

1 Bisphenol A sorption on commercial polyvinyl chloride microplastics: Effects of UV-aging
2 and biofilm colonization on plastic behaviour in the environment

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9 **Abstract**

10 Plastic particles degrade in the natural environment resulting in the modification of their
11 physical and chemical characteristics. However, little is known about the effect of plastic
12 particle degradation on the behaviour of plastic additives and their environmental fate. In this
13 study, two types of commercial polyvinyl chloride (PVC₁ and PVC₂) microplastics were aged
14 by UV irradiation and biotic modification via biofilm colonization to investigate the sorption
15 and desorption behaviour of bisphenol A (BPA). The sorption capacity of microplastics
16 generally increased after biofilm colonization, which might be related to the new functional
17 groups generated by microorganisms enhancing the affinity for BPA. The opposite effect was
18 observed for desorption. Field studies suggested that both the properties of biofilms and
19 polymers might be important factors that determine contaminant sorption behaviour in surface
20 waters. Surface cracks and new functional groups were found on PVC₁ after UV irradiation,
21 which increased available sorption sites and enhanced H-bonding interaction, however, no
22 significant changes were observed for PVC₂. Suspect screening analysis showed that the
23 presence of antioxidants and UV stabilizers might be important factors controlling the UV
24 aging degree of PVC microplastics, and indirectly influencing microorganisms' colonization

25 on microplastics. This study provides important new insights into the evaluation of the fate of
26 plastic particles in natural environments.

27 **Keywords:** PVC; adsorption; desorption; bisphenol A; additives

28 **1.Introduction**

29 Commercial plastic products are widely used in both manufacturing and human
30 activities (Hahladakis et al., 2015; Singla et al., 2020). Although plastic products bring
31 convenience, they also result in large amounts of plastic waste. It has been reported only about
32 20 % of plastic waste is recycled or incinerated, with the majority of plastic wastes
33 accumulating in landfills or released into the environment (Geyer et al., 2017). It has been
34 estimated that around 8 million tons of plastic waste enter into the ocean annually, which
35 dramatically increases the exposure risks from plastics and pollutants in the aquatic
36 environment (Jambeck et al., 2015). Previous studies have suggested that plastics can adsorb a
37 wide range of compounds in the aquatic environment including polychlorinated biphenyls
38 (PCBs), polycyclic aromatic hydrocarbons (PAHs), etc. (Chen et al., 2020; Rios et al., 2010),
39 and so they are considered as an important transport vector.

40 Plastic wastes gradually age under abiotic processes (e.g., ultraviolet radiation) and
41 biotic processes (e.g., biofilm colonization) when they are released to the natural environment
42 (Bhagwat et al., 2021; Zhang et al., 2020). Such processes could be an important variable that
43 affects the interaction between plastics and pollutants as aging can alter the physicochemical
44 properties of plastics debris. Commercial plastics are polymers within which additives (e.g.,
45 plasticizers, flame retardants, antioxidants, etc.) are present with the additives having the
46 potential to affect the aging process of plastics (Luo et al., 2022). For example, a previous study
47 revealed that the presence of the Irgafos 168 (antioxidant) that is added to prevent the formation
48 of radicals and inhibit the UV aging effects for microplastics (Wu et al., 2021). In addition,

49 studies have revealed that plasticizers (e.g., phthalates) could increase the attachment of
50 microorganisms on plastic surfaces and promote the colonization of biofilms (Debroy et al.,
51 2021; Wang et al., 2022). The presence of additives might therefore affect the
52 sorption/desorption behaviour of plastics debris for chemical pollutants through controlling the
53 aging process of plastics. Up to now, most studies on additives have only focussed on their
54 leaching behaviour during the aging process, whilst few studies have illustrated how additives
55 could impact the sorption/desorption behaviour of chemical on plastics when plastic debris act
56 as vectors for pollutant transport in the environment. As additives are an integral part of
57 commercial plastic products, exploring the role of plastic additives on plastics' environmental
58 behaviour could better assess the exposure risks of plastic debris in the environment.

59 Polyvinyl chloride (PVC) is one of the most widely consumed plastics worldwide and
60 is known to contain a high number of additives compared to other polymers. For example,
61 plasticizers can make up over 50 % of the total weight of PVC plastics (Net et al., 2015). In
62 addition to that, PVC is one of the most difficult plastics to manage (Bell; and Takada, 2021)
63 as it is not easy to recycle (Liu et al., 2020; Ragaert et al., 2017). As a result, PVC has been
64 shown to result in a high environmental exposure risk and is an ideal material to investigate the
65 role of additives on environmental behaviour of plastics. In this study, two types of commercial
66 polyvinyl chloride (PVC) that were purchased from two different sources were modified by
67 abiotic (artificial UV), biotic (biofilms colonization) aging processes and their combination to
68 obtain more environmentally representative particles to investigate their interaction behaviour
69 with bisphenol A (BPA). BPA is one of the most commonly used chemicals for the production
70 of polycarbonate polymers, epoxy resins, food containers, medical equipment and electronics
71 (Vandenberg et al., 2007). In addition, BPA is widely detected in many personal care products
72 such as body lotions, face wash, shampoo, etc, along with river, seawater, sediment and human
73 urine samples (Huang et al., 2020; Jala et al., 2022; Tschersich et al., 2021; Xie et al., 2022).

74 As an endocrine disrupting chemical (EDC) its toxicity and bioavailability have also been
75 widely studied. BPA was therefore chosen as a model target contaminant that coexists with
76 PVC in aqueous environments. In addition, mass spectrometry based suspect screening
77 analysis was used to reveal the effect of additives on the aging process of PVC microplastics.
78 The objectives of this study were therefore to (i) probe the role and function of plastic additives
79 in the aging process of commercial PVC microplastics and determine how plastic additives can
80 effect sorption/desorption behaviour of PVC microplastics in the aquatic environment; (ii)
81 explore different aging pathways for their effect on sorption and desorption behaviour of BPA
82 on PVC microplastics, and to investigate the interaction mechanism between BPA and PVC
83 microplastics to clarify the potential relationship between the ageing of plastics and the
84 uptake/release behaviour of BPA.

85 **2. Materials and methods**

86 2.1 chemicals and reagents

87 Acetonitrile and Methanol (HPLC grade) were purchased from Fisher Scientific Ltd
88 (UK). Bisphenol A (BPA, purity $\geq 99\%$) was purchased from Sigma-Aldrich Co. LLC (UK)
89 and the detailed information of BPA is shown in Table S1. Stock BPA solution (100 mg/L)
90 was prepared in methanol and kept at 4 °C. Crystal violet solution was purchased from Sigma-
91 Aldrich Co. LLC (UK).

92 2.2 Preparation of commercial microplastics and samples characterization

93 2.2.1 Fresh microplastic samples

94 Two types of PVC plastic (PVC₁ and PVC₂) were obtained from a market (Guangzhou,
95 China) and Hilltop Products Ltd (UK). PVC₁ is a soft material used in table mats and PVC₂ is
96 a granule used in the construction industry and present in the electrical component

97 (e.g., electrical insulation, wires, and cable coatings). The structures of PVC plastic polymers
98 are given in Fig. S1. PVC₁ was firstly cut to small pieces (approximately 3-5 mm) to get the
99 similar particle size with plastics with PVC₂. All PVC microplastic samples were washed with
100 ultrapure water to remove surface impurities and then air-dried before use.

101 2.2.2 UV aged microplastic samples

102 Fresh PVC₁ and PVC₂ microplastic materials were placed into crimp cap quartz vials
103 (7 pieces of microplastics in each vial). All quartz vials were placed into a Suntest CPS+ xenon
104 chamber (Atlas Material Testing Technology LLC (USA)) for the accelerated aging
105 experiments. The Xenon arc lamp produced an irradiance of 750 W m⁻². The wavelength of
106 radiation ranged from 300 nm to 800 nm, temperature was set at 35 °C and performed for one
107 week (7 days).

108 2.2.3 Biofilm colonized microplastic samples

109 Fresh and UV aged PVC₁ and PVC₂ microplastics were incubated in flasks and shaken
110 (110 rpm) with the addition of activated sludge obtained from the Lancaster Wastewater
111 Treatment Plant (WWTP) at 23 ± 1 °C for four weeks (28 days). After four weeks incubation,
112 the biofilms colonized microplastics were separated from the sludge and washed with ultrapure
113 water and kept sealed at 4 °C until further analysis. In addition, the two types of PVC plastic
114 sample were also incubated in ultrapure water for four weeks as the control group.

115 In addition, field deployments were also carried out to colonize biofilms on fresh and
116 UV aged PVC₁ and PVC₂ microplastics to study the effect of different environmental factors
117 on microorganism attachment and sorption/desorption behaviour. Two in situ sites selected
118 were the River Conder (54°00'29.8"N 2°46'17.9"W, Lancaster, UK) and the active sludge plant
119 of WWTP (54°00'29.8"N 2°46'17.9"W, Lancaster, UK). Fifty fragments of fresh and UV aged
120 microplastics were packed in filter bags (8 cm × 10 cm). Filter bags were placed into a large

121 mesh nylon bag (11 cm × 17 cm) to exclude large organisms. All bags were finally loaded into
122 metal cages, details are shown in Fig. S2. After incubation for four weeks (May-June), the
123 metal cages were transported to the laboratory. The microplastics samples were washed with
124 ultrapure water and kept at 4 °C for further analysis.

125 2.2.4 Microplastics characterization

126 PVC₁ and PVC₂ microplastic samples after the different aging treatments were
127 characterized by Fourier-transform infrared spectroscopy (FTIR, Agilent, USA) and recorded
128 in the range of 4000–400 cm⁻¹ to identify transformations of the surface functional groups. In
129 addition, microplastics after removal of biofilms were also characterized by FTIR to assess
130 biodegradation. The cleaning method of biofilm colonized microplastics followed the
131 previously reported protocol of (Supporting Information-M1) (Sandt et al., 2021), which was
132 demonstrated to have minimal impact on the oxidation of microplastics. Biofilm biomass was
133 quantified with a modified crystal violet (CV) method and illustrated in Supporting
134 Information-M2 (Lobelle and Cunliffe, 2011). Scanning electron microscopy (SEM, JEOL
135 JSM 7800F) was performed to characterize the surface changes of PVC microplastics after UV
136 irradiation and biofilms colonization.

137 2.3 Suspect screening for microplastic samples using LC-MS

138 Suspect screening was conducted on solvent extracts produced from both fresh and UV
139 aged PVC₁ and PVC₂ microplastics to determine the additives present in the microplastics.
140 Samples of each PVC microplastic (100 mg) were extracted with 5 mL methanol (ME), n-
141 hexane and dichloromethane (DCM) respectively by ultrasonication for 30 min at room
142 temperature. ME, n-hexane and DCM without microplastic samples were used as a control. In
143 addition, fresh PVC₂ microplastics with colonized biofilms were also analysed with the same
144 method using suspect screening analysis to identify plasticizers present and changes compared

145 with fresh counterparts. During the extraction, glassware was used throughout to prevent the
146 contamination of exogenous plastic additives. Solvent extracts were filtered by PTFE and the
147 volume adjusted to approximately 800 μL prior to liquid chromatography-mass spectrometry
148 (LC-MS) analysis. The extracts were analyzed using a HPLC system (Waters ACQUITY™,
149 USA) coupled to a QTOF MS system (Waters Xevos G2-S, USA). The analysis and qualitative
150 method were modified from our previously published method (Qiu et al., 2021) and details are
151 listed in Supporting Information-M3.

152 The presence of chemical additives was quantified according to changes in instrument
153 response. Higher response number indicated higher concentration of the compound. In order
154 to guarantee the accurate and credibility of the data, all extraction samples were run in one
155 batch that ensure the instrument to ensure consistent running conditions.

156 2.4 Adsorption experiments

157 BPA stock solution (100 mg/L) was diluted to 100 $\mu\text{g/L}$ with ultrapure water, the
158 volume ratio of methanol kept below 0.01 % to reduce solvent effects. Before the adsorption
159 experiments, 10 mL 100 $\mu\text{g/L}$ BPA solution was placed into glass tubes to assess the loss of
160 BPA caused by volatilization and adsorption to glass surfaces. Results showed that the loss of
161 bisphenols in centrifuge tubes was less than 1 %.

162 For the adsorption kinetic study, 50 mg of microplastics and 10 mL 100 $\mu\text{g/L}$ BPA were
163 added into glass tubes. All tubes were placed on the shaker at 140 rpm (25 ± 1 °C). The
164 supernatants were collected after 12 h, 24 h, 48 h, 72 h, 96 h, 120 h, 168 h, 216 h, 264 h, and
165 filtered through a 0.2 μm PTFE membrane. All the experiments were performed in triplicate.
166 In addition, the sorption behaviour of biofilms colonized microplastics (between laboratory
167 and field work) was also investigated.

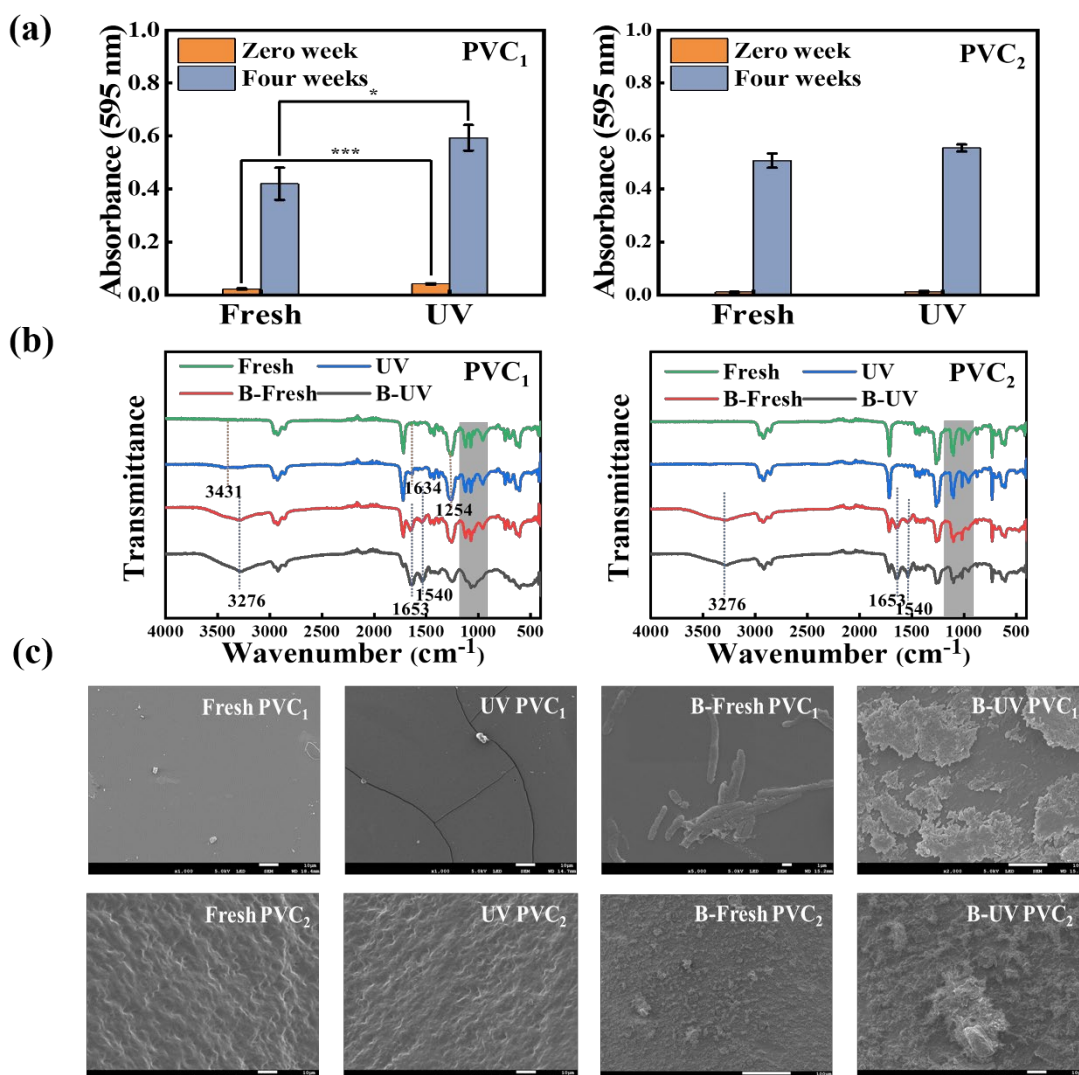
168 2.5 Desorption experiments

169 After sorption equilibrium was achieved, microplastics from the sorption experiments
170 were transferred into glass tubes containing 10 mL ultrapure water, and shaken at 140 rpm. For
171 the biofilms colonized microplastics environment (laboratory and field) the desorption capacity
172 of BPA was also assessed. Three replicates were conducted for each treatment. The
173 supernatants were collected from 0 h to 120 h. All supernatants were analysed by a Shimadzu
174 NexeraX2 ultra high-performance liquid chromatography (UHPLC), details about UHPLC
175 conditions are presented in Supporting Information-M4.

176 2.6 Statistical analysis

177 T-test and ANOVA were used to analyse significant differences. All statistical analysis
178 was performed using SPSS 22.0 software and Microsoft Office Excel 2020. Figures were
179 plotted with Origin 2019. All calculation equations are listed in the Supporting Information-
180 M5.

181 **3. Results and discussion**

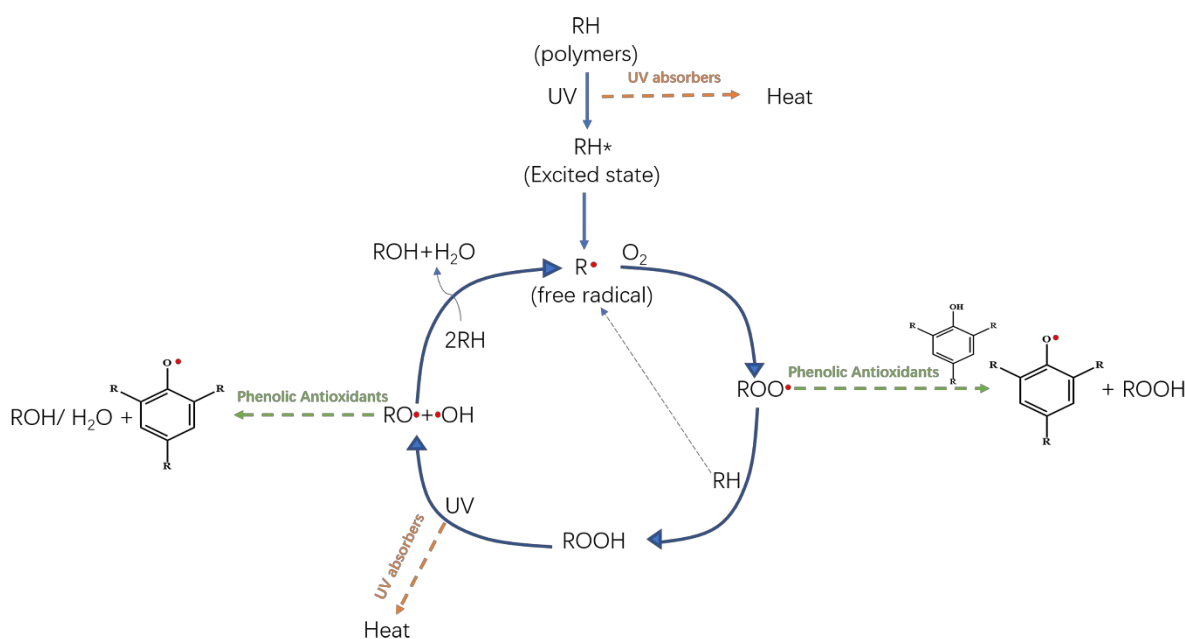


183 **Fig. 1.** (a) Changes in absorbances of crystal violet dye for fresh and UV aged PVC1 and PVC2
 184 microplastics that incubated biofilms in the laboratory. Error bars are the means \pm standard
 185 deviation (SD) of three repeats. * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. (b) FTIR spectrogram
 186 of fresh, UV aged, biofilms colonized fresh (B-Fresh) and UV aged (B-UV) microplastics. (c)
 187 SEM images of microplastics with different aging treatment.

188 3.1.1 UV aging

189 UV irradiation results in obvious changes to PVC₁ microplastics. As illustrated in Fig. 1b,
 190 slight vibration occurred at 3431 cm⁻¹ (O-H), a new peak appeared at 1634 cm⁻¹ (C=C) and the

191 vibration of C–Cl at 1254 cm^{-1} reduced slightly after UV aging, which might indicate that
 192 dehydrochlorination and oxidation reactions occurred for PVC₁ during the UV aging process
 193 (Wang et al., 2020). In addition, the crystal violet (CV) method also suggests the changes of
 194 functional groups of PVC₁ microplastics after UV aging (Fig. 1a). The initial binding of CV
 195 significantly increased after UV aging for PVC₁ microplastics (T-test, $p < 0.05$). The generation
 196 of new functional groups (e.g., O–H, C=C, C=O, etc.) allows the bonding (H-bonding
 197 interaction, π - π interaction) with the dye molecules (Bhagwat et al., 2021; Yi et al., 2021).
 198 Moreover, the SEM images also suggest changes after UV aging as the surfaces of fresh PVC₁
 199 microplastics were smooth, whilst in contrast, the surfaces were cracked after UV irradiation
 200 (Fig. 1c). However, few changes could be characterized by FTIR spectrum and SEM images
 201 for PVC₂ microplastics after UV aging treatment (Fig. 1b and 1c), suggesting that UV aging
 202 resulted in very few changes to the structures and properties of PVC₂. The different changes
 203 between PVC₁ and PVC₂ microplastics after UV aging might be related to the additives used
 204 in the production of the plastics.



205 **Fig. 2.** The aging mechanism of plastics and the function of antioxidants and light stabilizers

206 Antioxidants (e.g., phenolic antioxidants, amine antioxidants, phosphorus antioxidants,
 207 etc.) and light stabilizers (e.g., UV absorbers, hindered amine light stabilizers (HALS),
 208 quenchers, etc.) are the most widely used additives to resist oxidation, UV degradation and
 209 improve the life cycle of polymers (Rani et al., 2017). According to the results of suspect
 210 screening analysis, a range of antioxidants and light stabilizers were found in fresh PVC₁ and
 211 PVC₂ microplastics (Table 1). However, for fresh PVC₁ microplastics, only Irganox 245
 212 (phenolic antioxidants) was detected, which functions by capturing and removing free radicals
 213 (e.g., RO•, ROO•, etc.), resulting in the prevention of chain degradation reactions and further
 214 radical oxidation, see Fig. 2. Irganox 1076 (phenolic antioxidants), Isonox 132 (phenolic
 215 antioxidants), Tinuvin 144 (HALS) and Tinuvin 234 (UV absorber) were detected in the
 216 solvent extracts of fresh PVC₂. After UV aging, the antioxidants cannot be detected in the
 217 extracts of PVC₁ microplastics (Fig. S3), which indicates that phenolic antioxidants were all
 218 consumed and converted to their degradation products (Fig. 2). However, all of the antioxidants
 219 and UV absorbers still remained in UV aged PVC₂ extracts (Fig. S3). It's known that UV
 220 stabilizers can absorb UV and transfer irradiation to heat (Fig. 2), with a previous study
 221 reporting a synergistic effect between UV stabilizers and antioxidants (Jiang et al., 2021),
 222 which might improve the UV aging resistance of PVC₂. As a result, with the protection of
 223 antioxidants and light stabilizers, PVC₂ showed less changes to its properties compared with
 224 PVC₁ after UV irradiation.

225 **Table 1.** Antioxidants and light stabilizers identified in fresh PVC₁ and PVC₂ microplastics.

Microplastics type	Antioxidants	Light stabilizers	
	Phenolic antioxidants	UV absorbers	HALS
PVC ₁	Irganox 245	-	-

226

227 3.1.2 Colonization by biofilms

228 The estimation of biomass using the CV method indicated an obvious colonization of
229 biofilms after incubation over four weeks (Fig. 1a). In addition, it was observed that biomass
230 growth was higher on UV aged PVC₁ microplastics compared with fresh microplastics, whilst
231 there was no significant difference ($P < 0.05$) for PVC₂ microplastics, as shown in Fig. 1a.
232 Recent studies showed that the increased roughness and hydrophilicity (generation of O-
233 containing functional groups) of microplastics could promote the colonization of
234 microorganisms on microplastics (Ho et al., 2020; Hossain et al., 2019). In the natural
235 environment, the degradation of plastics is probably initiated with UV aging to reduce
236 molecular weight and size of plastics, which can then be metabolized by microorganisms (Ali
237 et al., 2021). Therefore, UV degradation might be an important factor affecting the attachment
238 of microorganisms on microplastics. As antioxidants and light stabilizers are vital factors to
239 control the UV aging degree of microplastics, they could also indirectly affect the formation of
240 biofilms on microplastics.

241 The FTIR spectrum illustrated new peaks were generated at 3293 cm^{-1} (N-H), 1653 cm^{-1}
242 (C=O , amide I) and 1540 cm^{-1} (N-H and C-N, amide II) for both PVC₁ and PVC₂
243 microplastics after biofilms colonization (Fig. 1b), which represent the characteristic peaks
244 from proteins, and as an indicator of biofilm formation (Sandt et al., 2021). In addition, the
245 intensity of a spectral region between $1180 - 900\text{ cm}^{-1}$ (shaded in grey) obviously changed
246 after colonization by biofilms, which represents vibrations from polysaccharides (Sandt et al.,
247 2021). For both PVC₁ and PVC₂ microplastics surface changes and microorganisms (e.g., rod-

248 like bacteria) were observed in SEM images (Fig. 1c), which confirmed biofilm formation on
249 microplastics.

250 It is worth noting that the peak at 1720 cm^{-1} (C=O) of FTIR spectrum for fresh PVC₁
251 and PVC₂ microplastics represents the characteristic peak for plasticizers (Fig. S9), which
252 could also be observed in other plasticized PVC plastics but does not exist in the pure
253 experimental unplasticized PVC plastics (Altenhofen da Silva et al., 2011; Patil and Jena, 2021).
254 However, the intensity of C=O clearly reduced after removing the biofilms (Fig. S9, red
255 spectrum-b). The FTIR spectrum of PVC microplastic samples incubated in ultrapure water
256 showed no obvious change of C=O (Fig. S10), which excludes the effect of possible leaching
257 behaviour of plasticizers during the biofilm's incubation process. It suggests that the
258 plasticizers could be metabolized by microorganisms. As biofilms colonized fresh PVC₂
259 microplastics showed the most obvious changes of C=O bonding, they were also subjected to
260 suspect screening analysis to further investigate any changes to the plasticizers after biofilm
261 formation. The results from Fig. S4 suggest that the presence of plasticizers decreased after
262 biofilms colonization. Dimethyl phthalate, Dibutyl phthalate, and Diethyl phthalate could not
263 be detected in the extracts of PVC₂ microplastics after biofilms colonization, which indicates
264 that plasticizers were consumed by microorganisms. Previous studies have suggested that
265 plasticizers could act as a carbon source that can be utilized by many fungi or bacteria, hence
266 promoting the initial colonization of microorganisms on PVC plastics (Ru et al., 2020; Singh
267 Jadaun et al., 2022; Wang et al., 2022). This indicates that the presence of plasticizers might
268 also be important for the formation of biofilms on microplastics.

269 3.2 Adsorption and desorption behaviour of BPA on microplastics

270 3.2.1 UV aging

271 The sorption kinetics curves for BPA on PVC microplastics are shown in Fig. S5. The
272 kinetics data demonstrate that sorption equilibrium for BPA on fresh PVC₁ microplastics were
273 achieved within 168 h (one-way ANOVA analysis, $p > 0.05$), and the time needed to reach
274 sorption equilibrium became shorter after UV irradiation (72 h). This suggested UV aging
275 could accelerate the sorption of BPA on PVC₁ microplastics. In addition, the fitting model
276 suggested that the sorption behaviour of fresh PVC₁ microplastics could be better described by
277 a pseudo-first-order model, whilst better described by a pseudo-second-order model after UV
278 irradiation (Fig.S6). This indicates that the rate-limiting step was a physical process for fresh
279 PVC₁, but relies on chemical processes which involve the adsorption between the adsorbent
280 and adsorbate after UV aging treatment (Mohan et al., 2006). The sorption capacity of BPA on
281 PVC₁ microplastics significantly increased after UV aging (Fig. 3a). The generation of new
282 functional groups (e.g., O–H) could potentially have enhanced the H-bonding between
283 microplastics and BPA (Zhou et al., 2020). In addition, the cracks in UV aged microplastics
284 can offer more available sorption sites and enhance the sorption capacity (Chen et al., 2022).
285 However, the sorption behaviour for PVC₂ microplastics didn't show such obvious changes
286 after UV irradiation as the sorption equilibrium time (both achieved equilibrium within 96 h
287 before and after UV irradiation, Fig. S5), sorption rate-limiting step (both better described by
288 a pseudo-first-order model and sorption behaviour was dominated by physical process, Fig.
289 S6) and sorption capacity (Fig. 3a) showed no significant changes after irradiation (T-test, $p >$
290 0.05). With the protection of antioxidants and light stabilizers, most chain degradation reactions
291 could have been prevented leading to few changes in the physicochemical properties of PVC₂
292 microplastics (Fig. 1), and thus further limiting changes in the sorption behaviour.

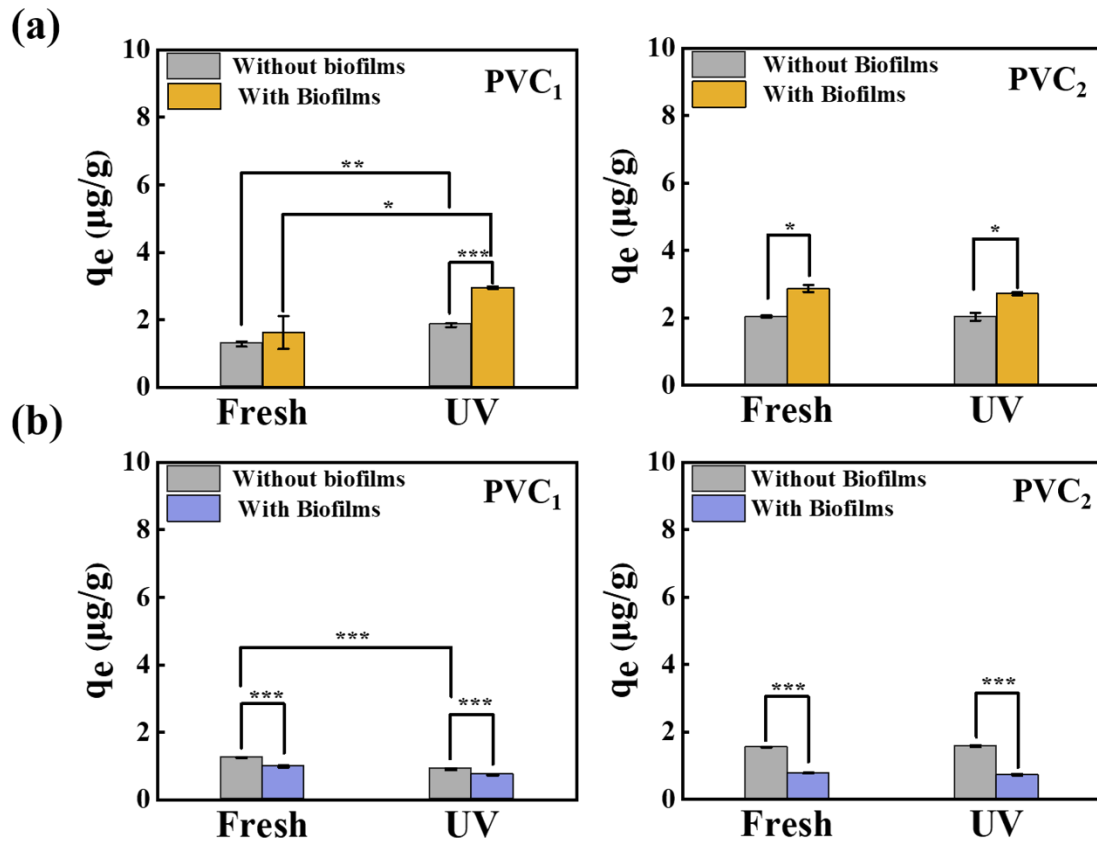
293 The aging degree also impacted the desorption behaviour of BPA on microplastics. As
294 shown in Fig. 3b, the desorption capacity of PVC₁ reduced after UV aging (T-test, $p < 0.001$),
295 where the cracks in the microplastics allowed more BPA to diffuse into the structure or narrow

306 pores rather than surface sorption. This suggests it is more difficult for UV aged PVC₁
307 microplastics to release BPA compared to fresh microplastics (Fan et al., 2021; Sun et al.,
308 2021). In contrast, no significant change was observed for PVC₂ after UV aging (T-test, $p >$
309 0.05). This could also be attributed to no obvious changes to the physicochemical properties of
300 PVC₂ after irradiation. As a result, plastic additives (antioxidants and light stabilizers) could
301 not only affect the UV aging behaviour of polymers but also indirectly impact the sorption and
302 desorption behaviour of pollutants on polymers by controlling the aging process.

303 3.2.2 Biofilms colonization

304 The pseudo-second-order model better described the sorption process of BPA for both
305 PVC₁ and PVC₂ microplastics after biofilm colonization (Fig. S6), which indicates that the
306 adsorption process might mainly be controlled by chemical processes (Y.S. Ho, 1999). The
307 sorption capacity was enhanced (although no significant difference for fresh PVC₁) for both
308 fresh and UV aged microplastics after the colonization with biofilms (Fig. 3a). This might be
309 due to the formation of new functional groups (e.g., N-H, C=O, etc.) corresponding to biofilms
310 that can further promote affinity for BPA. Fig. S7 illustrates the FTIR spectrum of
311 microplastics after adsorption of BPA. The intensity and vibration of the biofilm characteristic
312 peaks (e.g., N-H, amide I, amide II) changes after sorption. For example, decreased intensity
313 of the peak at 3276 cm⁻¹ (N-H), 1653 cm⁻¹ (amide I) and 1540 cm⁻¹ (amide II) could be observed
314 for biofilms colonized on fresh and UV aged PVC₁ and PVC₂ microplastics after adsorption,
315 which indicates interactions (e.g., H-bonding interaction, π - π interaction, etc.) may occur
316 between BPA and biofilms colonized PVC microplastics. As BPA shows aliphatic C-H
317 vibration at around 2962 cm⁻¹ (Fig. S8), the enhanced peak of C-H for biofilm colonized PVC₁
318 and PVC₂ microplastics after adsorption might also indicate the binding of BPA on PVC
319 microplastics (Fig. S7). As a result, sorption behaviour might be impacted by microorganisms
320 for both fresh and UV aged microplastics after biofilm colonization. As shown in Fig. 3b, the

321 desorption capacity decreased for both fresh and UV aged PVC microplastics after colonization
 322 with biofilms. The enhanced H-bonding attraction could increase the affinity between BPA and
 323 PVC microplastics, which might result in the reduction of the desorption ability.

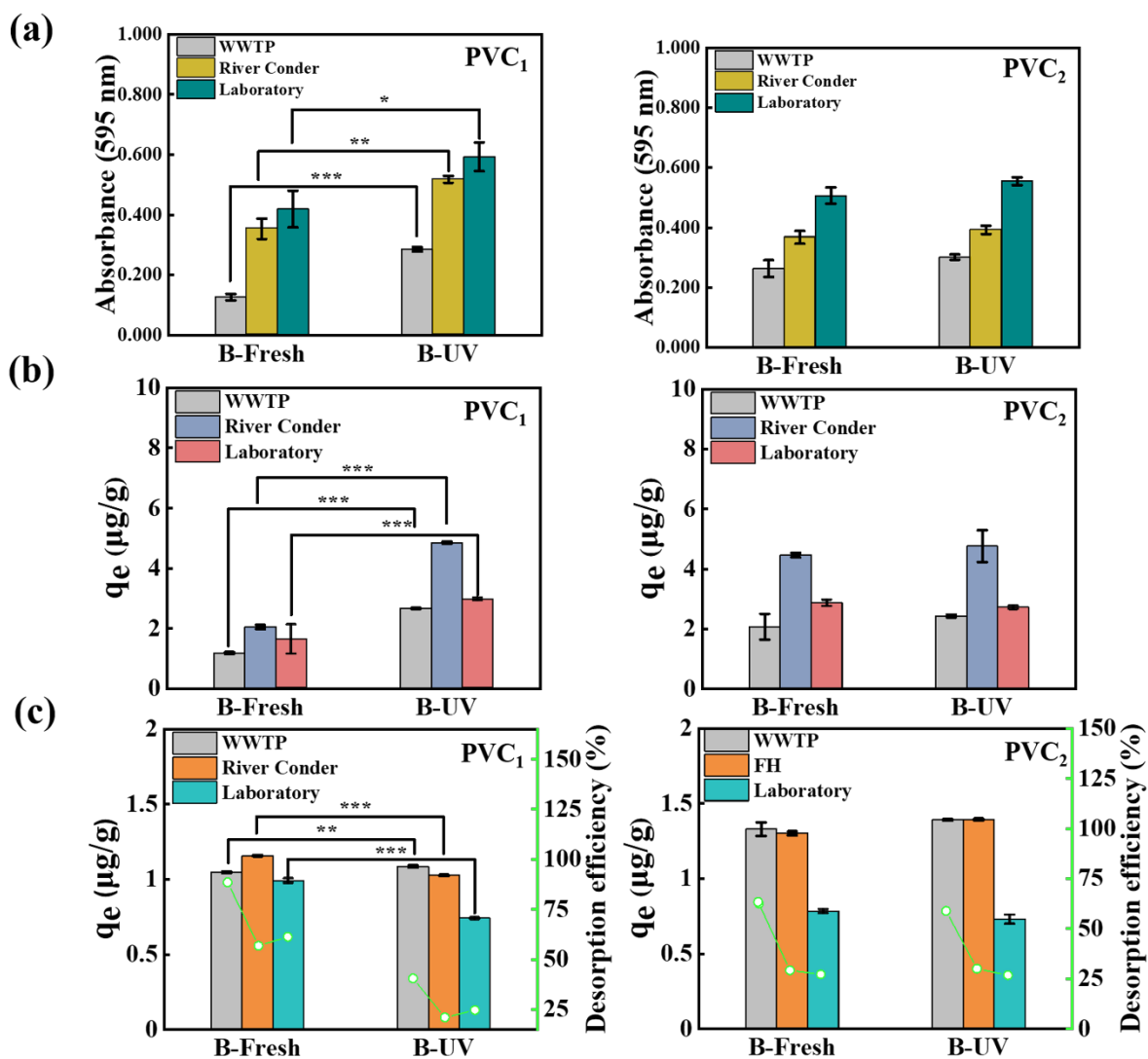


324 **Fig. 3.** (a) The sorption capacity of BPA on fresh and UV aged PVC₁ and PVC₂ with or without
 325 the colonization of biofilms. (b) The desorption capacity of BPA on fresh and UV aged PVC₁
 326 and PVC₂ with or without the colonization of biofilms. Error bars are the means ± standard
 327 deviation (SD) of three repeats. (50 mg microplastics, 10 mL 0.1 mg/L BPA, 25 °C, 140 rpm).
 328 * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

329 3.3 Field colonization by biofilms

330 Additional field work was carried out to further explore the interaction behaviour between
 331 BPA and biofilms colonized microplastics. As shown in Fig. 4a, field derived biofilms
 332 successfully colonized the microplastics. The intensity of C=O reduced after removing the

333 biofilms from PVC₁ and PVC₂ microplastics samples that were incubated in the River Conder
 334 and WWTP (Fig. S9, orange spectrum-d, green spectrum-f), which further suggests that
 335 plasticizers may be degraded by microorganisms during the biofilm's colonization process.



336 **Fig. 4.** (a) Changes in absorbance of crystal violet dye for biofilms colonized fresh (B-Fresh)
 337 and UV aged (B-UV) PVC₁ and PVC₂ microplastics that incubated in active sludge plant of
 338 wastewater treatment plant (WWTP), River Conder. (b) The sorption capacity of BPA on
 339 biofilms colonized (field and lab) fresh and UV aged PVC plastics. (c) The desorption capacity
 340 of BPA on biofilms colonized (field and lab) fresh and UV aged PVC plastics. (n=3, 50 mg
 341 microplastics, 25 °C, 140 rpm). * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

342 When considering the same biofilm incubation site, the sorption capacity of PVC
343 microplastics was positively correlated with biofilm biomass (Fig. 4a and 4b), suggesting that
344 higher biomass indicates higher affinity of BPA to PVC microplastics. Both field and
345 laboratory studies showed that UV aging could promote the colonization of biofilms on PVC₁
346 microplastics (Fig. 4a), which also verifies that the physiochemical properties changes as a
347 result of UV irradiation could enhance the attachment of microorganism and further alter the
348 sorption behaviour. However, across the different biofilm incubation sites, biomass and
349 sorption capacity didn't show a positive correlation for both PVC₁ and PVC₂ microplastics,
350 which indicates that the properties of polymers might also play an important role for the
351 sorption behaviour. As illustrated in Fig. S9, the characteristic peaks of biofilms (e.g., N-H,
352 amide I, amide II) disappeared after cleaning the microplastic surfaces, whilst the vibration of
353 the C-H stretching and C-Cl reduced for PVC₁ and PVC₂ compared with the microplastics
354 without biofilms. This indicates that biodegradation occurred after biofilm colonization. As a
355 result, the formation of biofilms not only introduces the biological signals (e.g., new functional
356 groups from protein and polysaccharide) but could also cause the biodegradation of
357 microplastics and change the properties of polymers. Both factors might affect the
358 environmental behaviour of PVC microplastics, leading to complex sorption mechanisms.

359 The data on desorption behaviour suggested that UV aged PVC microplastics showed
360 lower desorption efficiencies than fresh microplastics after colonization with biofilms under
361 both field and laboratory conditions (Fig. 4c). However, it is worth noting that the desorption
362 capacity for PVC₁ microplastics with WWTP incubated biofilms increased after UV aging (T-
363 test, $p < 0.05$), which is explained by enhanced sorption capacity. The sorption capacity of BPA
364 on UV aged PVC₁ with WWTP incubated biofilms was significantly higher than fresh
365 microplastics (Fig. 4a), although the desorption efficiency decreased sharply from 88.0 % to
366 40.7 %, the desorption capacity still increased owing to the increased sorption capacity. As a

367 result, UV aging might result in microplastics accumulating higher biomass, leading to higher
368 pollutant loadings and potentially greater pollutant release.

369 **4. Conclusion**

370 In this study, two types of PVC microplastics were modified by abiotic, biotic processes
371 and a combination of both, to obtain more realistic polymers for the investigation of the
372 sorption/desorption behaviour of BPA. Special emphasis was placed on the influence of
373 microplastic additives on the aging process and environmental behaviour. Although PVC₁ and
374 PVC₂ were the same type of polymer, they were produced with different type of antioxidants
375 and light stabilizers (chemical additives), which resulted in different aging profiles (UV aging
376 degree and microorganism colonized level) under the same aging conditions. In addition, both
377 field and laboratory biofilms incubation investigations provided evidence that plasticizers can
378 be metabolized after the formation of biofilms, which suggests that plasticizers could effect the
379 colonization behaviour of microorganisms on PVC microplastics. As the aging of microplastics
380 influences the sorption/desorption behaviour of BPA with interaction mechanisms involving
381 H-bonding interaction, π - π interaction, etc. our results highlight that plastic additives can affect
382 their environmental behaviour as a vector of pollutant transport) as they undergo ageing. This
383 is the first study to profile the role of plastic additives on sorption/desorption behaviour of
384 plastic particles, and thereby lays a foundation for further study on the fate, potential exposure
385 risk and toxicity of microplastics.

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