

EFFECTS OF ALGAE ORGANIC MATTER ON THE RELEASE OF POLYCYCLIC AROMATIC HYDROCARBONS FROM MICROPLASTICS

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Introduction

Plastic products have been widely used in commercial packaging and building materials due to their excellent properties, and are flooding all aspects of modern life.^{1,2} However, there is a serious imbalance between plastic production and recycling. In the end, only about a quarter or less of the plastic is recycled or properly disposed of, and a large amount of plastic waste is released into the environment.^{3,4} It is foreseeable that these disordered plastics discharged into nature will be affected by many natural factors, including hydrolysis, photo-degradation, mechanical abrasion and biodegradation.^{1,5,6} Under the influence of physical, chemical and biological processes, plastic products discharged into nature will be broken down into smaller plastic fragments.^{7,8} Surface changes occur during the crushing of plastic fragments, including the peeling of the plastic surface coating, the formation of pores, and changes in mechanical strength, oxygen content and molecular weight.^{9,10} Among these processes, mechanical abrasion and photochemical degradation are considered to be important processes in the aging of hydrocarbon polymers.^{11,12}

The aging mechanism of polymers under different environmental conditions has been extensively studied.^{9,12,13} Some studies have explained the interaction mechanism between ultraviolet aging microplastics and organic pollutants.¹⁴⁻¹⁶ We use the commonly used plastic modification technology in the industry, chromic acid etching, to oxidize the surface of the plastic. Polyethylene plastics that are frequently detected in marine and freshwater environments are used as model plastic particles.¹⁷ Microplastics in the aquatic environment can be combined with persistent organic pollutants or heavy metals.^{18,19} The concentration of pollutants in microplastics may even be 10⁵ to 10⁶ times the concentration of pollutants in environmental seawater.^{20,21} Our previous study used polyethylene (PE) as a model material to study the influence of different modified microplastics on the free dissolved concentration (C_{free}) of organic pollutants in water.²² The results of the study initially revealed the effects of organic pollutants and microplastics in the water environment.

However, the surface of the microplastics entering the water environment may come into contact with different organisms, thereby affecting the diffusion of pollutants carried in the microplastics. Especially after the surface of the microplastics is covered with a layer of biofilm, for each microplastic particle, it is bound to affect the external mass transfer process of the pollutants it carries. Since effective diffusion in biofilms is slower than in water, external mass transfer will slow down. Therefore, our research starts from this point, using *Microcystis aeruginosa* as a model algae, extracting the intracellular and extracellular organic matter to simulate the environmental conditions when algal blooms occur in nature. Passive dosing devices were used to determine the partition coefficients of two common polycyclic aromatic hydrocarbons, phenanthrene and pyrene, on the intracellular and extracellular organic matter of *Microcystis aeruginosa*. Finally, based on the semi-analytical mass transfer model proposed by Seidensticker et al., the influence of algae-derived organic matter on the effectiveness of polycyclic aromatic hydrocarbons on microplastics was explored.²³

Materials and methods

Materials

Clear high density polyethylene microspheres (150-210 μm, 0.96 g cm⁻³) were purchased from Cospheric LLC. (Goleta, CA, U.S.A.). An EPA610 standard polycyclic aromatic hydrocarbon (PAH) mixture in methanol and methylene chloride (1:1, v/v) with individual PAH concentrations in the range from 100 to 2000 mg L⁻¹ was obtained from Supelco (Bellefonte, PA, U.S.A.).

Modified microplastic particle preparation

Pristine MPs were washed three times with deionized water, and dried in a 40 °C oven for 48 h before sample preparation to ensure that the particles were dry and clean. A total of 150 ml of chromic acid was added to a glass beaker and incubated in a 65 °C water bath. A total of 25 mg of pristine MPs was added to 65 °C of chromic acid for 15 min. During this process, the reaction solution was continuously stirred with a glass rod to bring the MP into full contact with chromic acid. After the reaction was completed, the etched microplastics (EMPs) were washed and recovered. The particles were tiled to be achieve even dispersal in the glass petri dishes. The dishes were then transferred to a dark box containing ultraviolet light bulbs (4×15 W UVC bulbs, λ_{max} = 254 nm) and exposed to ultraviolet light for 30 days.

Passive dosing measures the partition coefficient between pollutants and algae media

Through the polydimethylsiloxane polymer preloaded with chemical substances, passive dosing devices were used to control the chemical activity of hydrophobic organic pollutants in the aqueous solution. Then measure the

concentration of hydrophobic organic pollutants in the equilibrium solution. Phenanthrene and pyrene are regarded as model pollutants, while humic acid, IOM, and EOM are model medium components.

Results and discussion

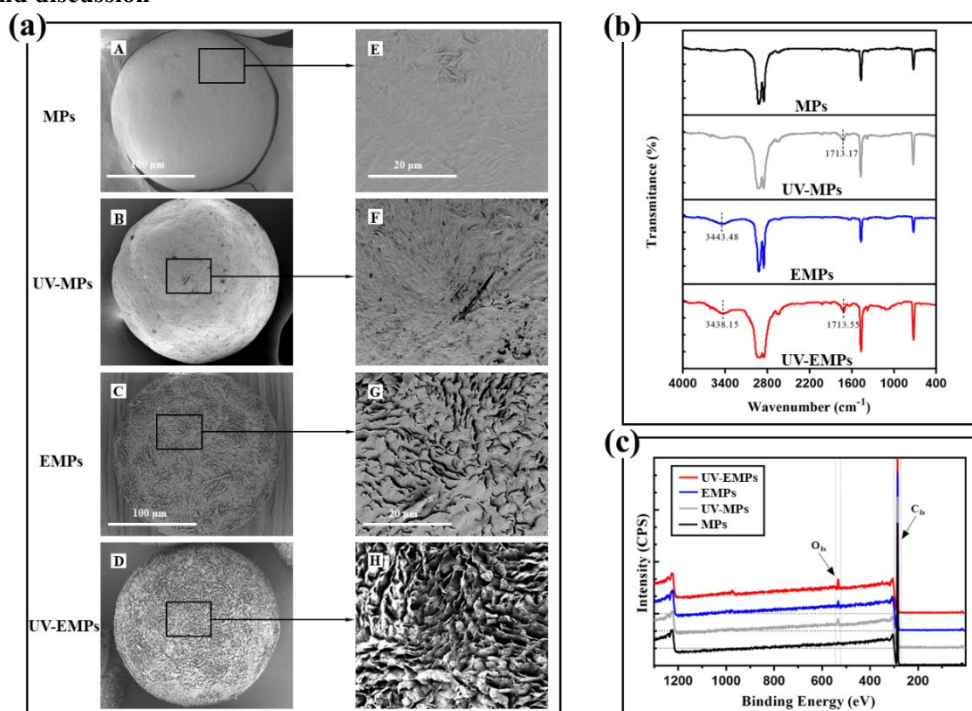


Figure 1. (a) SEM images of different modified MPs and surface structures. The scale bars for (A, B, C, D) and (E, F, G, H) are 100 μm and 20 μm, respectively. (b) FTIR spectra of MPs, EMPs, UV-MPs and UV-EMPs. (c) XPS spectra of different modified MPs.

Characterization of modified microplastics

The surface morphology of the different modified microplastics was characterized by SEM, as shown in Fig. 1a (A-H). It can be clearly found that the surface of the pristine microplastics (MPs) is relatively smooth, and after ageing by ultraviolet light, the surface ripple structures deepen. The FTIR spectrum of pristine MPs matched the standard structure spectrum of polyethylene (Fig. 1b). One or more O-containing absorption bands appeared in the other three modified MPs. According to a previous study²⁴, the stretching band of EMPs at 3417 cm⁻¹ can be attributed to O-H stretching vibration. The spectrum of UV-MPs shows a tensile vibration peak of carbonyl groups at 1725 cm⁻¹, while that of UV-EMPs shows the tensile vibration of hydroxyl and carbonyl groups.

The surface area of the MPs was significantly improved (1.67 m² g⁻¹) after chemical etching. The surface area of UV-EMPs (2.37 m² g⁻¹) is significantly (five times) higher than that of pristine MPs, and the pore volume (0.89 cm³ g⁻¹) is increased by twice. The pore surface area distribution shown in Fig. 2b (A3-D3) indicates that the surfaces of the pristine MPs have fewer pores and the surfaces of the MPs after ultraviolet ageing have enlarged original pores in addition to an increased number of small pores. The observed increase in the pore surface area and pore volume of pores smaller than 150 nm is critical to the change in MPs adsorption capacity.²⁵ It is foreseeable that micro-plastics in the natural world that are worn or heavily etched on the surface will absorb more pollutants upon contact when the MPs have been exposed to UV for a long time.

Sorption isotherms and desorption kinetics of phenanthrene on modified microplastics

The Freundlich model is better at describing the sorption of phenanthrene in EMPs and UV-EMPs. Such results are also foreseeable as the increase in pores shifts the isotherm toward nonlinear sorption.^{26, 27} This result verified what we concluded by the nd-SPME method that the sorption of PAHs on MPs is mainly based on partitioning; however, a mechanism of adsorption also likely takes place in EMPs and UV-EMPs due to pore sorption. We use the semi-analytical model described by Seidensticker et al. to describe the kinetic mass transfer between aqueous solutions of organic contaminants and spherical particles of polyethylene.²³ This model is a good explanation for the dominant mechanism in the desorption process of PAHs from different modified microplastics. Figure 2 shows the measured concentration time series and the model results of the fitted complete model (blue solid lines), considering only the model prediction of the external mass transfer using the full model parameters (red dashed line) and considering only the intraparticle diffusion. In the initial stage of desorption, this part of the experimental data is lacking due to the difficulty of experimental sampling and instrumental analysis conditions. For all PE

microplastics, early models at the beginning of desorption showed that external mass transfer always controlled overall mass transfer. When approaching equilibrium, intraparticle diffusion becomes the rate limiting step. Especially for the etch-modified microplastics, it is more obvious that it is more affected by the intraparticle diffusion at a later stage. Therefore, the intraparticle diffusion coefficient obtained by the model fitting is smaller than that of the unmodified microplastic. In the study by Sven Seidensticker et al., it has been shown that as the particle size increases, the probability of long-range transport of pollutants increases, and as the diffusion coefficient within the particles increases, the probability of long-range transport of pollutants decreases²⁸. Our results show that the desorption kinetics of the modified polyethylene microplastics is still dominated by film diffusion.

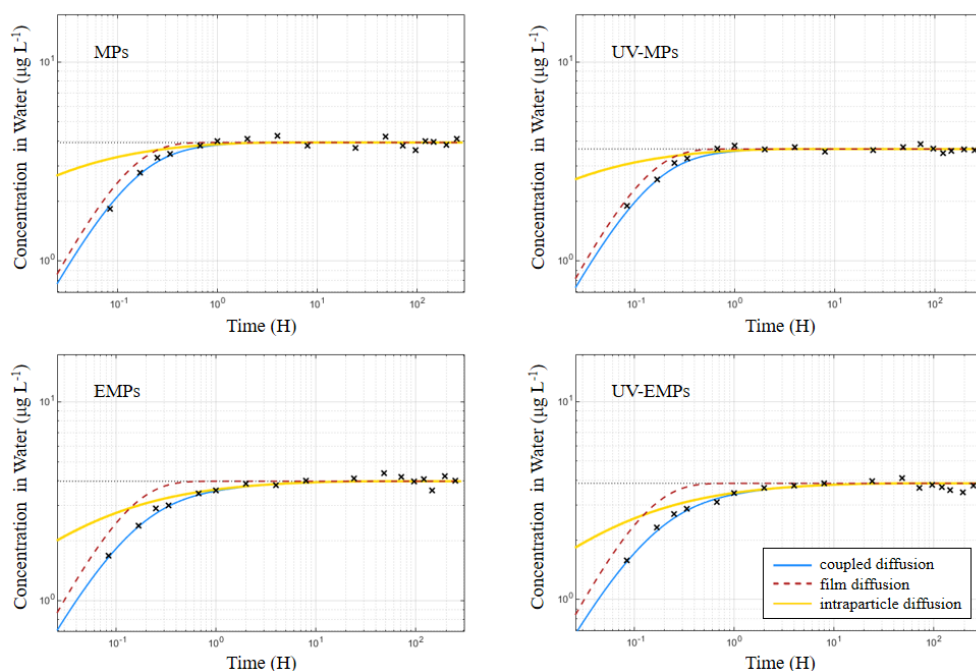


Figure 2. Desorption kinetics of phenanthrene from different modified microplastics. Models for film diffusion, intraparticle diffusion, and the coupled diffusion are shown with the red dashed, the solid yellow lines, and the solid blue lines, respectively. The horizontal black dotted line shows the equilibrium concentration.

Acknowledgements

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