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Published version:

The formal publication is available via its DOI: https://doi.org/10.1016/j.nexres.2026.101928

Journal: Next Research (Next Res.)
Published: 2026, volume 10, article 101928

Nano-Adsorbents for Microplastic Removal – Cross-Material Insights, Performance and Practical Applications

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Abstract

The widespread pollution of ecosystems by microplastics poses a major environmental and health crisis. Conventional remediation technologies remain largely ineffective for removing these minute and persistent pollutants, resulting in a critical "microplastic–nanoplastic gap." This review evaluates nano-adsorbents as a promising solution to address this challenge. It presents a comprehensive classification of nano-adsorbents, including carbon-based nanomaterials, metal–organic frameworks, magnetic nanoparticles, and sustainable bio-based nanomaterials, alongside a critical evaluation of their structure–function relationships. Key adsorption mechanisms, such as hydrophobic interactions, electrostatic forces, hydrogen bonding, π–π stacking, and physical entrapment, are systematically analyzed, along with commonly employed modeling approaches. Furthermore, comparative analysis of adsorption capacities and process efficiencies across studies is carried out to address inconsistencies in the literature. The review also discusses the performance of nano-adsorbents in real-water matrices and their application in continuous-flow systems, highlighting the influence of complex environmental conditions on adsorption behavior. Although nano-adsorbents demonstrate superior adsorption capacity, rapid kinetics, and tunable selectivity compared to conventional materials, significant challenges, including high production costs, scalability limitations, potential ecotoxicity, and post-treatment recovery, remain critical barriers to practical implementation. By integrating material-level insights with process-level considerations, this review provides a critical framework to guide the rational design, evaluation, and translation of nano-adsorbents for scalable and sustainable microplastic remediation.

Keywords:

Mechanism, nanoparticles, metal-organic framework, adsorption capacity, wastewater treatment, continuous-flow systems, real water

1. Introduction

The excessive reliance on plastics, driven by their versatility, cost-effectiveness, and durability, has led to a drastic surge in plastic waste. This resulted in the emergence of a new class of persistent environmental contaminants: microplastics (MPs) and nanoplastics (NPs). These particles, typically defined as being smaller than 5 mm and 100 nm, respectively, present a global environmental challenge, infiltrating terrestrial, aquatic, and atmospheric ecosystems [1]. Primary MPs are intentionally manufactured for use in products, such as cosmetics and industrial abrasives. However, the vast majority of MPs and NPs are secondary in origin, produced by the degradation and fragmentation of larger plastic debris through a combination of physical, chemical, and biological processes [2,3]. This constant breakdown ensures a continuous flux of MPs and NPs into the environment. Their small size, low density, and high persistence make them difficult to contain and allow for their ubiquitous widespread dispersal from ocean sediments to mountain peaks [1].

The environmental and health risks associated with MPs and NPs are multifaceted and alarming. These particles can evade conventional filtration systems, facilitating their transport through aquatic systems and incorporation into the food web, where they pose a significant threat to all trophic levels, including humans [4,5]. Mistaken for food, these indigestible particles can accumulate in the digestive tracts of organisms, causing direct harm, such as physical blockages, reduced feeding, starvation, internal abrasions, and even death [2,6]. Due to high surface area and hydrophobic nature, MPs and NPs tend to adsorb and accumulate other harmful pollutants, such as heavy metals, pesticides, polycyclic aromatic hydrocarbons, pharmaceutical residues, and pathogens from the surrounding environment [1,7]. Once ingested, these contaminants can desorb in the gut, leading to bioaccumulation and biomagnification up the food chain [4]. Additionally, experimental studies have revealed a range of adverse effects linked to exposure to MPs, which include oxidative stress, DNA damage, organ dysfunction, metabolic disorders, endocrine disruption, and reproductive and developmental toxicity [8,9]. The presence of these particles in human tissues, including the lungs, small intestine, large intestine, and tonsils [10], highlights the urgent need for effective treatment strategies.

Existing remediation approaches, particularly conventional wastewater treatment plants (WWTPs), are inadequate to address the concerns posed by MPs and NPs. Processes such as primary sedimentation, coagulation, dissolved air flotation, and filtration can remove 70-99%

of larger MPs. However, a residual amount of microplastics, typically ranging from 1 to 50% of the total MPs, remains in the treated water [11,12]. Reports have shown that WWTPs are largely ineffective in capturing MPs smaller than 20 μm and are almost entirely unable to retain NPs [13]. These smaller particles can bypass conventional treatment stages, leading to their discharge into aquatic ecosystems as part of treated effluent. This technological constraint creates a "microplastic-nanoplastic gap", a size domain where traditional physical separation methods fail. The limitations of existing methods have prompted interest in nanomaterials for innovative solutions that offer the potential to effectively remove these minute, highly mobile plastic fragments.

Adsorption, a phenomenon where pollutants (the adsorbate) bind to the surface of a solid material (the adsorbent), is particularly advantageous for removing small plastic particles from aqueous environments. In this regard, nano-adsorbents are emerging as promising alternatives for removing MPs and NPs owing to a simple, efficient, reliable, and cost-effective process [14]. Nano-adsorbents are engineered materials with at least one dimension in the nanoscale range (1-100 nm), designed to adsorb/bind pollutants on their surface. Their exceptional efficacy is attributed to unique intrinsic properties that differ from those of their bulk counterparts. The most significant of these properties is an extremely high surface-area-to-volume ratio, which exponentially increases the number of available active sites for adsorption per unit mass of material, resulting in significantly higher adsorption capacities [15]. Due to tunable surface chemistry, nano-adsorbents can be precisely modified or functionalized to promote specific interactions with MPs, thereby enabling the design of highly selective adsorbents with affinity for target pollutants. This leads to enhanced reactivity, resulting in higher adsorption capacities and faster removal kinetics than those of conventional adsorbents [14]. Moreover, adsorbents can be regenerated and reused, thereby improving sustainability, economic feasibility and minimizing secondary wastes [11].

In recent years, a substantial body of literature has emerged addressing the applications of nanomaterials for MP and NP remediation. However, the reviews from the last five years predominantly fall into one of three categories: (i) broad surveys of nanotechnology applications for MP remediation that lack material-specific depth [14,16]; (ii) focused reviews on single material classes with no cross-material comparison [11,17,18]; and (iii) general overviews of MP removal technologies that treat adsorption as one among many mechanisms without rigorous quantitative analysis [1,3,7]. There is no existing review that systematically

compares diverse classes of nano-adsorbents while simultaneously evaluating their real-world applicability. Although adsorption mechanisms are discussed, a cross-material analysis that explicitly links adsorbent surface properties to dominant adsorption pathways across material classes remains limited.

A key limitation of the nano-adsorbent literature is the absence of standardized comparative approaches. Adsorption data is usually presented as isolated performance metrics from individual studies, making cross-study comparisons difficult and potentially misleading [19]. While adsorption mechanisms and modeling approaches are frequently discussed, their interpretation is often presented descriptively, without critical evaluation of their applicability, limitations, or consistency across studies [16]. In addition, although studies involving real-water matrices have been reported, existing reviews have not systematically compiled the findings [17], resulting in a limited understanding of nano-adsorbent performance under practical conditions.

This review addresses these gaps by adopting a critical and integrative framework that distinguishes it from prior literature. First, it presents a normalized comparative dataset of nano-adsorbents, standardizing key operational parameters and incorporating the MP:adsorbent (MP:Ads) ratio as an important yet underrepresented metric linking material performance to practical feasibility. Second, it moves beyond material-centric classification by identifying cross-material design principles that govern adsorption behavior across diverse systems. Third, it critically evaluates adsorption models, emphasizing their limitations and the need for cautious interpretation. Finally, it consolidates and analyzes available evidence from studies conducted in realistic water matrices and continuous-flow systems, providing a more coherent perspective on practical applicability. Collectively, this integrated approach enables a more rigorous comparison of nano-adsorbents and offers clearer direction for their rational design and implementation.

2. Nano-adsorbents – Types and Properties

Various materials are explored as nano-adsorbents, each with unique chemical and physical properties and potential applications. This diversity allows the selection of an adsorbent tailored to the characteristics of the target MPs or NPs and the conditions of the water to be treated. The main categories of nano-adsorbents are carbon-based nanomaterials, metal-organic frameworks, metal and metal oxide nanoparticles, and bio-based nano-adsorbents [16]. Each

of these categories encompasses a wide variety of specific materials with different structures, surface chemistries, and adsorption mechanisms (Figure 1).

2.1 Carbon-based nanomaterials

Carbon-based nanomaterials are among the most widely studied adsorbents for MP removal owing to their tunable surface chemistry, diverse morphologies, chemical stability, versatile and scalable production methods, and cost-effectiveness [5]. However, their performance is not inherently superior under all conditions; it depends strongly on specific surface area, pore architecture, surface modification, and compatibility with target polymer types [11,20]. This class of nano-adsorbents uniquely spans a wide spectrum of materials, encompassing conventional carbons (activated carbon, biochar) to engineered nanostructured carbons (carbon nanotubes, graphene derivatives). While conventional carbons rely primarily on surface area and porous networks, advanced nanomaterials offer more accessible adsorption interfaces and greater control over surface functionality. Surface modification plays a critical role in enhancing adsorption efficiency by increasing the number of active binding sites and altering the surface charge and properties for specific MPs. Common strategies include oxidation, magnetic functionalization, and incorporation of metal or metal oxides into the carbon matrix [5,21]. This reflects a broader shift in adsorbent design, i.e., from simply maximizing surface area to engineering surface characteristics to optimize interactions with target MPs and NPs.

(a) **Activated carbon:** Activated carbon, the most established carbonaceous adsorbent, is produced from carbon-rich precursors, like coal or wood, via pyrolysis followed by activation. The process creates a network of micropores, making the material highly porous and conferring a very high specific surface area, often exceeding 1000 m^2/g [11]. It demonstrates consistently high adsorption efficiencies for smaller MPs and pretreated samples, particularly in column-based systems [22]. However, its performance is hindered by limited pore accessibility, especially for larger MPs that cannot diffuse into the micropores, resulting in under-utilized internal surface area [5]. This highlights a critical limitation that high surface area does not always translate into high adsorption efficiency and depends on the target contaminants. Moreover, energy-intensive production methods and regeneration challenges make it a relatively expensive material and reduce its long-term sustainability [11].

(b) **Biochar:** Biochar, a carbon-rich material produced by pyrolysis of biomass, such as agricultural wastes, wood chips or manure [23], offers a more sustainable and economical

alternative. It is characterized by heterogeneous pore structure and diverse surface functionalities. Although it has a lower specific surface area (8-132 m^2/g) than activated carbon [24], its performance can be enhanced through modification strategies, such as magnetic functionalization or iron doping [25]. These modifications not only improve adsorption efficiency but also facilitate recovery via magnetic separation [26]. Mg/Zn-modified magnetic biochars leverage the formation of positively charged $Mg(OH)_2$ and ZnO to capture the negatively charged MPs. Additionally, these biochars can facilitate the thermal degradation of adsorbed microplastics into smaller, less harmful molecules, offering dual functionality- removal and degradation [25]. However, highly variable performance is due to the synthesis conditions, such as pyrolysis temperature, residence time, and the nature of the feedstock, which have been reported to govern its physicochemical characteristics, surface area, and pore-size distribution [23,27], leading to challenges in reproducibility and standardization.

(c) **Graphene and its derivatives:** Graphene, along with its functional derivatives graphene oxide (GO) and reduced graphene oxide (rGO), represents a class of highly engineered carbon nanomaterials. These possess an exceptionally high accessible surface area and flexible surface chemistry suitable for adsorption [28,29]. Three-dimensional architectures prevent graphene sheet restacking and maximize exposure of adsorption sites, resulting in some of the highest reported adsorption capacities [30]. Beyond surface area, the planar structure and modifiable surface chemistry enable selective affinity toward specific polymer types, especially aromatic plastics such as polystyrene [29]. However, these high-performance systems are typically evaluated under controlled laboratory conditions, and their behavior in complex environmental matrices remains insufficiently explored. Moreover, challenges in recovery and high production costs currently restrict large-scale application.

(d) **Carbon nanotubes (CNTs):** CNTs are hollow cylindrical structures with diameters of 1-50 nm, made of rolled graphene sheets, which can be single-walled (SWCNTs) or multi-walled (MWCNTs). The high aspect ratio, excellent mechanical strength and chemical stability, and strong hydrophobic nature render them very effective for adsorbing non-polar pollutants [31]. Their performance is further enhanced when integrated into composite systems, particularly with magnetic nanoparticles, enabling efficient post-treatment recovery [32]. CNT-based materials consistently exhibit high removal efficiencies, including near-complete removal of polyamide, polyethylene terephthalate, and polyethylene MPs in some systems [33]. However, as with graphene-based materials, their

widespread application is limited by high production costs and concerns about environmental and biological safety.

Cross-material insights and design implications

A comparative evaluation of carbon-based nano-adsorbents reveals that adsorption performance is governed less by the material category itself and more by key design parameters, including: (i) pore architecture and accessibility, which controls interactions with particle size, (ii) surface functionalization that determines affinity for MP types, (iii) 2D and 3D structural morphology affecting the availability of active sites, and finally (iv) recovery and reusability that is required for practical applicability and sustainability. Notably, materials with extremely high surface area but poor accessibility (e.g., microporous activated carbon) may underperform relative to materials with moderate surface area but better structural accessibility (e.g., rGO aerogels, modified biochars). Similarly, advanced nanomaterials (graphene, CNTs) offer superior performance but face scalability and cost barriers. Besides this, adsorption capacities for these materials vary widely across studies and are frequently influenced by different experimental conditions, including MP size, initial concentration, and water matrix composition. As a result, direct comparison of performance metrics without normalization can be misleading.

2.2 Metal-organic frameworks (MOFs)

MOFs are crystalline porous materials constructed as a hybrid of metal ions/clusters coordinated to organic ligands or linkers to form one-, two- or three-dimensional structures [34]. They represent a highly engineered class of nano-adsorbents characterized by ultrahigh porosity, large surface area, and abundant active sites, which make them promising candidates for MP and NP adsorption. Unlike conventional porous materials, their performance is not dictated only by surface area. It is strongly influenced by pore accessibility, surface functionalization, and structural stability under aqueous conditions [35,36]. The selection of metal nodes (zirconium, iron, chromium) and organic linkers (di- or tri-carboxylic acids) allows precise tuning of these physicochemical characteristics in MOFs, enabling them to be designed to target specific pollutants [37,38].

A critical consideration in MP/NP adsorption using MOFs is the size mismatch between the pores and the plastic adsorbate. While MOFs possess well-defined microporous or mesoporous

structures, most MPs are larger than the internal pores, thereby limiting adsorption predominantly to external surfaces or defect sites [39,40]. This shifts the design focus from porosity to surface engineering and hierarchical structuring, including the development of composite MOFs, to enhance accessibility and facilitate strong interactions [41]. However, this tunability introduces trade-offs related to synthesis complexity, cost, and long-term stability, particularly in aqueous and chemically complex environments. As a result, while MOFs demonstrate high performance under controlled conditions, their translation to real-world systems remains constrained.

(a) **Zirconium-based MOFs:** UiO-66 series (UiO stands for Universitetet i Oslo), composed of $Zr_6O_4(OH)_4$ clusters linked by terephthalic acid (1,4-benzenedicarboxylic acid) ligands, are among the most studied MOFs due to their excellent chemical and thermal stability. The arrangement arising from strong metal-ligand coordination creates a highly porous architecture with a large surface area. Zirconium clusters in UiO-66 render the framework resistant to degradation in aqueous environments, making it structurally robust and apt for water treatment procedures. Since adsorption is largely restricted to surface regions, the performance gains depend heavily on improving structural accessibility. Modifications of the organic linker with various functional groups (e.g., amine groups) have been reported to improve affinity for specific MPs and facilitate broad pH stability [42-44]. Additionally, the development of mesoporous UiO-66 derivatives by introducing surfactants such as CTAB or P123 has addressed challenges related to pore accessibility, thereby significantly enhancing MP/NP removal [45].

(b) **Chromium- or Iron-based MOFs:** The MIL-101 series (MIL stands for Materials of Institut Lavoisier) is another prominent class of MOFs, known for its exceptionally large pore sizes and high specific surface areas, often exceeding 3000 m^2/g [46]. It is typically synthesized using chromium (Cr) or iron (Fe) as the metal center and terephthalic acid as the linker. Such features contribute to high adsorption capacities, making them attractive candidates for MP/NP removal [39]. Moreover, these MOFs are derivatized into composites by incorporating metal nanoparticles, including iron oxide. Such composites are reported to exhibit abundant active sites with high surface area, exceptional adsorption efficiency, stability, reusability, and ease of recovery via magnetic separation [47]. However, the use of chromium-based variants raises environmental and health risk concerns due to potential metal leaching, while iron-based analogs offer a comparatively safer alternative.

(c) **Cobalt-based MOFs:** Zeolitic imidazolate frameworks, such as ZIF-67, exhibit rapid adsorption performance. Their structural features enable fast uptake kinetics, as low as 20 min, and effective interaction with aromatic polymers under controlled conditions [48]. However, these systems are often limited by moderate surface area compared to other MOFs and reduced stability under varying environmental conditions. Additionally, cobalt-based systems raise concerns regarding metal toxicity and long-term environmental impact [49,50].

Cross-material insights and design implications

Across different subclasses, MOFs demonstrate that adsorption performance is governed less by intrinsic porosity and more by accessible surface area, structural stability, and functional tunability. While pristine MOFs offer exceptional theoretical properties, their practical performance is often constrained by (i) limited accessibility of internal pores for larger MPs, (ii) sensitivity to aqueous environments and potential structural degradation, (iii) high synthesis cost and complexity, and (iv) challenges in recovery and reuse. Consequently, current research is shifting toward hierarchically structured and composite MOFs, where accessibility, stability, and recoverability are simultaneously optimized, which are essential for translating laboratory performance of these MOFs into practical water treatment applications.

2.3 Metal nanoparticles

This category comprises inorganic nanoparticles having high reactivity, functional versatility, catalytic potential, and in some cases, unique properties like magnetism. Unlike carbon-based materials and MOFs, whose performance is largely governed by structural features such as surface area and porosity [11,39,47], metal nanoparticles are primarily defined by their surface activity and functional adaptability. However, the tendency of these nanoparticles to aggregate in aqueous systems reduces their effective surface area and limits adsorption performance over time. Additionally, concerns about metal-ion leaching and long-term ecotoxicity pose significant barriers to practical implementation [51].

(a) **Magnetic nanoparticles:** Magnetic nanoparticles, particularly iron oxide (Fe_3O_4)-based systems, exhibit strong superparamagnetic properties with low toxicity. These are among the most widely explored metal nanoparticles due to their ease of separation from treated

water using an external magnetic field, which also enables their regeneration and reuse [52]. This process is comparatively more efficient than centrifugation or filtration, and further prevents the generation of secondary pollutants [9]. However, the adsorption capability of bare Fe_3O_4 nanoparticles is limited by a relatively low surface area and affinity for hydrophobic MPs. Consequently, surface functionalization with a hydrophobic agent, such as hexadecyltrimethoxysilane, is often required to enhance performance [53]. Studies have shown excellent removal efficiencies of 88-100% for polystyrene, polyethylene, polyvinyl chloride, and polypropylene MPs using magnetic nanoparticles and their derivatives [54,55].

(b) **Zeolites:** Zeolites are composed of SiO_4 and AlO_4 tetrahedra linked to form a three-dimensional network of channels and cages. This provides a highly ordered, microporous, and crystalline architecture. The net negative charge in the zeolite framework is compensated by exchangeable cations (such as Na^+, K^+, or Ca^{2+}) located within the pores, giving them well-known ion-exchange properties. The uniform pore size, typically 0.4 to 0.7 nm, enables them to selectively adsorb molecules based on their shape and size via physisorption [56]. Furthermore, their performance is highly sensitive to surface properties, which must be carefully tuned for effective interaction with polymeric particles. The content of silica, alumina, and polar groups on the zeolite's surface is responsible for the hydrophilicity/hydrophobicity of zeolites. These can be modified to exhibit hydrophobicity by maintaining a high Si/Al ratio and reducing the number of OH groups, thereby enhancing their affinity for non-polar microplastics [57]. Despite having a lower adsorption capacity than other advanced nanomaterials, its facile synthesis, eco-friendly nature, and recycling properties make it a potential strategy for large-scale applications [58].

(c) **Metal oxide nanoparticles:** Metal oxide nanoparticles, such as titanium dioxide and zinc oxide are among the widely used nanoparticles for environmental applications. They are known for their photocatalytic activity, which involves the degradation of organic pollutants via the generation of reactive oxygen species on exposure to UV or visible light [59]. Employing these materials offer dual-functionality-(i) adsorption of MPs, and (ii) breakdown of polymer chains of MPs into smaller and less harmful byproducts, thereby providing complete and effective mineralization of plastics [3]. However, their performance is governed by external factors, including light availability and extent of penetration, water chemistry and the presence of other radical-scavenging species [60,61].

Nanoparticle aggregation and surface fouling can further reduce the effectiveness over time, limiting their applicability in complex environmental matrices.

(d) **MXenes:** MXenes are an emerging class of two-dimensional materials derived from selective etching of the A-layer from MAX ($M_{n+1}AX_n$) phases. MAX are layered ternary carbides and nitrides composed of transition metals, carbon, and/or nitrogen. The general formula of MXenes is $M_{n+1}X_nT_x$, where M is an early transition metal (e.g., Ti, V, Nb, Cr), X is carbon or nitrogen, and T represents surface functional groups (e.g., –OH, –O, –F) [62]. This distinct layered architecture provides MXenes a unique combination of high metallic conductivity, chemical stability, thermal conductivity, hydrophilicity, large specific area with functionalizable surfaces and environmental compatibility [63]. Their tunable surface chemistry and 2D morphology make them potentially effective adsorbents for MPs. In one study, Urso et al. (2022) developed MXene-derived γ-Fe_2O_3/Pt/TiO_2 microrobots for 'on-the-fly' capture of NPs in the three-dimensional space [64]. However, their applications are still at an early stage with limited studies on long-term stability, scalability, and environmental impacts. Additionally, synthesis methods can be complex and may involve hazardous chemicals, raising concerns regarding sustainability and large-scale implementation [65,66].

Cross-material insights and design implications

Across metal nanoparticle-based systems, adsorption performance is governed not only by surface reactivity but also by stability, accessibility, and environmental safety. Several key design considerations are of paramount importance, including (i) aggregation control, crucial for maintaining active surface area, (ii) surface modification to enhance functionality and stability, (iii) recovery (e.g., magnetic systems) and reusability, essential for practical use, and (iv) environmental safety (metal leaching, toxicity). Owing to these constraints, metal nanoparticles are rarely optimal as standalone adsorbents. Instead, their role is increasingly shifting towards functional components within composite or hybrid systems, where their reactivity can be effectively utilized while minimizing associated risks.

2.4 Bio-based nanomaterials and composites

Bio-based nano-adsorbents have emerged as a promising class of materials for MP/NP removal, driven by sustainability, biodegradability, and environmental compatibility. Derived from

renewable and biodegradable resources, such as polysaccharides, proteins, and other natural polymers, these materials are preferred over synthetic nanomaterials owing to their low toxicity, cost-effectiveness, and potential for the circular economy [67]. A key strength of bio-based nanomaterials lies in their tunable surface chemistry, enabled by the abundance of reactive functional groups, which allows easy modification without complex synthetic routes. Their relatively soft, flexible, and porous architecture facilitates better interactions with irregularly shaped heterogeneous MPs.

(a) **Nanocellulose:** In the form of nanofibers or nanocrystals, nanocellulose is one of the most widely studied bio-based nano-adsorbents due to its high surface area, hydrophilicity, and abundance of surface functional groups that facilitate interactions with MPs [68]. It can be easily processed into various forms, such as aerogels, membranes, and sponges. These are highly porous networks providing structural versatility to effectively trap and degrade MPs [69]. Despite these advantages, pristine nanocellulose often exhibits moderate adsorption efficiency, especially for non-polar MPs. These are overcome by cationic functionalization (e.g. ammonium salts) to increase the density of positive charge on the surface, which enhance the affinity and adsorption capacity [70].

(b) **Nanochitosan:** Chitosan, a natural biopolymer derived from the deacetylation of chitin (found in the exoskeletons of crustaceans), is one of the leading candidates for bio-based MP removal. These adsorbents exhibit excellent biocompatibility, biodegradability, and ease of functionalization [71]. The presence of reactive moieties, like hydroxyl and amine groups, enables chemical modification, thereby providing active binding sites for functionalized or weathered MPs [72]. A particularly effective strategy of combining chitosan with magnetic nanoparticles yields composites with dual advantages: high adsorption capacity and ease of magnetic recovery [73]. Such systems demonstrate improved operational feasibility compared to individual biopolymers. However, chitosan-based materials are sensitive to environmental conditions such as pH and ionic strength, which can affect their structural integrity and adsorption efficiency. Additionally, their relatively low mechanical strength may limit long-term reuse.

(c) **Biopolymer-based sponges and aerogels:** These are advanced three-dimensional porous structures fabricated from materials such as alginate, cellulose, proteins, and other natural polymers, which possess excellent biodegradability and adsorption capacity to capture MPs across a range of sizes [68]. These materials are often engineered to form composites, sponges, hydrogels, and aerogels through (i) blending or crosslinking with other

biopolymers, such as starch, pectin, lignin, acrylamide, and proteins, or (ii) doping with metal nanoparticles to enhance stability and performance to remove various MP types [74-78]. Furthermore, their lightweight and highly porous nature makes them particularly suitable for filtration-based or batch systems [75,79]. However, their efficiency is strongly dependent on structural integrity and resistance to degradation in aqueous environments. In addition, large-scale production with consistent properties remains a challenge due to variability in raw materials and processing conditions.

Cross-material insights and design implications

Among bio-based nano-adsorbents, sustainability and environmental compatibility are prioritized alongside MP removal capacity. Key factors governing their effectiveness include: (i) surface functional group density, which enables tunability without complex synthesis, (ii) structural architecture (e.g., aerogels, sponges) that controls accessibility and capture efficiency, (iii) mechanical and chemical stability, crucial for reusability and durability, and (iv) composite integration (e.g., magnetic systems) to enhance operational feasibility. Their applicability is often constrained by variability in physicochemical properties depending on the source material and synthesis conditions. While these materials offer sustainability benefits, challenges related to mechanical stability, structural integrity, and adsorption efficiency often necessitate blending or modification, thereby increasing costs to some extent. Nevertheless, their long-term stability and scalability must be addressed for practical implementation.

3. Mechanism of adsorption

The remarkable efficiency of nano-adsorbents in capturing MPs and NPs is dictated by a complex interplay of physicochemical forces acting at the interface between the adsorbent surface and the plastic particle. One mechanism may dominate under certain conditions; however, strong and effective binding often results from a synergistic combination of multiple interactions. These include physical entrapment, intermolecular forces, electrostatic interactions, and hydrogen bonding. Factors such as surface area, pore size, charge, polymer type, surface functionalization, and water chemistry affect these interactions and their contribution to the sequestration of MPs and NPs [11]. Figure 2 depicts the various mechanisms of MPs adsorption onto nano-adsorbents.

3.1 Physical adsorption and pore-filling mechanisms

The physical adsorption, or physisorption, mechanism plays a significant role in porous nano-adsorbents, such as activated carbon, nanobiochar, MOFs, and aerogels [11]. The mechanism is non-specific and relies on the physical entrapment of particles within the porous framework of the adsorbent. The process begins with diffusion of MP particles from the bulk solution to the external surface of the adsorbent, a process known as *film or boundary-layer diffusion*. This is followed by migration into the internal pore structure, a process referred to as *intraparticle diffusion*. This is often the rate-limiting step of the overall adsorption process. The intraparticle diffusion can occur through two primary pathways: pore diffusion, where the particles move through the liquid-filled pores, and solid diffusion, where the particles migrate along the pore walls. Inside the pores, particles are retained through a combination of steric hindrances and weak van der Waals forces [80].

The efficacy of physical adsorption depends heavily on the adsorbent's pore-size distribution and specific area, as well as on the size of the plastic particles. While high surface area is often correlated with enhanced adsorption capacity, the relationship is not always linear. Instead, the presence of interconnected meso- and macro-pores and their accessibility play a crucial role in facilitating particle transport and retention. This is particularly relevant for materials with very narrow, well-defined pores, such as zeolites [11,25,81]. Such nano-adsorbents can be used to selectively capture very small particles or NPs while excluding larger MPs, thereby exhibiting a size-exclusion or molecular-sieving effect. However, this selectivity also imposes inherent limitations. In several cases, particularly for larger MPs, the particle size exceeds the pore dimensions, restricting access to internal pore networks and confining adsorption to the external surface. This limitation is pronounced in highly microporous materials, such as MOFs, where a large fraction of the surface area may remain inaccessible for MP adsorption [39,40]. Therefore, hierarchical pore structures that combine macro-, meso-, and micropores are often more effective, as they provide pathways for transport as well as retention sites for MPs and NPs [33,82]. This highlights that adsorption performance is governed not only by surface area but also by pore architecture and accessibility.

3.2 Chemical and physicochemical interactions

Beyond physisorption, the removal of MPs is significantly influenced by the diverse chemical and physicochemical interactions between the adsorbent surface and the polymeric chains of

plastic. These include hydrophobic interactions, π-π stacking, hydrogen bonding, and van der Waals forces. Though the interactions depend on the chemical nature of the materials involved, their cumulative effect often results in a higher adsorption capacity than that achieved by physical adsorption alone.

Hydrophobic interactions act as a key driving force for the adsorption of MPs, typically composed of non-polar hydrocarbon polymers like polyethylene and polypropylene [83]. The phenomenon is predominantly an entropic effect, rather than an attractive force. Water molecules form a highly uniform cage-like structure around hydrophobic surfaces. The non-polar MPs and NPs, being thermodynamically unstable in such an aqueous environment, tend to minimize contact with water molecules. Due to this hydrophobic effect, these particles are easily adsorbed onto a hydrophobic surface, thereby excluding water molecules from the interface, and attaining an energetically favorable state [84]. Adsorbents such as carbon nanotubes, graphene, and untreated biochar possess inherent hydrophobicity due to sp2-hybridized carbon structures, making them a popular choice for capturing non-polar MPs [11,85]. However, attributing adsorption solely to hydrophobicity may oversimplify the system, especially in complex aqueous environments where dissolved organic matter or surfactants can alter surface properties and interaction behavior [19]. Additionally, the strength of hydrophobic interactions depends on the relative hydrophobicity of both the adsorbent and the plastic, which is not always systematically evaluated.

π–π interactions, one of the important non-covalent interactions, are particularly relevant for plastics containing aromatic rings, such as polystyrene and polyethylene terephthalate. [84]. Nano-adsorbents like graphene, biochar, and CNTs possess large, electron-rich π systems capable of strong, stable, and attractive interactions with these plastics through π- π orbital overlap [30,86]. This mechanism creates a face-to-face or edge-to-face stacking configuration, thereby providing a degree of selectivity for aromatic polymers over non-aromatic ones.

van der Waals forces, which are weak, non-specific, short-range electrostatic attractions, arise from transient dipoles formed by temporary fluctuations in electron density. While individually weak, the collective effect of these forces over a large contact area can significantly contribute to overall adhesion. The MP particles are brought into close proximity to the adsorbent by van der Waals forces, after which they are held by stronger forces [87]. However, these forces alone are generally insufficient to account for high adsorption capacities and provide a supportive

additional layer of binding energy for adsorption, irrespective of the materials' chemical nature [88].

3.3 Electrostatic forces and hydrogen bonding

While physical and hydrophobic interactions are crucial, the most specific and tunable interactions in the adsorption of MPs are electrostatic attraction and hydrogen bonding. These are highly influenced by environmental parameters, such as the pH and ionic strength of the water, as well as the surface chemistry of the adsorbent and MPs [89]. Electrostatic interactions arise from the attraction between oppositely charged species [90]. Hydrogen bonding involves a specific dipole-dipole interaction in which a hydrogen atom is shared between a donor group (like –OH or $–NH_2$) and an acceptor atom, like oxygen or nitrogen [84]. While frequently cited, hydrogen bonding is often inferred indirectly, typically from spectroscopic observations. The presence and density of functional groups on the adsorbent surface are paramount for these interactions to occur.

Many nano-adsorbents inherently possess or are functionalized with hydroxyl, carboxyl, carbonyl, and amine groups, which act as potent hydrogen bond donors or acceptors, forming strong, directional bonds with complementary groups on the MP surface or with water molecules at the interface. These functional groups also introduce a surface charge on the adsorbents, governed by the point of zero charge, which determines whether the surface is positively or negatively charged under given conditions. The surface charge can thus be tuned by adjusting the surrounding pH to align with the properties of the target MP/NP for enhanced removal [84,87]. This pH-dependent adsorption behavior has been widely exploited in the design of adsorbents [39,91]. In addition, electrostatic interactions are highly sensitive to ionic strength. Dissolved ions can screen surface charges, thereby reducing effective attraction between adsorbent and MPs. These interactions are a key advantage of using functionalized nano-adsorbents, as they can be engineered to target specific MPs and NPs with high affinity and selectivity [2,84].

A recent study, investigating the adsorption of various MPs by Fe_3O_4 nanoparticles of different sizes, demonstrated that surface chemistry can play a more decisive role in governing adsorption performance. Variations in surface charge and functional groups can significantly alter interaction strength, even when surface area differences are minimal, thereby leading to the highest removal efficiency with large-sized nanoparticles [92]. This emphasizes the

importance of chemical functionality over purely structural parameters in designing effective adsorbents.

3.4 Synergistic and complex mechanisms

In most practical scenarios, the adsorption of MPs is not dominated by a single isolated mechanism, but by a complex synergistic combination of multiple interactions, as described earlier. Advanced materials are often designed to leverage this mechanism by integrating structural features with tailored surface chemistry to yield high-performing nano-adsorbents. For example, the MOF ZIF-67 relies on hydrogen bonding, electrostatic interactions, and π-π stacking to strongly bind polystyrene MPs [48]. Magnetic CNTs use hydrophobic interactions to capture polyethylene but also engage in complexation and π-π stacking for polyethylene terephthalate [33]. Similarly, biochars are engineered to combine pore-filling mechanisms with electrostatic interactions [93]. Such a multi-pronged approach leads to stronger and more robust binding of the MPs than any single mechanism could achieve on its own.

From a design perspective, the most effective nano-adsorbents are those that strike a balance among accessible pore structures that facilitate transport, surface functional groups that enable selective interactions, and adaptability to environmental conditions such as pH and ionic strength. Therefore, a comprehensive understanding of adsorption requires not only identification of possible interactions but also critical evaluation of their relevance under specific conditions. This is essential for developing robust and scalable nano-adsorbent systems.

4. Adsorption behavior: kinetics, isotherm, and thermodynamic analysis

The performance of nano-adsorbents in MP/NP removal is dictated not only by the nature of physical-chemical interactions, but also by the rate at which adsorption occurs, the equilibrium distribution of particles between phases, and the underlying energetic drivers. Adsorption kinetics, isotherm models, and thermodynamic parameters collectively provide a quantitative framework to interpret these processes, thereby yielding insights into the adsorption behavior of nano-adsorbents [39,91,94].

4.1 Adsorption kinetics

Adsorption kinetics describes the rate at which adsorbates are removed from solution and provides insight into the rate-controlling steps of the adsorption process. In addition to

elucidating adsorption mechanisms, kinetic analysis is critical for designing effective nano-adsorbent systems, as it directly influences contact time requirements, reactor configuration, and operational costs in water treatment applications [95,96]. Typically, adsorption proceeds through sequential stages: bulk transport, film diffusion, intraparticle diffusion, and final attachment to active sites [39,97]. The relative contribution of each step depends on both material properties and system conditions. Kinetic behavior is strongly influenced by parameters such as initial plastic concentration, adsorbent dosage, particle size, pH, and temperature, which collectively govern mass transfer and interaction dynamics [95].

Among kinetic models, the pseudo-second-order model (PSO) is the most frequently reported for describing MP/NP adsorption onto nano-adsorbents, often yielding high correlation coefficients, exceeding 0.98, across studies [47,48,91,94]. This model is commonly interpreted as indicative of chemisorption involving strong surface interactions such as electrostatic attraction, hydrogen bonding, or surface complexation. For example, adsorption of polystyrene NPs onto granular activated carbon (GAC) and CNT-based systems is often well described by this model, underscoring the importance of surface-controlled processes over sole diffusion-limited transport [33,98].

The pseudo-first-order (PFO) model, often associated with physisorption, is less frequently successful. In systems with a high availability of active sites and strong concentration gradients, early-stage adsorption is often dominated by external mass transfer, where PFO behavior may be observed [33,39,99,100]. As adsorption progresses and surface sites become occupied, the process may transition toward interaction-controlled behavior better described by PSO kinetics. Here, PFO generally fails to capture the full adsorption profile, especially in systems where surface functionalization enhances the strength of chemical interaction [91,98].

The intraparticle diffusion model (Weber–Morris) provides additional insight into transport limitations. Multi-linear behavior in adsorption plots indicates that adsorption is governed by multiple steps rather than a single rate-limiting mechanism. Typically, an initial rapid phase corresponds to boundary layer diffusion, followed by a slower stage associated with diffusion into internal pores [39]. The extent of intraparticle diffusion is strongly influenced by adsorbent structure, including pore size distribution, tortuosity, and particle size, which determine the accessibility of internal adsorption sites [101,102]. Reduced adsorbent size has been shown to increase the intraparticle diffusion, as shorter pore channels facilitate faster transport of target contaminants to adsorption sites [103]. In contrast, highly porous adsorbents, like GAC,

graphene oxide, and MOFs, exhibit rapid boundary-layer diffusion followed by slower intraparticle diffusion. The intercept reflects the contribution of external mass-transfer resistance, highlighting the role of hydrodynamics and particle size [39,98,104].

Additional models, such as the Elovich equation and Bangham model, have also been applied in specific cases to describe adsorption behavior on heterogeneous surfaces or systems dominated by pore diffusion [91,105]. However, these models see limited application in MP/NP removal literature compared to the PSO and intraparticle diffusion frameworks. Although kinetic analysis demonstrates that the adsorption of MPs/NPs involves a complex interplay between mass transport and surface interaction processes, the influence of nano-adsorbent surface properties, such as charge heterogeneity, roughness, and functional group density, remains insufficiently quantified [19].

4.2 Adsorption isotherm

Adsorption isotherms describe the equilibrium relationship between the adsorbate concentration in solution and the amount adsorbed on the solid surface. These models are essential for estimating maximum adsorption capacity and evaluating surface heterogeneity [106,107].

The Langmuir isotherm has emerged as the predominant model for describing MP/NP adsorption onto nano-adsorbents, with many studies reporting it as the best fit to equilibrium data [5]. The model assumes monolayer adsorption on relatively uniform surfaces and no interaction between adsorbed molecules. High adsorption capacities reported for materials such as activated carbon, biochar, rGO, and MOFs are often interpreted within this framework [27,30,94,98]. However, the assumption of a homogeneous surface and monolayer coverage is rarely fully valid for nano-adsorbents, which often exhibit structural and chemical heterogeneity [108]. Therefore, the apparent success of Langmuir fitting may reflect mathematical convenience rather than a true physical behavior.

In contrast, the Freundlich isotherm accounts for multilayer adsorption on heterogeneous surfaces and finds selective application in MP/NP removal. Systems involving mixed plastic types, modified surfaces, or composite nano-adsorbents predominantly exhibit Freundlich-type behavior due to variations in binding-site energies [33,39]. The model does not predict maximum adsorption capacity and is not applicable at high pressure or concentrations [109].

In many adsorption studies on MP/NP removal, the correlation coefficient for the Freundlich model is often lower than that for the Langmuir model. Consequently, Langmuir is frequently reported as the better fit, whereas the Freundlich model is either overlooked or discussed only in passing [98]. As nano-adsorbent surfaces are inherently heterogeneous, a lower statistical fit for the Freundlich model does not necessarily imply its inapplicability. It further highlights the limitation of relying solely on correlation coefficients without considering the underlying surface characteristics [92]. Alternative models such as Sips, Toth, Temkin, and MLSE offer greater flexibility by accounting for both heterogeneity and interaction effects. Despite their relevance, very few studies have utilized these models to study MP adsorption behavior [39,91].

4.3 Thermodynamic analysis

Thermodynamic parameters provide insight into the energy changes, spontaneity, feasibility and nature of adsorption processes. The three pillars of thermodynamic characterization, the Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), are typically derived from temperature-dependent equilibrium data [110]. The spontaneity of MP/NP adsorption onto nano-adsorbents is indicated by negative ΔG° values and is consistently reported across diverse studies. However, the magnitude of ΔG° varies depending on adsorbent type, plastic properties, and environmental conditions [111-113]. In one study, iron-impregnated biochar exhibited more negative ΔG° values for polystyrene adsorption than unmodified biochar, indicating greater spontaneity and stronger adsorption affinity. This improvement was attributed to increased positive surface charge and enhanced surface functionality resulting from iron incorporation [114]. Endothermic adsorption ($\Delta H^\circ > 0$) suggests that energy input facilitates adsorption, potentially due to desolvation or structural rearrangements. Several studies have reported positive enthalpy values for the adsorption onto carbon-based materials [91,94]. In contrast, exothermic behavior ($\Delta H^\circ < 0$) indicates that adsorption is energetically favorable and may be dominated by weaker physical interactions [114].

Entropy changes (ΔS°) further elucidate adsorption mechanisms. Adsorption is typically associated with decreased entropy ($\Delta S^\circ < 0$) due to reduced randomness at the solid-liquid interface, resulting from restricted mobility of adsorbed species, confinement within pores, or a lack of significant structural changes [94,113,114]. However, this trend can differ in aqueous systems. MP surfaces are often hydrated, with structured water molecules present at the interface. During adsorption, these water molecules are displaced by the adsorbate, leading to

an overall increase in disorder. This entropy gain ($\Delta S^\circ > 0$) is therefore attributed to the release of bound water molecules rather than increased mobility of the adsorbed species. The magnitude of ΔS° can vary with temperature and surface chemistry. Hydrophobic polymers tend to show stronger temperature dependence due to weaker water binding, whereas MPs with charged functional groups retain strongly bound water molecules, resulting in a smaller change in entropy [111,115]. Despite their importance, thermodynamic analyses are often limited in scope and rely on a narrow temperature range. Additionally, the parameters are rarely integrated with kinetic and isotherm analyses to provide a unified mechanistic interpretation.

4.4 Limitations of adsorption models

Despite their widespread application, adsorption models require careful interpretation in MP/NP removal systems. Kinetic, isotherm, and thermodynamic models are inherently based on simplified assumptions that may not fully represent the complexity of nano-adsorbent–plastic interactions. For instance, the PSO model is frequently interpreted as evidence of chemisorption, while Langmuir fitting is often taken to imply monolayer adsorption on homogeneous surfaces [94]. In practice, nano-adsorbents exhibit significant structural and chemical heterogeneity, and multiple interaction mechanisms operate simultaneously, making such direct associations potentially oversimplified. Moreover, different models may adequately describe the same experimental data, leading to ambiguity in mechanistic interpretation. High correlation coefficients alone do not necessarily validate a specific adsorption mechanism [98], as similar fitting behavior can arise from distinct underlying processes leading to model overlap. This highlights the need to interpret model parameters in conjunction with material properties, surface chemistry, and environmental conditions, rather than relying solely on statistical fitting.

A further challenge lies in the comparability of reported adsorption parameters across studies. Variations in experimental conditions, including plastic type, particle size distribution, concentration range, and water matrix composition, significantly influence kinetic constants, adsorption capacities, and thermodynamic values [19]. As a result, direct comparison of model parameters without normalization may lead to misleading conclusions regarding adsorbent performance. Finally, most adsorption models are derived from batch systems under controlled laboratory conditions and may not directly translate to dynamic, real-world environments where transport limitations, heterogeneous particles, and fluctuating conditions play a dominant role [19,116]. Bridging this gap requires integrating adsorption modeling with realistic system design considerations and environmentally relevant testing conditions.

5. Comparative analysis of nano-adsorbents and structure-property relationships

Table 1 describes distinct nano-adsorbent systems targeting a diverse array of polymer types within MPs. To enable meaningful comparison across studies, the data were standardized by converting key parameters (e.g., adsorbent dosage, MP concentration, contact time, and adsorption capacity) into consistent units (e.g., g/L, min, mg/g) wherever possible. This normalization facilitates cross-study comparison; however, some variability persists due to differences in experimental design and reporting practices in the original literature. Beyond performance comparison, this dataset also allows identification of structure–property relationships linking material architecture, surface chemistry, and adsorption behavior.

5.1 Performance: removal efficiency vs adsorption capacity

Two primary performance indicators dominate the literature: removal efficiency (%) and adsorption capacity (q_m, mg/g). These metrics, while related, reflect fundamentally different operational realities. Removal efficiency indicates the fraction of MPs eliminated from solution under specific conditions, whereas q_m represents the mass of MPs adsorbed per unit mass of adsorbent. The compiled data reveal a wide range of performance among nano-adsorbents: removal efficiencies range from 66.63 to 100%, while q_m span from 5.898 to 1650 mg/g. Moreover, q_m and RE do not exhibit a direct correlation. For instance, the activated carbon@MIL-100(Fe) composite achieves 99.97% removal of polystyrene with a capacity of 349.9 mg/g, while the 3D rGO aerogel exhibits a higher capacity (617 mg/g) but substantially lower removal efficiency (66.63%) [30,40]. The magnetic CNTs reported by Tang et al. (2021) represent an exceptional case, achieving both complete removal and ultra-high capacity (1100–1650 mg/g), attributed to their large surface area, hydrophobic character, and multi-polymer targeting capability [33].

It is important to note that q_m and removal efficiency are not antagonistic parameters; their divergence in specific studies reflects differences in experimental design, including initial MP concentration, adsorbent dosage, and contact time. Since removal efficiency is concentration-dependent, at higher initial MP concentrations, the same adsorbent may exhibit greater capacity while achieving lower fractional removal. From a structural perspective, high q_m values are typically associated with materials possessing high surface area, π-electron-rich domains, dense functional groups, or abundant active sites, such as graphene-based systems, metal oxide nanoparticles, and CNTs [33,92,119]. However, these morphological features do not guarantee

efficient active site utilization under all operational conditions. Mass-transfer limitations, particle aggregation, or pore inaccessibility may reduce the effective fraction of sites contributing to adsorption within experimental contact times. Conversely, high removal efficiency is readily achieved in systems with favorable (typically low) adsorbent-to-pollutant ratios and readily accessible surface sites, even when the intrinsic capacity to adsorb is low [98,117].

The relative importance of these metrics depends entirely on the application. In continuous-flow water treatment, where contact time is limited by hydraulic residence time, kinetic performance and the capacity achievable within that window may outweigh absolute equilibrium capacity. In batch remediation of concentrated microplastic-laden effluents, absolute capacity becomes paramount to minimize adsorbent mass requirements and subsequent waste generation. The magnetic sponge carbon reported by Li et al. (2023) offers a pragmatic compromise, achieving 98.63% removal with 369.07 mg/g capacity within only 10 min [118], suggesting surface-dominated adsorption mechanisms without significant pore-diffusion limitations.

5.2 The MP:Adsorbent ratio as a critical economic and operational variable

While q_m characterizes the intrinsic potential of an adsorbent material, the concentration ratio of MP to adsorbent (MP:Ads) is an underreported yet critical operational parameter that determines whether this potential is economically and practically accessible. A high q_m material deployed at unfavorable MP:Ads ratio may achieve high removal efficiency but with high material costs, excessive waste generation, and inefficient utilization of binding sites. Conversely, a moderate-q_m material operated at optimal MP:Ads ratio may deliver economically superior process despite lower intrinsic capacity. The MP:Ads ratio thus serves as a critical bridge between laboratory material characterization and engineering system design, enabling assessment of material efficiency, process robustness, secondary waste burden, and lifecycle cost that q_m alone cannot provide. The compiled data exhibit extraordinary variation in MP:Ads ratio, ranging from 0.006 to 300 (Table 1).

At one extreme, 1.5 g/L biochar was applied against an initial MP concentration of 0.01g/L, yielding MP:Ads ratio of 1:150 (= 0.006) [27]. This substantial excess of adsorbent ensures that binding sites remain in vast surplus relative to microplastic particles, driving removal efficiency toward completion through mass-action effects. However, this approach generates

150 grams of spent adsorbent per gram of microplastic removed, creating significant secondary waste-management challenges and material costs that may limit large-scale application. Similarly, CINPs@MXene/PU/PDMS sponge, NH_2-MIL-101(Fe)/CS/GO, chitin-cellulose foams and zeolites are high-adsorbent dosage systems which achieve excellent removal efficiency but at substantial operational cost [123,125,127,131]. However, excessive adsorbent dosage can induce particle aggregation, reducing specific surface area and effective active sites, thereby diminishing capacity per unit mass [132].

Several nano-adsorbents, including magnetic sponge carbon, magnetic activated carbon, Fe_3O_4@PDA and Fe_3O_4@AC, has been utilized at moderate MP:Ads ratio indicating efficient adsorbent utilization with high removal efficiency [118,124,126,129]. Magnetic CNTs (MP:Ads = 1) represent a unique case with stoichiometric equivalence, complete removal efficiency, and exceptionally high capacity of ~1650 mg/g [33]. This suggests near-complete utilization of available binding sites without excess adsorbent. This is economically ideal; however, it requires precise matching of adsorbent capacity to MP loading, which may be impractical in variable real-world influents.

The Fe_3O_4 nanoparticles (MP:Ads = 300) reported by Hu et al. (2025) represent the other extreme among the compiled data [92]. Rather than adsorbing MPs into internal pores or onto high-surface-area scaffolds, these nanoparticles attach to MP surfaces via electrostatic interactions, forming a magnetically responsive coating that enables subsequent magnetic separation. The extreme MP:Ads ratio reflects this surface-coating mechanism, where nanoparticle dose is minimal relative to the MPs' mass. The reported adsorption capacity of 784–1460 mg/g, therefore, does not represent conventional pore saturation but rather the mass of MPs that can be rendered magnetically separable per unit mass of coating nanoparticles [92]. The modest removal efficiency reflects collision-limited coating efficiency at extreme concentrations, rather than adsorbent-site exhaustion.

5.3 Other parameters for adsorption

(a) **pH dependence and surface charge:** pH is one of the crucial operational variables in MP adsorption, affecting both the surface charge of the adsorbent and the electrostatic character of the MP-solvent interface. The dataset reveals adsorption across a broad pH spectrum, from strongly acidic to mildly alkaline environments. The MXene-derived γ-Fe_2O_3/Pt/TiO_2 microbots achieve 99% polystyrene removal at pH 3, suggesting

protonation of surface functional groups enhances electrostatic attraction to negatively charged MP surfaces [64]. Notably, several systems, including magnetic sponge carbon, Fe_3O_4@AC, biochar, rGO, and aerogels, demonstrate effective performance in near-neutral conditions (pH 6-8) without requiring stringent pH adjustments and are able to target multiple polymers with high adsorption capacity [27,30,118,124,130]. This suggests that surface functional groups are effective under environmentally relevant pH conditions, although their charge state and interaction strength may vary. Besides this, non-electrostatic mechanisms, likely hydrophobic interactions and π-π stacking between the graphitic carbon surface and aromatic polystyrene rings, may also dominate the adsorption process. MIL-101(Cr) nano-adsorbent exhibited operation across an exceptionally broad window of pH ranging from 5 to 10, attributable to the chemical stability of the chromium-based MOFs and its Lewis acidic sites that remain active across diverse proton activities [39]. This pH resilience contrasts with many bio-derived adsorbents whose surface functionality, and consequently adsorption performance, varies substantially with proton concentration.

(b) **Contact time and kinetic regimes:** With respect to adsorption kinetics, two distinct regimes are observable: rapid (<60 min) and slow (>240 min). The rapid systems, such as magnetic sponge carbon, magnetic sepiolite, and MXene-derived microbots, typically involve external surface adsorption or magnetic field-assisted mass transfer, facilitating adsorption within 10 min [64,118,128]. In contrast, the activated carbon@MIL-100(Fe) composite and chitin-cellulose foams require 20-24 h, suggesting intra-particle diffusion limitations within the porous MOF structure [40,131]. While such extended times may be acceptable in static batch remediation scenarios, they are not preferred in continuous-flow treatment systems where hydraulic residence times are typically limited to minutes. Furthermore, large contact times may promote aggregation or structural rearrangement of either adsorbent or microplastic particles, potentially altering apparent capacity through physical entrapment rather than true adsorption [132].

(c) **MP/NP size and polymer specificity:** The target sizes range from few nano to thousands of micron. A general trend suggests that nano-adsorbents are most effective for MPs within specific size windows. Nano-adsorbents with porous architectures exhibit good efficiency for MPs having a size less than their pore diameter, which facilitates easy diffusion. However, larger MPs are often demonstrated to physically adsorb onto the surface of nano-adsorbents due to diffusion limitations [39,118,127]. Polymer specificity varies considerably. Early-generation carbon-based adsorbents like biochar and activated carbon

is applied to target single polymer, predominantly polystyrene, whereas advanced systems demonstrate multi-polymer capability [27,117,120-122]. The CINPs@MXene/PU/PDMS sponge targets six polymer types, while magnetic CNTs address polyethylene, polyethylene terephthalate, and polyaminde simultaneously [127]. This multi-polymer capability is essential for real-world applications where wastewater contains heterogeneous MP assemblages.

5.4 Trade-offs affecting material selection

The comparative analysis reveals several inherent trade-offs linked to material structure:

(a) **Kinetics vs capacity:** A fundamental trade-off emerges between adsorption capacity and kinetic performance. High-capacity systems, such as magnetic CNTs, MIL-101(Cr), and 3D rGO aerogel, typically require extended contact times, ranging from 300–1200 min. Conversely, rapid systems exhibit comparatively moderate capacities [27,33,92,124]. This inverse relationship reflects the distinction between surface-area-dominated capacity (requiring pore diffusion) and surface-reaction-dominated kinetics (limited to external sites).

(b) **Efficiency vs dosage:** High removal efficiencies are often achieved at elevated adsorbent dosages. Moreover, multi-polymer systems (magnetic CNTs, CINPs@MXene sponge, chitin-cellulose foams) sacrifice some single-polymer efficiency for broader applicability. The CINPs@MXene/PU/PDMS sponge, targeting six polymer types, exemplifies this versatility but requires substantially higher adsorbent dosage [127].

(c) **Performance vs scalability:** Advanced materials such as MOFs and graphene derivatives provide high performance due to engineered surface chemistry and porosity, thereby enhacing synergistic interactions between components, but may face challenges related to cost, large-scale synthesis, regeneration, and reuse [119,121,122].

(d) **Magnetic recovery vs stability:** Magnetic functionality (Fe_3O_4, γ-Fe_2O_3, or metallic components) enables facile separation via external magnetic fields, a critical practical advantage. However, magnetic components may undergo oxidative degradation or iron leaching under acidic conditions. Xia et al. (2025) reported measurable Fe^{2+} and Fe^{3+} leaching (5.85 mg/g total) from magnetic biochar composites, increasing to 10.83 mg/g after four regeneration cycles [132]. While leaching rates of 1–3% per cycle may be acceptable for some applications, they raise concerns regarding secondary contamination and adsorbent longevity.

These trade-offs indicate that no single structural design is universally optimal, and material selection must consider both performance and operational feasibility. Based on the observed structure–property relationships and practical applications, several design principles can be proposed: (i) balance between accessibility and capacity to minimize diffusion limitations, (ii) surface functionalization to enhance adsorption through electrostatic interactions and hydrogen bonding, particularly for weathered or functionalized MPs, (iii) hierarchical porosity to improve mass transfer and adsorption across different MP sizes, (iv) composite architectures with integrated multiple functionalities, (v) operational compatibility for efficient and cost-effective performance under realistic conditions, including neutral pH, optimized adsorbent dosage and environmentally relevant concentrations, and (vi) scalability, regeneration and lifecycle considerations. These principles emphasize that effective adsorbent design requires integration of structural features with functional performance, rather than optimization of a single parameter.

5.5 Limitations in cross-study comparison

Despite normalization of key parameters, direct comparison of nano-adsorbent performance remains challenging due to inconsistencies in data reporting and experimental conditions. Not all studies report a complete set of adsorption parameters; while removal efficiency is commonly provided, adsorption capacity, kinetic modeling, and especially thermodynamic analysis are often missing or selectively reported [122,125], limiting comprehensive evaluation across materials. In addition, adsorption performance is highly sensitive to operational factors such as adsorbent dosage, contact time, initial MP concentration, and pH, which vary widely across studies [39,40]. This condition heterogeneity means that reported performance metrics are not directly comparable without explicit normalization, which itself introduces assumptions and potential distortions. Many systems, which report high removal efficiencies, operate under optimized or non-comparable conditions, making it difficult to distinguish intrinsic material performance from experimental influences. Furthermore, complexity arises from differences in material characteristics, including structure, morphology, porosity, and surface functionalization. Variations in composite design and modification strategies introduce additional heterogeneity, complicating direct comparison of structure–property relationships across material classes. Finally, disparities in testing conditions, particularly MP size (nano- vs micro-scale), polymer type, and water matrix (e.g., ultrapure water vs real wastewater), add another dimension of variability [33,92,124]. These factors collectively highlight the need for

more standardized methodologies and consistent reporting to enable meaningful cross-study comparison.

While the present analysis focuses on comparative evaluation within nano-adsorbent systems, it is important to contextualize these findings relative to conventional adsorbents. Traditional materials such as activated carbon, charcoal, clays, untreated agricultural wastes, sand filtration, and coagulation-based processes establish the operational baseline for MP removal, particularly in large-scale water treatment systems. However, these systems are primarily effective for larger MPs and often exhibit slower kinetics and lower removal efficiencies under comparable conditions [133-136]. Moreover, conventional adsorbents face significant regeneration challenges and are prone to a loss of adsorptive capacity over cycles due to chemical, energy-intensive processes [11]. In contrast, the structure–property relationships among nano-adsorbents highlight their ability to achieve enhanced performance through engineered surface chemistry, high specific surface areas, hierarchical porosity, multifunctional interactions, and efficient recovery [30,33,39,92,137]. Such performance advantages are frequently demonstrated under controlled batch conditions and may vary when translated to practical systems. Besides this, advanced nano-adsorbents, including zeolites, MOFs, magnetic CNTs, and graphene oxide derivatives, require complex, multi-step synthetic procedures and are expensive [11,138]. Therefore, nano-adsorbents should be viewed not as direct replacements but as complementary materials, particularly for targeting smaller MPs/NPs that remain challenging for conventional technologies.

6. Towards practical implementation of nano-adsorbents

6.1 Continuous-flow systems

The translation of nano-adsorbent technologies from batch laboratory studies to continuous-flow systems represents a critical transition toward practical remediation of MPs/NPs. While batch experiments frequently report high adsorption capacities under controlled conditions, such systems do not adequately capture the dynamic water conditions, mass transfer, and operational constraints that govern performance in continuous-flow environments. In these systems, adsorbents must maintain removal efficiency under limited hydraulic residence times, continuous loading, and progressive saturation, making process-level evaluation essential for assessing real-world applicability.

(a) **Reactor configurations:** Reactor configuration strongly influences the performance of nano-adsorbents in continuous systems. These are typically implemented as fixed-bed reactors (FBRs) or fluidized-bed systems (FBSs), each offering distinct advantages and limitations [139]. FBRs are widely used due to their operational simplicity and compatibility with existing treatment infrastructure (e.g., GAC and biochar filters). These systems can achieve high removal efficiencies under controlled flow conditions and are relatively easy to design and operate. In MP removal, these systems often behave more like deep-bed filters than purely adsorptive columns. However, particle accumulation leads to cake formation, clogging, and an increased pressure drop, necessitating periodic backwashing to maintain operational stability. Adsorbent exhaustion necessitates replacement or regeneration [22,140,141].

FBSs, in contrast, promote enhanced mixing, reduced clogging, and improved external mass transfer through particle suspension. A fluidized-bed study using slag-derived adsorbents reported adsorption capacities up to ~1400 mg/g and removal efficiencies up to 99%, with slightly improved utilization compared to fixed beds. The improved performance is attributed to reduced external mass-transfer resistance and more uniform contact between MPs and adsorbent surfaces [142]. However, nano-adsorbents exhibit distinct challenges in such systems. Their low density and fine size increase the risk of entrainment, attrition, and material loss, requiring stabilization through composite structures or supports. Magnetic nano-adsorbents partially address this issue by enabling recovery via external fields, but repeated cycling may affect aggregation and performance [33]. Thus, the choice between these configurations depends on balancing removal efficiency, energy consumption, operational stability, and ease of scale-up. For MP/NP removal, where particle size and aggregation behavior influence transport dynamics, reactor selection must also account for potential fouling and particle retention.

(b) **Design constraints:** Designing continuous-flow systems for nano-adsorbent-based MP removal requires balancing adsorption performance with hydraulic and mechanical constraints. Classical parameters such as bed height, flow rate, and empty bed contact time (EBCT) remain central, but their interpretation differs for particulate systems [143-145]. Experimental studies consistently show that increasing bed height improves removal efficiency by extending residence time and increasing sorbent inventory. In GAC columns treating polyethylene MPs (0.2–1.0 g/L), removal efficiency reached ~95% at lower

concentrations and longer bed lengths, but decreased at higher loading due to faster saturation [22]. Similarly, biochar columns showed improved performance at lower flow rates (e.g., 3 mL/min) and increased bed height (e.g., 6 cm), confirming the importance of contact time [141].

However, nano-adsorbents introduce additional constraints. Their small particle size can lead to high pressure drop, poor packing stability, and risk of particle washout, making direct use in packed beds impractical. To address this, nano-adsorbents are often immobilized into granules, composites, or porous monoliths (e.g., biochar, aerogels, supported nanomaterials). While this improves hydraulic performance, it may reduce accessible surface area and alter adsorption behavior relative to dispersed systems [130,141,146,147]. Besides this, many nano-adsorbent systems require relatively long EBCTs to achieve high removal, whereas real wastewater treatment processes operate under significantly shorter hydraulic constraints. In a study, Shen et al. (2021) showed a significantly higher removal efficiency of polyethylene and polyamide MPs by zeolites modified with a cationic surfactant compared to an unmodified adsorbent, even at a higher flow rate of 7 ml/min [147]. This highlights the importance of optimizing materials not only for adsorption capacity but also for rapid kinetics, transport efficiency, and structural compatibility under realistic flow conditions.

(c) **Breakthrough behavior:** Continuous-flow systems are governed by breakthrough behavior, where adsorption is constrained by residence time, transport limitations, and progressive site saturation. Breakthrough curves (C_t/C_0 vs time) provide a more realistic measure of adsorbent performance than equilibrium capacity alone, revealing the transition from effective adsorption to column exhaustion. Initially, C_t/C_0 remains low as adsorption sites are readily available. As adsorption progresses, a mass transfer zone (MTZ) develops, depicting the region of active adsorption, and propagates through the column until breakthrough occurs. Breakthrough is the point at which MPs first appear in the effluent at a detectable concentration, typically ranging from 5 to 10% of C_0 (Figure 3). Unlike equilibrium-based batch studies, breakthrough analysis reflects the dynamic interplay between adsorption kinetics, transport phenomena, and reactor design [139].

In nano-adsorbent systems, breakthrough dynamics deviate from classical dissolved-contaminant behavior due to the particulate nature of MPs. Unlike molecular adsorbates, MPs are removed through a coupled mechanism of adsorption and filtration/straining,

where particles are trapped between adsorbent grains, attached via hydrophobic or electrostatic interactions, or retained through physical entanglement [147]. For example, a banana-peel biochar fixed-bed column achieved ~92% removal of 150–300 μm polystyrene MPs under optimized conditions, with removal governed by both surface interactions and physical trapping within the bed structure [141].

The hybrid adsorption mechanism "*stick, trap, and entangle*" is very crucial, as high surface area alone does not guarantee delayed breakthrough. Nano-adsorbents typically provide abundant external active sites, enabling rapid initial removal, but may also saturate quickly if adsorption is surface-limited. Furthermore, the aggregation of nano-adsorbents or MPs under flow conditions can reduce the effective surface area and alter mass-transfer pathways [146]. Consequently, the trade-off between capacity and kinetics, as identified in batch systems, becomes quite significant in continuous operation, where insufficient transport leads to early breakthrough despite high intrinsic capacity.

(d) **Industrial feasibility:** Despite promising laboratory results, several challenges limit the large-scale implementation of nano-adsorbent-based continuous-flow systems. It depends not only on removal efficiency but also on cost, scalability, operational stability, and regulatory acceptance [139]. Most available data are derived from single-component systems using synthetic MPs or surrogate contaminants [140,148]. In real-world applications, adsorption occurs in complex matrices that can alter surface interactions, block adsorption sites, and accelerate breakthrough. For example, competitive adsorption and surface charge modification in such environments may significantly reduce effective adsorption capacity compared to laboratory conditions. However, very few studies have been conducted under realistic conditions [149]. Fouling and clogging are particularly significant for MP systems due to the particulate nature of the pollutant [146]. Accumulation within the bed can lead to pore blockage and a reduction in effective adsorption sites. While backwashing can restore performance in systems such as GAC or biochar columns, repeated cycles may degrade adsorbent structure or lead to loss of fine particles [22,146]. Another critical issue is material stability and environmental safety. Free nano-adsorbents (e.g., metal oxides, CNTs) may pose risks of release into treated water, necessitating immobilization or incorporation into stable matrices [147]. This transformation from nano-scale materials to macro-scale structures introduces trade-offs between adsorption performance and process feasibility. Overall, successful scale-up of

continuous systems requires integration of adsorption, filtration, hydrodynamics, and regeneration strategies, supported by pilot-scale validation under realistic conditions. Current literature on MP removal remains limited in such integrated assessments, indicating that the translation of nano-adsorbents from laboratory systems to practical water treatment technologies is still at an early stage.

6.2 Real Water Matrices

The evaluation of nano-adsorbents in real-water matrices represents an important step towards their practical applicability for MP/NP removal. While most investigations at bench scale consistently demonstrate superior performance, necessary for large-scale water treatment, these conditions do not capture the complexity of environmental systems. In real wastewater scenarios, complex matrix effects, such as fluctuating physicochemical conditions, natural organic matter (NOM), high ionic strength, microbial communities, and competing contaminants, significantly influence adsorption behavior and surface thermodynamics [25,108,131]. Moreover, MPs often acquire a coating of biomolecules, humic acids, or proteins known as 'eco-corona', which alter their zeta potential towards more negative values, thereby influencing the electrostatic interactions. These layers can also block pores in adsorbents [98,150]. These factors alter the adsorption behavior, often leading to inconsistent results. Recently, studies have begun to address this gap by testing nano-adsorbents in diverse real matrices, providing critical insight into robustness and limitations.

(a) **Drinking and grey-water systems:** These represent controlled aqueous environments with moderate complexity, often containing domestic wastes, dissolved ions, NOM, surfactants, oils, and microorganisms. Nano-adsorbents' performance in these matrices reflects a balance between intrinsic adsorption mechanisms and matrix-induced interactions. Drinking water systems impose strict constraints. Here, MP concentrations are very low, and removal must be carried out without altering water quality or introducing secondary contaminants. Integrating NH_2-MIL-101(Fe) nano-adsorbents into ultrafiltration membranes has demonstrated 90% removal efficiency, with reductions from 70 particles L^{-1} to 8 particles L^{-1} in polyethylene terephthalate-bottled water, along with >83% removal after 8 cycles [151]. Minor variation in water chemistry also affects adsorption performance. Ionic species such as Cl^- and SO_4^{2-} reduce adsorption efficiency through charge screening, while Ca^{2+} and Na^+ can enhance removal via bridging interactions between negatively charged MPs and adsorbent surfaces [123,151]. This

sensitivity underscores that, in drinking water systems, performance is prominently governed by surface stability and selectivity. Furthermore, filtration and retention dominate over adsorption capacity, and nano-adsorbents are most effective when immobilized within process-compatible structures.

Greywater, such as kitchen wastewater, introduces additional complexity due to the presence of oils, fats, surfactants, elevated COD, high organic load, and a wide range of interfering ions, including ammonia and phosphate [33]. In such systems, nano-structured CINPs@MXene sponges maintain excellent removal efficiencies (>90%) by leveraging hydrophobic interactions and structural entrapment [127]. However, these sponges rely on non-specific interactions, including co-removal with oil phases or organic aggregates. Yakout et al. (2026) also reported high removal of polyethylene terephthalate MPs using a hybrid NH_2-MIL-101(Fe)/CS/GO nano-adsorbent under elevated ionic strength and organic load, reflecting that adsorption is not the sole governing mechanism. Divalent cations (e.g., Ca^{2+}, Mg^{2+}) and organic matter promote MP aggregation, thereby increasing particle size and facilitating removal through interception and filtration-like processes [123]. Magnetic CNTs, which combine the high adsorption efficiency of CNTs with the easy recovery of iron oxides, achieved 100% removal of suspended MPs, particularly polyethylene, polyethylene terephthalate, and polyamides, from the kitchen effluent and maintained 80% efficiency for four consecutive cycles, indicating a potential for a cost-effective strategy [33].

(b) **Natural water:** Water from rivers, lakes, and coastal environments presents a fundamentally different challenge due to its dynamic and heterogeneous nature. Unlike engineered/simulated systems, these matrices exhibit fluctuations in salinity, turbidity, organic matter content, and biological activity, all of which influence nano-adsorbent behavior. Experimental studies have demonstrated that nano-adsorbents, such as MOFs and nanoporous GAC, can maintain high MP removal efficiencies (>70%) across diverse natural waters, including freshwater and seawater [98,123].

In saline environments, increased ionic strength compresses the electrical double layer, weakening electrostatic interactions but promoting aggregation of MPs. Similarly, the presence of suspended sediments and NOM influences adsorption behavior. Although NOM usually interferes with MP adsorption by competing for active sites on nano-adsorbents [25,108], studies have demonstrated the synergistic effects of divalent cations

like Mg^{+2} and NOM through complex formation, which facilitates MP transport by preserving colloidal stability [81,98,123,152]. Adsorption sites may be blocked by organic coatings or fouled by particulate matter, reducing the effective surface availability. Conversely, these same components can facilitate co-flocculation and bridging, thereby capturing aggregated MPs [131,150]. The net effect is governed by system-level interactions rather than material-specific properties. Furthermore, removal efficiencies reported under one set of environmental conditions may not translate directly to another, even within the same water body.

(c) **Agricultural runoffs and industrial effluents:** Agricultural runoff and irrigation waters are characterized by high particulate load, nutrient enrichment, and the presence of agrochemicals and heavy metals, creating conditions that differ significantly from both domestic and natural surface waters. Removal efficiencies in agricultural waters can reach 98–99% for MPs/NPs, often exceeding those observed in controlled laboratory systems. This enhancement is primarily attributed to the formation of complex aggregates involving MPs, metal ions, and microbial biofilms. For example, heavy metal ions such as Pb^{2+} can bridge between negatively charged MPs and chitin-cellulose nano-adsorbent surfaces, while microbial communities contribute to biofilm formation on MPs, leading to increased particle size and retention [131]. While this enhances overall removal efficiency, it also complicates mechanistic interpretation. Salinity variations further influence performance, either via ionic interference at low concentrations or via enhanced aggregation and capture efficiency at higher salinity [131]. This dependence on aggregation-driven mechanisms implies that performance may vary significantly with seasonal and environmental conditions, limiting predictability.

Industrial waste streams represent the most complex and demanding environments for nano-adsorbent applications due to high MP concentrations, the presence of oils and surfactants, and elevated chemical and particulate loads. In these systems, removal is governed not only by adsorption but also by process-level factors such as fouling, phase separation, and hydrodynamics [153]. Nano-structured adsorbents and sponges have demonstrated the ability to maintain high removal efficiencies (>90%) in such environments, including oil-rich wastewaters [127]. However, these systems rely heavily on hydrophobic partitioning and structural entrapment, with adsorption playing a secondary role. Rapid accumulation of MPs and associated contaminants leads to fouling,

pore blockage, and reduced mass transfer, limiting long-term performance [126]. In this context, engineered nano-adsorbents provide selectivity. Through specific linkers, such as the imine-decorated magnetic nanoparticles developed by Rushdi et al. (2025), materials can be targeted to specific polymers while simultaneously scavenging dissolved organic pollutants [154]. However, wastewater treatment plants rarely rely on single-particle adsorption as it is not economically viable. Continuous-flow pilot systems have been developed to remove MPs via induced heteroaggregation, achieving removal efficiencies exceeding 97%. Here, functionalized nanomaterials composed of amine-grafted silica or organosilanes bind to dispersed MPs and NPs, neutralize the repulsive forces, and induce the formation of large floating flocs that can be easily separated via filtration, skimming, or magnetic sedimentation [155]. Magnetic nano-adsorbents offer additional advantages in such environments by enabling simultaneous removal of MPs and associated pollutants, followed by magnetic recovery [33,127]. However, issues related to aggregation, stability, and regeneration become more pronounced under high loading conditions, raising concerns about scalability and operational reliability. Furthermore, as matrix complexity increases, removal efficiency becomes more dependent on system-level interactions and process design than on intrinsic adsorption properties.

Overall, across these real-water systems, a consistent pattern emerges: the performance of nano-adsorbent is governed not by a single mechanism but by a matrix-dependent combination of adsorption, aggregation, filtration, and co-removal processes [123]. The relative importance of these mechanisms shifts systematically with increasing complexity of the water matrix. While the synergistic mechanism enhances MP removal, it also introduces variability and reduces the direct correlation between laboratory-derived adsorption capacity and real-world performance. Nevertheless, nano-adsorbents are most effective as a part of integrated treatment systems, where their exceptional properties complement the physical and chemical removal processes inherent to real-water environments.

7. Challenges

Despite the remarkable performance of nano-adsorbents in laboratory settings, several hurdles must be overcome to utilize these for large-scale microplastic remediation. These challenges span economic, technical, and environmental domains; hence, a critical assessment is required for the sustainable and responsible adoption of this technology.

7.1 High cost and scalability

The most important barriers to the real-world applications of many advanced nano-adsorbents are their high production costs and the difficulty of scaling up their synthesis from the laboratory to an industrial level [18]. As mentioned earlier, the production of high-purity materials like MOFs, CNTs, and graphene often requires expensive precursors, specialized equipment, and complex, energy-intensive, multi-step processes. Furthermore, the purification and functionalization of these materials can be complex and require advanced separation techniques. These factors render the approach economically infeasible compared with conventional adsorbents, such as activated carbon, for treating large volumes of water [11,138]. Other sustainable, lower-cost materials, such as biochar, offer a viable alternative. However, optimizing their performance and production with consistent quality at an industrial scale is a challenge [156]. Issues related to heat and mass transfer, precise control over reaction parameters, and the maintenance of product yield and quality become much more critical at larger scales. Continuous-flow synthesis, in which reactants are continuously pumped through a reactor, is being explored to address these scalability challenges, as it provides better control over reaction conditions and easier scale-up.

7.2 Post-treatment recovery

Another hurdle in using free nanoparticles and other nano-adsorbents is their removal after water treatment. Once nano-adsorbents bind to MPs, the agglomerate must be efficiently recovered from the treated water to prevent the generation of secondary pollutants [157]. Conventional methods like filtration have limited applicability when treating large quantities of water. Moreover, they are not efficient to trap particles belonging to nanoscale. In this context, magnetic nanoparticles and their derived nano-adsorbents, such as magnetic biochar, magnetic CNTs, and magnetic MOFs, possess the additional advantage of easy recovery by applying an external magnetic field [158]. However, the infrastructure required for the large-scale magnetic separation does not yet exist and would require significant capital investment [159]. Furthermore, the recovered adsorbent must be regenerated for reuse to make it an economically viable and environmentally sustainable strategy. Low-cost and efficient regeneration processes that do not affect adsorption capacity are another challenge [7].

7.3 Potential ecotoxicity

The most critical concern is the long-term environmental and toxicological impact of nano-adsorbents, primarily due to their release into the water. If not properly contained or recovered, these nanomaterials could become a new class of pollutants, potentially harming aquatic organisms and ecosystems [160]. Reports suggest that nanomaterials have a tendency to cross biological membranes, accumulate in organisms, disrupt cellular processes, cause oxidative stress, elicit immune responses, and exert other toxic effects. The potential for bioaccumulation in the food web is another serious risk [160,161]. Furthermore, the use of metal-based nano-adsorbents raises concerns about the potential leaching of toxic metal ions into the water, which could have long-term consequences for environmental and human health [51]. These must be thoroughly investigated through life-cycle assessments (LCA) and ecotoxicology studies. An LCA is a systematic analysis of the environmental impacts of a product or process throughout its entire life cycle, from the extraction of raw materials to its final disposal. Designing a nano-adsorbent that is merely effective at capturing MPs is no longer sufficient. The entire lifecycle of the material, i.e., its synthesis using sustainable methods, operational use to ensure stability and no leaching, and its end via safe recovery, regeneration, or benign degradation, must be critically considered to achieve holistic environment remediation [162].

7.4 Real-world applicability

Lastly, there is a significant gap between the high adsorption capacities reported in controlled laboratory environments and the potential performance of these nano-adsorbents in real-world systems [3]. Most studies are conducted using clean, distilled, or synthetic water spiked with individual or mixtures of uniform-shaped MPs [25,163]. In contrast, the composition of real wastewater, textile effluent, river water, etc., is very complex and difficult to simulate in controlled environments. Besides this, environmental MPs are non-uniform, weathered or oxidized, and often coated with biofilms, which alter their interactions with nano-adsorbents [150]. Studies evaluating performance in real water matrices have only recently begun and require thorough analysis to accurately predict adsorption behavior with respect to water chemistry, organic/inorganic content, microbial communities, and seasonal variations.

8. Conclusions and future prospects

Nano-adsorbent technology has evolved rapidly due to environmental needs and continuous advances in materials science. A wide range of materials is transformed into nano-adsorbents, which have provided solid proof of concept for the remediation of MPs and NPs from aquatic

systems. The path forward must address the key challenges of cost, safety, operational feasibility, scalability, and recovery while improving material performance and functionality. Green and sustainable synthetic methods should be developed that use natural and renewable precursors, environmentally benign solvents, and reduce energy requirements. Designing hybrid systems that combine adsorption with catalytic degradation (photocatalysis or the Fenton reaction) within a single platform could offer a more effective approach to MP destruction than physical removal alone. Another thrust area of research is the development of smart materials that respond to external stimuli, such as changes in pH, temperature, or light. These materials can be used to capture and release MPs by modulating the external environment. Additionally, the integration of artificial intelligence and computational modeling can provide fundamental insights into interactions at the nano-interface, guiding the rational design of adsorbents with optimized surface chemistry and pore structures. These in-silico tools will enable researchers to screen a large number of potential materials and identify the most promising candidates for synthesis and testing, significantly shortening the development cycle for new, high-performance adsorbents. The success of any new technology is dictated by its real-world performance. Hence, the most critical aspect of future research is translating small-scale studies into realistic conditions to develop a tangible solution to the global MP crisis.

Declaration of use of AI-assisted tools

During the preparation of this manuscript, the author used ChatGPT (v5.2) to assist with reference formatting and readability. Subsequently, the author reviewed and edited the content as needed and takes full responsibility for the content.

CRediT

RS was involved in conceptualization, investigation, analysis, manuscript drafting, reviewing and final editing.

Competing interests

Author declare no competing interest.

Funding declaration

This work did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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Table 1. Nano-adsorbents for the removal of MPs

Nano-adsorbent	Polymer type	Size (µm)	Key conditions				Removal (%)	Adsorption capacity (mg/g)	MP:Ads ratio	Adsorption behavior	Ref.
			MPs /NPs (g/L)	Adsorbent (g/L)	pH	Contact time (min)					
Activated carbon@MIL-100 (Fe) composite	PS	0.5	0.1	0.43	7	1200	99.97	349.9	0.23	PSO Freundlich	[40]
Chitosan activated carbon	PS	-	0.05	1.5	6	120	99	129.87	0.03	PSO + IPD Langmuir Spontaneous + exothermic	[117]
3D rGO aerogel	PS	5	0.6	0.75	6	120	66.63	617	0.8	PSO Langmuir Spontaneous + endothermic	[30]
Magnetic CNTs	PE, PET, PA	48	5	5	7	300	100	1100 – 1650	1	PFO (PE); PSO (PET, PA) Freundlich	[33]
Magnetic sponge carbon	PS	1	0.2	0.5	-	10	98.63	369.07	0.4	PSO Langmuir + Freundlich	[118]
Chitin-graphene oxide sponge	PS	1	0.001	-	6	720	92.9	5.898	-	PSO + IPD Langmuir Spontaneous + exothermic	[119]
Granular activated carbon (GAC)	PS	0.09	0.02	5	8.4	240	90	6.33	0.004	PSO + IPD	[98]
Biochar	PS	< 0.5	0.01	1.5	7.5	5	>90	44.9	0.006	PFO + IPD Langmuir Spontaneous + exothermic	[27]
ZIF-67	PS	1–3	0.005	0.4	8	20	92.1	11.6	0.0125	PFO Freundlich	[48]
MIL-101(Cr)	PS	< 1	0.005 – 0.07	-	5-10	-	96	800	-	PFO Freundlich	[39]

UiO-66-OH MOF	PVDF, PMMA, PS	0.18 – 0.33	1	-	-	-	> 85	-	-	-	[120]
Zn-TPA-MOF-5	PVC, PMMA	0.075 – 0.095	0.25	2.5	-	40	95-97	33 – 57	0.1	PSO Langmuir	[121]
ZIF-8@Aerogel	PVDF, PS	0.06 –0.14	0.5	-	-	-	85-92	-	-	-	[122]
NH_2-MIL-101(Fe)/CS/GO	PET, PS	25 – 30	0.015	10	6.2	40	89-94	255 – 322	0.0015	PSO Langmuir + Freundlich	[123]
Fe_3O_4@AC	HDPE, LDPE, PP	1 - 3000	1	1	6	30	80	23.72	1	PSO Sips	[124]
Fe_3O_4 (300 nm)	PET, PS, PP, HDPE, LDPE, PVC	100 – 1000	30	0.1	-	1200	≥70	784 – 1460	300	PSO Langmuir + Freundlich	[92]
Zeolites: H-USY, H-β, X, clinoptilolite	PS	0.2	0.100 & 0.200	2.5 to 50		20	77-92	80 – 190	0.002 – 0.04	-	[125]
MXene-derived γ-Fe_2O_3/Pt/TiO_2 microbots	PS	0.050	6 x10^{12} MPs/L	0.75	3	5	99	-	-	-	[64]
Fe_3O_4@PDA	PS	1	0.01	0.02	7	20	98.5	-	0.5	-	[126]
CINPs@MXene/ PU/PDMS sponge	PS, PP, PE, PET, PMMA	5 – 1000	1	50	-	480	-	400	0.02	PFO + IPD Freundlich	[127]
Magnetic sepiolite	PE	48	10	40	-	10	98	-	0.25	-	[128]
Oat-protein based sponges	PS	1	0.001	0.2	6	720	81.2	6.579	0.005	PSO Langmuir	[75]

Magnetic pineapple waste activated carbon	PE, PS, PET	355	5	20	-	30	86.53 - 89.05	-	0.25	-	[129]
Bi-CS-CNF-PDA Aerogels	PS, PP, PE, PMMA	0.2 – 1	1.5	3	7	240	-	300 - 450	0.5	PFO Freundlich	[130]
Chitin-cellulose foams	PS, PP, PET, PMMA	3	1	50	-	1440	> 90	300 - 585	0.02	PSO Freundlich Spontaneous + exothermic	[131]

Abbreviations: intra-particle diffusion (IPD), microplastic (MP), polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polyvinyl chloride (PVC), polyamide (PA), polystyrene (PS), polyvinylidene fluoride (PVDF), pseudo-first-order (PFO), pseudo-second-order (PSO)

Figure Captions

Figure 1. Types of nano-adsorbents for MP removal and their key attributes.

Figure 2. Mechanistic pathways governing MP adsorption onto nano-adsorbents. The figure illustrates the synergistic contribution of physical adsorption, pore-filling, hydrophobic interactions, π–π stacking, electrostatic interactions, and hydrogen bonding.

Figure 3. Schematic illustration of a continuous-flow adsorption system for MP removal and its corresponding breakthrough curve. The figure depicts the operation of a fixed-bed column packed with nano-adsorbents, where influent containing MPs (at concentration C_0) passes through the bed and adsorption occurs along the column length. The associated breakthrough curve (C/C_0 vs. time) highlights key operational parameters, including breakthrough point (t_b), complete saturation point (t_s), and mass transfer zone (MTZ).

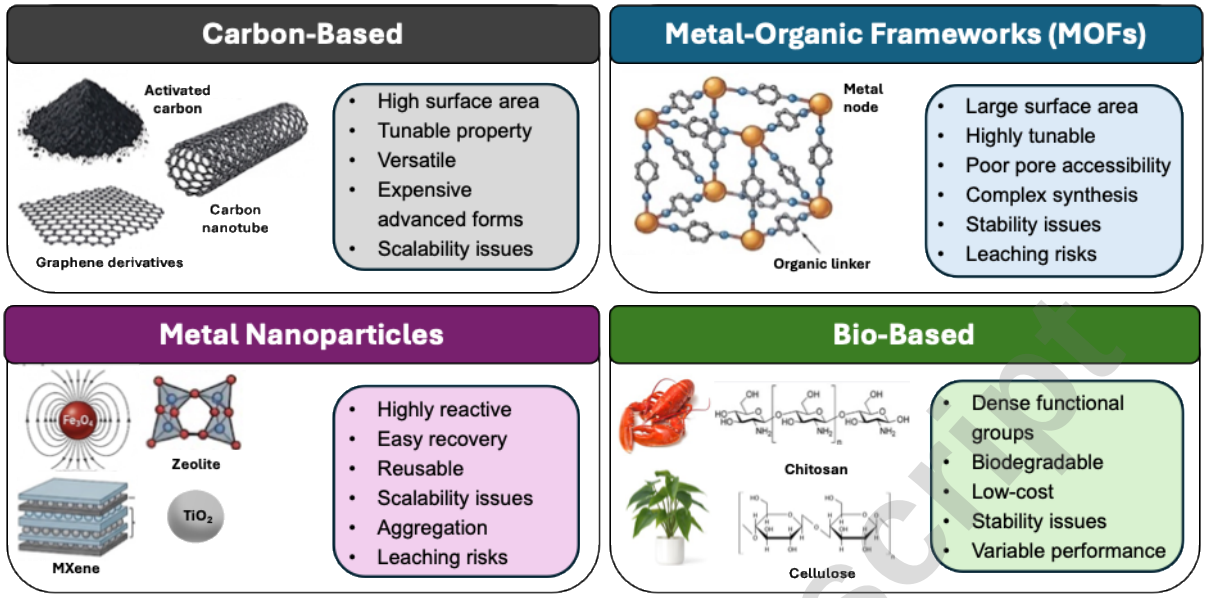

Figure 1

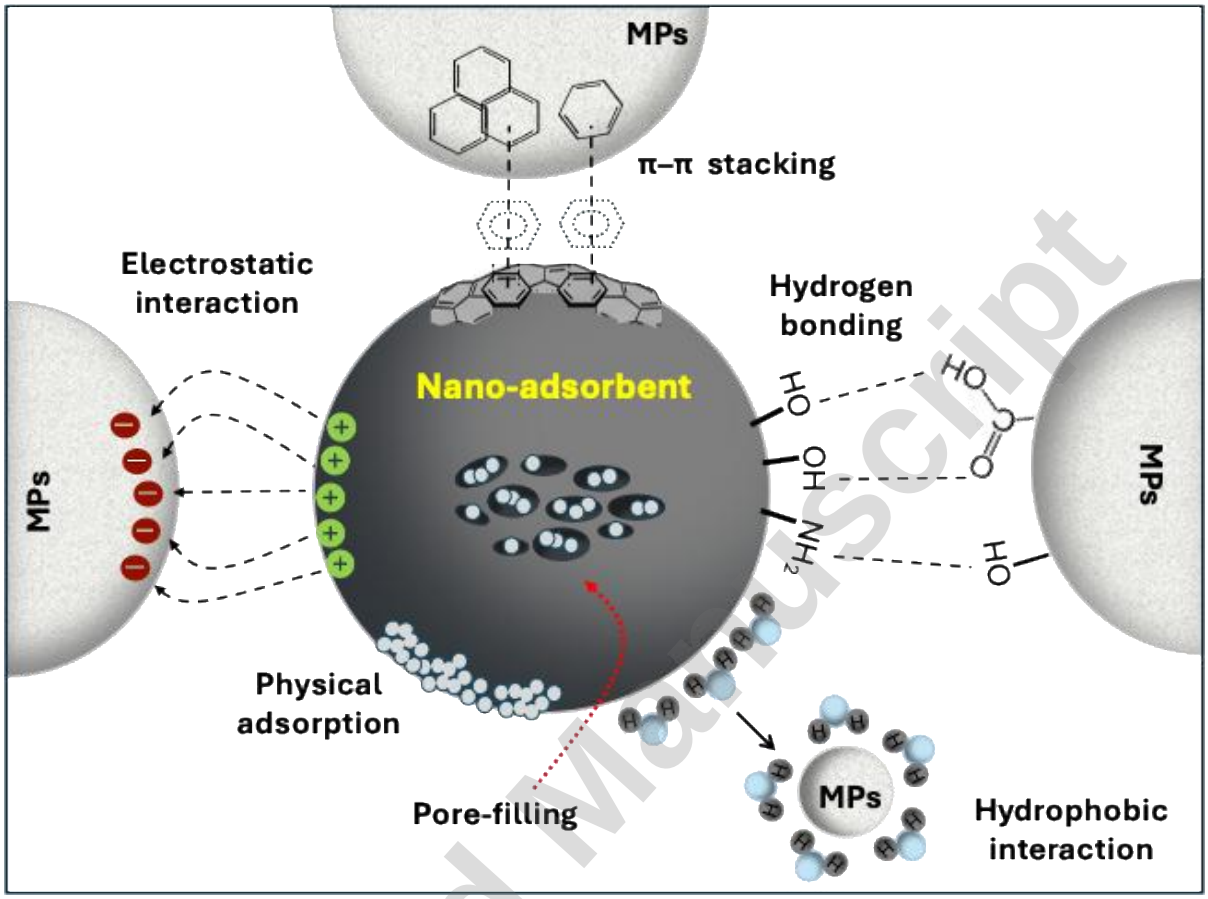

Figure 2

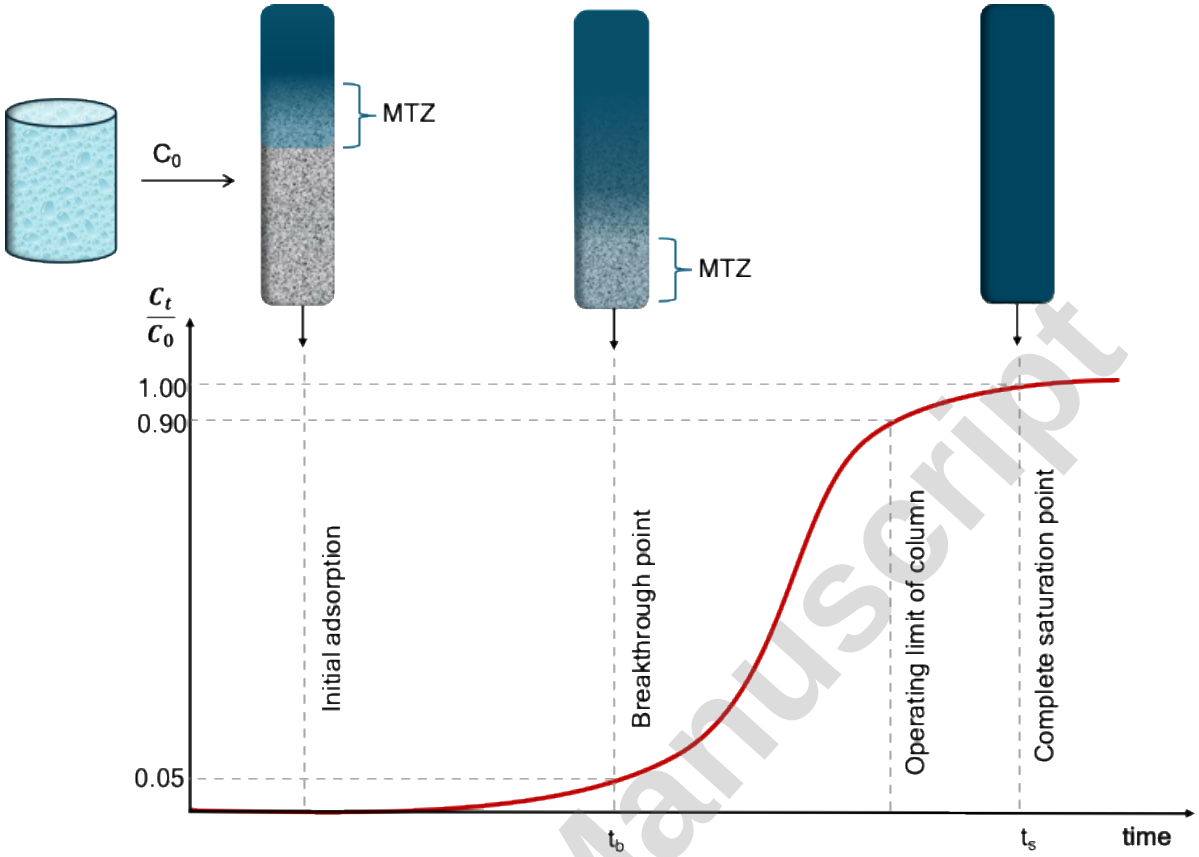

Figure 3