

Aging Characteristics of PET Microplastics under Interaction of Environmental Factors and Their Adsorption Behavior toward Ciprofloxacin

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Abstract: The environmental risks of microplastics as pollutant vectors have garnered extensive attention. This study investigates the interactive effects of illumination, temperature, and oxidation on the surface morphology, functional groups, and adsorption behavior of conventional non-biodegradable polyethylene terephthalate (PET) using a Box-Behnken design. SEM and FTIR characterized the physicochemical properties, while kinetic and isotherm models evaluated ciprofloxacin (CIP) adsorption onto pristine and weathered PET. Results reveal that PET, inherently possessing an aromatic backbone, exhibits pronounced thermo-driven and chemical oxidative degradation. Optimal weathering occurred under UV irradiation, 60 °C, and Fenton oxidation. Post-weathering, PET displayed edge erosion, increased specific surface area, and an enrichment of secondary oxygen-containing polar sites at the solid-liquid interface triggered by polymer backbone cleavage. CIP adsorption followed pseudo-second-order kinetics, shifting from the Langmuir to the Freundlich model post-weathering. Consequently, the weathered PET achieved a 50.7% increase in adsorption capacity. This study provides critical data support for evaluating the long-term combined ecological risks of conventional microplastics and co-contaminants.

1 Introduction

Polyethylene terephthalate (PET) microplastics, formed through the fragmentation of recalcitrant PET waste, accumulate in the environment and frequently act as transport vectors for co-contaminants^[1]. Environmental factors, including temperature, ultraviolet (UV) irradiation, and chemical oxidation, interactively induce PET weathering. This process generates surface physical defects and secondary oxygen-containing polar groups, which subsequently govern the interfacial adsorption behavior of PET toward co-contaminants like the antibiotic ciprofloxacin (CIP). Currently, systematic research on PET weathering characteristics and its adsorption mechanisms under multifactorial interactive conditions is limited.

This study investigates pristine and interactively weathered PET microplastics (exposed to coupled UV, thermal, and oxidative conditions) using CIP as the target co-contaminant. The objective is to evaluate the interactive effects of these environmental factors on the PET weathering trajectory and surface physicochemical evolution. Furthermore, kinetic and isothermal adsorption models are utilized to analyze the CIP adsorption characteristics and mechanisms pre- and post-weathering. These findings provide empirical data for assessing the long-term combined ecological risks of microplastics and associated co-contaminants in environmental matrices.

2 Materials and Methods

2.1 Materials and instruments

Polyethylene terephthalate (PET) films (thickness: 0.01 mm) and PET microplastic particles (average diameter: 180 μm) were purchased from Xinjiang Lanshan Tunhe Sci-Tech Co., Ltd. (China). Ciprofloxacin hydrochloride (CIP, purity ≥ 98%) was obtained from Shanghai Macklin Biochemical Co., Ltd. (China). All other chemical reagents used in the experiments were of guaranteed reagent (GR) grade, and ultrapure water was utilized throughout the study.

2.2 Experimental methods

2.2.1 Interactive effects of environmental weathering factors

To elucidate the interactive effects of diverse environmental factors on the weathering of PET, the pristine PET films were initially fragmented into uniform 1 cm × 1 cm squares. The present study employs thin-film aging condition screening, which makes it possible to more accurately simulate the actual aging process of plastics in natural environments, thereby rendering the experimental design more representative of real-world scenarios. Response surface methodology (RSM) was

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subsequently employed to investigate the interactive impacts of illumination, temperature, and oxidative conditions on the PET films.

Specifically, a three-factor, three-level Box-Behnken design (BBD) matrix was constructed (Table 1), comprising a total of 17 distinct experimental runs. The independent variables and their designated categorical/numerical levels were as follows: illumination [darkness (0), natural light (1), and UV irradiation (2)], temperature (20 °C, 40 °C, and 60 °C), and oxidative conditions [control/no oxidation (0), H₂O₂ oxidation (1), and Fenton oxidation (2)].

Following a 14-day continuous weathering period for each experimental cohort, the surface carbon-to-oxygen (C/O) atomic ratio of the specimens was quantified utilizing an energy-dispersive X-ray spectrometer (EDS). The C/O ratio was selected as the aging indicator because it encompasses oxygen-containing functional groups (e.g., C-O and O-H) that may not be fully captured by the carbonyl index (CI)^[2].

Table. 1 The Factor and Level Table of the Response Surface

Factor	Level		
	1	2	3
A-Illumination	Darkness(0)	Natural light(1)	UV irradiation(2)
B-Temperature	20 °C	40 °C	60 °C
C-Oxidative condition	No oxidation(0)	H ₂ O ₂ oxidation(1)	Fenton oxidation(2)

Upon completion of the interactive weathering trials, three-dimensional response surface plots were constructed based on the experimentally derived C/O atomic ratios. These analytical models were employed to systematically evaluate the degree of PET weathering driven by the interactive effects of the selected environmental variables. Ultimately, this statistical approach facilitated the identification of the optimal parameter combination for maximizing the weathering extent of the PET microplastics.

2.2.2 Characterization of PET weathering

Guided by the response surface optimization results, the identified optimal conditions were applied for the scaled-up batch weathering of PET. Subsequently, the alterations in the surface morphology and functional groups of the pristine and weathered PET were systematically characterized utilizing SEM and FTIR, respectively.

2.2.3 Adsorption kinetics and isotherm experiments

For adsorption kinetics, 25 mg of pristine or weathered PET microplastics was mixed with 25 mL of CIP solution (2 mg/L) and agitated at 180 r/min and 298 K. Aliquots were sampled at predetermined intervals to quantify residual absorbance. For adsorption isotherms, a CIP concentration gradient (0.1–10 mg/L) was employed. Suspensions were agitated under identical conditions for 6 h to reach complete adsorption equilibrium.

2.2.4 Adsorption models and data analysis

The adsorption kinetic data were fitted employing the pseudo-first-order [Eq. (1)] and pseudo-second-order [Eq. (2)] models:

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (1)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \quad (2)$$

where q_e and q_t (mg/g) denote the adsorption capacities of the pristine and weathered PET for CIP at equilibrium and at any given time t , respectively; k_1 (min⁻¹) and k_2 [g/(mg·min)] represent the adsorption rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively.

The isothermal adsorption data were further fitted employing the Langmuir [Eq. (3)] and Freundlich [Eq. (4)] isotherm models:

$$q_e = \frac{q_{\max} K_L \rho_e}{1 + K_L \rho_e} \quad (3)$$

$$q_e = k_f \rho_e^{1/n} \quad (4)$$

where ρ_e (mg/L) represents the equilibrium mass concentration of CIP; q_e (mg/g) and q_{\max} (mg/g) denote the equilibrium adsorption capacity and the theoretical maximum monolayer adsorption capacity of the pristine and weathered PET, respectively; K_L (L/mg) is the Langmuir affinity constant related to the free energy of adsorption; while k_f (L/g) and $1/n$ are the Freundlich constants indicative of the adsorption capacity and adsorption intensity, respectively.

3 Results and discussion

3.1 Interactive effects of environmental factors on PET weathering

The experimental design matrix and the corresponding outcomes of the response surface optimization are summarized in Table 2. The three-dimensional response surface plots are illustrated in Figure 1. For PET microplastics, exposure to strong oxidative systems constitutes the primary driving force for their weathering. Specifically, the highly reactive free radicals generated by the Fenton reagent effectively attack and cleave the vulnerable sites along the PET macromolecular chains. Concurrently, elevated temperatures accelerate the microscopic segmental motion of the polymer. This enhanced molecular mobility enables the internal structure to more readily surmount the activation energy barrier, thereby facilitating thermal degradation.

Table. 2 The Optimization Experimental Results of the Response Surface

Illumination	Temperature	Oxidative condition	C/O
Darkness	40°C	Fenton oxidation	3.32
UV irradiation	20°C	H ₂ O ₂ oxidation	4.15
Natural light	40°C	H ₂ O ₂ oxidation	4.20
UV irradiation	60°C	H ₂ O ₂ oxidation	3.42
Natural light	20°C	Fenton oxidation	3.72

Natural light	40°C	H ₂ O ₂ oxidation	4.18
Darkness	60°C	H ₂ O ₂ oxidation	3.73
Darkness	40°C	No oxidation	4.85
Natural light	60°C	Fenton oxidation	3.05
Darkness	20°C	H ₂ O ₂ oxidation	4.55
Natural light	60°C	No oxidation	4.40
Natural light	40°C	H ₂ O ₂ oxidation	4.19
Natural light	40°C	H ₂ O ₂ oxidation	4.21
UV irradiation	40°C	Fenton oxidation	3.08
UV irradiation	40°C	No oxidation	4.58
Natural light	40°C	H ₂ O ₂ oxidation	4.20
Natural light	20°C	No oxidation	4.87

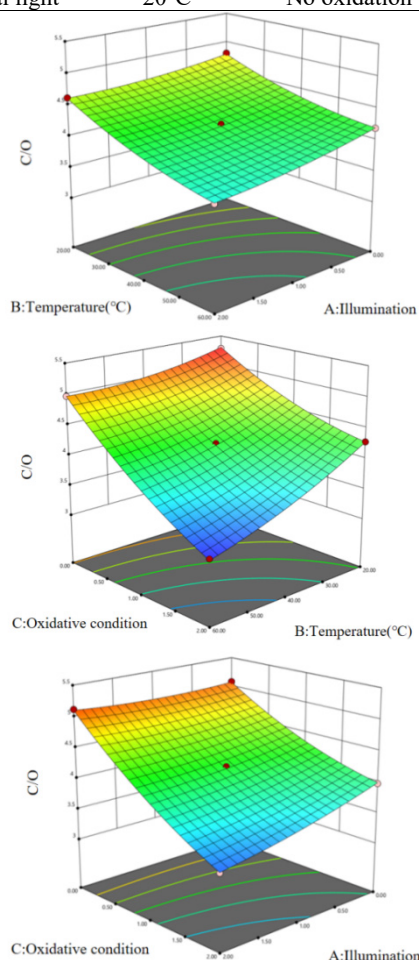


Figure 1 Response Surface Plot of C/O Ratio Variation for PET

The analysis of variance (ANOVA) revealed that the linear terms of illumination (A), temperature (B), and oxidative conditions (C) exerted highly significant effects on PET weathering ($P < 0.01$). The relative impact weight of these individual factors on the weathering extent followed a descending order: chemical oxidation > environmental temperature > illumination. Furthermore, the intensity of the bipartite interactions exhibited the following hierarchy: temperature \times oxidative conditions > illumination \times oxidative conditions > illumination \times temperature.

The interactive weathering behavior of PET exhibits a hierarchical response, governed primarily by a coupled thermo-chemical oxidation mechanism. Owing to its rigid aromatic backbone, PET requires thermal activation to overcome the energy barrier for chain segment mobility. When thermal input is synergistically combined with a

strong oxidative system, the polymer undergoes enhanced depolymerization and surface degradation. Regression analysis identified UV irradiation, 60°C, and Fenton oxidation as the optimal conditions to induce maximal weathering of PET.

The temperature-oxidation interaction arises from thermal activation enhancing radical attack. Elevated temperatures increase PET chain mobility and reduce bond cleavage energy, facilitating $\bullet\text{OH}$ diffusion into the matrix. Radicals preferentially attack ester linkages and methylene groups adjacent to aromatic rings. This coupled mechanism accelerates chain scission and generates oxygen-containing functional groups. The weaker illumination-temperature interaction indicates UV primarily affects surfaces without oxidants. These insights explain why UV, 60°C, and Fenton oxidation produced the lowest C/O ratio, indicating maximal degradation.

3.2 Physicochemical characterization of pristine and weathered PET

3.2.1 Surface morphology analysis

For precise quantification in experiments, standardized 100-mesh microplastic particles were used instead of manually cut films to eliminate shape-induced inconsistencies and ensure data reliability. The pristine PET microplastics exhibited an irregular blocky morphology with distinct mechanical fracture planes and sharp edges, attributable to the polymer's intrinsic crystallinity and mechanical hardness. The original surfaces were smooth and structurally dense, indicating low porosity and high physical compactness.

However, following combined weathering (UV irradiation, 60°C, and Fenton oxidation), significant physical deterioration of the PET surface was evident from edge rounding, dissolution pitting, and the generation of cracks and debris via surface exfoliation. Ultimately, the proliferation of these physical defects increased the surface roughness and porosity of the weathered PET, thereby providing favorable spatial conditions for the diffusion and physical entrapment of CIP molecules^[3].

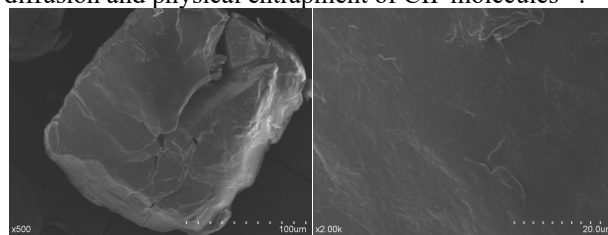


Figure 2 Pristine PET electron microscopy analysis Figure

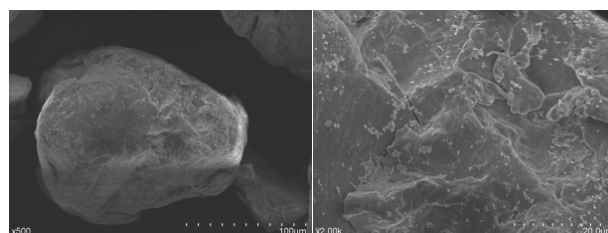


Figure 3 Aged PET electron microscopy analysis Figure

3.2.2 Evolution of surface functional groups

The FTIR spectrum of pristine PET exhibited the characteristic intact polyester backbone, featuring the C–H bending vibration of the benzene ring at 725 cm⁻¹ and the C–O–C stretching vibrations of the ester groups at 1018–1100 cm⁻¹. Inherently, these structural features impart distinct hydrophobicity and adsorption inertness.

Under the combined influence of various environmental factors, PET microplastics undergo degradation, and their surface polarity characteristics also change. Specifically, the intensities of the absorption peaks at 1100 cm⁻¹ and 1240 cm⁻¹, characteristic of ester groups, diminished significantly, indicating the cleavage of ester bonds induced by hydroxyl radicals ($\cdot\text{OH}$). Concurrently, the intensity of the carbonyl absorption peak at 1715 cm⁻¹ intensified markedly. Furthermore, a distinct broad-band signal indicative of terminal hydroxyl (–OH) or free carboxyl groups emerged in the high-frequency region around 3420 cm⁻¹. Ultimately, this transition toward an oxygen-rich, polar surface provided abundant hydrogen bond donors/acceptors and dipole-interaction anchoring sites for CIP molecules, thereby enhancing the interfacial affinity^[4].

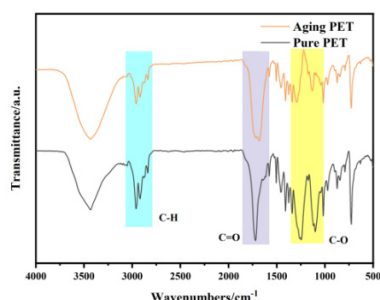


Figure 4 FTIR Spectra of PET

3.3 Adsorption experimental results

3.3.1 Adsorption kinetics

The adsorption kinetic curves are illustrated in Figure 4. The parameters derived from the model fittings are summarized in Table 3. The fitting results reveal that the adsorption of CIP onto both pristine and weathered PET conforms to the pseudo-second-order kinetic model ($R^2 = 0.998\text{--}0.999$). This high degree of correlation suggests that the adsorption process is predominantly governed by chemisorption^[5].

Owing to its inherent rigid aromatic ring structure, PET demonstrated a rapid initial mass transfer response toward CIP, attaining adsorption equilibrium within approximately 60 min. Notably, while environmental weathering did not alter the temporal scale required to reach equilibrium, it substantially augmented the adsorption capacity. Specifically, the equilibrium adsorption capacity escalated from 0.65 mg/g to 0.98 mg/g, corresponding to an increment of 50.7%^[6].

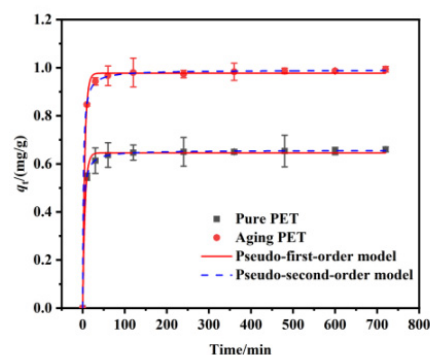


Figure 5 Fitting Plots of Adsorption Kinetic Models for PET

Table 3 Fitting parameters of kinetic models for pure and aging PET

Microplastics	Pseudo-first-order model			Pseudo-second-order model		
	$q_e/(mg/g)$	k_1/min^{-1}	R^2	$q_e/(mg/g)$	$k_2/[mg/(g \cdot min)]$	R^2
Pure PET	0.645	0.185	0.9959	0.656	0.752	0.9998
Aging PET	0.977	0.200	0.9978	0.990	0.607	0.9997

3.3.2 Adsorption isotherms

The adsorption isotherm curves are depicted in Figure 5, with the derived modeling parameters summarized in Table 4. The equilibrium data reveal that pristine PET is well-described by the Langmuir model, whereas the weathered PET aligns more closely with the Freundlich model. This transition signifies a shift from predominantly monolayer adsorption to a coexistence of monolayer and multilayer adsorption post-weathering. Derived from the Langmuir model, the theoretical maximum monolayer adsorption capacity (q_{max}) of PET escalated from 3.93 mg/g to 5.11 mg/g after the weathering treatment.

Furthermore, the $1/n$ parameter within the Freundlich model decreased from 0.602 for the pristine PET to 0.451

for the weathered counterpart. Mechanistically, the terephthalate units along the PET backbone can engage in robust π - π electron-donor-acceptor (EDA) interactions with the fluoroquinolone aromatic rings of CIP. Compounded by the hydroxyl and free carboxyl moieties exposed during the weathering process, these interactive forces promote the multilayer stacking and aggregation of CIP molecules^[7]. Concurrently, the Freundlich affinity constant (k_f) surged from 1.054 to 2.001, indicating a strong specific binding capacity of aromatic-rich PET in receiving waters. As show in figure 6.

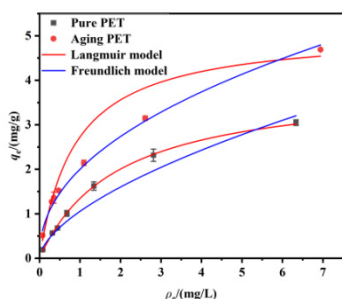


Figure 6 Fitting Plots of Adsorption Isotherm Models for PET

Table. 4 Fitting parameters of adsorption isotherms for pure, aging PET

Microplastics	Langmuir model			Freundlich model		
	$q_{max}/(mg/g)$	$k_L/(L \cdot mg)$	R^2	$k_f/(L/g)$	$1/n$	R^2
Pure PET	3.93	0.519	0.9883	1.05	0.602	0.9762
Aging PET	5.11	1.143	0.9732	2.00	0.451	0.9808

4 Conclusions

(1) Environmental factors differentially affect PET weathering, with impact significance ordered as: chemical oxidation > temperature > illumination. The maximum weathering condition is UV irradiation, 60 °C, and Fenton oxidation, which yields the lowest surface carbon-to-oxygen (C/O) atomic ratio.

(2) Weathering modifies the physicochemical properties of PET. Morphologically, initial dense and smooth surfaces transform into rough and porous structures with microcracks.

(3) Post-weathering, CIP equilibrium adsorption capacity increases by 50.7%. Adsorption follows pseudo-second-order kinetics (equilibrium at ~60 min), with isotherms shifting from the Langmuir to the Freundlich model.

References

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