the actual experimental q_e (68.0 μg/g) (Table 1). The good fit of the PSO model to experimental data of pristine PE-MP implies that the process was mainly dominated by sharing of π-π electrons via non-polar hydrophobic interactions (Olu-Owolabi et al., 2014, 2015); this was absent in aged MPs.

Comparing the same good fit parameters from the models for the sorption of TBA on aged PE-MP (Table 1) showed that the IPD model fits the data best and could explain the sorption process. The IPD model assumes that sorption is a multi-step process involving the transport of TBA from the solution to the external surface and then into the interior pores of the sorbent (Morris and Weber, 1964). The IPD model r^2 value is the highest (0.97) with the lowest χ^2 (0.98) and AIC (7.5) values. The calculated C (16.2 μg/g) value (equivalent to the MPs surface adsorbed TBA) was lower than the actual experimental q_e (29.0 μg/g) (Table 1), implying that the sorption process occurred both on aged MP surfaces (≈56%) and as within the pores (≈44%). This also buttresses the assumption that aging induced physical changes on the MP particles (as observed on the SEM images for aged PE-MP but not the pristine;

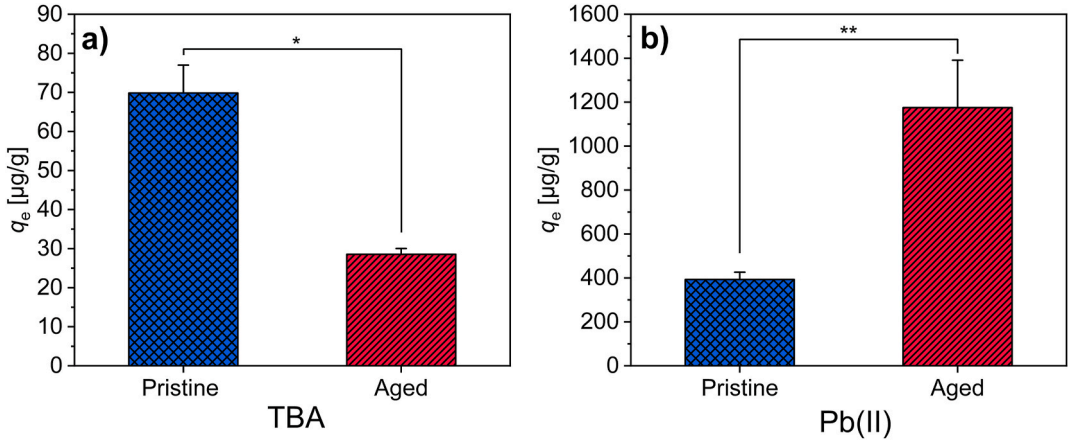

Fig. 2. Comparisons of preliminary sorption of (a) TBA and (b) Pb(II) of pristine and aged PE-MP.

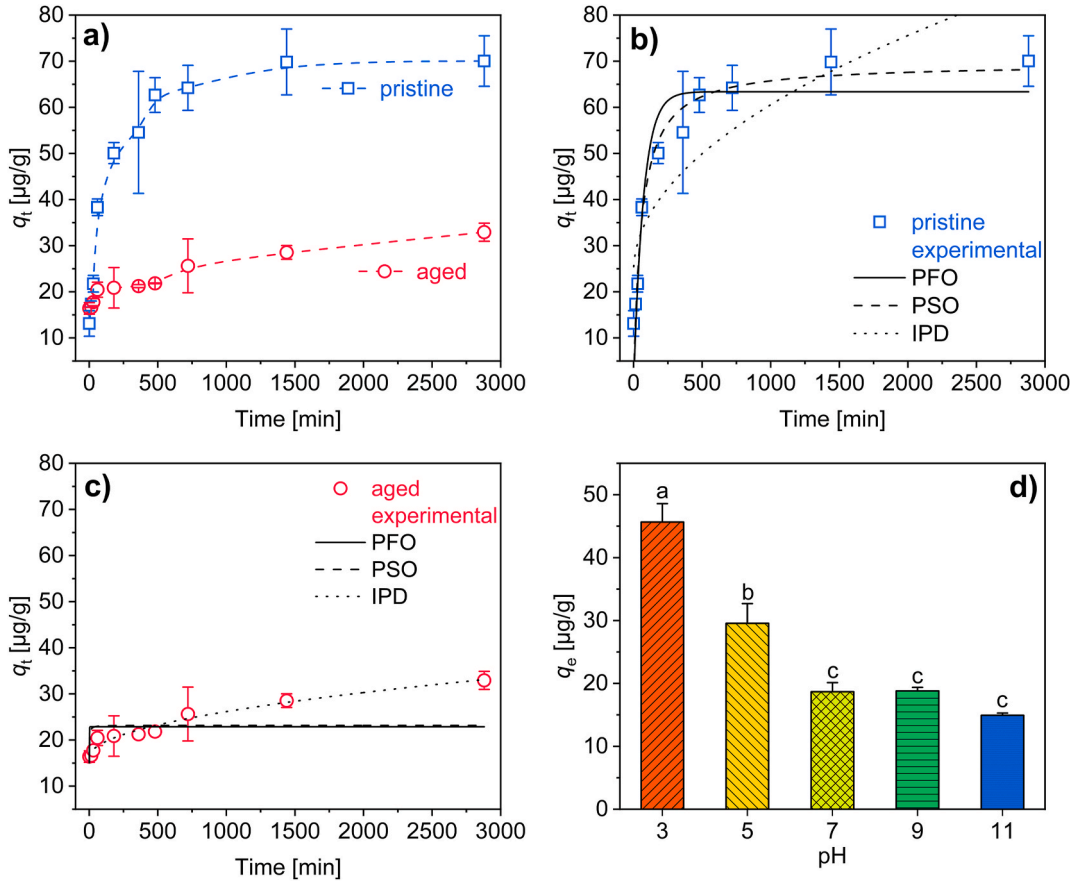

Fig. 3. (a) Sorption rate trends of TBA on pristine and aged PE-MP; kinetics modeling of the rate data for (b) pristine PE-MP, (c) aged PE-MP; (d) effect of pH on the sorption of TBA on aged PE-MP.

Table 1
Kinetics model parameters for pristine and aged PE-MP adsorption.

Model of kinetics	Parameter	Pristine PE-MP	Aged PE-MP
PFO	q_e (µg/g)	63.4	22.9
	k_1 (/min)	0.013	1.264
	r^2	0.91	0.15
	χ^2	51.1	27.5
	AIC	47.1	40.9
PSO	q_e (µg/g)	69.5	23.2
	k_2 (g/µg/min)	2.499×10^{-4}	0.080
	r^2	0.95	0.20
	χ^2	26.5	25.9
	AIC	40.6	40.3
IPD	*C* (µg/g)	24.33	16.23
	k_i (g/µgmin$^{1/2}$)	1.146	0.314
	r^2	0.75	0.97
	χ^2	134.9	0.98
	AIC	56.8	7.5
Experimental	q_e (µg/g)	68.0	29.0

Fig. S2), such as mechanical fragmentation and surface cracking, resulting in a more porous polymer surface that could allow for TBA sorption. The IPD plot (Fig. 3c) exhibited a multi-linear graph implying that the TBA sorption process occurred via a several-step mechanism (Akpotu et al., 2023). These include the fast transfer of TBA molecules from solution to the external surfaces of MPs (diffusion step) (within 60 min), followed by the slower diffusion of the molecules into the pores of the MPs (intra-particle diffusion step) which is the rate-limiting step, and finally, the equilibrium stage where the rate of molecules diffusing in and out of the polymer pores is balanced (Olu-Owolabi et al., 2021; Weber and Morris, 1963).

3.2.3. *Effect of pH on terbuthylazine sorption onto aged polyethylene microplastics*

Understanding the effect of solution pH on contaminant uptake is vital because pH is known to influence the extent of contaminant and adsorbent surface charge speciation, and thus the degree of adsorption (AttahDaniel et al., 2023). Hence, the effect of pH on the sorption of TBA on aged PE-MP was experimentally evaluated (Fig. 3d). The trend shows that the sorbed amount of TBA at equilibrium (q_e) decreased significantly ($p < 0.05$) as pH increased. Consequently, sorption was highest at pH 3 (45.7 µg/g) and decreased significantly ($p < 0.05$) toward pH 7 (18.7 µg/g). While the sorption between pH 7 (18.7 µg/g) and pH 9 (18.8 µg/g) did not differ significantly, a further reduction in sorption to 14.9 µg/g was observed at pH 11 (Fig. 3d).

The molecules of TBA, an ionisable compound, exhibit different chemical species (cations, anions, and zwitterions) depending on the ambient solution pH, and this can influence the sorption process by influencing the type(s) of interaction(s) involved (Zhao et al., 2020). Like all other triazines, TBA is a weak base with a logarithmic acid dissociation constant (pKA) of 1.9 (Ronka, 2016). The experimentally tested pH range (3–11) was above the pKA of TBA, suggesting that mainly neutral TBA species were present, and electrostatic interactions are likely to have little effect on the sorption process (Zhao et al., 2020). Nevertheless, a higher sorption efficiency was observed for TBA at a higher hydrogen ion concentration (lower pH) (Fig. 3d); thus, other types of interactions must have predominated, and this may be linked to the polymer surfaces. Recall that a comparison between TBA sorption on pristine and aged PE-MP (Fig. 2a) showed significantly higher sorption on pristine PE-MP, and this was attributed to the formation of more effective hydrophobic interactions on non-polar surfaces of pristine PE-MP by TBA molecules. On the other hand, due to oxidation of these

surfaces on aged PE-MP and formation of negatively charged sites (resulting from functional groups such as aldehydes, ketones and carboxylic acids) (Al Harraq et al., 2022; Feldman, 2002; Mylläri et al., 2015) the surfaces are polarized, and formation of hydrophobic interactions, and consequently, TBA adsorption is significantly reduced. However, for aged MPs, the non-polar surfaces almost similar to those of pristine MPs may be simulated by protonation (H^+) of the charged surfaces at lower solution pH values (AttahDaniel et al., 2022), and a more effective formation of hydrophobic interactions is re-established resulting in higher sorption observed at lower pH. As solution pH increases, the amount of H^+ and protonation gradually decreases, continuously re-initiating the charged surfaces and reducing the efficiency of hydrophobic interactions between MPs and uncharged TBA molecules.

A similar sorption trend has been reported by Ronka (2016) for TBA sorption on poly(divinylbenzene): This trend was attributed to the more effective formation of hydrogen bonds at lower pH between the hydroxyl hydrogen atom of the carboxyl group and the nitrogen of the terbuthylazine ring (O–H···N). It has also been suggested that the N-heteroaromatic ring of TBA serves as both a π-donor and π-acceptor (Keiluweit and Kleber, 2009) and is believed to interact with the negatively charged functional groups of aged PE-MP. Thus, hydrophobic interactions, hydrogen bonding, and π-π interactions are implicated in the overall sorption of TBA on aged PE-MP.

3.2.4. *Thermodynamics of terbuthylazine on sorption onto aged polyethylene microplastics*

TBA sorption trends on aged PE-MP at varying solution concentrations (100–500 μg/L) and temperatures (20–40 °C) are presented in Fig. 4a. The trends show enhanced TBA sorption at any temperature as concentration increased until a saturation point for aged PE-MP, which was attained at 300 μg/L. This enhanced TBA sorption until saturation can be ascribed to the transfer of TBA from the solution phase to aged PE-MP sorption sites as concentration increases. Once sorption site saturation is attained, further TBA uptake is not permissible and an increase in concentration leads to no further sorption. On the other hand, an increase in temperature from 20 to 40 °C showed a reduction in sorption of TBA (Fig. 4a). For low solubility organic compounds such as TBA, the reduced sorption has been attributed to enhanced solubility at higher temperatures and a subsequent increase in kinetics; thus, TBA films at the MP sorption sites re-dissolve into solution, ultimately leading to lower sorption (Olu-Owolabi et al., 2014).

To obtain more information about the sorption behavior, a desorption/hysteresis study of TBA from aged PE-MP was investigated at 20 °C. Fig. 4b shows the TBA sorption and desorption at 20 °C, as well as the undesorbed TBA (sorption minus desorption) remaining on the aged MPs (all in μg/g). The figure illustrates that only a small fraction of TBA was desorbed, with an average of 2.9 (±1.2) μg/g (≈15.6%) throughout the concentration range; thus, hysteresis was high. This suggests that TBA is strongly sorbed onto the aged MPs surfaces and crevices, and re-release into the environment (e.g., water bodies, soil) is unlikely. Moreover, ToF-SIMS depth profiles shown in Fig. S5 suggest that the TBA is incorporated in the near surface region of the PE, which would hamper the release rate and contribute to the observed hysteresis. The incorporation of chemicals into polypropylene is reported, for example, by Kern et al. (2020).

The results also suggest that at higher ambient temperatures, TBA could be partly desorbed due to the increased solubility, resulting in TBA release from aged PE-MP into the environment. Reduced sorption at higher temperature (Fig. 4a) is suggestive of an exothermic process. This was examined by calculating the thermodynamic parameters (Table 2). The ΔH° value was negative, implying and confirming the experimentally observed exothermic sorption of TBA. The magnitude of ΔH° obtained in this study (−8.19 kJ/mol) was in the size range associated with weak forces of interaction(s) (Olu-Owolabi et al., 2014), such as those between hydrophobic organic compounds and non-polar surfaces, π-π interactions, and other Van der Waals interactions. The ΔS° value (−49.08 J/mol/K) was also negative (Table 2), suggesting a decreased disorderliness of TBA molecules on the aged MP-solution interface as the TBA sorption proceeded toward equilibrium. This was ascribed to the ordered assembling of TBA molecules on the MP surface. The ΔG° value indicates the spontaneity of the sorption process; when the value is negative, it implies a spontaneous process. Low positive values imply that the sorption may require additional energy input to enhance the process. However, in this case, an increase in energy, in the form of temperature, increased kinetic energy, resulting in higher TBA solubility, and lowered sorption from the solution. The increasing trend in the values of ΔG° (Table 2) with increasing temperature suggests that sorption became less favorable at higher temperatures. Clearly distinguishing sorption processes that are on the borderline of spontaneity is difficult because inherent errors associated with the linear model thermodynamic parameters calculations may become significant when dealing with low energy surfaces, thus, shifting low negative values to positive values (Unuabonah et al., 2008).

Table 2
Sorption thermodynamic parameters for aged PE-MP.

Temperature	ΔG° (kJ/mol)	ΔH°(kJ/mol)	ΔS° (J/mol/K)
293.15K (20 °C)	6.20	−8.19	−49.08
303.15K (30 °C)	6.67		
313.15K (40 °C)	7.18		

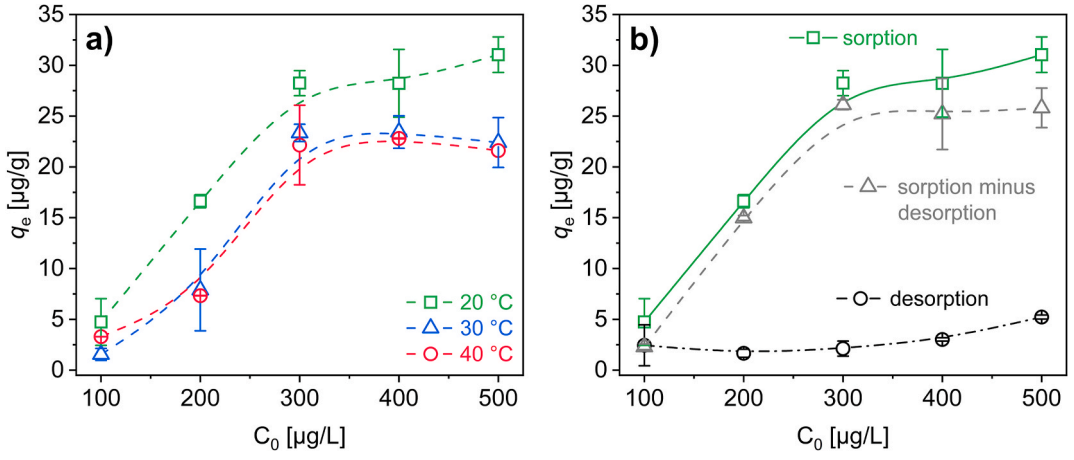

Fig. 4. (a) Effect of temperature (20–40 °C) on the sorption of TBA on aged PE-MP; (b) comparison of TBA sorption and desorption at 20 °C.

3.2.5. Adsorption isotherms at varying temperatures

The adsorption isotherm models described by Freundlich, Langmuir and Sips at varying temperatures are presented in Figs. S6a–c (see SI-3), while the fitting parameters are listed in Table 3. The Langmuir model describes monolayer adsorption onto adsorbents with homogeneous adsorption surfaces having equal affinity for the adsorbates, while the Freundlich model describes the sorption of adsorbates on heterogeneous adsorbent surfaces with dissimilar affinity for the adsorbents and the possibility of multi-layer adsorption occurring (Diagboya et al., 2021; Olu-Owolabi et al., 2022). On the other hand, the Sips model is a combination of both models yielding a more complex system, which is a more realistic description of most sorption processes on heterogeneous surfaces (Foo and Hameed, 2010).

Similar to the kinetics fittings above, a good fit is predicated on the r^2 value closer to unity, the lowest χ^2 and AIC values, and closeness of calculated q_e value to the experimental q_e. Comparing these parameters in Table 3 and it was observed that both the Langmuir and Freundlich models did not fit the experimental data at any temperature due to their poor r^2 values ($\leq$0.88) and high χ^2 ($\geq$19.7) and AIC ($\geq$45.3) values compared to the Sips model, which had r^2, χ^2, and AIC values $\geq$ 0.97, $\leq$5.8, and $\leq$24.6, respectively. This suggests complex sorption interactions on heterogeneous binding surfaces possibly comprising hydrophobic interactions on non-polar surfaces, hydrogen bonding on hydroxyl groups, π-π interactions, and possibly pore filling within the cracked surfaces resulting from the MPs aging process.

The Freundlich non-linear constant $1/n$ indicates the degree of favorability for the interaction between the sorbent and a pollutant (Tseng and Wu, 2008): when the value is $0.01 < 1/n < 0.1$, it indicates strongly favorable sorption; for values between $0.1 < 1/n < 0.5$, it indicates favorable sorption, while $1/n > 1$ points to unfavorable sorption. A 1/n value between 0.5 and 1 implies a pseudo-linear sorption process (Tseng and Wu, 2008). According to the Sips model, the $1/n$ value at 20 °C suggested a favorable process (0.26), while it suggested strongly favorable processes at 30 °C and 40 °C with values of 0.01 and 0.04, respectively (Table 3). In addition, values less than 1 suggest that the sorption process occurred on heterogeneous surfaces (Foo and Hameed, 2010).

3.2.6. Limitations and perspectives

While this study contributes to the understanding of the complex interaction between MPs and organic pollutants in an aqueous medium, considering several environmentally significant factors such as pH, temperature and pollutant concentration, it is essential to note that under real conditions additional parameters (such as natural dissolved and particulate organic matter, salinity, complex formation, pollutant competition) can influence sorption. Therefore, future studies should perform experiments in multi-solute systems to investigate the impact of these factors on the interaction between PE-MP and TBA. Since MP pollution in the soil environment is critical (Xu et al., 2019), there are already efforts underway to investigate the sorption of pollutants in MP-contaminated soils (Castan et al., 2021; Li et al., 2021; Šunta et al., 2020). As TBA remains present in soils (Silva et al., 2019), future studies should address this issue.

4. Conclusion

Sorption of TBA onto pristine and artificially aged PE-MP was investigated under simulated environmental conditions. Comparative characterization showed that artificial aging is associated with chemical and morphological changes to the polymer, which are comparable to natural weathering. The aging process resulted in increased polarity and decreased hydrophobicity and affected the sorption behavior of the particles for the hydrophobic pesticide TBA, thus leading to significantly less sorption on aged PE compared to pristine PE. Analysis of the sorption data revealed complex interactions for TBA sorption comprising hydrophobic interactions, hydrogen bonding, π-π interactions, and pore filling. Hysteresis was high for aged MPs with low desorption. However, data suggest that at higher temperatures (such as may be associated with global warming), sorbed TBA on the MPs could be re-mobilized into the environment. This study provides a valuable contribution to the interactions between TBA and PE-MP, which is one of the most commonly used plastics worldwide.

Table 3
Adsorption isotherm model parameters for TBA sorption on aged PE-MP.

Adsorption isotherm model	Parameter	20 °C	30 °C	40 °C
Freundlich	K_F(L/g)	0.08	0.01	0.02
	$1/n$	0.99	1.26	1.19
	r^2	0.87	0.78	0.79
	χ^2	20.3	31.8	24.7
	AIC	45.7	52.4	48.6
Langmuir	K_L (L/μg)	2.9×10^{-4}	2.2×10^{-7}	1.3×10^{-6}
	q_{max} (μg/g)	285.1	239326	41015
	r^2	0.88	0.75	0.77
	χ^2	19.7	35.0	26.3
	AIC	45.3	53.8	49.6
Sips	q_{max} (μg/g)	32.3	23.1	22.2
	$1/n$	0.26	0.01	0.04
	K_S (L/μg)	0.005	0.004	0.004
	r^2	0.98	0.99	0.97
	χ^2	4.9	1.5	5.8
	AIC	22.1	4.7	24.6

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CRediT authorship contribution statement

Johannes Junck: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Paul N. Diagboya:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Aleksander Peqini:** Writing – review & editing, Validation, Investigation, Formal analysis. **Marcus Rohnke:** Formal analysis, Investigation, Methodology, Validation, Writing – review & editing. **Rolf-Alexander Düring:** Writing – review & editing, Supervision, Resources, Project administration, 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

Akpotu, S.O., Diagboya, P.N., Lawal, I.A., Sanni, S.O., Pholosi, A., Peleyeju, M.G., Mtunzi, F.M., Ofomaja, A.E., 2023. Designer composite of montmorillonite-reduced graphene oxide-PEG polymer for water treatment: Enrofloxacin sequestration and cost analysis. Chem. Eng. J. 453, 139771.

Akpotu, S.O., Lawal, I.A., Diagboya, P.N., Mtunzi, F.M., Ofomaja, A.E., 2022. Engineered Geomedia Kaolin clay-reduced graphene oxide-polymer composite for the Remediation of Olaquindox from water. ACS Omega 7 (38), 34054–34065.

Al Harraq, A., Brahana, P.J., Arcemont, O., Zhang, D., Valsaraj, K.T., Bharti, B., 2022. Effects of weathering on microplastic Dispersibility and pollutant uptake Capacity. ACS environmental Au 2 (6), 549–555.

Al-Maliky, E.A., Gzar, H.A., Al-Azawy, M.G., 2021. Determination of point of zero charge (PZC) of Concrete particles adsorbents. IOP Conf. Ser. Mater. Sci. Eng. 1184 (1), 12004.

Álvarez, P.M., Quiñones, D.H., Terrones, I., Rey, A., Beltrán, F.J., 2016. Insights into the removal of terbuthylazine from aqueous solution by several treatment methods. Water Res. 98, 334–343.

Andrady, A.L., Neal, M.A., 2009. Applications and societal benefits of plastics. Philosophical transactions of the Royal Society of London. Series B, Biological sciences 364 (1526), 1977–1984.

Ateia, M., Zheng, T., Calace, S., Tharayil, N., Pilla, S., Karanfil, T., 2020. Sorption behavior of real microplastics (MPs): insights for organic micropollutants adsorption on a large set of well-characterized MPs. Sci. Total Environ. 720, 137634.

AttahDaniel, E.B., Dikio, E.D., Ayawei, N., Wankasi, D., Mtunzi, F.M., Diagboya, P.N., 2023. Adsorption investigation of a composite of metal-organic framework and polyethylene oxide hydrogel. Proc. Inst. Mech. Eng., Part N: Journal of Nanomaterials, Nanoengineering and Nanosystems.

AttahDaniel, E.B., Mtunzi, F.M., Wankasi, D., Ayawei, N., Dikio, E.D., Diagboya, P.N., 2022. Relative empirical evaluation of the aqueous sequestration of Methylene Blue using Benzene-1,4-dicarboxylic acid-linked Lanthanum and Zinc metal organic Frameworks. Water Air Soil Pollut. 233 (11).

Beneš, P., Paulenová, M., 1973. Surface charge and adsorption properties of polyethylene in aqueous solutions of inorganic electrolytes. Kolloid-Z.u.Z.Polymere 251 (10), 766–771.

Bhagat, K., Barrios, A.C., Rajwade, K., Kumar, A., Oswald, J., Apul, O., Perreault, F., 2022. Aging of microplastics increases their adsorption affinity towards organic contaminants. Chemosphere 298, 134238.

Bigalke, M., Fieber, M., Foetisch, A., Reynes, J., Tollan, P., 2022. Microplastics in agricultural drainage water: a link between terrestrial and aquatic microplastic pollution. Sci. Total Environ. 806 (Pt 4), 150709.

Binda, G., Zanetti, G., Bellasi, A., Spanu, D., Boldrocchi, G., Bettinetti, R., Pozzi, A., Nizzetto, L., 2023. Physicochemical and biological ageing processes of (micro) plastics in the environment: a multi-tiered study on polyethylene. Environ. Sci. Pollut. Res. Int. 30 (3), 6298–6312.

Bottoni, P., Grenni, P., Lucentini, L., Caracciolo, A.B., 2013. Terbuthylazine and other triazines in Italian water resources. Microchem. J. 107, 136–142.

Brandon, J., Goldstein, M., Ohman, M.D., 2016. Long-term aging and degradation of microplastic particles: Comparing in situ oceanic and experimental weathering patterns. Mar. Pollut. Bull. 110 (1), 299–308.

Campanale, C., Savino, I., Massarelli, C., Uricchio, V.F., 2023. Fourier transform infrared spectroscopy to assess the degree of alteration of artificially aged and environmentally weathered microplastics. Polymers 15 (4).

Castan, S., Henkel, C., Hüffer, T., Hofmann, T., 2021. Microplastics and nanoplastics barely enhance contaminant mobility in agricultural soils. Commun Earth Environ 2 (1).

Diagboya, P.N., Heyde, B.J., Düring, R.-A., 2023a. Efficient decontamination of aqueous glyphosate using Santa Barbara Amorphous-15 (SBA-15) and graphene oxide-SBA-15 poly-amidoamine functionalized composites. Chem. Eng. J. 466, 143263.

Diagboya, P.N., Junck, J., Akpotu, S.O., Düring, R.-A., 2023b. Isolation of aqueous pesticides on surface-functionalized SBA-15: glyphosate kinetics and detailed empirical insights for atrazine. Environmental science. Processes & impacts.

Diagboya, P.N., Mtunzi, F.M., Adebowale, K.O., Düring, R.-A., Olu-Owolabi, B.I., 2022. Comparative empirical evaluation of the aqueous adsorptive sequestration potential of low-cost feldspar-biochar composites for ivermectin. Colloids Surf. A Physicochem. Eng. Asp. 634, 127930.

Diagboya, P.N., Mtunzi, F.M., Düring, R.-A., Olu-Owolabi, B.I., 2021. Empirical assessment and reusability of an eco-friendly Amine-functionalized SBA-15 adsorbent for aqueous ivermectin. Ind. Eng. Chem. Res. 60 (6), 2365–2373.

EFSA, 2011. Conclusion on the peer review of the pesticide risk assessment of the active substance terbuthylazine. EFSA J. 9 (1).

Fairbrother, A., Hsueh, H.-C., Kim, J.H., Jacobs, D., Perry, L., Goodwin, D., White, C., Watson, S., Sung, L.-P., 2019. Temperature and light intensity effects on photodegradation of high-density polyethylene. Polym. Degrad. Stabil. 165, 153–160.

Feldman, D., 2002. Polymer weathering: Photo-oxidation. J. Polym. Environ. 10 (4), 163–173.

Foo, K.Y., Hameed, B.H., 2010. Insights into the modeling of adsorption isotherm systems. Chem. Eng. J. 156 (1), 2–10.

Fotopoulou, K.N., Karapanagioti, H.K., 2012. Surface properties of beached plastic pellets. Mar. Environ. Res. 81, 70–77.

Fu, Q., Tan, X., Ye, S., Ma, L., Gu, Y., Zhang, P., Chen, Q., Yang, Y., Tang, Y., 2021. Mechanism analysis of heavy metal lead captured by natural-aged microplastics. Chemosphere 270, 128624.

Guo, X., Pang, J., Chen, S., Jia, H., 2018. Sorption properties of tylosin on four different microplastics. Chemosphere 209, 240–245.

Guo, X., Wang, J., 2019. Sorption of antibiotics onto aged microplastics in freshwater and seawater. Mar. Pollut. Bull. 149, 110511.

Guo, X., Wang, X., Zhou, X., Kong, X., Tao, S., Xing, B., 2012. Sorption of four hydrophobic organic compounds by three chemically distinct polymers: role of chemical and physical composition. Environ. Sci. Technol. 46 (13), 7252–7259.

Halle, A. ter, Ladirat, L., Martignac, M., Mingotaud, A.F., Boyron, O., Perez, E., 2017. To what extent are microplastics from the open ocean weathered? Environ. Pollut. 227, 167–174. Barking, Essex : 1987.

Hohenblum, P., Liebmann, B., Liedermann, M., 2015. Plastic and Microplastic in the Environment, vol. 27. Report/Umweltbundesamt. Umweltbundesamt, Vienna.

Hu, B., Li, Y., Jiang, L., Chen, X., Wang, L., An, S., Zhang, F., 2020. Influence of microplastics occurrence on the adsorption of 17β-estradiol in soil. J. Hazard Mater. 400, 123325.

Hüffer, T., Metzelder, F., Sigmund, G., Slawek, S., Schmidt, T.C., Hofmann, T., 2019. Polyethylene microplastics influence the transport of organic contaminants in soil. Sci. Total Environ. 657, 242–247.

Hüffer, T., Weniger, A.-K., Hofmann, T., 2018. Sorption of organic compounds by aged polystyrene microplastic particles. Environ. Pollut. 236, 218–225. Barking, Essex : 1987.

ICH, 2006. Harmonised tripartite guideline: validation of analytical procedures: text and methodology. Q 2 (R1). International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use.

Ji, Z., Huang, Y., Feng, Y., Johansen, A., Xue, J., Tremblay, L.A., Li, Z., 2021. Effects of pristine microplastics and nanoplastics on soil invertebrates: a systematic review and meta-analysis of available data. Sci. Total Environ. 788, 147784.

Keiluweit, M., Kleber, M., 2009. Molecular-Level Interactions in Soils and Sediments: The Role of Aromatic π-Systems. Environ. Sci. Technol. 43 (10), 3421–3429.

Kern, C., Kern, S., Henss, A., Rohnke, M., 2023. Secondary ion mass spectrometry for bone research. Biointerphases 18 (4).

Kern, S., Kern, C., Pradja, M.M., Düring, R.-A., Rohnke, M., 2020. Spatially resolved indiffusion behavior of Cu 2+ and Ni 2+ in polypropylene. J. Appl. Polym. Sci., 49655

Khatib, I., Horyn, O., Bodnar, O., Lushchak, O., Rychter, P., Falfushynska, H., 2023. Molecular and Biochemical Evidence of the toxic effects of terbuthylazine and Malathion in Zebrafish. Animals : an open access. journal from MDPI 13 (6).

Klementova, S., Keltnerova, L., 2015. Triazine herbicides in the environment. In: Price, A., Kelton, J., Sarunaite, L. (Eds.), Herbicides, Physiology of Action, and Safety. InTech.

Köck-Schulmeyer, M., Ginebreda, A., Postigo, C., Garrido, T., Fraile, J., López de Alda, M., Barceló, D., 2014. Four-year advanced monitoring program of polar pesticides in groundwater of Catalonia (NE-Spain). Sci. Total Environ. 470–471, 1087–1098.

Lara, L.Z., Bertoldi, C., Alves, N.M., Fernandes, A.N., 2021. Sorption of endocrine disrupting compounds onto polyamide microplastics under different environmental conditions: Behaviour and mechanism. Sci. Total Environ. 796, 148983.

Li, J., Guo, K., Cao, Y., Wang, S., Song, Y., Zhang, H., 2021. Enhance in mobility of oxytetracycline in a sandy loamy soil caused by the presence of microplastics. Environ. Pollut. 269, 116151. Barking, Essex : 1987.

Li, J., Zhang, K., Zhang, H., 2018. Adsorption of antibiotics on microplastics. Environ. Pollut. 237, 460–467.

Li, S., Yuan, Y., Wang, X., Cai, L., Wang, J., Zhao, Y., Jiang, L., Yang, X., 2023. Bioaccumulation and toxicity of terbuthylazine in earthworms (Eisenia fetida). Environ. Toxicol. Pharmacol. 97, 104016.

Liu, P., Qian, L., Wang, H., Zhan, X., Lu, K., Gu, C., Gao, S., 2019. New insights into the aging behavior of microplastics accelerated by advanced oxidation processes. Environ. Sci. Technol. 53 (7), 3579–3588.

Liu, P., Zhan, X., Wu, X., Li, J., Wang, H., Gao, S., 2020. Effect of weathering on environmental behavior of microplastics: properties, sorption and potential risks. Chemosphere 242, 125193.

Ma, H., Pu, S., Liu, S., Bai, Y., Mandal, S., Xing, B., 2020. Microplastics in aquatic environments: toxicity to trigger ecological consequences. Environ. Pollut. 261, 114089. Barking, Essex : 1987.

MacLeod, M., Arp, H.P.H., Tekman, M.B., Jahnke, A., 2021. The global threat from plastic pollution. Science 373 (6550), 61–65.

Metcalfe, C.D., Wright, D.A., Hodson, P.V., 2022. In: Campbell, P.G.C. (Ed.), Organic Compounds, Ecotoxicology. Cambridge University Press, Cambridge, United Kingdom, New York, NY, USA, pp. 274–325.

Morris, J.C., Weber, W.J., 1964. Removal of biologically-resitant pollutants from wasters by adsorption. In: Advances in Water Pollution Research. Elsevier, pp. 231–266.

Mosca Angelucci, D., Tomei, M.C., 2020. Uptake/release of organic contaminants by microplastics: a critical review of influencing factors, mechanistic modeling, and thermodynamic prediction methods. Crit. Rev. Environ. Sci. Technol. 1–45.

Motulsky, H., Christopoulos, A., 2004. Fitting Models to Biological Data Using Linear and Nonlinear Regression: A Practical Guide to Curve Fitting. Oxford University Press, Oxford, New York, p. 351.

Müller, A., Becker, R., Dorgerloh, U., Simon, F.-G., Braun, U., 2018. The effect of polymer aging on the uptake of fuel aromatics and ethers by microplastics. Environ. Pollut. 240, 639–646.

Mylläri, V., Ruoko, T.-P., Syrjälä, S., 2015. A comparison of rheology and FTIR in the study of polypropylene and polystyrene photodegradation. J. Appl. Polym. Sci. 132 (28), 1–6.
Navarro, S., Vela, N., Giménez, M.J., Navarro, G., 2004. Persistence of four s-triazine herbicides in river, sea and groundwater samples exposed to sunlight and darkness under laboratory conditions. Sci. Total Environ. 329 (1–3), 87–97.
Nelms, S.E., Galloway, T.S., Godley, B.J., Jarvis, D.S., Lindeque, P.K., 2018. Investigating microplastic trophic transfer in marine top predators. Environ. Pollut. 238, 999–1007.
OECD, 2000. Test No. 106: Adsorption - Desorption Using a Batch Equilibrium Method.
Olu-Owolabi, B.I., Diagboya, P.N., Adebowale, K.O., 2014. Evaluation of pyrene sorption-desorption on tropical soils. J. Environ. Manag. 137, 1–9.
Olu-Owolabi, B.I., Diagboya, P.N., Adebowale, K.O., 2015. Sorption and desorption of fluorene on five tropical soils from different climes. Geoderma 239–240, 179–185.
Olu-Owolabi, B.I., Diagboya, P.N., Mtunzi, F.M., Adebowale, K.O., Düring, R.-A., 2022. Empirical aspects of an emerging agricultural pesticide contaminant retention on two sub-Saharan soils. Gondwana Res. 105, 311–319.
Olu-Owolabi, B.I., Diagboya, P.N., Mtunzi, F.M., Düring, R.-A., 2021. Utilizing eco-friendly kaolinite-biochar composite adsorbent for removal of ivermectin in aqueous media. J. Environ. Manag. 279, 111619.
Olu-Owolabi, B.I., Diagboya, P.N., Unuabonah, E.I., Alabi, A.H., Düring, R.-A., Adebowale, K.O., 2018. Fractal-like concepts for evaluation of toxic metals adsorption efficiency of feldspar-biomass composites. J. Clean. Prod. 171, 884–891.
Petersen, F., Hubbart, J.A., 2021. The occurrence and transport of microplastics: the state of the science. Sci. Total Environ. 758, 143936.
PlasticsEurope, 2023. Plastics - the Fast Facts 2023. PlasticsEurope. https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2023/. (Accessed 10 January 2024).
Queirós, L., Vidal, T., Nogueira, A.J.A., Gonçalves, F.J.M., Pereira, J.L., 2018. Ecotoxicological assessment of the herbicide Winner Top and its active substances-are the other formulants truly inert? Ecotoxicology 27 (7), 945–955.
Rochman, C.M., 2018. Microplastics research-from sink to source. Science 360 (6384), 28–29.
Ronka, S., 2016. Removal of triazine-based herbicides on specific polymeric sorbent: batch studies. Pure Appl. Chem. 88 (12), 1167–1177.
Rubin, A.E., Sarkar, A.K., Zucker, I., 2021. Questioning the suitability of available microplastics models for risk assessment - a critical review. Sci. Total Environ. 788, 147670.
Salehi, M., Jafvert, C.T., Howarter, J.A., Whelton, A.J., 2018. Investigation of the factors that influence lead accumulation onto polyethylene: Implication for potable water plumbing pipes. J. Hazard Mater. 347, 242–251.
Sarkar, A.K., Rubin, A.E., Zucker, I., 2021. Engineered polystyrene-based microplastics of high environmental relevance. Environ. Sci. Technol. 55 (15), 10491–10501.
Seidensticker, S., Grathwohl, P., Lamprecht, J., Zarfl, C., 2018. A combined experimental and modeling study to evaluate pH-dependent sorption of polar and non-polar compounds to polyethylene and polystyrene microplastics. Environ. Sci. Eur. 30 (1), 30.
Silva, E., Daam, M.A., Cerejeira, M.J., 2015. Aquatic risk assessment of priority and other river basin specific pesticides in surface waters of Mediterranean river basins. Chemosphere 135, 394–402.
Silva, V., Mol, H.G.J., Zomer, P., Tienstra, M., Ritsema, C.J., Geissen, V., 2019. Pesticide residues in European agricultural soils - a hidden reality unfolded. Sci. Total Environ. 653, 1532–1545.
Sun, Y., Yuan, J., Zhou, T., Zhao, Y., Yu, F., Ma, J., 2020. Laboratory simulation of microplastics weathering and its adsorption behaviors in an aqueous environment: a systematic review. Environ. Pollut. 265, 114864. Pt B.
Šunta, U., Prosenc, F., Trebše, P., Bulc, T.G., Kralj, M.B., 2020. Adsorption of acetamiprid, chlorantraniliprole and flubendiamide on different type of microplastics present in alluvial soil. Chemosphere 261, 127762.
Tasca, A.L., Puccini, M., Fletcher, A., 2018. Terbuthylazine and desethylterbuthylazine: recent occurrence, mobility and removal techniques. Chemosphere 202, 94–104.
Tourinho, P.S., Kočí, V., Loureiro, S., van Gestel, C.A.M., 2019. Partitioning of chemical contaminants to microplastics: sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation. Environ. Pollut. 252 (Pt B), 1246–1256.
Tseng, R.-L., Wu, F.-C., 2008. Inferring the favorable adsorption level and the concurrent multi-stage process with the Freundlich constant. J. Hazard Mater. 155 (1–2), 277–287.
Unuabonah, E.I., Adebowale, K.O., Olu-Owolabi, B.I., Yang, L.Z., Kong, L.X., 2008. Adsorption of Pb (II) and Cd (II) from aqueous solutions onto sodium tetraborate-modified Kaolinite clay: equilibrium and thermodynamic studies. Hydrometallurgy 93 (1–2), 1–9.
Uurasjärvi, E., Hartikainen, S., Setälä, O., Lehtiniemi, M., Koistinen, A., 2020. Microplastic concentrations, size distribution, and polymer types in the surface waters of a northern European lake. Water Environ. Res.: a research publication of the Water Environment Federation 92 (1), 149–156.
Wang, F., Gao, J., Zhai, W., Liu, D., Zhou, Z., Wang, P., 2020. The influence of polyethylene microplastics on pesticide residue and degradation in the aquatic environment. J. Hazard Mater. 394, 122517.
Wang, J., Liu, X., Li, Y., Powell, T., Wang, X., Wang, G., Zhang, P., 2019. Microplastics as contaminants in the soil environment: a mini-review. Sci. Total Environ. 691, 848–857.
Weber, W.J., Morris, J.C., 1963. Kinetics of adsorption on Carbon from solution. J. Sanit. Eng. Div. 89 (2), 31–59.
Wu, C., Zhang, K., Huang, X., Liu, J., 2016. Sorption of pharmaceuticals and personal care products to polyethylene debris. Environ. Sci. Pollut. Res. Int. 23 (9), 8819–8826.
Xu, B., Liu, F., Cryder, Z., Huang, D., Lu, Z., He, Y., Wang, H., Lu, Z., Brookes, P.C., Tang, C., Gan, J., Xu, J., 2019. Microplastics in the soil environment: occurrence, risks, interactions and fate – a review. Crit. Rev. Environ. Sci. Technol. 1–48.
Zha, F., Shang, M., Ouyang, Z., Guo, X., 2022. The aging behaviors and release of microplastics: a review. Gondwana Res. 108, 60–71.
Zhang, H., Wang, J., Zhou, B., Zhou, Y., Dai, Z., Zhou, Q., Chriestie, P., Luo, Y., 2018. Enhanced adsorption of oxytetracycline to weathered microplastic polystyrene: kinetics, isotherms and influencing factors. Environ. Pollut. 243 (Pt B), 1550–1557.
Zhao, L., Rong, L., Xu, J., Lian, J., Wang, L., Sun, H., 2020. Sorption of five organic compounds by polar and nonpolar microplastics. Chemosphere 257, 127206.
Zvekic, M., Richards, L.C., Tong, C.C., Krogh, E.T., 2022. Characterizing photochemical ageing processes of microplastic materials using multivariate analysis of infrared spectra. Environmental science. Processes & impacts 24 (1), 52–61.