Supplementary Information

Enhanced sorption of the UV filter 4-methylbenzylidene camphor on aged PET microplastics from both experimental and theoretical perspectives

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Text S1. Climate conditions for outdoor experiments

Bot-PET samples were placed on the roof of the Graduate Institute of Environmental Engineering (GIEE) building (GPS coordinates: 25.0180, 121.5433; Taiwan) and climate information about the sampling site is shown in Table S1.

Table S1. Climate information for the GIEE building in Taipei

Taipei	**2019.04**	**2019.05**	**2019.06**	**2019.07**	**2019.08**	**2019.09**	**2019.10**	**2019.11**	**2019.12**	**2020.01**	**2020.02**	**2020.03**
Average Temp. (℃)	24.2	25	28.5	30.3	30.5	27.3	25.3	22	19.1	17.9	18.7	20.8
Relative Humidity (%)	76	77	77	73	72	79	74	75	77	75	72	75
Sunshine hours (hr)	105	80	91	146	187	160	139	103	81	113	126	87
Solar Irradiance (MJ/m^2)	340	331	381	490	515	479	403	324	255	306	364	365
Precipitation (mm)	115	335	419	439	212	377	27	13	136	39	30	246

The Env-PET sample was a PET bottle collected on a beach in Yilan, Taiwan (GPS coordinates: 24.8567, 121.8327; Taiwan), in February 2019, and climate information about the sampling site is shown in Table S2.

Table S2. Climate information for Yilan

Yilan	2018.03	2018.04	2018.05	2018.06	2018.07	2018.08	2018.09	2018.10	2018.11	2018.12	2019.01	2019.02
Average Temp. (℃)	20.5	22.6	27	27.8	29.2	29.1	27.7	22.8	22	19.3	18.4	19.4
Relative Humidity (%)	72	74	76	79	75	76	77	77	87	85	84	85
Sunshine hours (hr)	149	108	191	144	212	187	170	76	65	103	62	66
Solar Irradiance (MJ/m^2)	478	426	623	550	669	621	521	277	231	239	215	253
Precipitation (mm)	40	26	33	245	92	145	165	535	436	307	447	56

Text S2. LC-MS/MS conditions

The concentrations of target compounds in experimental samples were analyzed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) with an Agilent 1200 liquid chromatograph (Agilent, Palo Alto, CA, USA) equipped with a ZORBAX Eclipse XDB-C_{18} column (150 × 4.6 mm, 5 µm pore size). A binary gradient with a flow rate of 0.9 mL/min was used. Mobile phase A was composed of 0.1% (v/v) formic acid in Milli-Q water, and mobile phase B was composed of 0.1% (v/v) formic acid with methanol. The mobile phase gradient and mass spectrometer conditions for mass spectral analysis is shown in Table S3-4.

Table S3. LC-MS/MS gradient for 4-MBC analysis

ESI: positive mode Mobile Phase A: 0.1% formic acid (v/v) in DI Mobile Phase B: 0.1% formic acid (v/v) in MeOH			
Time (min)	Flow rate (mL/min)	A (%)	B (%)
0	0.9	95	5
0.5	0.9	95	5
1.5	0.9	5	95
5	0.9	5	95
5.5	0.9	95	5
8.5	0.9	95	5

Table S4. Mass spectrometry parameters of 4-MBC in the LC−MS/MS system.

Compound	Retention time (min)	Precursor ion (m/z)	DP (Volt)	**Quantitation**			**Confirmation**		
				Product ion (m/z)	CE (Volt)	CXP (Volt)	Product ion (m/z)	CE (Volt)	CXP (Volt)
4-MBC	5.56	$[M+H]^+$=255	18.5	105	25	10.5	157	25	11.5

Sample injection was carried out by the autosampler with a 20 μL injection volume at room temperature. Mass spectra were acquired using a SCIEX API 4000 mass spectrometer (Applied Biosystems, Foster City, CA, USA) that was equipped with an electrospray ionization (ESI) interface. Multiple reaction monitoring (MRM) mode was used to acquire secondary mass spectra with a dwell time of 50 ms and unit mass resolution by MS/MS. The quantitation of 4-MBC was reported for the mass transition of m/z 255 → 105.

Text S3. Data analysis of sorption experiment

The pseudo-first-order[1] and pseudo-second-order[2] models were used to fit the sorption kinetic data.

$$\text{Pseudo-first-order equation: } \ln(q_e - q_t) = \ln q_e - k_1 t \text{ eq.} \qquad (1)$$

Pseudo-second-order equation: $\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$ eq. (2)

For the pseudo-first-order equation, the formula can be plotted as t vs $\ln(q_e - q_t)$, where the slope is k_1, q_e (mg/g) and q_t (mg/g) are the sorption capacity at equilibrium and at time t, respectively, and k_1 (1/h) is the reaction rate constant of the pseudo-first-order model. For the pseudo-second order equation, the formula can be plotted as t vs $\frac{t}{q_t}$, where the slope is $\frac{1}{q_e}$, q_e (mg/g) and q_t (mg/g) are the sorption capacity at equilibrium and at time t, respectively, and k_2 (g/mg·h) is the reaction rate constant for the pseudo-second order model.

Sorption isotherms of 4-MBC on microplastics were established by the Langmuir[3] and Freundlich[4] models.

Langmuir model: $q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$ eq. (3)

Freundlich model: $q_e = K_F \cdot (C_e)^n$ eq. (4)

where q_e (mg/g) is the concentration of 4-MBC adsorbed onto the microplastics at equilibrium, C_e (mg/L) is the residual aqueous concentration of 4-MBC at equilibrium, q_m is the total number of surface sites per mass of sorbent, which is usually the same as $C_{is,max}$, K_L and K_F are the Langmuir and Freundlich isotherm coefficients, respectively, and n is the Freundlich exponent, which is often applied as an indicator of isotherm nonlinearity.

Also, the linear form of Langmuir and Freundlich models, shown in Equations (5) and (6), were used to better evaluate the sorption isotherms data.

Langmuir model: $\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}$ eq. (5)

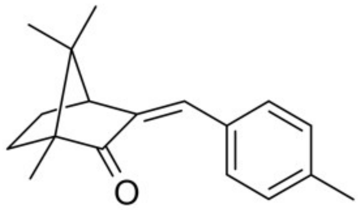
Freundlich model: $\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$ eq. (6)

The Arrhenius law [5] was used to fit the sorption activation energy between 4-MBC and the microplastics. The formula can be derived from

$$\ln\frac{k_2}{k_1} = \frac{-E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \text{ eq.} \quad (7)$$

where T_1 and T_2 were set at 20 °C and 50 °C, respectively, E_a (kJ·mole^{-1}) is the activation energy, K_1 is the reaction rate constant at 20 °C, and K_2 is the reaction rate constant at 50 °C.

4-methylbenzylidene camphor (4-MBC)



Physicochemical Properties	
Molecular mass	Molecular formula
254.4 (g/mol)	$C_{18}H_{22}O$
Solubility in water	pKa
5.1 mg/L	-
Log Kow	λ
4.95	300 (nm)

Figure S1. Physicochemical properties of 4-MBC

Figure S2. Scheme of the sorption experiment

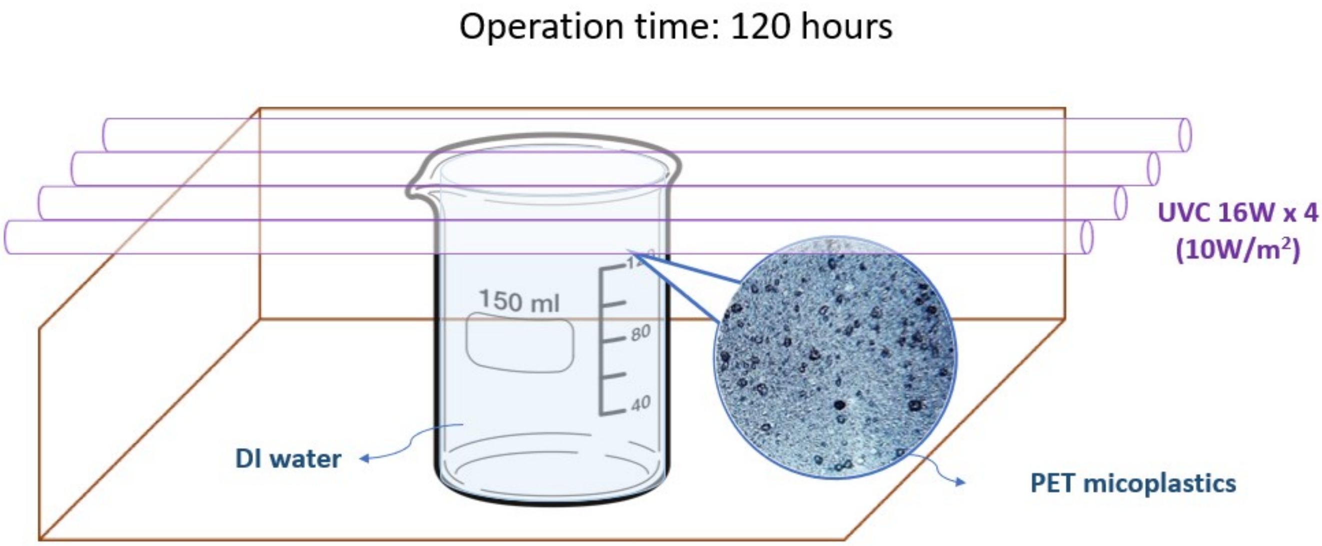


Figure S3. Experimental setup for a homemade aging system equipped with UVC lamps (254 nm)

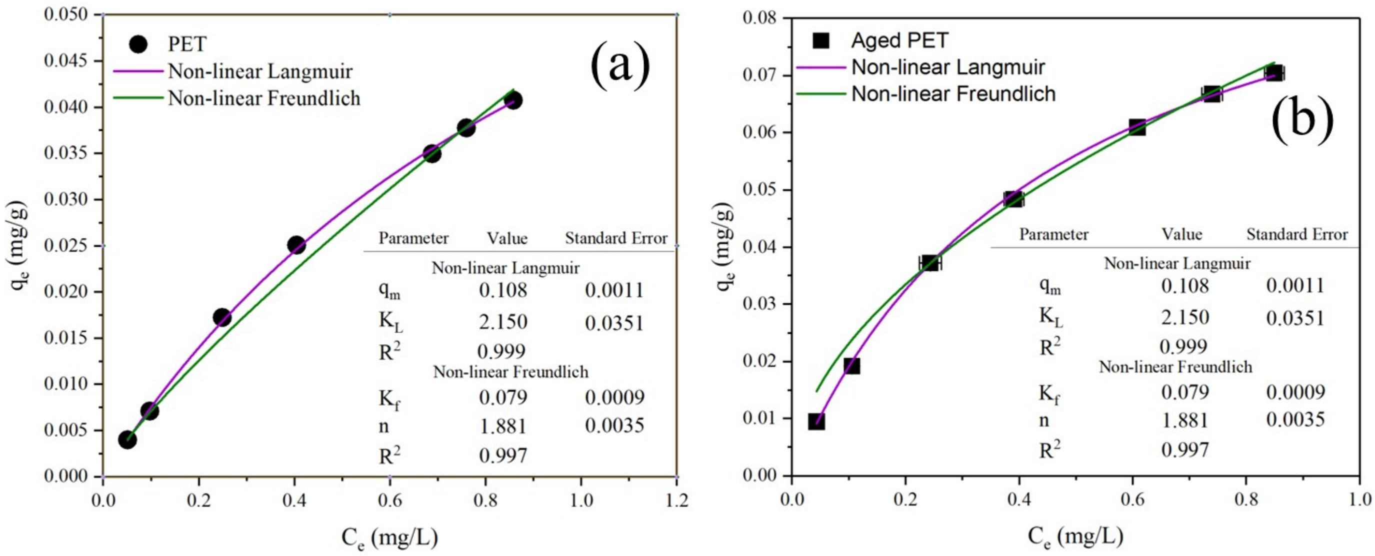


Figure S4. Langmuir and Freundlich isotherm plots for the sorption of (a) PET and (b) aged PET microplastics with 4-MBC

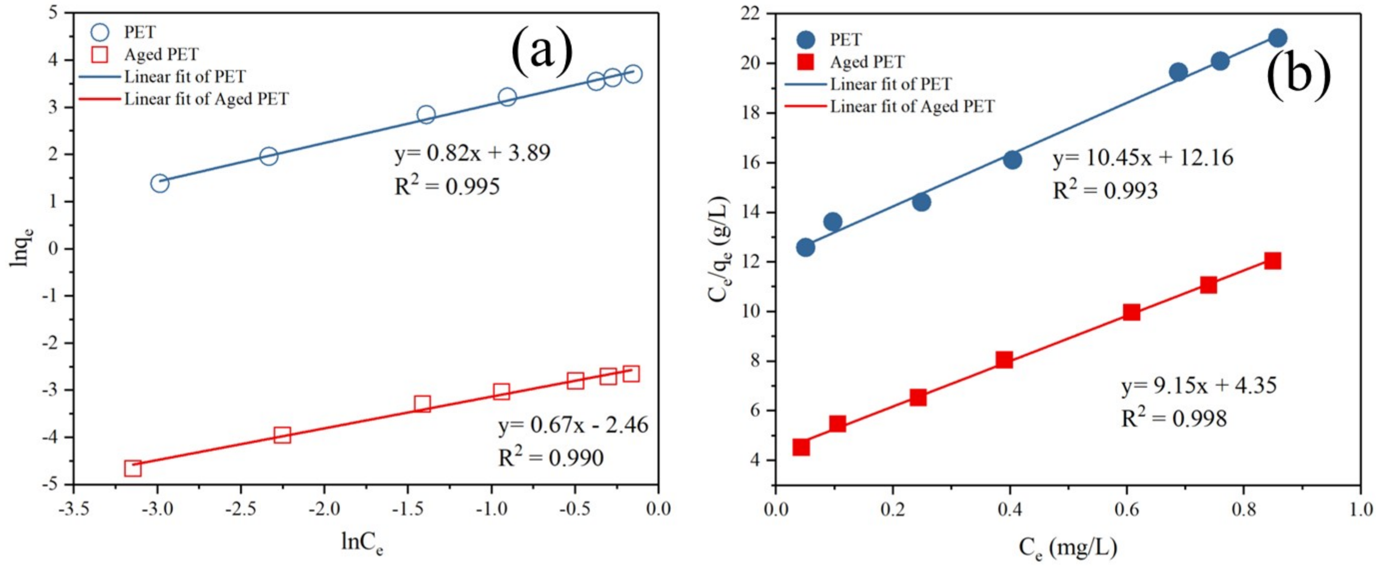


Figure S5. Sorption isotherm of 4-MBC on PET microplastics with the linear isotherm model: (a) Freundlich (b) Langmuir

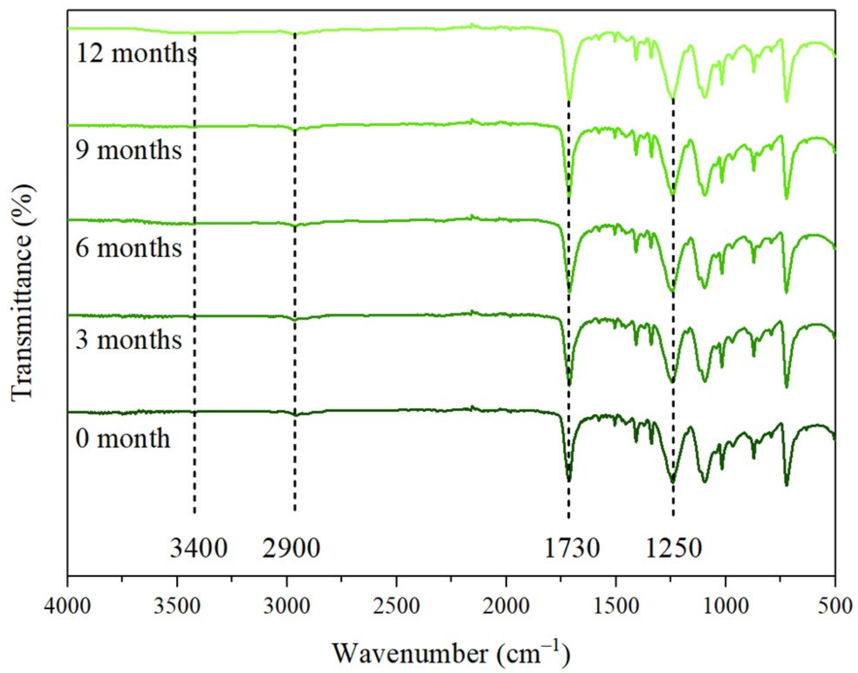


Figure S6. FTIR spectra of Bot-PET for 0, 3, 6, 9, and 12 months

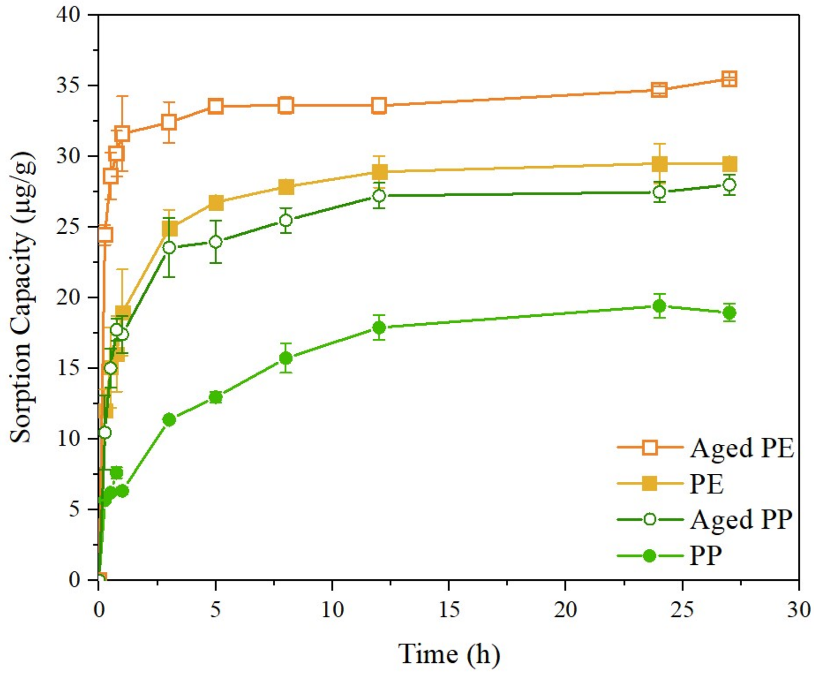


Figure S7. Sorption kinetics of virgin and aged PE and PP microplastics with 4-MBC over 27 h ($[4\text{-MBC}]_0$ = 50 ppb, $[\text{microplastics}]_0$ =100 mg, temperature = 20 °C, initial pH = 7, salinity = 0.)

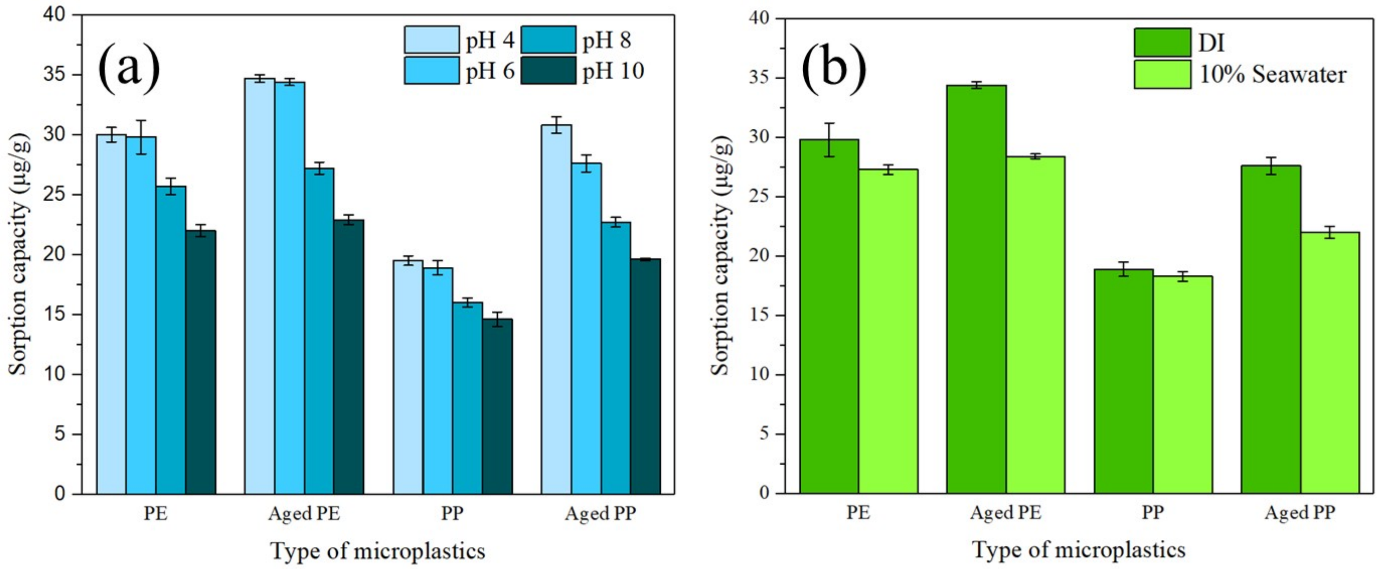


Figure S8. Sorption capacity of virgin and aged PE and PP microplastics for 4-MBC (a) at different pH values and (b) in the presence of salinity. ($[4\text{-MBC}]_0$ = 50 ppb, $[\text{microplastics}]_0$ =100 mg, temperature = 20 °C, initial pH = 7 (with the exception of the control pH), salinity = 0 (with the exception of the salinity effect).)

Table S5. XPS data of virgin and aged PET microplastics.

Element	**C 1s (%)**			**Total C**	**Total O**	**O/C ratio (%)**	**Carbonyl Index**
Assignments	**C–C (C–H)**	**C–O**	**C=O**				
PET	63.5	15.2	21.4	63.5	36.6	0.576	0.61
Aged PET	61.1	16.7	22.2	61.1	38.9	0.637	0.72

Table S6. Regression parameters for the sorption kinetics of 4-MBC on PET microplastics with pseudo-first order and pseudo-second order models.

	Pseudo-First-Order		
	q_e **(μg/g)**	k_1 **(1/hr)**	**R^2**
PET	3.20 ± 0.10	0.10 ± 0.004	0.88
Aged PET	3.95 ± 0.50	0.25 ± 0.045	0.97
	Pseudo-Second-Order		
	q_e **(μg/g)**	k_2 **(g/μg·hr)**	**R^2**
PET	6.54 ± 0.92	$1.12 \times 10^5 \pm 5.13 \times 10^3$	0.99
Aged PET	12.33 ± 0.53	$1.34 \times 10^5 \pm 4.10 \times 10^3$	0.99

Table S7. Activation energy of the 4-MBC sorption process onto PET microplastics

	Cal. q_e (μg/g) at 20 ℃	**Cal. q_e (μg/g) at 50 ℃**	**k (g/μg·hr) at 20 ℃**	**k (g/μg·hr) at 50 ℃**	**Activation Energy (KJ/mole)**
PET	6.54 ± 0.92	5.25 ± 0.77	$1.12 \times 10^5 \pm 5.13 \times 10^3$	$3.51 \times 10^5 \pm 1.12 \times 10^4$	28.68
Aged PET	12.33 ± 0.53	6.25 ± 0.52	$1.34 \times 10^5 \pm 4.10 \times 10^3$	$2.64 \times 10^5 \pm 1.13 \times 10^4$	18.29

Table S8. Binding energy of functional groups with 4-MBC by DFT

	eV	**kJ/mol**
R–COOH (Carboxylic)	**-0.50**	**-47.73**
H_2O	**-0.27**	**-26.44**
RCHO (Aldehyde)	**-0.26**	**-24.79**
RCOH (Alcohol)	**-0.30**	**-28.53**

Table S9. pH_{PZC} of virgin and aged microplastics

pH_{PZC}	PE	PE	PP
Virgin	3.88	4.02	3.85
Aged	3.89	4.03	3.87

Table S10. Sorption capacity of Bot-PET and Env-PET for 4-MBC ($[4\text{-MBC}]_0$ = 50 ppb, $[\text{microplastics}]_0$ = 100 mg, temperature = 20 °C, initial pH = 7 and salinity = 0.)

	Bot-PET					Env-PET
	Summer months			Winter months		-
month	0 month	3 months	6 months	9 months	12 months	-
q_e in DI (µg/g)	0.43	0.49	0.82	0.73	0.99	2.3

References

1. Lagergren, S., Zur theorie der sogenannten adsorption geloster stoffe. **1898**.
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