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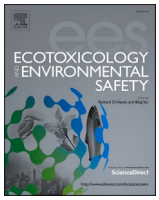

Effect of ultra-high-density polyethylene microplastic on the sorption and biodegradation of organic micropollutants

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ABSTRACT

Microplastics and organic micropollutants are two emerging contaminants that interact with each other in environmental and engineered systems. Sorption of organic micropollutants, such as pharmaceuticals, pesticides and industrial compounds, to microplastics can modify their bioavailability and biodegradation. The present study investigated the capacity of ultra-high density polyethylene particles (125 μm in diameter), before and after aging, to sorb 21 organic micropollutants at different environmentally relevant concentration. Furthermore, the biodegradation of these organic micropollutants by a biofilm microbial community growing on the microplastic surface was compared with the biodegradation by a microbial community originating from activated sludge. Among all tested organic micropollutants, propranolol (70%), trimethoprim (25%) and sotalol (15%) were sorbed in the presence of polyethylene particles. Growth of a biofilm on the polyethylene particles had a beneficial effect on the sorption of bromoxynil, caffeine and chloridazon and on the biodegradation of irbesartan, atenolol and benzotriazole. On the other hand, the biofilm limited the sorption of trimethoprim, propranolol, sotalol and benzotriazole and the biodegradation of 2,4-D. These results showed that ultra-high density polyethylene particles can affect both in a positive and negative way for the abiotic and biotic removal of organic micropollutants in wastewater. This project highlights the need for further investigation regarding the interaction between microplastics and organic micropollutants in the aquatic environment.

1. Introduction

Microplastics and organic micropollutants (OMPs) are two emerging contaminants that threaten environmental and human health. Microplastic is a novel type of pollution that receives increasing interest from both the public and scientific community over the last decades (Andrady, 2011). These plastic particles range in size from 10 μm to 5 mm and are commonly created by weathering or breakdown of larger plastic particles or leakage of industrial wastes in the water (Kumar et al., 2023). The emerging concern of the presence of microplastic in water is due to the rapid development of industrialized production, an increase of the worldwide plastic consumption and an improper disposal of waste (Lu et al., 2021). A large portion of microplastics that end up in the ocean are made by high molecular polymers, and they could be recalcitrant in water bodies for decades (Hitchcock and Mitrovic, 2019).

OMPs are xenobiotics present throughout the water cycle at trace concentrations. They mostly enter the water body by anthropogenic activities such as agriculture, medicinal treatment, and industrial production (Yu et al., 2019). Even though OMPs are present at extremely low concentrations varying from ng/L to several μg/L, they can have diversified adversary effects as they contain a broad category of human-induced chemical substances, for example, herbicides, industrial compounds, and pharmaceuticals (Horton et al., 2018; Liu et al., 2019; Mak et al., 2019; Walpitagama et al., 2019).

The interaction between microplastic and OMPs in the environment and in wastewater has important implications for the fate of each of these contaminant classes. OMPs can directly adsorb on the surface of microplastic particles by physical forces, including hydrogen bonding, hydrophobic interaction, van der Waals force, and electrostatic interaction (Atugoda et al., 2021). In these binding mechanisms, microplastic particles could be the vectors to transport OMPs, which can be referred to as a "Trojan horse" effect (Abdolahpur Monikh et al., 2020). As a

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result, this mechanism could also lead to a decrease in the bioavailability of OMPs in water compartments, resulting in a lower biodegradation efficiency and an increased half-life.

Natural aging of plastic particles in the environment is an important process that will affect the particles sorption activity towards organic compounds and OMPs. Plastic is aged by sunlight radiation, physical abrasion, temperature fluctuation and microbial transformation (Yu et al., 2021). Aging processes not only change the particles size, but also the surface morphology and the microstructure of the plastic particles (Mao et al., 2020). The majority of all microplastics pollution consists of aged microplastics and the abundance will increase alongside the continuing input of plastic debris in the environment (Li et al., 2018).

On the other hand, the development and formation of microbial biofilms on the surface of microplastic might influence the sorption and biodegradation of OMPs as well (Girard et al., 2020). Microplastic provides an appropriate surface for the attachment of biofilms (Almendros and Dorado, 1999; Holman et al., 2002; Lee et al., 2011; Singh et al., 2019, 2020; Xie et al., 2017). These microbial biofilms, that are sometimes referred to as the plastisphere (Zettler et al., 2013) when growing on microplastics particles, might be able to degrade OMPs by growth-linked or co-metabolic degradation in conjunction with microplastic consumption (Sivan, 2011). In this scenario, microplastic particles act as an absorbent material for organic compounds, such as OMPs and dissolved organic matter (DOM), and a growth surface for microbial biofilms.

Municipal wastewater treatment plants are one of the main recipients of microplastics and organic pollutants (Deblonde et al., 2011; Liu et al., 2021). Although wastewater treatment plants are capable of removing up to 99% of the microplastics from the aqueous phase thanks to adsorption to sludges, wastewater effluent is still considered as an important contamination pathway by carrying 50% of the monitored microplastics contamination (Liu et al., 2021). In wastewater treatment plants, microplastics are in contact with a wide range of diverse microbial communities, leading to the growth of a biofilm on the microplastic particles and potential biodegradation. Colonization of microplastics by a microbial biofilm increases the bioavailability of microplastics towards some organic (Wang et al., 2021) and inorganic (Guan et al., 2020) pollutants. Therefore, microplastic supporting the growth of a biofilm can facilitate the transfer of pollutants towards downstream ecosystems (Wang et al., 2021). However, very few studies have been conducted regarding the biodegradation activity of biofilm-developed microplastics on organic micropollutants, especially using activated sludge microbial communities.

In this study, the impact of microplastics on the sorption and biodegradation of organic micropollutants in aqueous environments was systematically explored. Specifically, the research focused on the sorptive capacities of ultra-high-density polyethylene (PE), a plastic widely utilized within the industry, towards a diverse array of 21 OMPs at concentrations typical of those found in wastewater treatment facilities (ranging from 1 to 500 μg/L). Additionally, the effects of artificial aging on these processes were meticulously examined under controlled laboratory conditions. Concurrently, the biodegradation activities of both activated sludge and a biofilm community, which developed on microplastic particles, were rigorously compared employing the same set of OMPs. Biodegradation kinetics served as the metric for assessing and comparing biodegradation activity. This research makes a significant contribution to the understanding of how microplastic pollution influences the sorption and biodegradation behaviours of organic micropollutants within wastewater treatment systems. The findings not only highlight the complex interactions between microplastics and environmental contaminants but also underscore the pressing need for innovative strategies to manage microplastic pollution in wastewater treatment contexts. This study is pioneering in its simultaneous examination of the aging effects on microplastics and their consequential interactions with biodegradative microbial communities, thereby providing novel insights into the mitigation of micropollutant impacts in aquatic systems.

2. Methodology

2.1. Microplastics

Ultra-high-density polyethylene (PE) was bought from Sigma-Aldrich (Schnelldorf, Germany). The PE was of analytical quality with an average size of 125 μm in diameter.

2.1.1. Pre-treatment aging procedure

The PE particles were aged with a combination of two methods. First, 70 g of PE was placed on an aluminium foil tray at 60 cm under a UV-C-254 nm lamp of 18 W for 72 hours (Cai et al., 2018). The particles were stirred every 12 h to ensure even UV-radiation distribution. After this, the particles were stored at room temperature in a dry and dark place, after which an adapted Fenton oxidation method of Munoz et al. (2021) was used to chemically oxidise the microplastic particles. A 3 L glass reactor was used on a continuous stirrer, in which 140 mL of a 50 g/L Fe-stock solution and 700 mL H_2O_2 were added. After 20 h, the H_2O_2 concentration was measured and an additional dose of 52.5 mL H_2O_2 was added. Next to that, an additional dose of 10.5 mL Fe-stock was added. After 48 h, the H_2O_2 was measured a last time, and the Fenton oxidation was stopped by filtering the plastic particles and washing with ultrapure water. The formed iron sludge was vacuum filtered and 200 mL 37% HCl was added to remove the iron overnight. Finally, the aged plastic was washed, vacuum filtered and dried at room temperature before storage at room temperature in a dark and dry place.

2.2. OMP selection

A total of 21 OMPs were selected in this research, including 6 herbicides (chloridazon, methyl-desphenyl chloridazon “MDCH”, desphenyl chloridazon “DCH”, 2,4-dichlorophenoxyacetic acid “2,4-D”, bentazone, and bromoxynil), 13 pharmaceuticals (caffeine, sulfamethoxazole, carbamazepine, metformin, guanylurea, propranolol, metoprolol, irbesartan, atenolol, trimethoprim, sotalol, clofibric, and diclofenac), and 2 industrial compounds (perfluorooctanoic acid "PFOA", and benzotriazole). These compounds were selected due to their broad variety of physicochemical properties, known biodegradation rates and applications. It should be noted that MDCH and DCH are transformation products of chloridazon, while guanylurea is a transformation product of metformin.

The detailed information on OMPs is listed in the Table1. All OMPs were commercially bought from Sigma-Aldrich (Schnelldorf, Germany). A mixed stock solution of 21 OMPs, with an individual concentration of each OMPs of 500 mg/L, was prepared in acetonitrile (LC/MS grade) and stored at -20 °C.

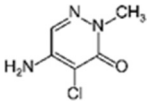
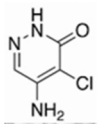
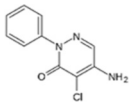
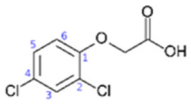
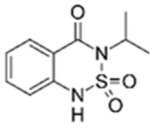
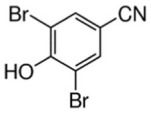
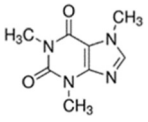
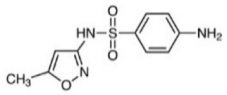
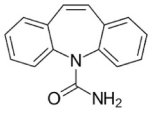
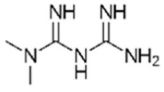
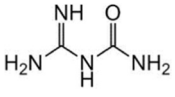
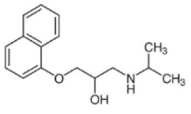
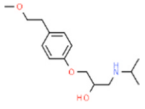
2.3. Inoculum

Activated sludge was collected from the secondary tank from a local municipal wastewater treatment plant (Bennekom, the Netherlands). The inoculum was collected within 3 days before starting the experiment to ensure its microbial quality and was stored at 4 °C to limit metabolic activity. The dissolved organic carbon and the dry matter content in the inoculum were measured as 95.6 ± 1.3 mg/L and 5.0 ± 0.18 g/L, respectively.

2.4. Medium preparation

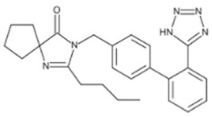
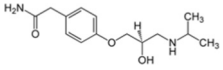
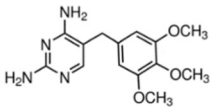
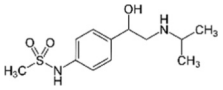
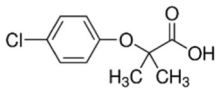
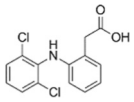
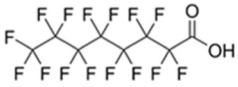
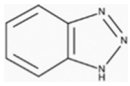
Chemicals for medium were bought from Sigma-Aldrich (Schnelldorf, Germany). The pH buffer stock solution contained 0.5 g/L Na_2HPO_4 and 1.9 g/L KH_2PO_4, to achieve a neutral environment at pH=7.2. Macronutrient stock medium contained 8 g/L $CaCL_2.2\ H_2O$, and 9 g/L $MgSO_4.7\ H_2O$. The stock for microelements included 11

Table 1
Physicochemical properties and the chemical structures of the 21 selected OMPs.

Name	CAS No.	Molecular form	Chemical structure	Neutral Molecular weight (g/mol)	pKa	LogP
Methyl-desfenyl chloridazon	17254–80–7	$C_5H_6ClN_3O$		159.573		-1.38
Desphenyl chloridazon	6339–19–1	$C_4H_4ClN_3O$		145.55		-1.14
Chloridazon	1698–60–8	$C_{10}H_8ClN_3O$		221.6	3.38	1.14
2,4-Dichlorophenoxyacetic acid	94–75–7	$C_8H_6Cl_2O_3$		221.033	2.73	2.81
Bentazone	25057–89–0	$C_{10}H_{12}N_2O_3S$		240.277	3.3	2.34
Bromoxynil	1689–84–5	$C_7H_3Br_2NO$		276.91	3.86	2.70
Caffeine	58–08–2	$C_8H_{10}N_4O_2$		194.194	14	-0.07
Sulfamethoxazole	723–46–6	$C_{10}H_{11}N_3O_3S$		253.279	pKa1 = 1.6 pKa2 = 5.7	0.89
Carbamazepine	298–46–4	$C_{15}H_{12}N_2O$		236.269	13.9	2.77
Metformin	1115–70–40	$C_4H_{11}N_5$		129.167	12.4	-2.6
Guanylurea	141–83–3	$C_2H_6N_4O$		102.1		-1.4
Propranolol	525–66–6	$C_{16}H_{21}NO_2$		259.34	9.42	3.48
Metoprolol	37350–58–6	$C_{15}H_{25}NO_3$		267.364	9.7	1.88

(*continued on next page*)

Table 1 (*continued*)

Name	CAS No.	Molecular form	Chemical structure	Neutral Molecular weight (g/mol)	pKa	LogP
Irbesartan	138402–11–6	$C_{25}H_{28}N_6O$		428.5	4.08	4.5
Atenolol	29122–68–7	$C_{14}H_{22}N_2O_3$		266.336	9.6	0.16
Trimethoprim	738–70–5	$C_{14}H_{18}N_4O_3$		290.32	7.12	0.91
Sotalol	3930–20–9	$C_{12}H_{20}N_2O_3S$		272.37	pKa1=8.3 pKa2=9.8	1.1
Clofibric Acid	882–09–7	$C_{10}H_{11}ClO_3$		214.645	3.2	2.6
Diclofenac	15307–86–5	$C_{14}H_{11}Cl_2NO_2$		296.148	4.15	4.51
Perfluorooctanoic acid	335–67–1	$C_8HF_{15}O_2$		414.07	-0.5–4.2	6.3
Benzotriazole	95–14–7	$C_6H_5N_3$		119.127	8.37	1.44

chemicals, as listed in the supplementary material A (Table. S1). Medium was prepared by adding pH buffer stock solution (50 mL/L), macronutrient solution (6 mL/L), and microelements (0.6 mL/L) in ultrapure water.

2.5. Batch assays

Serum bottles (250 mL) with a final medium volume of 100 mL were used for all tests. Each tests contained the same medium and five different OMPs concentrations (1,10, 50, 100, 500 μg/L), added as an acetonitrile solution, were tested. The acetonitrile concentration was equalized in all bottles. Tests with microplastic were performed with a concentration of 5 g/L of ultra-high-density polyethylene (PE or aged PE) in each bottle. All bottles were immediately closed with butyl rubber stoppers and sealed with aluminium caps. The headspace of the bottles was flushed with atmospheric air and the oxygen concentration in the headspace was monitored to ensure aerobic conditions. All bottles were transferred to shakers with a speed of 80 rpm, in the dark and either at 4 °C or 20 °C. Every condition was assessed in triplicate.

For both abiotic and biotic tests, a temperature of 4 °C was used to inhibit the biodegradation activity of the inoculum without modifying the chemical composition of the medium and without autoclaving. This approach has already successfully been used to investigate the sorption capacity of biologically activated carbon (Piai et al., 2020).

The abiotic removal tests consisted of five different groups, two at 4 °C with PE and aged PE and three at 20 °C, with PE, aged PE and without any microplastic.

Prior to the biotic removal tests, around 200 mL of fresh activated sludge was transferred to a sterile flask and kept for 24 hours on a shaker (80 RPM) at 20 °C and under aerobic conditions. Biotic removal tests were conducted with and without PE in the medium at 20 °C and 4 °C. Only non-aged PE was tested, as effect of aging on the surface of the plastic particles might influence the biofilm growth and diversity. This experiment consisted of three different phases: 1) a 5 days growth/acclimation phase at 20 °C without OMPs, 2) a 7 days abiotic removal phase at 4 °C in presence of OMPs and 3) a 42 days biotic removal phase at 20 °C, still with OMPs. For the test that contained PE, 5 g/l of PE was added to each bottle at the beginning of phase 1. Serum bottles were inoculated with 10 mL of activated sludge and had a final volume of 100 mL. During the phase 1, bottles were placed on a shaker at 80 rpm for 5 days at 20 °C in the dark, to promote biofilm development on the PE particles or acclimation of the activated sludge. The bottles were spiked with OMPs, at the beginning of phase 2, to achieve the five different concentrations, 1, 10, 50, 100 and 500 μg/L, before to be transferred to a shaker at 4°C. The same bottles were then transferred back to a shaker at 20 °C for phase 3, to measure the biodegradation activity of the biofilm developed during phase 1. A schematic representation of the experimental setup of the biotic test can be found below (Fig. 1). Microscopic pictures of the microplastic particles and biofilm are presented in the supplementary material A (Fig. S1).

2.6. Analytical methods

2.6.1. Microplastic particles quantification

Microplastic particles concentration in the biodegradation tests were determined using Nile-Red staining combined with fluorescence microscopy and image analysis. An aliquot of a 1.5 mL liquid sample was filtered over a 25 mm Cyclopore treck etched membrane with a pore size of 0.2 μm in a filtration set-up using vacuum. The sample was washed with 100 mL of particle free Milli-Q water. The particles were stained

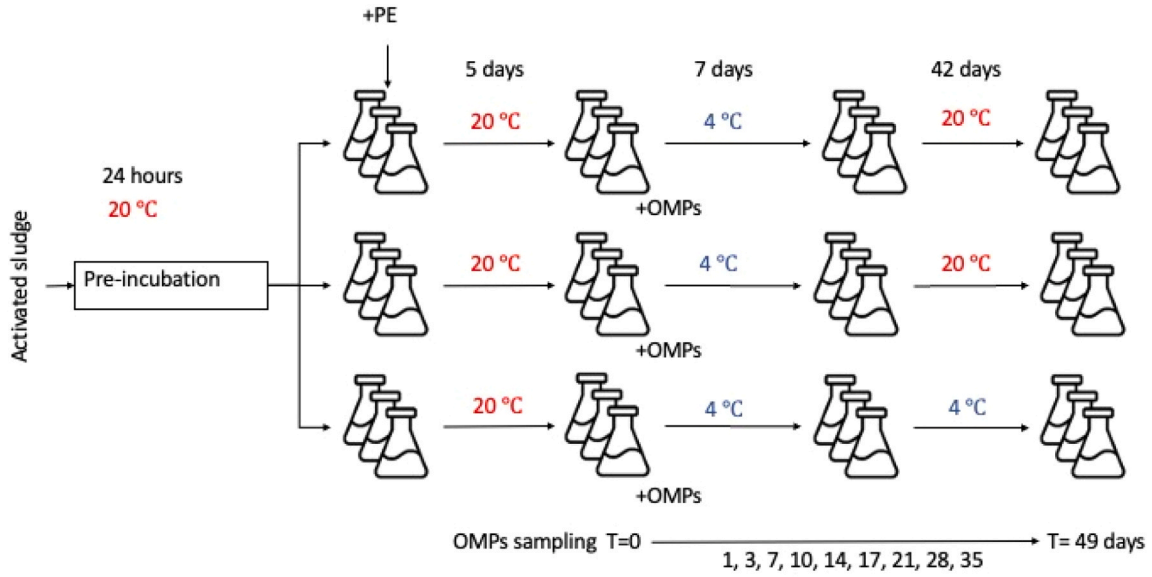


Fig. 1. Schematic representation of the biotic batch test.

on-filter using a selective fluorescent dye (Nile Red) in ethanol. Using fluorescence microscopy, field images were collected from 21 areas on the filter and the images are processed with ImageJ and a script to count and size the particles. The results of the image analysis were combined and reported in Excel. Finally, the particle mass concentration of the microplastics particles in the aqueous samples was calculated. Details of the method are described elsewhere (Vitali et al., 2022).

2.6.2. OMPs quantification

Sampling was performed at 0, 1, 3 and 7 days during the abiotic test and at 0, 1, 3, 7, 10, 14, 17, 21, 28, 35 and 49 days during the biotic test. Less samples were taken during the biotic test in absence of microplastic (activated sludge controls at 4 °C and 20 °C). 2 mL liquid samples were taken with a syringe from each batch to quantify OMPs. The samples were immediately filtered through a 1.2 μm glass microfiber membrane filter (Puradisc 6822–1312 Syringe Filters, Whatman, Germany) and then transferred to amber LC vials. The glass microfiber membrane filter was tested to confirm that it did not adsorb any OMPs during the filtration process. The filtered samples were diluted with ultrapure water and 5% acetonitrile to a nominal concentration of 1 μg/L prior to quantification by LC-MS/MS.

An Ultra High Performance Liquid Chromatography (UHPLC) system equipped with a triple quad mass spectrometer (SCIEX Triple Quad™ 5500, Nieuwerkerk aan den IJssel, Netherlands) was used for detection and quantification of the OMPs. The injection volume was 25 μL and the analytes were separated using a Kinetex 1.7 μm Phenyl-Hexyl 100 Å, 30 ×2.1 mm column (Phenomenex, USA) and a gradient of ultrapure water (MilliQ) with 0.1% formic acid (A) and acetonitrile with 0.1% formic acid (B). Details of the LC method can be found in the supplementary materials A (Text. S1). OMPs were ionized using a Turbo Ion Spray electrospray ion source. Multiple reaction monitoring (MRM) parameters, fragment masses of all analytes and UHPLC parameters can be found in the supplementary materials A (Table. S2). Analysed data were processed by SCIEX OS-MQ (version 1.7) software. The obtained calibration standard curve of OMPs showed a good linearity ($R^2 > 0.99$). The limit of quantification (LOQ) in the sample matrix was 25 ng/L, while the limit of detection was not determined in this experiment.

2.6.3. Surface area measurements

To measure the effect of aging on the surface area, two 0.5 g samples of each aged and non-aged PE were taken. These measurements were done by a DVS automated gravimetric vapor sorption analyser (TGA Q5000 SA) (TA instrument, Etten-Leur, The Netherlands), where the plastic surface was measured with increasing water humidity. The procedure was set as follows: equilibration at 25°C; set humidity at 0% relative humidity (RH); start isothermal segment 240 min; step humidity 10%RH for 720 min to 80% RH, abort humidity step if weight change < 1% for 60 min. To obtain the surface area, the BET theory was used for calculations and is described in the supplementary material A (Text. S2).

2.6.4. Oxygen concentration

Oxygen content in the biodegradation assays was monitored by using gas chromatography coupled with a flame ionization detector (GC-FID). Before the measurement, 25 μL gas samples were collected from each batch bottle using a glass syringe and needle. Afterward, the samples were injected into the GC instrument (GC-2010, Shimadzu, Japan). The instrument used two parallelly connected columns, which were Porabond Q (50 m x 0.53 mm; 10μm; Varian; Part.no. CP7355) and Molsieve 5 A (25 m x 0.53 mm; 50μm; Varian; Part.no. CP7538) for parallelle separation of CO_2, CH_4 and O_2.

2.7. Data analysis

Data analyses and figures production were performed using R (vers. 4.0.2) and the package ggplot2 (vers. 3.3.5).

The oxygen consumption was calculated with ideal gas law, as shown in Eq. 1.

$$PV = nRT \quad (1)$$

Where P is the absolute pressure of the gas in the batch bottles, V is the volume of the gas, N is the number of moles of oxygen molecules, and T is the absolute temperature. The R is the universal gas constant with a value of 8.3144598 J. mol^{-1}. K^{-1}

In the abiotic and biodegradation tests, the removal efficiency of a single OMP compound in the batch assays was calculated by the difference of the original concentration and the one measured at sampling time, as shown in Eq.2.

$$R(\%) = \frac{C_0 - C_x}{C_0} \times 100 \quad (2)$$

Where R is the removal efficiency of single OMP (%), C_0 and C_x are the concentration of single OMP at day 0 (ng/L) and day X (ng/L), respectively.

Once an OMP was removed in the abiotic tests, the Freundlich model was used to simulate the sorption isotherm, as shown in Eq.3.

$$q_{eq} = K_f C_{eq}^{\ \frac{1}{n}} \quad (3)$$

Where C_{eq} is the equilibrium concentration of the OMPs on the liquid phase (μg/L) and q_{eq} is the amount of adsorbate adsorbed per unit mass of PE (μg/g). K_f is the distribution coefficient and n is the correction factor (Khayyun and Mseer, 2019).

The sorption capacity (SC) load at equilibrium was calculated based on the mass balance as shown in Eq.4.

$$q_{eq} = \frac{(C_0 - C_{eq}) * V}{m_A} \quad (4)$$

Where q_{eq} is the SC load at equilibrium (μg/g) and C_0 is the initial OMP concentration (μg/g). C_{eq} is the OMP concentration at equilibrium (μmol/g) and V is the liquid volume (L) and m_A is the mass of PE (g).

Pseudo-first-order kinetic models (Eq. 5) were applied to analyse the biodegradation processes of OMPs under different conditions in this study.

$$C_t = C_0 e^{-kt} \quad (5)$$

where C_t (ng/L) and C_0 (ng/L) are the concentrations of OMPs at a sample and the original measured concentration; t (d) was the sampling time and k (day^{-1}) was the first-order rate constant. Constant k (day^{-1}) was then calculated following Eq. 6

$$k = -\frac{\ln\left(\frac{C_t}{C0}\right)}{t} \quad (6)$$

3. Results and discussion

3.1. Effect of ultra-high-density polyethylene on the sorption of organic micropollutants

High-density polyethylene particles can promote the removal of three organic micropollutants. The removal efficiency of propranolol in presence of PE was from 70% to 75% after seven days while it was of maximum 20% in absence of PE for all tested concentrations (Fig. 2). This phenomenon suggests that the high removal of propranolol was an effect of PE. The presence of PE also affected the removal of trimethoprim and sotalol, as 25% of trimethoprim and 15% of sotalol were removed after seven days in the presence of PE, and this for all OMPs concentration (see supplementary materials B). The constant removal of propranolol is evident, regardless of the initial concentration (1, 10, 50, 100, 500 μg/L). This suggests that adsorption equilibrium is attained at the lowest concentration (1 μg/L), and there is no observable competition at higher concentrations.

PE may provide sufficient surface area to adsorb propranolol (Wang et al., 2017). PE has a multi-layer structure with pores on the surface, in which propranolol might be extensively adsorbed in the edges or pores of exposed layers because of the electrostatic and hydrophobic interactions (Ali et al., 2016; Burke et al., 2013; McDougall et al., 2022;

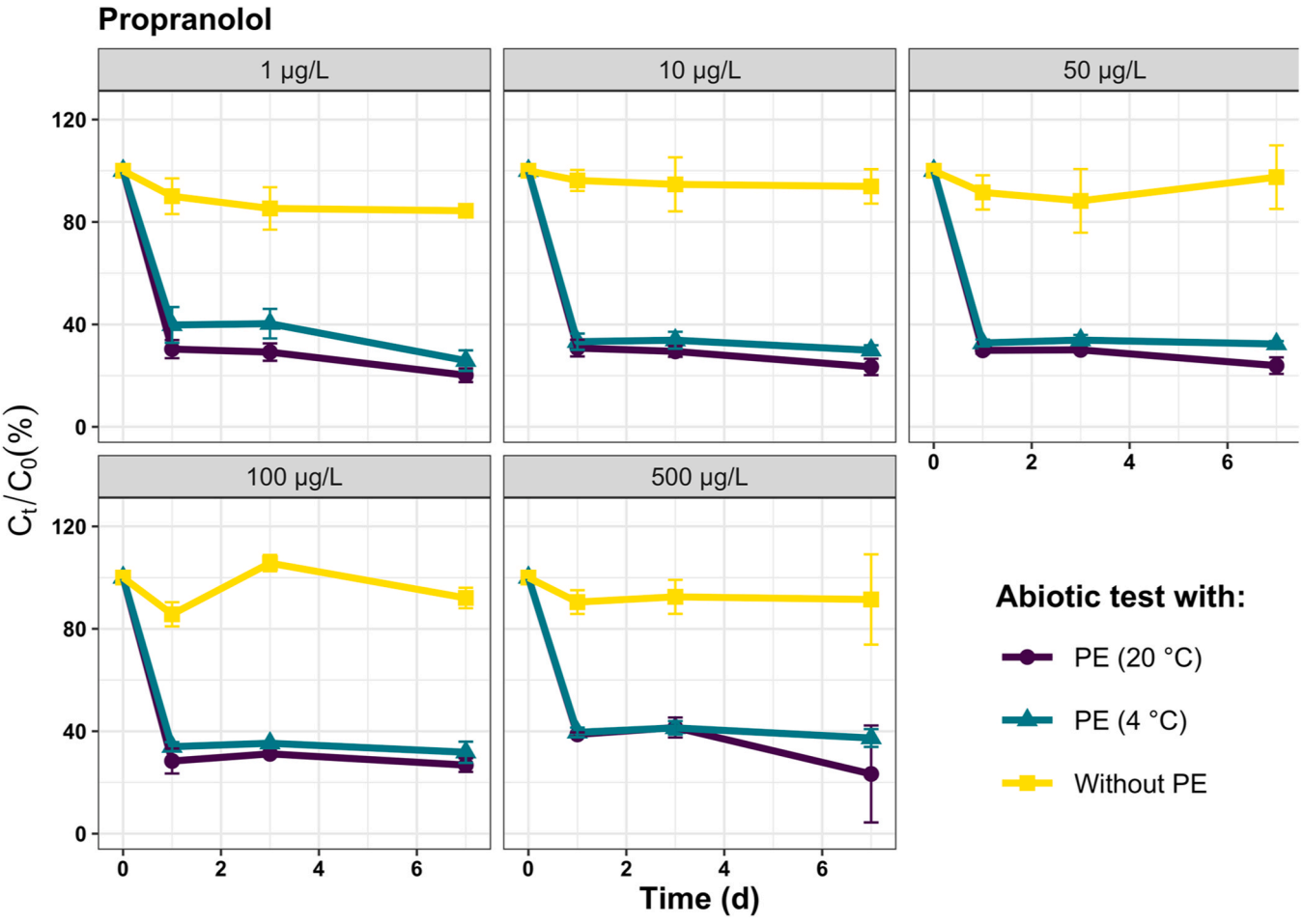


Fig. 2. Fraction of propranolol (%) remaining in abiotic removal tests. Points and lines represent the average (n=3) of each test over time (d). Error bars represent the standard deviation between the triplicate.

Razanajatovo et al., 2018). The surface of PE is negatively charged at the pH of this study (pH=7.8), while propranolol is present in cationic form (pKa=9.42). McDougall et al. (2022) found that sorption favored compounds in cationic form, such as fluoxetine and propranolol, while Razanajatovo et al. (2018) concluded that the sorption of sertraline and propranolol was enhanced by their positive charge. Sotalol is another example of a cationic compound that was removed in presence of PE. Nonetheless, there is no significant removal of atenolol, metoprolol, metformin and its transformation product, guanylurea (GAS) (supplementary materials B), which are also cationic compounds (Table 1), which indicates that chemical structures and physicochemical properties of OMPs may contribute to the discrepancies in OMP adsorption behaviour. The molecular size and flexibility of propranolol and sotalol may allow for more effective interactions with the polymers that make up microplastics, which larger and more flexible molecules can better adjust their conformation to fit into the spaces on and within the microplastic surfaces (Teuten et al., 2007). Moreover, the presence of reinforced aromatic structure in propranolol and sotalol might facilitate π-π interactions with microplastics more significant than chemicals such as atenolol, metoprolol, metformin (Shin et al., 2021).

There was no significant removal of several neutral and anionic compounds, most likely due to charge repulsion and low hydrophobicity. The anionic diclofenac is considered to be more hydrophobic than propranolol but no sorption was measured. Previous research showed that diclofenac could be adsorbed by ultra-high density polyethylene at 25°C and pH=7 (Munoz et al., 2021) or to aged low-density polyethylene (Miranda et al., 2022). Yet, this research also suggests diclofenac desorption at a pH ranging from 7.5 to 8, which could be an explanation for the low diclofenac sorption in this study (pH=7.8). This shows that the speciation of OMPs is important for interpretation of sorption to PE microplastics, but this needs to be considered together with their hydrophobicity. Among the other OMPs tested in the present study, sulfamethoxazole (Razanajatovo et al., 2018) and carbamazepine (Atugoda et al., 2021) were not removed as well, while they are known to adsorb to polyethylene. To elucidate the limited removal of sulfamethoxazole and carbamazepine through adsorption onto PE microplastics, it is essential to consider the impact of the wastewater matrix on this process. Previous literature has evidenced that competitive adsorption from a range of other contaminants was present in wastewater effluent (Shin et al., 2021), which might substantially diminish the available binding sites on polyethylene, thereby reducing its capacity to adsorb these specific organic micropollutants. Additionally, the physicochemical properties of the wastewater, such as pH and ionic strength, play crucial roles in influencing the adsorption efficiency (Ahmed et al., 2017). These conditions can alter the charge and solubility of sulfamethoxazole and carbamazepine, potentially reducing their affinity for the hydrophobic surfaces of polyethylene microplastics. Understanding these interactions is vital for assessing the efficacy of using microplastics as adsorbents in wastewater treatment and for developing strategies to enhance the removal of such persistent pollutants.

Further investigation should be conducted to truly assess the sorption and desorption capacity of polyethylene for OMPs in wastewater. According to Bakir et al. (2012), PE microplastics were classified as rubbery microplastics, which showed a high relevance between their morphology and their sorption behaviour. The surface of PE microplastics should be rough and porous, and the shape of PE should be pellet-like. Therefore, hydrophobic OMPs are more likely to be adsorbed on their surface due to electrostatic reactions. However, if the used PE was different in size and shape, the sorption behaviour of OMPs may be different (Gui et al., 2021). The potential hypothesis is that the electrostatic interactions between PE and OMPs may be strengthened if PE has a larger surface area, as this provides more opportunities for the attachment of OMPs.

3.2. Effect of aging on the sorption capacity of ultra-high-density polyethylene microplastics

The aging procedure used in this project had an influence on the surface area of PE microplastics. The BET surface area of two collected non-treated microplastic samples is 123.9 and 151.0 cm^2/g, while the surface area of the aged samples is 398.8 and 302.2 cm^2/g. Compared to literature, the aging procedure was similar in technique and time, but a combination of two methods has not been done before. The most realistic laboratory simulation of microplastic aging is photo-oxidation and physical abrasion (Sun et al., 2020), while only UV radiation was used in the present study. Nonetheless, the change in surface area indicate that our procedure produced aged PE particles.

Aged PE adsorbs more sulfamethoxazole, chloridazon, caffeine and sotalol than non-aged PE (Fig. 3). At 20°C and with a starting concentration of 1 μg/L, aged PE adsorbs up to 50% more sulfamethoxazole than non-aged PE. For higher concentrations of sulfamethoxazole, this difference is around 30%. Sorption is the main removal mechanism as no biodegradation activity was observed in the unsterilized batches. Higher sorption activity of aged PE towards sulfamethoxazole has already been shown before (Guo and Wang, 2019). More abiotic removal by aged PE is also seen with irbesartan and bromoxynil (supplementary materials B). An explanation of this phenomenon is that aging increases the surface area of microplastics, making the surface rougher, which increases the surface to volume ratio and increase the sorption affinity to OMPs (Atugoda et al., 2021). Another explanation is that with aging, oxidation occurs which yields oxygen-containing functional groups (carbonyl, hydroxyl, ketone and ester). This increases the polarity of microplastics, which may increase the sorption of anionic OMPs (Guo and Wang, 2019; Wu et al., 2016), and could be verified with spectroscopic methods, such as ATR-FTIR. This is in line with our results and the speciation of the before-mentioned OMPs, which are neutral/anionic. Also the formation of hydrogen-bonds among oxygen-containing functional groups can cause more sorption by aged PE (Yu et al., 2019). However, in the case of propranolol, benzotriazole and trimethoprim, which all have oxygen containing functional groups, aged PE showed less absorption activity than the non-aged PE. This contradictory observation might be the result of the increased positive polarity, which may reduce the sorption of cationic chemicals such as propranolol, benzotriazole and trimethoprim.

3.3. Dual effects of biofilms and temperature on the sorption capacity of OMPs

Temperature incubation influenced the abiotic removal of most tested micropollutants (Supplementary material B). Isotherm analysis showed a higher removal of these substances at 4 °C with PE in comparison to 20 °C with PE. An increased abiotic removal or sorption at lower temperature was expected for most OMPs, as equilibrium sorption increases with decreasing temperature (ten Hulscher and Cornelissen, 1996).

The biofilm coating of the PE particles greatly increased the removal of some OMPs in comparison with PE particles without biofilm. During the abiotic test at 4℃, two OMPs showed more abiotic removal with the existence of biofilms, which were bromoxynil and caffeine (Fig. 3). Bromoxynil and caffeine did not reach their highest removal until the end of the experiment at 7 days, where they showed 80% and 60% removal, respectively. Furthermore, removal of caffeine is concentration-dependent and showed a proportionally lower sorption at 500 μg/L, which is the highest tested concentration (supplementary materials B).

Previous literature has intensively documented the complexity of sorption behaviour on biofilms and the properties influencing this mechanism (Johansen et al., 2019; Kalmokoff et al., 2001). Fresh water biofilm consists of communities of bacteria, fungi and algae, embedded in a complex extracellular polymeric matrix. This matrix is composed of diverse and simple organic matter, such as exopolysaccharides, nucleic

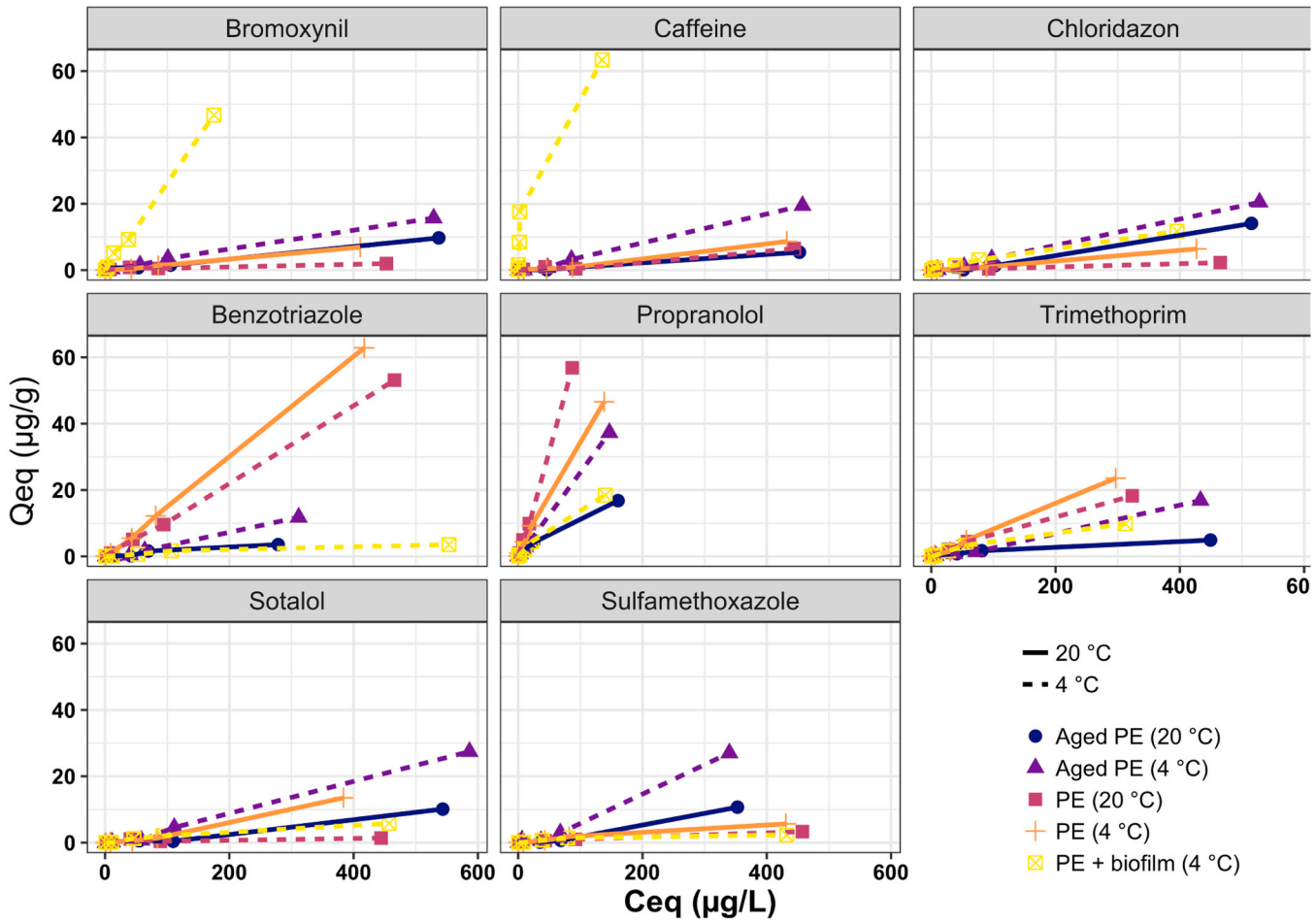


Fig. 3. Isotherm sorption analysis of eight selected OMPs. Dashed and full lines represent the experimental temperature (dashed= 4 °C, full= 20 °C). Colors and dot shape represent each individual experiment. PE + biofilm (4 °C) data were extracted from the 7 days of incubation at 4°C.

acids, lipids and proteins and is usually negatively charged (Flemming and Wingender, 2010; Lewis, 2001). Biofilm composition greatly influences its surface charge, surface area, shape, and hydrophobicity, which will affect its sorption capacity (Combarros et al., 2014; Li and Bishop, 2004; Wang et al., 2002).

Surface charge of the biofilm matrix may explain the sorption capacity of biofilms toward positively charged chemicals, such as caffeine, that have been reported to adsorb to organic matter in fresh water (Kiecak et al., 2020). However, higher sorption of other compounds in the presence of biofilms, such as bromoxynil, could not be explained by their charge in medium, hence, other properties influence their removal.

Microbial communities with a higher diversity have more chance to allow OMPs to diffuse and adsorb on the surface of the biofilm. This is due to a more diverse cell structure, which allow OMPs to interact with a higher diversity of cell membranes and bacterial metabolic products (Wang et al., 2020). Biofilms have a higher affinity than pure PE to both hydrophobic and hydrophilic compounds (Johansen et al., 2018; Wunder et al., 2011).

On the other hand, biofilms decreased the removal of trimethoprim, propranolol, sotalol and benzotriazole (Fig. 3). This phenomena could be due to (i) a low biofilm sorption capacity for these OMPs (Combarros et al., 2014; Li and Bishop, 2004), or (ii) an N-H bond on the OMPs making them simultaneously electrostatically attracted by the biofilm and the microplastic (Benjedim et al., 2020). This second explanation is likely as these OMPs are positively charged, resulting in competition between the biofilm and the PE to attract the OMPs. An alternative hypothesis is that the existence of biofilm diminishes the accessibility of active sorption sites on PE, thereby restricting the sorption of OMPs that exhibit an affinity for such sites.

Finally, no correlation between the OMPs concentration or removal could be found with the measured microplastic concentration. However, our microplastic quantification at the end of the experiment in the presence of biofilm showed a lower concentration than expected. All measured samples contained between 3.6 and 4.8 g/L of microplastic particles, instead of 5 g/L. This could be due to the formation of biofilm and a polysaccharide matrix on the coated particles, leading to an aggregation and sedimentation of microplastic (Michels et al., 2018). It should be noted that a microplastic concentration of 5 g/L of 125 µm PE represents a particle concentration of approximately $5 * 10^6$ particles/L. This is higher than any reported concentration in wastewater. For example, concentration ranging between $4 * 10^0$ to $4.5 * 10^5$ particles/m^3 have been measured in German wastewater treatment plant (Schmidt et al., 2020). Finally, not all microplastic will allow the development of a biofilm (Yang et al., 2022), hence, precaution should be taken before comparing the results of the present study with investigations using another type of plastic.

3.4. Ultra-high-density polyethylene promotes the biodegradation of irbesartan, benzotriazole, and atenolol

The presence of PE with biofilm enhanced the biodegradation of irbesartan, atenolol and benzotriazole. Oxygen consumption data confirm that a low bacterial aerobic metabolic activity took place during the first seven days of incubation at 4°C (supplementary material A, Fig. S2). Therefore, during these seven days mainly abiotic processes contributed to the removal of OMPs. Rapid increase in oxygen

consumption, when the batches were transferred to a shaker at 20℃, indicated that biofilms were active. No difference can be observed in term of oxygen consumption among the experiments with different initial OMP concentration. Furthermore, it should be noted that the initial biomass was equal in every test.

Having confirmed that the abiotic removal processes were dominant in the first 7 days at 4 °C (Fig. 4, blue solid line), the removal of irbesartan, atenolol and benzotriazole exhibited a higher degradation rate in the presence of PE, for every tested concentration (Fig. 4). Biodegradation of irbesartan and benzotriazole were profoundly enhanced in the presence of PE, while no difference could be observed for atenolol (Fig. 4). Biodegradation patterns for these three OMPs could not be associated with physico-chemical properties and might be related to the presence of microbial population that can degrade these compounds. Indeed, several bacteria are known to degrade irbesartan (Iranzo et al., 2018), benzotriazole (Larcher and Yargeau, 2011) and atenolol (Xu et al., 2017).

Propranolol was not removed or degraded in the presence of activated sludge or an active biofilm at 20 °C (Fig. 4). Activated sludge microbial communities are able to actively consume this chemical (Ribeiro et al., 2013), however, the presence of other carbon sources, such as humic acid or other dissolved organic matter, might have reduced the biodegradation activity toward propranolol (Lee et al., 2011). Whilst other OMPs were degraded in this experiment, limited differences were observed between the batches with activated sludge, and with PE particles coated with biofilm.

Finally, the presence of PE particles led to a catabolic activity inhibition of the microbial community, as shown by the decreased biodegradation kinetic of the pesticide 2.4-D. Removal kinetic for all concentration was higher when only activated sludge was used as inoculum and the experiment was conducted at 20°C (Figs. 4 and 5). 2.4-D is known for its biodegradability and was expected to be consumed by the activated sludge microbial community (Marrón-Montiel et al., 2006). This inhibition could either be the result of a loss of competent degraders during the biofilm formation, a toxic effect or of a limited diffusion of this compound to the biofilm by the presence of PE. This

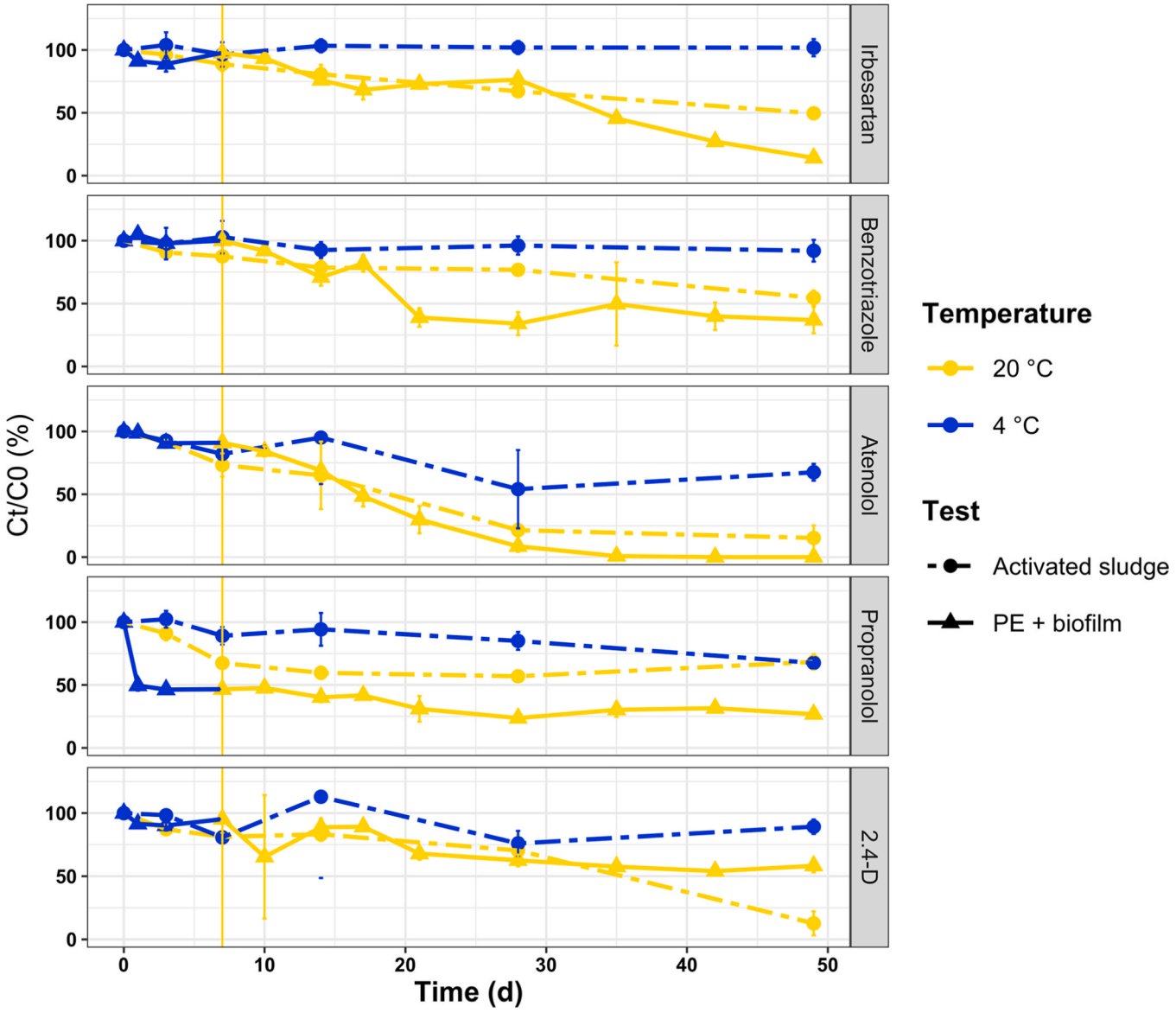


Fig. 4. Fraction (%) of irbesartan, benzotriazole, atenolol, propranolol, and 2.4-D remaining in batches over time (d). Lines and points represent the average of three replicates. Starting concentration was 1 µg/L, other concentration can be found in the supplementary materials A (Fig. S4). Error bars represent the standard deviation between the replicates. The vertical yellow line (7d) represents the temperature change from 4 °C (blue solid line, ▲) to 20 °C (yellow solid line, ▲) for the batches with PE + biofilm.

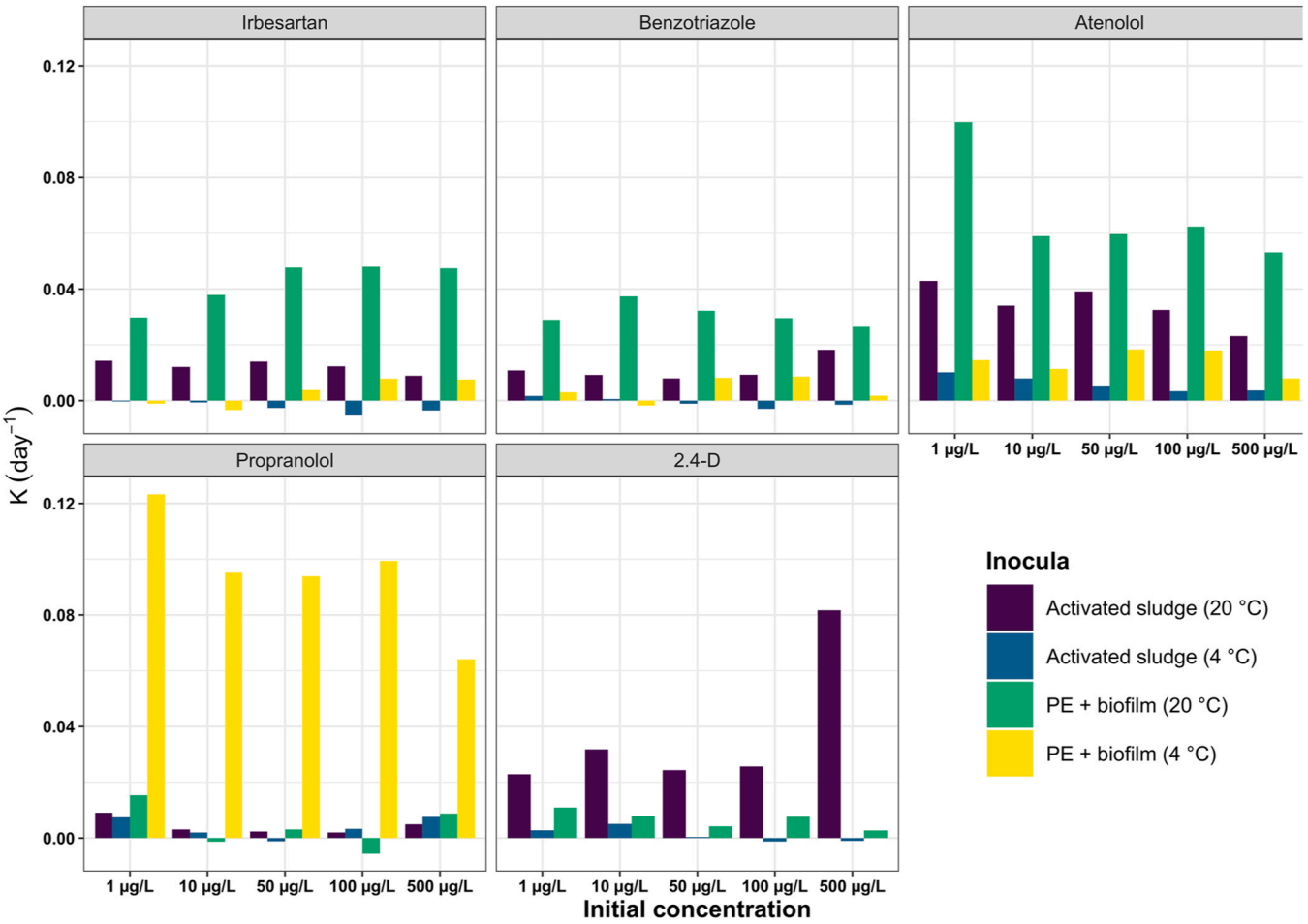


Fig. 5. Removal rate (k) (day^{-1}) for irbesartan, benzotriazole, atenolol, propranolol and 2,4-D as a function of initial concentration level. K was extracted from the pseudo-first-order kinetic models (Eq. 5). Batches with PE + biofilm were incubated at 4 °C for 7 d and then at 20 °C for 42 d.

shift could disturb the overall biodegradation activity of the original activated sludge community toward 2,4-D. Previous research evidenced that coexistence of PE microplastics with other substrates interfered with the development of specific organisms in wastewater treatments. For example, PO_4^{3-} removal by phosphorus-accumulating organisms in wastewater treatment was inhibited in presence of microplastics, even at lower concentration than the one used in the present study (Yang et al., 2022).

4. Outcomes

With this study, we confirmed that high density polyethylene microplastic particles can adsorb micropollutants, including propranolol, trimethoprim and sotalol. The presence of PE and the development of a biofilm promotes biodegradation of irbesartan, atenolol and benzotriazole but reduces the biodegradation of 2,4-D. Enhanced biodegradation of irbesartan, atenolol and benzotriazole is of interests as these three OMPs may be present in wastewater (Papageorgiou et al., 2016) and may interact with the various microplastics present in the wastewater treatment plant and activated sludge aeration tank.

Laboratory produced microplastic particles, such as the one used in this project, are not representative of the actual microplastic pollution in wastewater (Munoz et al., 2021), specially at this concentration (5 g/L). Furthermore, the used aging protocol may not produce aged-PE representative of field PE. Most environmental aging mechanisms are physical abrasion and photo-oxidation (Sun et al., 2020) while the Fenton reaction is infrequently used in conventional wastewater treatment primarily due to its high operational costs, complex handling requirements for hydrogen peroxide and iron salts, and significant safety concerns related to the storage and use of these reactive chemicals (Zhang et al., 2019). Additionally, the environmental burden of disposing of iron sludge generated during the process further limits its practical application (Shokri and Fard, 2022; Zhang et al., 2019). Despite these challenges, our study employs Fenton oxidation as a novel method to artificially age microplastics, leveraging its robust oxidative properties to simulate environmental degradation processes under controlled laboratory conditions. This approach allows us to model the weathering effects on microplastics, enhancing our understanding of their interactions with environmental pollutants and assessing their impact more accurately. By adopting this method, we aim to contribute valuable insights into the dynamics of microplastic degradation and its implications for ecological risk assessments, bridging the gap between laboratory research and real-world environmental scenarios. In this study, this method proved its feasibility of modifying the surface area of the PE particles and influencing their sorption behaviour, as expected.

The subsequent phase of this investigation should focus on determining the extent to which such aging procedures impact the microbial community composition, diversity, and biodegradation activity of the biofilms colonising microplastic particles. It is hypothesized that artificially aged polyethylene (PE) particles may exhibit an increased density of functional groups such as carbonyl, hydroxyl, ketone, and ester, thereby altering surface polarity and influencing biofilm community development. However, precise quantitative and qualitative assessments are essential to confirm these alterations. Such modifications to the microplastic surface might significantly affect the alpha diversity, biomass, and pathogen abundance of aged microplastics (Shan et al.,

2022), potentially altering the biodegradation efficiency of organic micropollutants. Future research needs rigorously evaluate these potential impacts to enhance our understanding of microplastic biodegradation processes in aquatic environments.

The high diversity of plastic, in their size, shape and composition, is an issue for water treatment performance and assessment as they may exhibit different adsorbent capacity toward OMPs or biofilms. This will modify the bioavailability of OMPs to microbial communities and therefore limit the biodegradation of these adsorbed OMPs (Yu et al., 2021). Microplastics might as well function as a type of biocarrier for microbial communities. This might be utilized to improve the removal of some organic micropollutants, as demonstrated in the present study. However, it could as well facilitate the spread of pathogens in sewage and surface water (Lai et al., 2022).

The potentially biased biodegradation of microplastics, when using activated sludge from wastewater treatment plants compared to biofilms developed on microplastics, requires further scrutiny. In municipal wastewater environments, the presence of abundant nutrient-rich carbon sources facilitates the co-metabolism of organic micropollutants alongside the primary metabolism of carbon nutrients by microbial communities. In contrast, microbiomes that colonise microplastics in carbon-limited settings may display a propensity to prioritize the metabolism of plastics as their primary carbon source. The presence of auxiliary carbon sources could thus serve as a confounding factor in accurately assessing the biodegradation capacities of microbiomes derived from differing origins. This distinction underscores the need for a rigorous evaluation of biodegradation processes, considering the environmental context and carbon availability, to ensure valid comparisons and enhance our understanding of microbial interactions with microplastics.

5. Conclusion

Ultra-high-density polyethylene microparticles and organic micropollutants are both emerging contaminants. Interaction between microplastics and organic micropollutants may lead to a modification of the bioavailability and biodegradation. Propranolol, trimethoprim and sotalol are micropollutants that were adsorbed by polyethylene microplastics. Aged microplastic particles adsorbed more sulfamethoxazole, chloridazon, caffeine and sotalol than the non-aged particles. Furthermore, the presence of a microbial biofilm on the microplastic particles affected the sorption capacity of the microplastic. This, combined with the catabolic activity shift of the microbial community in the presence of microplastic particles, is greatly affecting the bioavailability and biodegradability of organic micropollutants. Growth of the microbial community on microplastic particles positively or negatively modified the sorption of some micropollutants. With this study, we contribute to the understanding of microplastic pollution, and its associated microbial community, and the effect on the fate of organic micropollutants in wastewater.

CRediT authorship contribution statement

Baptiste Alan, Jean Poursat: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Alette A.M. Langenhoff:** Writing – review & editing, Supervision, Conceptualization. **Ruud J.B. Peters:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Conceptualization. **Nora B. Sutton:** Writing – review & editing, Validation, Supervision, Resources, Conceptualization. **Jiahao Feng:** Writing – original draft, Investigation, Data curation, Conceptualization. **Julianne Goense:** Writing – original draft, Investigation, Data curation, 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. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2024.116510.

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