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Research Progress on the Adsorption and Their Mechanisms of Heavy Metal in Soil By Microplastics

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ABSTRACT

Microplastics (MPs), as emerging global contaminants, have garnered increasing attention due to their persistent nature, ubiquitous distribution, and recalcitrance to degradation. The co-occurrence of microplastics (MPs) and heavy metals (HMs) in soil systems has emerged as a critical global environmental concern, posing synergistic threats to ecosystem integrity and human health. Nevertheless, their interaction mechanisms remain poorly characterized. This review systematically examines the interplay between MPs and HMs in terrestrial environments, with emphasis on two key aspects: Interaction mechanisms between microplastics (MPs) and heavy metals (HMs) adsorption, influence factors on adsorption including polymer type, aging status, particle size/concentration of MPs, and physicochemical properties of HMs/soil matrices. Furthermore, coordinated multidisciplinary efforts are urgently required to establish risk assessment for MPs and HMs in soil systems and develop targeted remediation strategies.

KEYWORDS

Microplastics; Heavy metals; Soil; Adsorption

1. INTRODUCTION

Microplastics (MPs, diameter <5 mm) are emerging high-risk pollutants in the natural environment [1]. Currently, global plastic production exceeds 320 million tons annually [2], and is projected to reach approximately 1.2 billion tons by 2050 [3]. Due to improper use and mismanagement, plastic waste generation has surged to 1.6 million tons per day since the COVID-19 outbreak, with over 79% of MPs being released into the soil annually [4]. Heavy metals (HMs) are also abundant in soil, and MPs as carriers of HMs can alter their transport or mobility [5]. Recent studies suggest that the complexation between MPs and HMs can produce significant ecological effects and environmental toxicity through food webs, meanwhile, their complex toxicity effects would be biotransformed and biological amplified, even pose potential threats to organisms and human health [6, 7]. Given the continuous accumulation of HMs and MPs in soil, it is urgent to understand their biological effects and physiological processes in detail to provide a theoretical basis for future strategy development and risk prediction.

In this paper, the adsorption mechanism of microplastics and heavy metals in soil were reviewed, and the effects of physical and chemical properties of microplastics, heavy metals and the soil environment on the adsorption behavior of microplastics were introduced. To better analyze and manage the impact of MP and HM pollution in soil, addressing existing gaps and meeting future research challenges is crucial. This study will reveal the mechanisms and influence factors of interaction between soil microplastics and heavy metals, providing a scientific basis for assessing the ecological and environmental risks of soil complex pollutants and promoting the risk control and management of soil pollution.

2. MECHANISMS OF THE HEAVY METAL SORPTION TO MICROPLASTICS

Microplastics have stronger hydrophobicity, larger surface area and stronger sorption capacity which can act as a carrier medium to help heavy metals migrate and store. It has been suggested that the physical and chemisorption mechanisms between MPs and heavy metals were the main reason on their interaction [8]. Physical sorption are mediated by weak interactions and covalent bonds. Chemical mechanisms is mainly composed of electrostatic interaction, surface complexation and coprecipitate. Additionally, hydrogen bonding, a special weak electrostatic interaction, affects HM adsorption on MPs in the presence of proton donor and acceptor groups [9].

Because the hydroxyl and carboxyl functional groups in MPs are highly prone to surface complexation, MPs adsorb HMs through metal cations via hydrogen bonding, surface complexation, and π-π interactions [10].

Furthermore, MPs can co-precipitate with HMs whose mobility may decrease due to changes in soil physicochemical properties, leading to enhanced adsorption. Through co-precipitation of MPs and MPs, the organic-bound fraction of metals was enhanced but exchangeable, carbonate-bound, and Fe-Mn oxide-bound fractions of heavy metals were reduced [11].

3. INFLUENCE FACTORS OF THE HEAVY METAL SORPTION TO MICROPLASTICS

3.1. Microplastics Characteristics

3.1.1. Physicochemical properties of unaged microplastics

The type, concentration, shape and particle size of microplastics all affect the interaction between microplastics and heavy metals in the soil [8]. Common microplastics in soil mainly include polyethylene (PE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyamide (PA), acrylonitrile butadiene styrene (ABS), chlorinated polyethylene (CPE) and polyurethane (PU). Due to the significant differences in type, specific surface area, polarity, and functional groups, plus the differences in the complexation reactions of functional groups with heavy metal cations, leading to different sorption capacities for heavy metals [8].

For example, PS mainly interacts with heavy metal cations through π-π bonds; PA has an amide group composed of C-N-H and N-H bonds, and the O-containing groups, C=C/C-C groups reinforce the complexation reaction with heavy metal cations including the C-O on PVC, C=O on PLA, and aromatic C-C on PU [8].

High dose of different type MPs increased available heavy metal concentrations and their phytotoxicity in soil compared with low doses [12]. Besides, some studies found that low dose of some MPs can conversely elevated the soil heavy metal concentrations due to that the addition of MPs influences soil physicochemical properties and then the form of heavy metals [11].

There are also some differences in the adsorption of organic pollutants by microplastics of different shape and particle size. MPs with different shapes affect soil properties which may alter heavy metal transport process [13]. MPs with larger particles were found decreasing sorption rates and increasing desorption rates. That is because larger-size MPs alter cation exchange and soil property, thereby promoting the transport of heavy metal in soil. Nanoscale plastics with larger specific surface area and aggregation trend had stronger adsorption capacity for heavy metal and posed increased toxicity to organisms [8].

The crystallinity degree of microplastics also affects the adsorption behavior for heavy metals. Zou et al. studied that the high-crystallinity PE had a higher sorption capacity for Cd^{2+}, Cu^{2+}, Pb^{2+} than the low-crystallinity PE [14]. In addition, Guo et al. the crystallinity degree of PE, PP, PS, PVC was gradually decreasing, but the adsorption capacity of showed the opposite sequence [15].

The point of zeta charges of most MPs is lower than 6.0, indicating the negatively charged MPs surface is favorable for cationic metal sorption [16].

3.1.2. Physicochemical properties of aging microplastics

Diverse abiotic and biotic aging processes such as ultraviolet (UV) radiation, high-temperature thermal radiation, biodegradation, and chemical oxidation and so on can change the surface properties (surface roughness, hydrophobicity, surface charge, biofilms and its extracellular polymeric substances), microstructure (porosity and pore volume), and physicochemical properties (color, size, shape, released additives, new functional groups, and crystallinity of MPs).

As the extension of aging time, the surface of microplastics will produce more pores, cracks and pits, become rough, and the specific surface area, sorption sites, and pores of the biofilms increases, enhancing heavy metal adsorption on MPs [17]. UV-irradiated MPs generate oxygenated functional groups (C–O, –OH, –COOH) through oxidation, enhancing electrostatic interactions and complexation [18]. Crystallinity affected by aging inversely correlates with adsorption capacity[8].

3.2. Physicochemical Properties of Heavy Metal

HM physicochemical properties significantly influence their interactions with MP. Heavy metals with higher atomic number (e.g., Pb^{2+}, Cu^{2+}, Cd^{2+}) with smaller hydrated ionic radius (Pb^{2+}: 0.401 nm; Cu^{2+}: 0.419 nm; Cd^{2+}: 0.426 nm) exhibit stronger electrostatic interactions with negatively charged MPs [8]. Moreover, different types of HMs have varying affinities for the same type of MP. Related studies have shown that Pb and Cr have the highest MP affinity than those of Ni and Co [19].

3.3. Physicochemical Properties of the Soil Environment

The adsorption of heavy metal by microplastics in soil depends on the pH, organic matter, salinity, soil hydrothermal condition, soil aggregates, soil organisms and other environmetal conditions.

Heavy metals have various ionic forms at different pHs. pH changes the heavy metal sorption location. Clay is an important component of soil, and its charge characteristics are affected by pH. Lower pH reduces clay mineral adsorption capacity, releasing exchangeable HMs [20]. pH not only affects the physicochemical properties of soil and heavy metals but also the surface charge of microplastics. An increase in pH enhances the electronegativity of microplastics, and thus the adsorption capacity formed by electrostatic forces is also increased. However, the effect of pH on adsorption also varies due to the different adsorption mechanisms between heavy metals and microplastics.

Soil organic matter can combine with MPs to form conjugated copolymers with high electron density, facilitating the sorption of HMs. Soil organic matter adheres to MPs is usually prone to fostering the microbes to form biofilms which facilitate the sorption and degradation of heavy metals by MPs [21]. Humus main stable component of soil organic matter is contain a large amount of carboxyl groups, phenolic hydroxyl groups, and other functional groups which can adsorb metal ions, leading to decreased sorption by MPs. Moreover, MPs adhered with humic substances would become copolymer of negative charges. Many observations indicated that the interaction between heavy metals and MPs were greatly enhanced when humic substances covered the surface of MPs [8].

Salinity influences HM adsorption via salting-out effect which increase in ionic strength lowers the solubility of heavy metals and thus promote precipitation of the heavy metal) and crowding-out (reducing adsorption via ion competition) effects. High salinity compresses electrical double layers, inducing MP aggregation and reducing HM adsorption [8]. When the salting-out effect is greater than the crowding-out effect, the adsorption capacity of MPs increases. Liu et al. [22] confirmed that under the influence of salt ions, the adsorption mechanism is primarily electrostatic interaction, surface complexation, and ion exchange. If electrostatic interaction is the main adsorption mechanism, Na^+ will compete with HMs for adsorption sites through electrostatic attraction. Soil salinity can also cause electrostatic shielding of metals and aggregation of MPs. An increase in salinity in HM solutions intensifies competition among cations, significantly prolonging the time for PE to adsorb HMs (lead, copper, cadmium, and zinc). It is worth noting that at a salinity of 0%, the adsorption and release rates are significantly higher than at salinities of 15% and 30% ($P < 0.05$) [8].

Hydrothermal treatment alters MP morphology, functional groups and aging degree, increasing heavy metal adsorption. Moreover, soil hydrothermal conditions influence the MPs and HMs migration [8].

Soil aggregates influence MP accumulation; 72% of MPs associate with aggregates, with abundance of higher at 92% fibers dominating in micro-aggregates [8]. HM speciation shifts occur earlier in macro-aggregates than that in smaller aggregates [11].

Microorganisms and fauna (e.g., laccase) harboring in soil oxidize MPs, increasing carbonyl groups, specific surface area of MPs and thus HM adsorption capacity [8]. Digestive enzymes in simulated gastrointestinal environments accelerate HM desorption from MPs, posing toxicity risks [23].

Cation exchange capacity (CEC), clay minerals, and amorphous Fe/Mn/Al oxides modulate HM adsorption. Higher CEC increases As adsorption on MPs [24]. Clay minerals enhance HM adsorption via surface area, while Fe (II) oxides reduces U(VI) mobility and thus decrease the U sorption by MPs [25].

4. SUMMARY

Electrostatic and non-covalent interactions, hydrogen bonding, surface complexation, π-π interactions and coprecipitate were main mechanisms for heavy metals adsorption on MPs. Physicochemical properties of unaged MPs and aging MPs, physicochemical properties of heavy metals and soil environmental conditions have different effects on the adsorption of heavy metal on MPs. Therefore, given the different land use types and soil physicochemical properties, future research should provide more targeted studies on the interactions of MPs and heavy metals co-contamination in soil across a broad range of environmental gradients.

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