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Research Progress on The Adsorption and Their Mechanisms of Polycyclic Aromatic Hydrocarbons in Soil by Microplastics

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Abstract: The physicochemical characteristics and refractory properties of microplastics can adsorb and enrich polycyclic aromatic hydrocarbons in the environment, and then release the adsorbed and accumulated pollutants into other organisms, which will cause harm to the soil ecosystem. In this paper, the effects of microplastics type, size, density, aging degree and soil environmental factors on the adsorption of polycyclic aromatic hydrocarbons by microplastics were reviewed. This paper will provide a theoretical basis for exploring and revealing the combined pollution of microplastics and polycyclic aromatic hydrocarbons in the soil environment.

Keywords: Microplastics; PAHs; soil; adsorption.

1. Introduction

Plastic waste pollution is sweeping the globe at an alarming rate, and the surge in the consumption of personal plastic protective equipment during the current COVID-19 outbreak has exacerbated the issue of plastic pollution. The pollution and disposal of plastic waste have become challenges faced by the world. In 2018, the global plastic waste generation was 34.8 million tons, and it is estimated that by 2050, the world will produce approximately 67.8 million tons of plastic waste. Plastic particles with a diameter less than 5mm are referred to as "microplastics," while nanoplastics (NPs) are particles that are less than 100nm in at least one dimension. Studies have shown that microplastics can be toxic to organisms, including inhibiting growth, reducing egg production, altering enzyme activity, and increasing mortality rates. Microplastics have relatively stable physicochemical properties, are difficult to naturally degrade, and persist widely in marine, freshwater, and soil environments, and they readily adsorb organic pollutants, heavy metals, pathogens, and antibiotic resistance genes in the environment. Enriched pollutants in microplastics are magnified through the food chain, enhancing their toxic effects and threatening ecosystems and human health, making them a recent focus and hot topic in the field of environmental research.

Currently, research on microplastic pollution has mainly focused on marine, coastal, estuarine, and lacustrine ecosystems. Terrestrial environments are significant sources and sinks for microplastic pollution. For instance, the application of sewage, sludge, and organic fertilizers, the use of plastic films, and atmospheric deposition can all lead to the accumulation of microplastics in the soil. Studies have estimated that the annual emission of microplastics to farmlands in Europe and North America reaches 110,000 and 730,000 tons, respectively. This figure even exceeds the average annual increase of microplastics in the surface waters of the ocean. The issue of soil microplastic pollution has become a global hot topic in recent years, and there is an urgent need for systematic research on its content, sources, migration and transformation, ecological and environmental effects, and health risks. Research on the accumulation and effects of microplastics in the soil environment is relatively scarce. Heavy metals, persistent organic pollutants (POPs), and antibiotics are common pollutants in the soil, with polycyclic aromatic hydrocarbons (PAHs) being the most severe and widespread among organic pollutants. Studies have shown that microplastics, as carriers for the migration of these pollutants in the environment, can concentrate hydrophobic organic substances, such as PAHs. Pollutants adsorbed by microplastics can be released back into the soil environment during the degradation process of microplastics, causing continuous harm to the soil. Research has shown that microplastics interact with organic pollutants and heavy metals in the soil, undergo migration and transformation, and may even be absorbed, accumulated, bioamplified, and biotransformed by organisms in the soil environment. In the future, they may accumulate in organisms and the human body through various exposure pathways, leading to complex toxicity effects and posing potential significant hazards to organisms and human health.

In this paper, the interfacial adsorption behavior and adsorption mechanism of microplastics and polycyclic aromatic hydrocarbons in soil were reviewed, and the effects of physical and chemical properties of microplastics on the adsorption behavior and mechanism of microplastics were introduced. As an agricultural powerhouse, our country's soil is crucial for human survival and development. This study will reveal the patterns and mechanisms of interaction between soil microplastics and pollutants, providing a scientific basis for assessing the ecological and environmental risks of soil complex pollutants and promoting the risk control and management of soil microplastic pollution.

2. Mechanisms of the PAHs Sorption to Microplastics

Microplastics will adsorb a variety of organic pollutants and act as a carrier medium to help organic pollutants migrate and store. Meantime Microplastics that adsorb pollutants can persist in soil for a long time and may pose potential ecological risks. It has been suggested that the hydrophobicity of microplastics plays a leading role in their adsorption of organic pollutants[1]. In addition, the changes in the physical and chemical properties of microplastics that have existed in the soil for a long time also affect their adsorption with polycyclic aromatic hydrocarbons due to abrasion and aging[2].

Numerous studies have shown that hydrophobic partitioning, electrostatic interaction, hydrogen bonding, π-π interaction, and Van der Waals force interaction are the main mechanisms affecting the adsorption between PAHs and microplastics. Polar interaction and π-π interaction are the key mechanisms of PAHs adsorption on PS microplastics[3].

Sun et al. studied the adsorption behavior and mechanism of polyethylene (PE) microplastics and polyvinyl chloride (PVC) microplastics on polycyclic aromatic hydrocarbons in soil. The results showed that physical adsorption dominated by hydrophobic partitioning was the main adsorption mechanism, and the equilibrium partition coefficient of PE microplastics for PAHs was significantly greater than that of PVC[4].

Rochman et al. [5] found that the adsorption capacity of microplastics such as polystyrene (PS), polyethylene (PE), and polyvinyl chloride (PVC) on PAHs varies greatly. Polypropylene (PP), PE and PS all had high adsorption capacity for nitropolycyclic aromatic hydrocarbons (NPAHs), among which PS had a higher adsorption rate for 9-nitroanthracene (9-NAnt), and its adsorption mechanisms mainly included partitioning, hydrophobic interaction and van der Waals force. PE has the best adsorption performance for 9-NAnt, and its possible adsorption mechanism is dissolution and micropore filling. Molecular chemisorption may be the mechanism of the interaction between PP and 9-NAnt[24]. PP and PS have a higher adsorption capacity for 2-nitrofluorene (2-NFlu), followed by PE, and their adsorption process for 2-NFlu is more complex, and the main mechanisms include partitioning, hydrophobic interaction, and intragranular diffusion[24].

3. Influence Factors of the PAHs Sorption to Microplastics

3.1. Microplastics characteristics

3.1.1. Physicochemical properties of unaged microplastics

The type, concentration, and particle size of microplastics all affect the interaction between microplastics and polycyclic aromatic hydrocarbons in the soil (Wan). Common microplastics in the environment mainly include polyethylene (PE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyamide (PA). Due to the significant differences in structure, functional groups, and charge properties of microplastics with different compositional components, plus the different degrees of chain arrangement density during the polymer formation process, leading to different adsorption capacities for pollutants [6, 7].

For example, PS mainly interacts with other aromatic organic compounds through π-π bonds; PA has an amide group composed of C-O and N-H bonds, which easily forms adsorption with pollutants through hydrogen bonds, and its adsorption capacity is much greater than that of other types of microplastics [8] .

Lo et al. sampled many MP samples in ten sandy beaches in Hong Kong and found PAHs concentrations were between 70.8 and 1509 ng/g (dry weight). Among the 16 PAHs, 3-4-ring PAHs were dominant: Phe had the highest average concentration in MP samples (121 ng/g), followed by Pyr(93.5 ng/g) and Flt (55.0 ng/g), which may be due to a variation in adsorption because of the different molecular weight of PAHs[9].

Sun 's research found that microplastics can enhance the adsorption and fixation of polycyclic aromatic hydrocarbons in soil. The types and dosages of microplastics will affect the relative allocation of PAHs in soil and microplastics to varying degrees[4]. Xu et al. found that PE and PP microplastics significantly increased the adsorption capacity of brick red soil and brown soil to phenanthrene at the addition ratio of 1% and 10% (w/w) ($p < 0.01$), and PS microplastics significantly increased the adsorption capacity of the two soils to phenanthrene at only 10% addition ($p < 0.01$)[10].

There are also some differences in the adsorption of organic pollutants by microplastics of different densities and types. Fries et al. investigated the adsorption effects of HDPE and low-density polyethylene (LDPE) on polycyclic aromatic hydrocarbons (PAHs) and found that LDPE had a higher diffusion coefficient and faster adsorption rate than HDPE[11].

Within a certain range, the particle size of microplastics is inversely proportional to their specific surface area and the number of effective adsorption sites, and the smaller the particle size, the stronger the adsorption capacity [12].

Su et al. investigated the adsorption characteristics of polyethylene microplastics (PE-MPs) to naphthalene (NAP), phenanthrene (PHE), and pyrene (PYR) in the soil environment, and compared the adsorption capacity of polyethylene (PE), polypropylene (PP), and polystyrene (PS) microplastics for the three PAHs. The experimental results show that the adsorption process conforms to the pseudo-second-order kinetic model. Factors affecting adsorption include pollutant concentration, microplastic particle size, and water-soil ratio. When the adsorption is not saturated, the concentration of PAHs increases, the microplastics particle size decreases, and the water-soil ratio increases, the adsorption capacity of PE-MPs for the three PAHs increases. The adsorption capacity of PE-MPs, PS-MPs, and PP-MPs for the three PAHs is PS > PP > PE[13].

The abundance of the rubber domain in microplastics also affects the adsorption behavior of microplastics. Under laboratory conditions (25°C), PE microplastics have the richest rubber domain. Pyrene sorption was higher to PE than to PS and PVC, which was related to surface area, but also because PE is a semi-crystalline polymer, while PS and PVC are glassy polymers with large crystalline regions.[14].

Plastic polymers usually contain amorphous and crystalline regions. For instance, PE and PP, containing both crystalline and amorphous regions, are both classified as semi-crystalline polymers, in which amorphous regions are favorable for the sorption of organic chemicals [15]. Guo et al. [16]reported that the sorption coefficients of phenanthrene, naphthalene, and lindane to PE decreased with increasing crystallinity of PE.(Microplastics in the soil environment Occurrence, risks, interactions and fate - A review)

3.1.2. Physicochemical properties of aging microplastics

Microplastics in the environment would be subjected to diverse abiotic and biotic aging processes such as ultraviolet (UV) radiation, high-temperature thermal radiation, biodegradation, and chemical oxidation and so on [17]. Those aging process can alter the surface properties, microstructure, and physicochemical properties such as color, size, shape, and crystallinity of microplastics.

The results show that with the extension of aging time, the surface of microplastics will produce more pores, cracks and pits, become rough, and the specific surface area increases. The chemical properties of microplastics, such as functional groups and crystallinity, will change, which in turn will change their adsorption properties. Many studies have shown that new oxygen-containing functional groups appear on the surface of aging microplastics, or their oxygen-containing functional groups (e.g., carbon-based, phenolic hydroxyl groups) increase, and the hydrophilicity is enhanced, which in turn enhances the adsorption of hydrophilic organic pollutants and reduces the adsorption capacity of hydrophobic pollutants [18]. Aging can also increase the surface negative charge of microplastics, affecting their electrostatic interactions with pollutants. Changes in surface properties caused by aging can also lead to irreversible adsorption of pollutants through polar interactions (e.g., hydrogen bonding), which further enhances the co-migration ability of microplastics and organic pollutants. Therefore, it is of great significance to carry out comparative research on the adsorption behavior between different types of aging microplastics and organic pollutants.

3.2. Physicochemical properties of the soil environment

The adsorption of persistent organic pollutants by microplastics in soil depends on the temperature, pH, ionic strength, salinity, and coexisting ions of the soil environment [19].

Li et al. studied the adsorption behavior and mechanism of polyethylene and polystyrene microplastics on 16 polycyclic aromatic hydrocarbons in soil. The study found that soil pH and HA concentration significantly affected the adsorption of PAHs by microplastics, and the adsorption capacity of PE and PS microplastics reached a peak at pH5.0 and pH7.0, respectively, and the increase of HA concentration inhibited the adsorption of PAHs on PE microplastics, but promoted the adsorption of PAHs on PS microplastics[20].

Zuo et al. found that salinity had a significant effect on phenanthrene sorption to microplastics which were in the rubber state (PE) rather than glass state (PS), while Bakir et al. (2014b) observed that pH had no effect on the adsorption of phenanthrene to PE in the rubber state[21, 22].

Sun 's research found that the physical and chemical properties of soil solutions significantly affect the adsorption process of microplastics and polycyclic aromatic hydrocarbons. The high salinity and low dissolved organic matter (DOM) content contribute to the adsorption of polycyclic aromatic hydrocarbons by microplastics, which are more easily desorbed[4].

4. Summary

Different microplastic types, sizes, densities, aging process and soil environmental proprieties have different effects on the adsorption of PAHs. The sedimentation of PAHs on microplastics in soil will change the fluidity of microplastics, PAHs and the toxic effects on organisms which may lead to more serious pollution. The interaction between microplastics and PAHs deserves further study. At present, there is still a lack of systematic comparative studies on the effects of different soil media and environmental factors on the adsorption/desorption/migration behavior of PAHs on microplastics, and the related mechanisms also need to be further explored.

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