

Review

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Carbon-based adsorbents for micro/nano-plastics removal: current advances and perspectives

Huifang Zheng¹, Qian Chen² , Zhijie Chen³

¹School of Resource and Safety Engineering, Wuhan Institute of Technology, Wuhan 430205, Hubei, China.

²School of Civil and Environmental Engineering, University of Technology Sydney (UTS), Sydney, NSW 2007, Australia.

³School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW 2052, Australia.

Correspondence to: Qian Chen, School of Civil and Environmental Engineering, University of Technology Sydney (UTS), City Campus, Broadway, Sydney, NSW 2007, Australia. E-mail: Qian.Chen-1@student.uts.edu.au; Dr. Zhijie Chen, School of Civil and Environmental Engineering, The University of New South Wales, High St, Kensington, Sydney, NSW 2052, Australia. E-mail: Zhijie.Chen1@unsw.edu.au

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Abstract

Carbon-based adsorbents, such as graphene, graphene oxide (GO), activated carbon/biochar (AC/BC), carbon nanotubes (CNTs), metal-modified carbon, and fly ash, are garnering increasing attention due to their exceptional structural properties, enabling their potential effectiveness in removing microplastics and nano-plastics (MPs/NPs) from aqueous solutions. A key attribute contributing to the efficacy of these carbon adsorbents in addressing MPs/NPs is their flexibly tunable surface properties. To advance the applicability of functionalized carbon adsorbents in the context of MPs/NPs removal, it is necessary to highlight their interactions with MPs/NPs in aqueous environments. The review commences by outlining the main adsorption mechanisms. Subsequently, the adsorption behavior of different types of MPs/NPs on carbon-based adsorbents is analyzed and how different factors influence their adsorption performance is examined. Finally, the review concludes by offering insights into prospective avenues for future research concerning functional carbon adsorbents for MPs/NPs removal.

Keywords: Carbonaceous adsorbents, microplastics/nanoplastics, adsorption mechanism, adsorption behavior



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INTRODUCTION

Plastics, which exhibit remarkable malleability, versatility, cost-efficiency, durability, exceptional oxygen resistance, and lightweight, have gained extensive usage^[1]. In the year 2020, global plastic production reached a staggering 367 million tons^[2], and an anticipated increase of 29% is projected for the year 2028^[3]. When subjected to environmental conditions, plastics gradually degrade into minute fragments due to factors such as weathering, mechanical wear, solar radiation, and microbial activities^[4,5]. These particles are categorized according to their size, shape, density, and the type of polymer from which they are made. Alimi *et al.*^[6], Ding *et al.*^[7], Jahnke *et al.*^[8], Lang *et al.*^[9], and Wright and Kelly^[10] mentioned that the classification of plastics based on size ranges from macro-plastics (larger than 25 mm), meso-plastics (5-25 mm), microplastics (MPs) (100 nm - 5 mm), to nano-plastics (NPs) (smaller than 100 nm) [Figure 1A-D]^[11]. MPs are commonly identified as particles between 1 µm and 5 mm, whereas NPs are defined as particles smaller than 0.1 µm^[12,13]. These newly recognized entities are now identified as emerging hazardous contaminants for their unique physical and chemical properties, intrinsic stability, and high resistance to biodegradation^[14-18]. They are ubiquitously present across diverse landscapes, encompassing sewage systems, wastewater treatment plants (WWTPs), sediment layers, oceans, groundwater reserves, estuaries^[19], drinking water sources^[6], the atmosphere^[20], soil^[21], food supplies^[22], and even the human body's bloodstream^[10,20].

Aquatic organisms, including mammals, birds, fish, zooplankton, and mollusks, are susceptible to mistakenly ingesting MPs/NPs^[23]. MPs/NPs can be made from a variety of plastic materials, including polypropylene (PP), polyvinyl chloride (PVC), polyester (PES), polycarbonate (PC), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polyurethane (PU), and polyethylene terephthalate (PET), among others^[24-26]. These particles, characterized by their aptitude for adsorbing harmful compounds, serve as carriers for toxic elements such as antibiotics, pharmaceuticals, heavy metals, pesticides, plasticizers, and pathogens^[27-29]. Facilitated by their high surface area, reduced dimensions, and pronounced hydrophobic properties^[20], these interactions significantly impact the availability, fate, and amplification of these pollutants within ecosystems. Furthermore, the small scale of MPs and NPs renders them prone to being ingested as sustenance by aquatic species, potentially propelling their movement up the food chain and posing a consequential toxicological threat across the entire ecological spectrum^[30-32]. Hence, the expeditious removal of MPs and NPs emerges as a pressing priority to safeguard the integrity of aquatic environments.

A diverse array of treatment technologies, encompassing adsorption^[33], coagulation^[34], advanced oxidation processes^[35], photocatalysis^[36], bioremediation^[37], and filtration^[38], has been devised to combat the presence of MPs and NPs in polluted waters. Among these methodologies, adsorption stands out as a cost-effective, straightforward, dependable, and efficacious approach for capturing both MPs and NPs from water sources and sewage systems^[15]. Conventional adsorbents encompass a spectrum of materials such as low-cost substances, carbonaceous materials, and modified materials^[39]. These versatile adsorbents offer an extensive range of choices and sources, rendering them adaptable to local conditions across diverse countries and regions^[40-42]. Significantly, the key attributes of adsorption, notably facile operational procedures, renewable adsorbents, and minimal toxicity, contribute to its broad potential for MPs/NPs removal in water, thereby promising prospects for its wide-scale application^[43,44]. Ali *et al.*^[2] and Chen *et al.*^[45,46] have both conducted reviews on the latest adsorbents for removing MPs/NPs from polluted water. Their reviews encompass a range of emerging adsorbents, including those based on sponge/aerogel, metals, biochar, and other innovative materials. They provide a thorough explanation of the characteristics and adsorption mechanisms of each adsorbent in relation to MPs/NPs. Notably, carbon-based adsorbents are highlighted as particularly promising due to their cost-effectiveness and high adsorption efficiency. However, there is still a

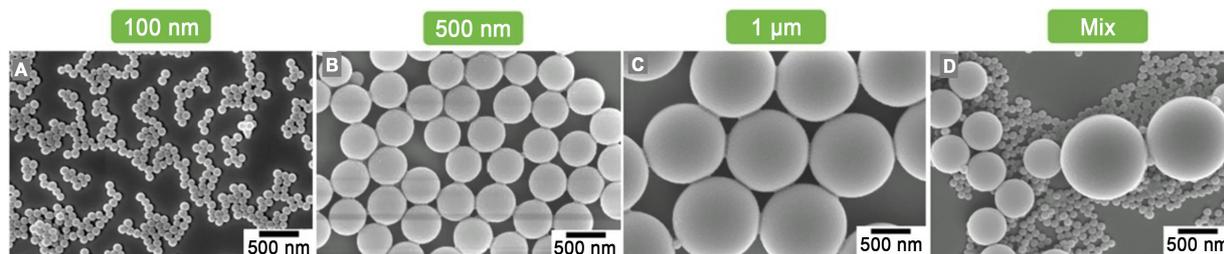


Figure 1. Morphology of PS MPs/NPs with different diameters at (A) 100 nm; (B) 500 nm; (C) 1 μm ; and (D) mixed sample^[11]. Copyright 2023, Elsevier. PS: Polystyrene; MPs: microplastics; NPs: nano-plastics.

lack of detailed information regarding the removal of MPs/NPs by carbon-based adsorbents. Additionally, a comprehensive and systematic explanation of the adsorption behaviors and mechanisms specific to each type of carbon-based adsorbent is yet to be fully explored.

Carbon-based materials, characterized by carbon as their primary constituent, exist in either powdered or bulk non-metallic solid forms. This category includes activated carbon/biochar (AC/BC)^[47,48], CNTs^[49], graphene^[46], graphene oxide (GO)^[50], metal-modified carbon^[51,52], and fly ash^[53], among others. AC stands as the foremost carbon-based adsorbent employed extensively in wastewater treatment. The versatility of AC allows for the preparation of a broad spectrum of adsorbents tailored to diverse environmental applications, including the removal of MPs and NPs from aqueous solutions^[47]. Given the elevated production costs associated with coal-based AC, biochar becomes a cost-effective alternative offering high efficacy in MPs/NPs adsorption^[51]. Biochar can be derived from an array of woody biomass sources, encompassing agricultural waste and byproducts such as peanut hulls and dairy manure^[54]. Notably, the utility of biochar extends beyond adsorption, encompassing roles such as carbon sequestration, soil fertility enhancement, and environmental remediation, thus establishing its multifunctionality in various domains. Graphene, constituting a single layer of a 2D hexagonal carbon network, is intricately investigated for its application prospects. Meanwhile, GO and reduced GO possess a high specific surface area and abundant surface functional groups, rendering it an ideal adsorbent for MPs/NPs removal^[50,55,56]. Carbon nanotubes (CNTs), on the other hand, manifest as cylindrical carbon tubes originating from one or multiple layers of graphene. Their well-defined hollow cylindrical structure, extensive surface area, hydrophobic characteristics, and amenability to surface modification contribute to their efficacy. Leveraging their exceptional physicochemical properties, GO and CNTs exhibit considerable advantages within the sphere of adsorption technology, particularly in addressing the removal of MPs/NPs^[49].

Although each carbon adsorbent exhibits distinct structural attributes and functionalities, a unifying trait present among all carbon adsorbents is their possession of abundant active surface functional groups. These groups play a pivotal role in shaping the surface chemical properties of carbon-based materials and facilitating the removal of MPs/NPs^[57]. The prevailing consensus is that the physical and/or chemical interactions occurring between MPs/NPs and the functional groups on adsorbents substantially contribute to the adsorption process of these minute pollutants. To align with the requirements of water quality criteria, substantial development and refinement efforts have been directed towards diverse carbonaceous materials and their derivatives. Consequently, a multitude of modification techniques have emerged to enhance the removal of MPs/NPs. These approaches include oxidation, magnetization, functional group grafting, and the incorporation of inorganic substances through compositional composites^[58].

Chemical and physical alterations to the surface of carbon materials can increase the variety and number of functional groups, enabling the addition of specific heteroatoms. This important area of research focuses on refining carbon materials' surface chemistry, specifically for the targeted capture of MPs/NPs.

These modifications enhance various characteristics of carbon-based adsorbents, such as pore distribution and volume, surface area, as well as increasing the number of functional groups and structural robustness. However, a thorough understanding of how the functional groups on the surface of carbon adsorbents interact with MPs/NPs is still lacking.

This study aims to thoroughly examine recent developments in carbon adsorbents, focusing on their surface functional groups and how these influence the removal and effectiveness against MPs/NPs in water. The papers published from 2015 till the present are summarized and reviewed (All of these papers are related to the MPs/NPs removal via carbon-based adsorbents). The review has two key goals: (1) To explore and clarify the basic processes that control the elimination of MPs/NPs by carbon adsorbents, emphasizing the complex interactions between functional groups and MPs/NPs; (2) To investigate the adsorption patterns of MPs/NPs on carbon adsorbents, highlighting their significant effects. Furthermore, the review will offer forward-looking views on future research into the use of functional groups in carbon adsorbents for the removal of plastic pollutants.

MECHANISM OF MPS/NPS ADSORPTION

The interaction between carbon adsorbents' functional groups and MPs/NPs is intricate, influenced by factors such as the carbon surface's diversity and chemistry, water's ionic composition, and adsorbate characteristics. Adsorbing MPs/NPs onto carbon materials involves various interactions: hydrophobic, hydrogen bonding, van der Waals forces, electrostatic attractions, π - π interactions, pore filling, and intraparticle diffusion [Figure 2]^[2,56,59]. The impact of these mechanisms on adsorption varies greatly, dependent on the MPs/NPs properties and the adsorbent type.

Chemisorption is important for removing MPs/NPs from water compared to physical adsorption interactions such as electrostatic interactions and pore filling. In specific water conditions, multiple mechanisms such as electrostatic interactions and surface complexation could simultaneously occur, influenced by electrostatic forces, binding site creation, and covalent bonding.

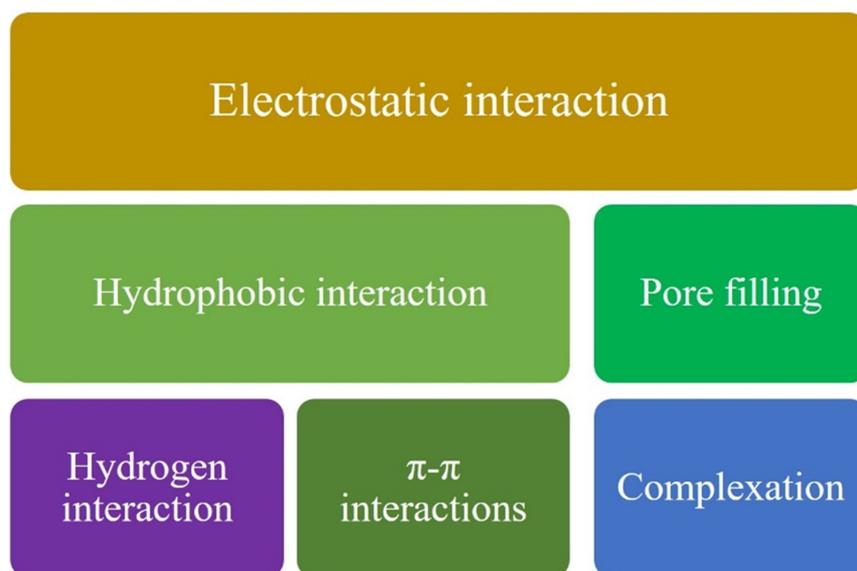
Physical adsorption, a relatively weaker process, involves MPs/NPs migrating into carbon adsorbents' pores and adhering to the carbon surface without forming chemical bonds. This mechanism is significantly affected by the surface area and porosity of carbon adsorbents^[47,51,60]. An increase in micropores enhances surface area, favoring physical adsorption, while more mesopores improve contaminant diffusion, thus accelerating adsorption kinetics.

The pore structure of carbon adsorbents plays a crucial role in the physical adsorption process, influenced by factors such as the raw materials used and the carbon synthesis method. This includes carbonization/pyrolysis temperatures for AC/BC^[61-63], as well as graphitization for GO and CNTs. The carbon surface's heterogeneity and polarity, along with associated functional groups, also significantly contribute to physical adsorption^[56,63]. These elements enable the transfer of MPs/NPs to the carbon surface through forces such as electrostatic attraction and ion-dipole interactions. Although common, physical adsorption is not typically the primary means of adsorbing MPs/NPs. Table 1 lists the recent typical carbon-based adsorbents for MPs/NPs adsorption^[47,49-53,64-68].

Table 1. The adsorption mechanism of MPs/NPs on carbon-based adsorbents

MPs/NPs	Carbon adsorbents	Mechanisms	Ref.
PS NPs	Granular activated carbon	Electrostatic attractions; Pore diffusion	[47]
PS MPs	3D RGO	π - π interaction	[50]
PS NPs	Biochar	Electrostatic attractions	[64]
PS NPs	Cu-Ni carbon materials	Electrostatic attractions	[66]
PS MPs	Zn-MBC	π - π interactions, hydrogen bonding, cooperative effect	[52]
PS MPs	Mg/Zn-MBC	Electrostatic interaction and chemical bonding	[51]
Polyethylene microbeads	Activated pine and spruce bark biochar	Physisorption	[67]
PS NPs	Iron-modified fly ash	Electrostatic attraction, complexation, π - π interactions	[53]
PS MPs, COOH-PS MPs, NH ₂ -PS MPs	ChGO	Electrostatic attraction, hydrogen bonding, π - π interactions	[65]
PE, PET, PA	Magnetic CNTs	Hydrophobic interactions, electrostatic attraction, hydrogen bonding, π - π interactions, complexation	[49]
PS NPs	Corn cob raw and oxidized biochar	Hydrophobic interaction and hydrogen bonding	[68]

MPs: Microplastics; NPs: nano-plastics; PS: polystyrene; 3D RGO: three-dimensional reduced graphene oxide; Zn-MBC: Zn modified magnetic biochar; Mg/Zn-MBC: Mg/Zn modified magnetic biochar; ChGO: sponge synthesized with chitin and GO; PE: polyethylene; PET: polyethylene terephthalate; PA: polyamide; CNTs: carbon nanotubes.

**Figure 2.** The main adsorption mechanisms of MNs/NPs by carbon-based adsorbents. NPs: Nano-plastics.

MPs/NPs tend to adhere to carbon-based adsorbents in water due to their hydrophobic nature, mainly through hydrophobic interactions. Hydrophobic molecules, which are non-polar, tend to aggregate and exclude water molecules in a polar environment due to hydrophobic interactions. The attachment of adsorbate molecules to the adsorbent's surface is not facilitated by strong ionic, hydrogen, or covalent bonds, but rather through weaker interactions like van der Waals forces^[69]. Many types of MPs/NPs exhibit significant hydrophobic characteristics. Similarly, carbon-based adsorbents, which are created at elevated temperatures, possess hydrophobic properties, enabling them to engage in potent hydrophobic interactions with MPs/NPs. For instance, CNTs are capable of bonding with MPs via either hydrophobic or π - π interactions, depending on the hydrophobicity of the MPs. When integrated with magnetic nanoparticles,

they form magnetic carbon nanotubes (M-CNTs), which allow for easy separation after absorbing MPs. M-CNTs have demonstrated high efficiency in removing MPs such as polyethylene (PE), PET, and polyamide (PA). They achieved complete adsorption of all MPs at a concentration of 5 g/L within just 5 h, with maximum adsorption capacities for PE, PET, and PA being 1,650, 1,400, and 1,100 mg/g, respectively. Remarkably, the adsorption process by M-CNTs remains effective even in the presence of substances like chemical oxygen demand, phosphate, and ammonia. M-CNTs also show the capability for thermal regeneration, maintaining their magnetic and adsorptive properties close to their original state. They retained about 80% efficiency even after four cycles of reuse^[49]. In the adsorption process, hydrophobic interactions were primarily responsible for the adsorption of PE and PET, while π - π interactions were significant in the adsorption of PA and PET. This underscores the versatility and effectiveness of M-CNTs in adsorbing and removing various types of MPs from the environment, highlighting their potential as a sustainable solution for tackling MP pollution^[49].

Iron-modified biochar is a notable example, especially when loaded with nanoparticles. It can be easily separated from mixtures using magnetic separation [Figure 3A]. The inclusion of iron species, particularly Fe_3O_4 , on the biochar creates active sites for surface complexation with nanoparticles, enhancing its adsorption capacity. This Fe-modified biochar is effective in rapidly removing all NPs from water in as little as 10 min and maintains its efficiency over four reuse cycles^[70].

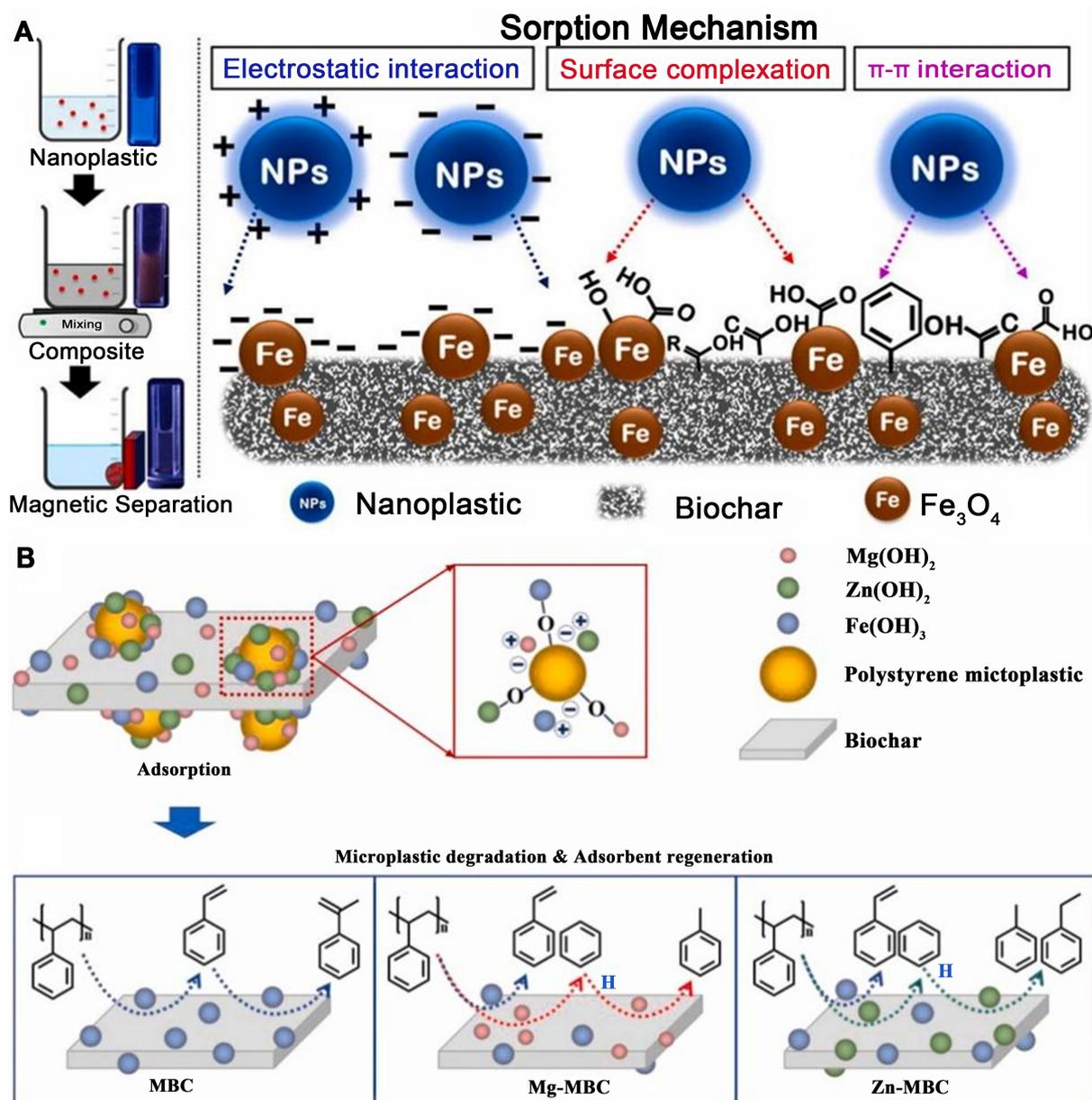
Similarly, biochar modified with magnesium and zinc leverages positively charged $\text{Mg}(\text{OH})_2$ and ZnO to enhance the adsorption of PS MPs. This improvement is primarily driven by electrostatic attraction and the formation of PS-O-metal bonds. Beyond its adsorptive qualities, Mg/Zn-MBC features catalytically active sites that exhibit significant hydrogenation activity. This property is particularly beneficial during the thermal treatment of PS MPs, facilitating the degradation of these plastics into smaller molecular compounds, as depicted in Figure 3B. This dual functionality not only aids in effectively removing MPs from the environment but also in breaking down and potentially repurposing these plastic materials^[51].

Ganie *et al.* discovered that BC, synthesized through pyrolysis at 750 °C, exhibited a positive surface charge of 2.85 mV. When this biochar was mixed with PS-based MPs/NPs that carried a negative charge of -39.8 mV, the zeta potential of the resulting combination rapidly shifted to -9 mV. This change signals a significant electrostatic attraction between the components^[64].

ChGO sponges demonstrate a remarkable capacity for reuse, maintaining high adsorption efficiencies even after three adsorption-desorption cycles. Specifically, these sponges have shown adsorption capacities of 89.8% for PS, 88.9% for PS-NH₂, and 72.4% for PS-COOH. The adsorption of PS, PS-NH₂, and PS-COOH onto ChGO sponges is facilitated by a blend of electrostatic interactions, π - π interactions, and hydrogen bond interactions. The presence of these varied interaction types is crucial to the sponges' ability to effectively adsorb different derivatives of PS, showcasing their versatility and efficiency as adsorbents in a range of applications^[65]. Graphite adsorbents can adsorb MPs/NPs via the π - π interactions. Yuan *et al.* found that the exceptional adsorption capacity (617.28 mg/g) of the three-dimensional reduced graphene oxide (3D RGO) towards polystyrene PS MPs was due to the strong π - π interactions between the graphite layers and the benzene rings in PS^[50]. Similarly, Zhou *et al.* reported that the π - π interaction between the sp²-hybridized carbon in CuNi@C and the aromatic rings in PS MPs promoted the removal of PS MPs^[71].

ADSORPTION BEHAVIOR OF MPS/NPS

Adsorption kinetic models are pivotal in evaluating the efficiency and identifying rate-determining steps in the removal of MPs/NPs onto carbon-based adsorbents, helping clarify the mechanisms involved in this



process^[72]. The adsorption kinetics generally encompass four steps^[73]: (1) bulk transport, which typically happens quickly; (2) film diffusion, a slower process; (3) intraparticle diffusion, also a slower step; and (4) adsorption attachment, which occurs rapidly. The generally used adsorption kinetic models for examining MPs/NPs adsorption on carbon-based adsorbents are the pseudo-first-order^[74], pseudo-second-order^[75], intraparticle diffusion, and film diffusion models^[76]. The pseudo-first-order and pseudo-second-order models are utilized to analyze the entire adsorption process. In contrast, the intraparticle diffusion and liquid film diffusion models are particularly useful for delineating the rate-limiting steps within this process. If the adsorption mechanism's complexity is not adequately captured by the pseudo-first-order and pseudo-second-order models, this can be further elucidated using the intraparticle and liquid film diffusion models,

providing a more comprehensive understanding of the adsorption dynamics.

The rate condition inherent in the direct form of both the pseudo-first and pseudo-second request templates can be represented as Q_e , as detailed in Equations (1) and (2)^[77,78].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

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

The q_t represents the adsorption capacity at time t , q_e denotes the adsorption capacity at equilibrium (mg/g), k_1 is the constant for the pseudo-first-order reaction, and k_2 stands for the pseudo-second-order reaction constant.

Extensive research [Table 2] indicates that both pseudo-first-order and pseudo-second-order kinetic models are effective in characterizing carbon-based adsorbents' adsorption behavior. However, their applicability depends on the specific properties of each adsorbent. The pseudo-first-order model is typically favored for rapid adsorption processes occurring primarily on the adsorbent's surface, and it is suitable for materials where surface interactions are predominant. In contrast, the pseudo-second-order model is better for processes where adsorption kinetics are governed by chemical adsorption mechanisms, involving electron sharing or transfer. This model fits adsorbents with complex surface chemistries or those engaged in deeper adsorption processes. The adsorbent's inherent properties, such as surface area, pore size, functional groups, and chemical structure, are crucial in determining the most suitable model.

Adsorption isotherms are essential for understanding the equilibrium behavior of adsorbents at constant temperature, influenced by the nature of the adsorbate, adsorbent, and adsorption solution properties such as pH, ionic strength, and temperature^[79]. Freundlich and Langmuir isotherm models are helpful in discerning the adsorption mechanism, whether linear monolayer coverage or multilayer adsorption^[74].

The Freundlich isotherm model, which is used to describe the adsorption characteristics of heterogeneous surfaces, can be expressed in both nonlinear and linear forms. The nonlinear form of the Freundlich isotherm is given by^[80]:

$$q_e = K_F C_e^{\frac{1}{N}} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{N} \log C_e \quad (4)$$

The Freundlich isotherm model is characterized by two coefficients: K_F (L/mg), which indicates the adsorption capacity, and N , which represents the strength of adsorption. These coefficients demonstrate that^[78]:

- (1) K_F quantifies the maximum amount of adsorbate that can be adsorbed per unit equilibrium concentration, reflecting the adsorbent's capacity to accumulate and retain the adsorbate.
- (2) N and its inverse $1/N$ measure the adsorption intensity or the bond strength between adsorbate and

Table 2. The adsorption capacity of MPs/NPs on carbon-based adsorbents and their corresponding adsorption behavior

Carbon adsorbents	Water matrix	Adsorption performance	Adsorption behavior	Ref.
Granular activated carbon	Lake water	Adsorption capacity 6.33 mg·g ⁻¹	Pseudo-second-order; Langmuir isotherm	[47]
3D RGO	Tap water	Adsorption capacity 448.60 mg·g ⁻¹	Pseudo-second-order; Langmuir isotherm	[50]
Biochar	River water	Adsorption efficiency 75%	Pseudo-first-order; Langmuir isotherm	[64]
Cu–Ni carbon materials	Synthetic wastewater	Adsorption efficiency 99.18%	Pseudo-first-order; Langmuir isotherm	[71]
Zn-MBC	Tap water	Adsorption efficiency >92%	Pseudo-second-order; Langmuir isotherm	[52]
Mg/Zn-MBC	Synthetic solution	Removal efficiency >94%	Pseudo-second-order; Langmuir isotherm	[51]
Iron-modified fly ash	Freshwater	Adsorption capacity 89.9 mg·g ⁻¹	Pseudo-first-order; Sips model	[53]
ChGO	Synthetic wastewater	Adsorption efficiency 89.8%	Pseudo-second-order; Langmuir isotherm	[65]
Magnetic CNTs	Synthetic wastewater	Adsorption capacity 1,650, 1,400, and 1,000 mg·g ⁻¹ for PE, PET, and PA, respectively	Pseudo-second-order; Freundlich isotherm	[49]
Corncob raw and oxidized biochar	Synthetic solution	Removal efficiency >90%	Pseudo-second-order; Langmuir isotherm	[68]

MPs: Microplastics; NPs: nano-plastics; 3D RGO: three-dimensional reduced graphene oxide; Zn-MBC: Zn modified magnetic biochar; Mg/Zn-MBC: Mg/Zn modified magnetic biochar; ChGO: sponge synthesized with chitin and GO; CNTs: carbon nanotubes; PE: polyethylene; PET: polyethylene terephthalate; PA: polyamide.

adsorbent, highlighting the surface's heterogeneity and the interaction's strength.

Unlike models predicting a saturation point, the Freundlich isotherm suggests an unlimited adsorption capacity, implying the potential for multilayer adsorption. The efficiency of the adsorption process under this model can be categorized as follows^[81]:

- (1) It is deemed efficient or favorable when $0 < 1/N < 1$, indicating a high affinity of the adsorbate for the adsorbent.
- (2) It is considered inefficient or unfavorable when $1/N > 1$, indicating a low affinity.
- (3) The process is seen as irreversible when $1/N = 1$, meaning the adsorbate, once adsorbed, remains firmly attached to the adsorbent.

The Langmuir model, assuming a uniform adsorbent surface with monolayer adsorption and no interaction between adsorbed molecules, is widely used^[72]. The nonlinear and linear forms of the Langmuir model are as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (6)$$

where q_m (mg/g) is the maximum adsorption capacity; K_L (L/mg) is the Langmuir isotherm constant.

Based on [Table 2](#), it is clearly seen that the Langmuir isotherm model is predominantly used for describing MPs/NPs adsorption on carbon-based adsorbents, suggesting monolayer adsorption on a homogeneous surface without significant interaction between adsorbed molecules.

EFFECT OF INFLUENCING FACTORS ON THE ADSORPTION PERFORMANCE

The elimination of MPs/NPs from water via adsorption is impacted by the characteristics of the adsorbent as well as the chemical properties of the water. While earlier discussions were centered on how the structure of the adsorbent influences its efficacy, we will now turn our attention to the particular elements that govern the adsorption process of MPs/NPs. These elements include pH level, dissolved organic matter (DOM), metal ions, and anions.

pH value

In aquatic environments, pH value significantly affects both the adsorbents' and MPs/NPs' surface charges, playing a key role in their adsorption process. This factor chiefly determines the electrostatic interactions between the MPs/NPs and carbon adsorbents and influences how the plastic particles cluster together. Research has consistently shown the pH-dependence of the MP/NP adsorption process, noting that a pH range slightly towards the acidic to basic side, usually around 4 to 8, is optimal for enhancing the electrostatic attraction during adsorption. Nonetheless, it is noteworthy that in instances where dominant adsorption mechanisms such as surface complexation are present, the pH's effect on the efficiency of MPs/NPs adsorption may be relatively insignificant.

Metal ions

Metal ions are frequently present in water resources, especially K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Fe^{3+} , and Al^{3+} . The impact of K^+/Na^+ ions on MPs/NPs adsorption is usually considered to be minimal^[53]. The effect of multivalent cations, including those with charges of +2 and +3, on the removal of MPs/NPs has been found to vary across different studies. One observed impact is that these high-valence cations can diminish the adsorption of MPs/NPs. This reduction in adsorption efficiency is attributed to the strong affinity these cations have for the adsorbents, which competes with and potentially hinders the binding of MPs/NPs to the adsorbent surfaces^[53,82]. Furthermore, certain metal ions, such as Mg^{2+} , Ca^{2+} , and Fe^{3+} , can improve the aggregation of MPs/NPs through electrostatic attraction. This aggregation process can restrict the diffusion of MPs/NPs into the porous structure of carbon adsorbents, potentially impacting the adsorption effectiveness. However, it is important to acknowledge that ions like Ca^{2+} and Mg^{2+} ions might also enhance the adsorption efficiency. They can create new adsorption sites on the adsorbents through a bridging effect, thereby potentially improving the overall removal efficiency of MPs/NPs [[Figure 4](#)]^[47].

Anions

Anions such as Cl^- , SO_4^{2-} , CO_3^{2-} , and PO_4^{3-} have an impact on the process of adsorbing MPs/NPs. These anions often obstruct the adsorbent-MPs/NPs interactions due to their propensity to bind with the adsorbents. Specifically, when using Cu-Ni/carbon materials for MPs/NPs removal, HCO_3^- largely alters the efficiency. This effect is attributed to the hydrolysis of HCO_3^- , which produces OH^- ions, subsequently raising the pH of the solution. This pH increase leads to stronger electrostatic repulsion between the MPs/NPs and the Cu-Ni carbon, affecting the adsorption dynamics. This relationship between different anions and the adsorption process is also reflected in the studies conducted by Ganie *et al.*^[64]. On the other hand, the efficacy of Zn-BMC in adsorbing PS MPs is negatively affected by the presence of anions, with their impact decreasing in the order: $NO_3^- < SO_4^{2-} < Cl^- < HCO_3^- < H_2PO_4^-$. It is suggested that the particularly strong effect of $H_2PO_4^-$ ions stems from their higher charge density, leading to more competitive adsorption on the surface of the adsorbent. This indicates the complexities involved in the adsorption process. Variables such as the concentration of anions, the surface characteristics of MPs/NPs, and the

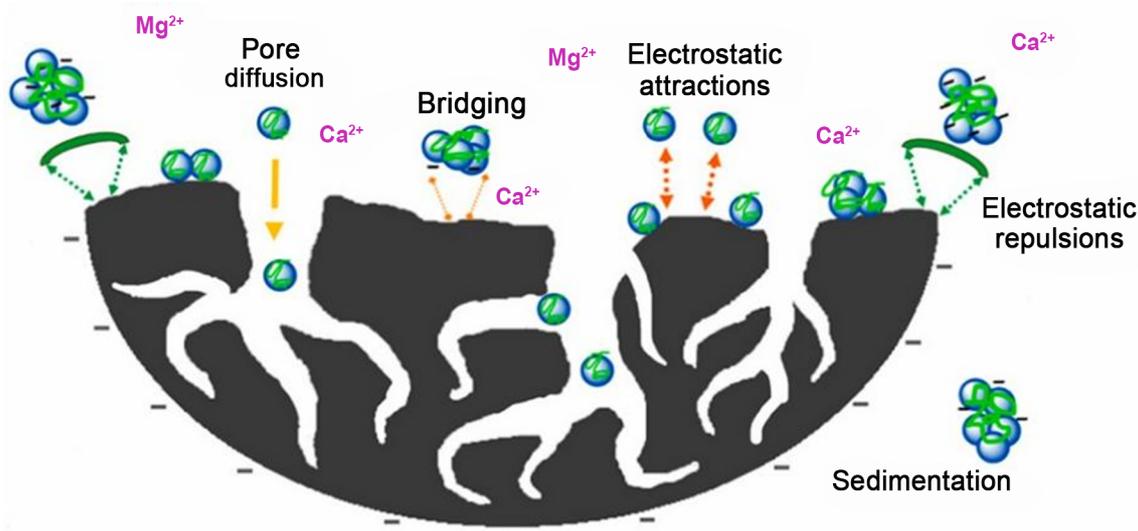


Figure 4. Potential adsorption mechanisms of PS NPs on AC, with the existence of Mg²⁺ and Ca²⁺ ions^[47]. PS: Polystyrene; NPs: nanoparticles; AC: activated carbon.

unique features of the adsorbents used contribute to diverse outcomes across different studies. These discrepancies underscore the importance of comprehensively understanding the environmental and material-specific factors that affect adsorption behavior in each distinct situation^[52].

DOM

DOM in water systems is a diverse and complex collection of polyelectrolytes. The way DOM interacts with MPs/NPs can affect how MPs adhere to adsorbents, as it changes the surface characteristics of both MPs/NPs and the carbon adsorbents. For example, research^[64] has demonstrated that humic acid can notably hinder the adsorption of PS NPs, causing a marked reduction in their removal efficiency (decreasing by 55%-75%). This reduction in adsorption is due to the coating and stabilization of the NPs and the adsorbents, such as BC-750, which creates strong electrostatic repulsion and consequently lowers the effectiveness of the adsorption process. It is important to mention, however, that even in an electrostatically unfavorable environment and in the presence of DOM at concentrations as high as 10 mg/L, sorption of NPs can still occur. This phenomenon can be explained by the more effective complexation of NPs on available adsorption sites, rather than their coverage by DOM^[70].

CONCLUSION AND PERSPECTIVES

In this comprehensive review, we delve into the recent advancements in carbon-based adsorbents and their role in eliminating MPs/NPs from water. A key focus is understanding the adsorption mechanism between these adsorbents and MPs/NPs. We then discuss the various methods of synthesizing these adsorbents and analyze their adsorption behaviors. Critical experimental parameters, such as pH value, anions, DOM, and metal ions, can impact the performance of carbon adsorbents to a different degree.

The removal of MPs/NPs from wastewater is crucial for reducing the harmful effects of plastics on various life forms. Despite some advancements, the field of MP/NP adsorption is still emerging, and current research is insufficient for fully resolving this issue. This section outlines challenges and future directions for MP/NP adsorption in water systems:

(1) For adsorbents to be practically viable, their ability to desorb and be reused is vital. Although

regeneration of adsorbents through thermal and chemical processes has been studied, more research is needed to efficiently desorb MPs/NPs, recycle adsorbents, and restore their adsorption capacity.

(2) The longevity and ecological implications of adsorbents are crucial factors. The degradation of adsorbents might result in metal leakage or nanoparticle emission, leading to secondary contamination. Moreover, adsorbents may react with other substances in water to form new pollutants. It is essential to evaluate adsorbents' stability in actual water environments and to develop efficient methods for their post-use removal.

(3) Although adsorption is effective for removing MPs/NPs, it can be influenced by water characteristics and might require significant time for optimal removal efficiency. Merging adsorption with other techniques such as magnetic separation or filtration could improve efficiency and cut costs. Notably, combining adsorption with magnetic separation using magnetic adsorbents has shown potential due to its high effectiveness and easy separation process. Future research should concentrate on creating such hybrid methods for various water environments.

(4) To enhance understanding of adsorbent-MP/NP interactions and facilitate the development of more effective adsorbents, it is necessary to combine the adsorption tests with computational tools. Such methods can assist in designing superior adsorbent materials by providing meaningful insights into adsorption mechanisms.

DECLARATIONS

Authors' contributions

Conceptualization, figures, table, and writing - original draft preparation: Zheng H

Writing - reviewing and editing: Chen Q, Chen Z

Supervision: Chen Z

Availability of data and materials

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Conflicts of interest

All authors declared that there are no conflicts of interest. Chen Z is an Editorial Board member of the journal *Water Emerging Contaminants & Nanoplastics*.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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