

Advances in Research of Adsorption and Desorption Behavior of Surfactants on Microplastics

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Abstract This paper summarizes the mechanisms and environmental effects of interactions between microplastics and surfactants; surfactants adsorb onto microplastics surfaces through hydrophobic interactions and electrostatic forces, changing their surface properties and transport behavior. In addition, microplastics act as carriers influencing surfactant distribution. Environmental factors (pH, ionic strength, *etc.*) significantly regulate this process. Current research still has limitations in areas such as desorption kinetics and combined pollution effects, necessitating in-depth studies under environmentally relevant conditions to provide a basis for risk assessment.

Key words Microplastics, Surfactant, Adsorption, Desorption, Interfacial interaction

0 Introduction

Plastics have become essential necessities and consumables for humans, and are almost ubiquitous in daily life. The production and use of plastics and their products lead to their release into the environment. Through long-term and continuous processes including abrasion, light exposure, high temperatures, oxidation, and fragmentation, they gradually break down to form plastic fragments or particles with a size smaller than 0.5 mm, which are termed secondary microplastics^[1–2]. Primary microplastics typically originate from industrial manufacturing and daily activities, such as microbeads in personal care products and resin pellets used as industrial raw materials^[3]. Microplastics come in numerous varieties; based on their composition, they can be classified as polystyrene, polyethylene, polyethersulfone resin, polyvinyl alcohol, polyurethane, *etc.*^[4].

Microplastic pollution in the environment has become a globally recognized hotspot issue. Microplastics are widely distributed in aquatic environments, having been detected in rivers, lakes, and oceans^[5–8]. Due to their stable nature, microplastics can persist in the environment for extended periods and can be transferred along the food chain, posing serious threats to the ecological environment and human health. In addition, daily-use detergents contain large amounts of surfactants. These surfactants enter the aquatic environment via domestic wastewater, and their increasing discharge volumes lead to persistent foam on water surfaces, causing water bodies to emit foul odors. They also increase the solubility of other pollutants, accelerate water eutrophication, and threaten human health^[9–10]. Therefore, studying the adsorption-desorption characteristics of surfactants onto microplastics is of significant importance for clarifying their transport behavior and eco-

logical risks in aquatic environments^[11].

1 Characteristics and interactions of microplastics and surfactants

Microplastics have small particle sizes and exist in a submicron-dispersed state, characterized by an extremely long half-life, strong hydrophobicity, and chemical inertness. Due to their large specific surface area, microplastics exhibit a strong adsorption capacity for pollutants. Surfactants are compounds with surface activity; at low concentrations, they can directionally adsorb at the surface of liquids or gases or other interfaces, significantly reducing surface tension or interfacial tension. Surfactants are amphiphilic compounds containing both hydrophobic and hydrophilic parts, possessing an "amphiphilic" structure^[12]; a small amount of surfactant causes a significant decrease in the interfacial tension of a solution. Surfactants can promote the migration of microplastics, primarily due to the adhesion work of surfactant molecules on the microplastic surface^[13]. The hydrophobic chains of surfactant molecules readily bind with microplastics, exposing the hydrophilic ends outward, thereby reducing the hydrophobicity of the microplastic surface^[14–15]. Surfactants can adsorb onto microplastics through hydrophobic interactions or electrostatic forces, increasing the solubility of microplastics in water^[4], promoting their dispersion and suspension in water, making them more easily transported by water flow, thus exacerbating the environmental risks of microplastics. Additionally, microplastics can act as carriers transporting surfactants and altering their distribution characteristics.

2 Migration characteristics of microplastics in surfactant solutions

Compared with polyethylene, polypropylene exhibits stronger migration capability in surfactant solutions due to its higher stability relative to polyethylene in such solutions^[16]. Differences in polymer monomers confer distinct hydrophobic properties to microplastic surfaces. Surface tension of microplastics is influenced by surfactants, altering their hydrophilicity. Both cationic surfactant

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(cetyltrimethylammonium bromide) and anionic surfactant (sodium dodecylbenzene sulfonate) enhance the suspension stability of polypropylene and polyethylene. However, in the presence of microplastics, sodium dodecylbenzene sulfonate demonstrates lower mobility compared to cetyltrimethylammonium bromide^[17].

Under surfactant exposure, the migration capacity of polyethylene microplastics increases with decreasing ionic strength and cation valence, and with increasing flow velocity. Migration capability also strengthens with rising surfactant concentration below its critical micelle concentration. Polyethylene displays higher migration capacity with cationic surfactant cetyltrimethylammonium bromide than with anionic surfactant sodium dodecylbenzene sulfonate. Previous studies indicate surfactants form a monomolecular layer on hydrophobic solid surfaces. Analogous to their adsorption behavior at air-water interfaces, surfactant molecules adopt increasingly upright orientations with rising concentration until achieving stable adsorption beyond the critical micelle concentration^[18].

The binding between microplastics and surfactant molecules features hydrophobic chains oriented inward and hydrophilic groups outward, similar to the micellar structure of surfactants. Micelles in solution possess an electrical double layer. Consequently, the electrical double layer formed by surfactant molecules on microplastic surfaces becomes compressed with increasing ionic strength in the solution, leading to a decline in the Zeta potential of microplastics. Additionally, elevated counterion concentration in the solution reduces the critical micelle concentration of surfactants, which constitutes a key cause for the decreased migration capability of microplastics at higher ionic strengths.

3 Adsorption behavior and influencing factors of microplastics on surfactants

Studies indicate that polystyrene microplastics adsorb nonionic surfactant Triton X-100, with adsorption capacity influenced by microplastic properties (*e.g.*, particle size), environmental factors (*e.g.*, temperature), and duration^[13]. Xia *et al.*^[15] reported a saturated adsorption capacity of 1 043 $\mu\text{g/g}$ for sodium dodecylbenzene sulfonate on polyvinyl chloride microplastics, consistent with Langmuir isothermal adsorption characteristics, though the underlying adsorption mechanism requires further exploration. Xu *et al.*^[19] investigated the kinetics and thermodynamics of SDBS and Tween-20 adsorption onto polyethylene terephthalate microplastics, examining pH effects and analyzing adsorption mechanisms via density functional theory. Experimental results revealed pH-dependent adsorption efficacy, with significantly higher adsorption of SDBS than Tween-20 involving both chemisorption and physisorption. Density functional theory calculations confirmed stronger affinity for SDBS, while electrostatic potential and independent gradient model analyses identified hydrogen bonding, van der Waals forces, and $\pi - \pi$ stacking as key mechanisms. Wang *et al.*^[20] demonstrated that cationic surfactants promote microplastic dispersion through hydrophilic positively charged groups

and reduce buoyancy via adsorption, with higher concentrations enhancing migration primarily due to increased adhesion on microplastic surfaces.

The influence of environmental factors on the adsorption process presents multi-dimensional characteristics: pH affects the migration of microplastics mainly by changing the surface potential of microplastics and porous media and promoting the deprotonation of surface functional groups of microplastics^[21]. The pH not only affects the morphological distribution of organic matter, but also changes the surface charge properties of microplastics. Thus affecting the adsorption capacity of microplastics to organic matter^[22]. The change of ambient temperature will also affect the adsorption capacity of microplastics to organic pollutants. Studies have found that as the temperature increases from 298 to 318 K, the adsorption capacity of microplastics to five pesticides carben-dazim, trichlorfon, diflubenzuron, malathion and difenoconazole increases, indicating that higher temperature is conducive to the adsorption of microplastics to pesticides^[23]. Salt concentration can lead to different adsorption results^[24], but there is still a lack of systematic research on the influence of these environmental factors on the adsorption surface activity of microplastics.

4 Association between biosurfactants and migration of polyethylene microplastics

Biosurfactant is an amphiphilic compound, which can reduce the surface and interfacial tension by forming micelles to promote the migration of hydrophobic substances in porous media. When the concentration of biosurfactant is less than critical micelle concentration, the recovery rate of polyethylene microplastics increases with the increase of the concentration of biosurfactant. The results show that, driven by electrostatic and hydrophobic interactions, biosurfactant molecules can cover the surface of microplastics and form an oil-in-water emulsion system, thus improving the dispersion and stability of polyethylene microplastics in aqueous solution and enhancing their migration ability in porous media. Due to the different relative contributions of hydrophobic and electrostatic interactions between biosurfactants and polyethylene microplastics, the promotion effect of nonionic biosurfactant sophorolipid on the migration ability of polyethylene microplastics is greater than that of anionic biosurfactant rhamnolipid. In addition, in the presence of biosurfactants, polyethylene microplastics with high surface roughness have stronger migration ability in porous media than those with low surface roughness. The migration of microplastics in porous media is affected by the chemical conditions of solution water^[25], and the change in chemical conditions of solution water will affect the migration of microplastics in porous media. Studies have shown that the mobility of original and aged microplastic particles in porous media can be significantly reduced by increasing the ionic strength of the solution, which is mainly attributed to the reduction of the thickness of the diffusion layer on the surface of the microplastic colloid due to the compression of the double electron layer on the surface of the microplastic colloid under salt stress^[26].

5 Conclusions and prospects

The coexistence of surfactants (SAAs) and microplastics (MPs) in aquatic environments has become widespread. Studies demonstrate that SAAs adsorbed onto MP surfaces significantly alter their hydrophilicity/hydrophobicity, thereby profoundly influencing MP migration behaviors in environmental media such as soils. Although existing research has achieved some progress, current understanding still exhibits notable deficiencies: firstly, studies on desorption behaviors of SAAs from MP surfaces (*e. g.*, desorption rates, extent, and conditions) remain insufficient; secondly, systematic reports are lacking on how key environmental factors (*e. g.*, pH, salinity, temperature, light, dissolved organic matter) affect MPs' adsorption and desorption capacities toward SAAs; finally, specific binding and release mechanisms between SAAs and MPs (*e. g.*, force types, binding sites) remain unclear. These knowledge gaps hinder comprehensive understanding of the environmental behavior of SAA-MP composite pollution.

Addressing these limitations, future research should focus on the following aspects: (i) Investigating dynamic effects of long-term coexistence on adsorption-desorption behaviors under simulated complex environmental conditions; (ii) Selecting typical SAAs (*e. g.*, LAS, AES) and MPs (*e. g.*, PE, PP, PS) with high detection rates in aquatic environments as primary research subjects; (iii) Systematically examining specific regulatory effects of multiple environmental factors (*e. g.*, pH, ionic strength, organic matter, aging degree) on MPs' adsorption and desorption capacities toward SAAs; (iv) Elucidating mechanisms: In-depth revelation of adsorption-desorption kinetics and underlying physicochemical mechanisms (*e. g.*, hydrophobic interactions, electrostatic attraction). Such research will establish a more robust scientific foundation for accurately assessing environmental risks of SAA-MP composite pollution.

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