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Metal-modified biochar: a sustainable approach for microplastics removal from drainage water

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Abstract

Environmental pollution from heavy metals, dyes, and emerging contaminants such as microplastics has prompted the exploration of low-cost, sustainable adsorbents. Biochar, derived from biomass pyrolysis, has emerged as a promising candidate due to its porous structure, surface functionality, and potential for chemical modification. This paper aims to review the current strategies employed in the synthesis and modification of biochar-based composites and assess their efficiency in environmental remediation applications. A comprehensive literature review was conducted, emphasizing recent developments in biochar modification techniques including metal impregnation, clay integration, hydrothermal processing, and mechanochemical treatments. Modified biochars showed substantial improvement in adsorption performance compared to their pristine forms. For heavy metals, Fe-impregnated biochar achieved Pb(II) removal efficiencies exceeding 95% with adsorption capacities up to 123.4 mg/g. MgO-doped biochar exhibited a methylene blue dye removal capacity of 216.7 mg/g. In microplastic remediation, Fe–Mn-modified biochar demonstrated an adsorption capacity of 34.29 mg/g and removal efficiency of 88% for polystyrene microplastics under optimized conditions (pH 7, 25°C). Ball-milled biochar composites achieved up to 3-fold increases in surface area and enhanced metal–carbon interactions, leading to higher adsorption via hydrophobic, electrostatic, and π–π interactions. Metal oxide-loaded biochars consistently outperformed pristine biochars, particularly in systems with electrostatic or ion-exchange dominant sorption mechanisms. Biochar-based composites present a versatile and effective platform for environmental remediation. Their performance depends strongly on synthesis parameters and functional modifications. Integration of metals, oxides, and structural tailoring can significantly enhance sorption capabilities, making them viable alternatives to conventional adsorbents.

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Introduction

The increasing industrialization, urbanization, and growing intensity of agriculture are manifesting themselves in worse and worse quality of water environments. This environmental disaster is compounded by the appearance of new, often unmonitored, contaminants (Amiri et al., 2015). The major sources of these pollutants are hospitals, industrial effluents, domestic wastes, and agricultural run-off entering the water bodies and many mixed contaminants (Figure 1). Emerging pollutants include endocrine-disrupting compounds (EDCs), MPs, pesticides, industrial flame retardants, nanomaterials, and pharmaceuticals and personal care products (PPCPs). All these contaminants have serious implications for the quality of drinking water and health of the ecosystem and thus call for advanced treatment solutions (Dong et al., 2023).

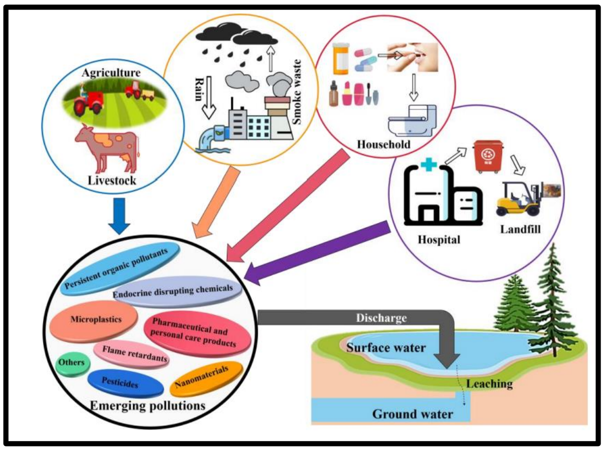

Fig 1. The sources and pathways of emerging pollutants into aquatic systems (Dong et al., 2023)

Plastic pollution has indeed reached critical proportions, and the world production exceeded 400 million metric tons (Alaghemandi, 2024). However, plastic poses serious environmental issues due to the materials' many applications such as flexibility, lightweight properties, durability, and cheap cost. Very low recycling rates current levels are horrendous at approximately 14% of all plastic wastes, and these dispose of plastic wastes through incineration, deposition in landfill sites, and environmental pollution. Poor disposal mechanisms increase the growth of MPs, defined as plastic particles below 5 mm in size, classified into two classes, one being intentional primary MPs built for use in consumer products and the other consisting of secondary MPs made from the fragmentation of larger plastic items under environmental weathering. They have been documented in virtually every environment, including marine and freshwater, terrestrial, atmospheric, and groundwater systems (Prata et al., 2019). In Figure 2, various mechanisms by which MPs proliferate in nature and invade the food chain are summarized. MPs can enter our food supply from many pathways, but the specific illustration emphasizes the aquatic one-the route by which MPs are entering the food chain via fish consumption, which is our major concern with respect to aquatic MPs (Mahmud et al., 2022).

Fig 2. Lifecycle of MPs generation to food chain (Mahmud et al., 2022)

In Iran, critical water bodies like the Caspian Sea and Persian Gulf face severe MP pollution due to industrial discharge and inadequate waste management (Razeghi et al., 2021). Compounding this issue, drought conditions exacerbate MP concentrations in water systems, straining conventional remediation methods (Bahrami et al., 2024). Despite advances in filtration and coagulation technologies, these approaches often lack cost-effectiveness, scalability, or sustainability, particularly in resource-limited regions (Klotz et al., 2023; Titone et al., 2024). Biochar, a carbon-rich material produced from biomass pyrolysis, has emerged as a promising adsorbent due to its tunable porosity, surface functionality, and eco-friendly production (Amiri et al., 2020; Qu et al., 2021; Seow et al., 2022). Recent studies highlight its efficacy in removing heavy metals and organic pollutants, yet its application for MP remediation remains underexplored. While pristine biochar exhibits moderate adsorption, metal modifications (e.g., Fe, MgO) enhance its capacity via electrostatic interactions, hydrophobic binding, and π–π electron donor-acceptor mechanisms (Ji et al., 2024; Wang et al., 2021a). For instance, Fe-modified biochar achieved 88% MP removal (Li et al., 2023), while ball-milled composites tripled surface area (Ganie et al., 2021). However, critical gaps persist: (1) limited understanding of competitive adsorption in complex wastewater matrices, (2) insufficient field-scale validation under drought conditions, and (3) unresolved ecotoxicological risks of metal leaching from modified biochars (Shrivastava et al., 2024). This study addresses these gaps by systematically reviewing metal-modified biochar synthesis, performance, and mechanisms for MP removal, with a focus on scalability and environmental safety. The primary goal of this paper is to critically review and synthesize current advancements in biochar-based composites for environmental remediation, focusing on their synthesis techniques, physicochemical modifications, and application efficacy in removing various pollutants including heavy metals, dyes, and microplastics. Special emphasis is placed on the role of metal doping, porosity engineering, and surface functionalization in enhancing the performance of biochar materials. This work also aims to identify key knowledge gaps and propose future research directions to optimize biochar composite design for practical and scalable applications.

Materials and Methods

The systematic investigation of biochar-based composites for microplastic removal employed a rigorously structured analytical framework. This comprehensive review focused on evaluating metal-modified biochar applications in environmental remediation, with particular emphasis on adsorption mechanisms, performance metrics, and scalability potential. The research methodology was executed through five distinct sequential phases: (1) Literature search and selection, (2) Data extraction and analysis, (3) Mechanistic evaluation, (4) Case studies and experimental validation, and (5) Knowledge gap identification. The investigation utilized prominent scientific databases, including Scopus, Web of Science, PubMed, and Google Scholar, focusing on peer-reviewed publications from 2015 to 2024 to ensure contemporary relevance. The literature assessment specifically examined various biochar modification techniques, including metal oxide incorporation, ball milling processes, and acid/base treatments. This systematic approach facilitated a thorough examination of modification strategies, their effectiveness in microplastic removal, and potential scalability for practical applications. The investigation particularly emphasized the relationship between modification techniques and enhanced adsorption performance, providing insights into optimization strategies for environmental remediation applications. The structured methodology enabled the identification of emerging trends, technical challenges, and opportunities for future research directions in biochar-based microplastic removal

Microplastic-Related Threat in Iran

Pollution from MPs in Iran is a problem increasingly acknowledged due to associated risks on ecosystems, wildlife, and human health. The origin of MPs is multiple, including degradation of larger plastic items, microbeads incorporated in personal products, and synthetic fibers shed from textiles. Such particles have an aquatic and terrestrial environment spread across regions and leave behind long-term risks. Iran has identified MP contamination in numerous environmental matrices such as rivers and lakes, coastal water, and urban air. Currently, the Caspian Sea and Persian Gulf, which are two very crucial aquatic ecosystems in Iran, are under stress from MP pollution, aggravated by increased industrial activities, urbanization, and poor waste management systems. Scientists have further shown that the sources of MPs in these areas are fishing activities, shipping, and land-based activities like mismanaged plastic waste. To address the situation of MPs in Iran, there is a need for a multi-pronged approach. Most of the challenges include lack of awareness among the public, not having contemporary legal frameworks in place, and the absence of advanced infrastructures for wastewater management. Iran could do the following: (1) strengthen waste management systems in such a way that leakage plastic into the environment is prohibited; (2) consider having campaigns on public awareness for responsible usage and disposal of plastics; (3) provide stricter legislation on single-use plastics and microbeads in consumer products; and (4) proper investments in research and monitoring related to better understanding sources, distribution, and impacts of MPs on Iran (Razeghi et al., 2021).

The critical need for MPs removal in drought-prone regions

Drought conditions affect MP removal in a way that poses enormous challenge to the otherwise smooth functioning of water treatment processes. It becomes extremely important to comprehend the mechanisms operational under drought and to develop adaptive management strategies. During periods of water scarcity, the usually reduced volume of drainage water creates a stimulus for increased concentration of pollutants, which include MPs; thus, the treatment of these pollutants would be affected seriously concerning efficiency and cost. Limited availability of water interferes with the natural diluting and transporting mechanisms that work favorably towards MP dispersal, leading to localized accumulation, hence exacerbating ecosystem impacts. The challenges that arise as a result of drought go beyond these treatment complications to include allocation of other resources and infrastructure management. Water management priorities during droughts often favor drinking water provision over wastewater treatment, putting at risk a return on investment for MP removal technology. The situation is then made worse by decreasing flow dynamics within aquatic systems, limiting the natural dispersal and attenuation of MPs and creating pollution hotspots with increased environmental hazards. There is, therefore, a need for an integrated approach incorporating all of these challenges. The wastewater treatment infrastructure is to be upgraded to ensure efficient MP removal under varying flow conditions, thus encouraging advanced filtration technologies and flexible operating protocols. The impending need now is to practice water-conserving options so that demand management can be exercised with a view toward maintaining treatment effectiveness. Nature-based solutions act as a good second line of defense to go along with technological approaches. Constructed wetlands/biofiltration systems provide that extra bit of filtration capacity while gliding along with natural attenuation. These systems are resilient during drought conditions and provide many other ecosystem service benefits besides MP removal. There are some very important regulatory and public outreach initiatives that will strengthen the role of MP management during times of drought. For example, the combination of strong regulatory deterrents to plastic use and disposal with widely recognized public campaigns to counter plastic pollution on a massive scale will help eliminate a large percentage of MP inputs to drainage systems. This preventive measure complements those aimed at treatment and supports sustainability objectives in the longer term. By integrating the diversity of these options, a formidable platform is therefore created for MP management under drought conditions. By synergistically combining technological, nature-based, and policy measures, communities will strengthen their capacity to tackle the scourge of MP pollution under the additional burden of water scarcity. Such an integrated approach acts as a buffer in favor of ecosystem health and human welfare against the mounting precariousness of the already tense MP removal processes by drought. MP management in drought periods must therefore encompass monitoring, research, and changes in treatment technology. Drought-proof technologies combined with good resource management practices will be fundamental in MP removal under sustainable water resource use.

Results and Discussion

Overview of Biochar and Its Modifications

Definition and Properties of Biochar

Biochar is best defined as a highly carbonaceous material, fine in particle size, and with an extremely porous structure. Biochar is produced through the thermal decomposition of various types of biomass, carried out in an oxygen-limited environment and at temperatures lower than 900°C. This remarkable material has emerged as a hot topic in scientific circles due to its environmental significance and various agricultural benefits. The structural and chemical properties of biochar are such that they are highly effective for purposes of environmental remediation. A very porous structure, combined with a variety of functional groups on the surface, including carboxyl, hydroxyl, and phenolic groups, promotes strong interactions with several environmental contaminants. These characteristics further translate into excellent adsorption properties for a wide variety of pollutants: heavy metals, organic compounds, and microplastic particles. The production of biochar offers a choice of feedstock, allowing a variety of different biomass sources to be used efficiently. These would comprise woody materials, e.g., bark; agricultural residues, e.g., rice husks and sugar beet waste; animal residues, e.g., dairy manure. The biochar properties can be tailored to specific environmental applications by controlling pyrolysis conditions (temperature levels, rates of heat transfer, and residence time). Beyond pollutants' remediation, biochar has very important agricultural and environmental advantages: carbon sequestration potential, crop productivity increases, greenhouse gas emissions reductions from soils, amelioration of soil quality parameters, reduced nutrient leaching, and optimum irrigation and fertilizer use efficiency. The combination of environmental remediation capacity with agricultural benefits hence makes biochar a sustainable option that can address several environmental problems simultaneously (Qu et al., 2021; Seow et al., 2022; Liu et al., 2022; Li et al., 2017). For instance, the morphological analysis conducted through SEM revealed distinctive structural characteristics of activated carbon derived from canola stalk biomass. The micrographic examination demonstrated a highly developed porous architecture characterized by surface irregularities and heterogeneous topography. The surface features of the canola stalk-derived activated carbon exhibited prominent macroporous structures and substantial cavity formations throughout the material matrix (Figure 3). This architectural development can be attributed to the thermal decomposition dynamics occurring during the pyrolysis process. The high-temperature treatment effectively degraded the primary biopolymer components of the canola stalk, specifically the long-chain polymeric structures of cellulose, hemicellulose, and lignin. The thermal degradation mechanism resulted in the systematic breakdown of these complex organic polymers, leading to the formation of well-defined void spaces and interconnected channel networks. This structural evolution during the pyrolysis process created an extensive network of pores and cavities, enhancing the material's potential for adsorption applications. The observed morphological features suggest efficient conversion of the agricultural biomass into a functional carbonaceous material with desirable surface characteristics for environmental applications. The development of these structural features indicates successful activation and carbonization of the canola stalk precursor, resulting in a material with enhanced surface area and accessibility to internal adsorption sites. These characteristics are fundamental for the material's effectiveness in various environmental remediation applications.

Figure 4 presents the SEM micrograph of bone char, confirming that the adsorbent particles exhibit an irregular shape with sharp edges and a rough surface. This morphology demonstrates the effective removal of the organic phase from the bone structure through burning.

Parameters Influencing Porosity and Sorption Capacity

The porosity and sorption capacity of biochars are governed by multiple interdependent factors, including feedstock properties, pyrolysis conditions, and post-treatment modifications. These factors collectively determine the biochar's structural and chemical characteristics, influencing its effectiveness in adsorption applications.

Feedstock Type

The composition of the raw biomass (e.g., lignin, cellulose, and hemicellulose content) significantly affects biochar porosity. Lignin-rich feedstocks (e.g., wood) typically yield biochars with higher surface area and microporosity compared to cellulose- or hemicellulose-dominated materials (e.g., grasses) due to their robust carbon structure (Bahrami et al., 2023).

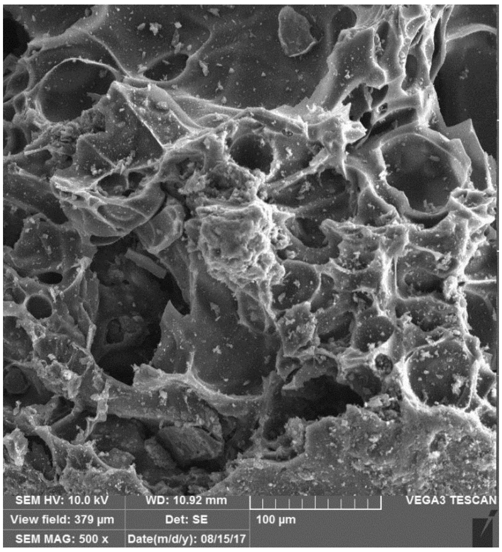

Fig 3. SEM images of canola stalk-derived activated carbon (Amiri et al., 2020)

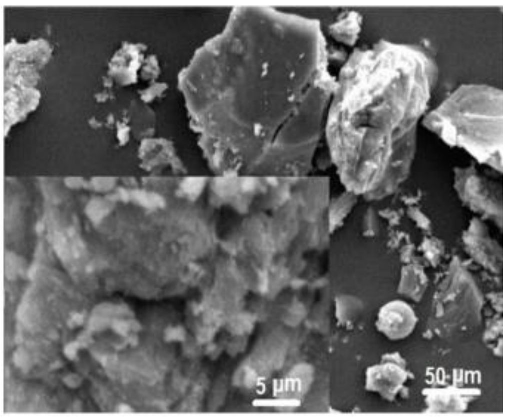

Fig 4. SEM images of bone char (Amiri et al., 2023)

Pyrolysis Temperature

Higher pyrolysis temperatures (typically 500–700°C) promote microporosity and surface area by enhancing carbonization and volatile matter removal. However, excessive temperatures (>800°C) may cause pore collapse or graphitization, reducing adsorption efficiency (Beigzadeh et al., 2020; Amiri et al., 2019).

Activation Methods

Chemical activation (e.g., KOH, H_3PO_4) introduces micropores and mesopores while enhancing oxygen-containing functional groups, whereas physical activation (e.g., steam, CO_2) selectively oxidizes carbon to enlarge pore structures (Patra et al., 2021). Chemical activation introduces a rich distribution of micropores and mesopores and increases oxygen-containing functional groups on the carbon surface, which can enhance adsorption properties and surface reactivity. Physical activation generally involves treating pre-carbonized materials with oxidizing gases such as steam or carbon dioxide at high temperatures. The activation proceeds via selective gasification reactions where carbon atoms are oxidized and removed, enlarging existing pore structures and developing new pores. This process tends to produce a larger fraction of mesopores and macropores by expanding the pore size of the original micropores (Nazbakhsh et al., 2025)

Post-Modification

Functionalization of adsorbent materials with nanoparticles (such as Fe_3O_4) or polymers is a widely used strategy to improve their selectivity and performance in removing specific contaminants, including heavy metals, from water and wastewater. Nanoparticle functionalization, for example with Fe_3O_4, introduces active sites that can selectively bind contaminants like heavy metals due to specific interactions between the metal ions and the nanoparticle surface. This can significantly boost the efficiency and specificity of adsorption processes. Polymer functionalization can tailor the surface chemistry and introduce functional groups that have a strong affinity for target pollutants. The nature of the polymer and its functional groups can be designed to interact selectively with certain contaminants, further enhancing the adsorbent's selectivity (Akhtar et al., 2024).

Particle Size and Structure

Smaller particles provide higher surface area-to-volume ratios, which significantly enhance adsorption kinetics by increasing the available surface for interaction with adsorbates. This higher surface area allows more binding sites to be exposed, facilitating faster and more efficient adsorption processes. For example, reducing particle size increases the surface-to-volume ratio dramatically, thereby improving the initial adsorption rate as molecules have more surface to interact with per unit volume. However, there is a critical balance to maintain. Excessive grinding or reduction of particle size can lead to the destruction or collapse of the pore network within the material. Pores are essential for adsorption because they provide internal surface area and pathways for adsorbate molecules to diffuse into the adsorbent. When the pore structure is damaged, the total accessible surface area may decrease despite smaller particle size, and diffusion pathways can be blocked or hindered, reducing the overall adsorption capacity and efficiency. Moreover, the thermodynamics and kinetics of adsorption are influenced by particle size. Studies show that as particle size decreases, adsorption equilibrium constants and rate constants increase, indicating more favorable adsorption energetics and faster kinetics. Conversely, parameters such as adsorption activation energy and adsorption enthalpy tend to decrease with smaller particle sizes, reflecting changes in surface interactions at the nanoscale (Osman et al., 2022)

Environmental Conditions

pH affects surface charge and ion-exchange capacity by influencing the protonation and deprotonation of functional groups. Meanwhile, ionic strength impacts electrostatic interactions, especially for charged adsorbates such as phosphate and heavy metals (Kumkum & Kumar, 2024).

Metal Modification of Biochar

The actual reform needed in improving biochar's physicochemical properties is through treatment methods for optimizing its performance in MP remediation. Basically, the changes are directed towards the fundamental characteristics of the material such as the specific surface area, pore architecture, and surface chemistry, thus improving adsorption capacity.

General Modification Techniques

Currently, the majority of methods for enhancement of the biochar adsorption power for MPs include modifications such as acid-base treatment, incorporation of metal oxides and metal salts, integration with clay minerals, and mechanical processing through grass milling (Cheng et al., 2021). In this regard, acid-base treatments are used to modify surface charge and increase the number of reactive sites. The incorporation of metal oxides and salts enhances interactions with charged microplastics (MPs). Integration with clay minerals improves the properties of the composite material. Additionally, mechanical processing methods, such as grass milling, increase surface area and expose more pores. Together, these techniques aim to enhance MP capture by improving interaction dynamics.

Role of Metals and Metal Oxides in Adsorption Enhancement

Loading biochar with specific metals or metal oxides introduces new active sites for complexation, electrostatic interaction, and ion exchange—mechanisms crucial for capturing MPs, especially those with charged or functionalized surfaces.

- Metal oxides: Fe_2O_3, MgO provide catalytic and adsorption properties.
- Metal salts: $FeCl_3$, $Al_2(SO_4)_3$ are used for their high reactivity and availability of cations.

Advanced Metal Incorporation Methods

More sophisticated modification techniques have been developed to improve the stability, distribution, and bonding of metals within the biochar matrix. These methods allow for fine-tuned control of the material's properties (Tong et al., 2020a; Ji et al., 2024):

a. Impregnation Method

Involves suspending biochar in a metal salt solution, allowing metal ions to penetrate and bind to the matrix. Subsequent heat treatment or chemical reduction finalizes the metal integration.

b. Co-precipitation

A process where metal precursors are mixed with the biomass before pyrolysis. During carbonization, metal species precipitate and integrate with the developing carbon matrix, producing well-distributed and stable particles. This approach ensures co-development of metal phases and biochar, enhancing durability and performance.

c. In-situ Hydrothermal Treatment

This one-step method combines biomass

and metal salts in an aqueous environment under elevated temperature and pressure. Biochar formation and metal/metal oxide incorporation occur simultaneously, resulting in intimate contact between metal species and carbon matrix. Yields materials with unique morphology and enhanced thermal/chemical stability.

d. Ball Milling

A mechanochemical technique where biochar is ground together with metal or oxide precursors under high-energy conditions. This causes mechanical bonding and embedding of metals within the carbon structure, resulting in strong metal-carbon interactions and distinct surface features. Highly effective for generating materials with superior adsorptive performance and mechanical integrity.

Toxicity Potential of Biochar-Based Composites

Despite the demonstrated efficacy of biochar-based composites in environmental remediation, significant concerns persist regarding their potential toxicity, which could undermine their long-term sustainability. These risks primarily stem from three sources:

Feedstock Contamination

Biochar derived from certain biomass sources (e.g., sewage sludge, industrial waste, or pesticide-treated agricultural residues) may retain harmful substances such as heavy metals (Pb, Cd, As), polycyclic aromatic hydrocarbons (PAHs), or dioxins. For instance, studies show that biochar produced from municipal waste can contain up to 120 mg/kg of lead, posing leaching risks in acidic environments (Liu et al., 2022; Majewska & Hanaka, 2025).

Synthesis-Induced Hazards

Chemical modifications during biochar production—such as metal doping (e.g., Fe, Mn) or nanomaterial integration (e.g., nano-MgO)—can introduce new toxicity pathways. While these enhancements improve adsorption capacity, they may also lead to:

(a) Metal Leaching: Under fluctuating pH or redox conditions, modified biochars can release toxic ions. Zhang et al. (2023) observed a 15–20% leaching rate of Fe from iron-modified biochar in saline water, exceeding EPA thresholds for aquatic life.

(b) Nanoparticle Release: Engineered nanocomposites (e.g., biochar-TiO_2) may generate reactive oxygen species (ROS), causing cellular damage in organisms (Wu et al., 2023).

Long-Term Ecological Impacts

Poorly stabilized composites can degrade over time, releasing contaminants into ecosystems. For example, in soil systems, residual metals may accumulate, disrupting microbial communities and reducing soil fertility (Shrivastava et al., 2024). In aquatic systems, leached toxins can bioaccumulate in fish, as demonstrated by Singh et al. (2021), who showed that nanoplastics coated with biochar-derived metals entered food chains.

To ensure the safe deployment of biochar-based composites, a comprehensive risk management approach must be implemented throughout the material's lifecycle. The process begins with rigorous pre-screening of feedstocks, where uncontaminated biomass sources such as crop residues should be prioritized and their metal content certified through analytical techniques like XRF or ICP-MS (Seow et al., 2022). This initial quality control step is crucial for preventing the introduction of contaminants that could later leach into the environment. Following feedstock selection, advanced stabilization techniques should be employed to minimize potential leaching risks. Metal-doped biochars can be coated with silica or bio-polymers, which have been shown to significantly reduce the release of toxic ions while maintaining adsorption capacity (Ji et al., 2024). These engineered barriers are particularly important for composites intended for use in variable environmental conditions where pH fluctuations or salinity changes might otherwise promote contaminant mobilization. Finally, complete lifecycle assessments are essential for quantifying long-term risks and guiding proper end-of-life management. Recent studies have demonstrated that improperly incinerated biochar composites can emit hazardous ultrafine particles (Shrivastava et al., 2024), underscoring the need for controlled disposal protocols. These lifecycle assessments should evaluate all stages from production to disposal, considering factors such as energy inputs, potential leaching scenarios, and optimal retirement pathways to minimize environmental impacts.

Microplastics and Their Removal Methods

Sources and Types of Microplastics

There are two main types of MPs based on their site of origin: primary MPs and secondary MPs. Primary Mps are intentionally manufactured to exist in small size as particles and are directly released to the environment. They are most commonly found in personal care products, industrial abrasives, and synthetic textiles. Secondary MPs are caused through physical, chemical, and biological processes from larger plastic items such as bottles, bags, and fishing nets. Over time these larger plastics undergo changes due to environmental stresses such as ultraviolet radiation, mechanical wear, and microbial degradation. How secondary microplastics are formed is not fully understood, making it all the more complicated to control factors such as size, shape, surface chemistry, and quantity (Enfrin et al., 2019). In present agricultural practices, plastics significantly enhance productivity and efficiency. These products include mulch films, greenhouse covers, irrigation tubes, drip lines, storage bags, silage films, and coatings for fertilizers, pesticides, and seeds. They are directly involved in increasing crop yield, conserving water, and controlling pests. Although beneficial in productivity, these plastics pose great challenges to the environment. Over time, some of these plastics degrade into MPs, which accumulate in both soil and water bodies, likely affecting soil health and disrupting aerobic communities as well as entering the food chain. MPs' economics in the agricultural systems necessitate the adoption of sustainable management practices intended to mitigate long-term effects associated with them (FAO, 2021). Figure 5 shows the morphological characteristics of MP particles as revealed by SEM analysis. The micrographs demonstrated a predominantly non-porous architecture interspersed with randomly distributed perforations across the particle surface. These microscopic observations highlighted the presence of irregularly shaped holes throughout the MP structure, exhibiting no discernible pattern or systematic arrangement. The heterogeneous distribution of these cavities presented a chaotic surface topology, with considerable variation in both the geometric configuration and dimensional aspects of the perforations. The stochastic nature of these structural features posed significant challenges in quantitatively characterizing the hole distribution patterns. The absence of uniformity in both the morphological

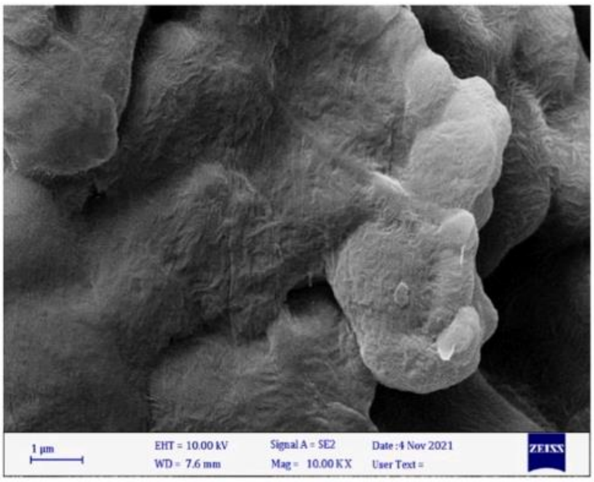

Fig 5. SEM images of MP (Bahrami et al., 2024)

characteristics and spatial arrangement of the cavities complicated the statistical analysis of their size distribution and shape parameters. This inherent structural complexity reflects the variable nature of MP degradation and formation processes in environmental systems.

Role of Biochar in Microplastic Removal

Recent studies have shown that biochar is effective in removing MPs from aquatic environments. For instance, Ganie et al. (2021) noted biochars produced from bagasse pyrolyzed at 350, 550, and 750 degrees Celsius as all being competent at adsorbing MPs. Biochars pyrolyzed at 750 degrees Celsius had the highest removal efficiency, which could be attributed to their enhanced porosity and surface area. Similarly, Wang et al. (2021a) noted that high-temperature biochars reached removal efficiencies above 95% for MPs, attributing this to the large abundance of honeycomb structures available in thin biochar chips created at 500 degrees. The application of magnetic biochar, one with modified iron oxides, also showed promising results, removing as much as 94.81% of polystyrene microspheres from aqueous solutions. The modification in magnetic property in iron-modified biochar enabled extraction of MPs from the solutions rapidly and effectively: hence, big chances for large-scale applications. Oxidized biochar showed a much higher adsorption capacity (>90%) compared to the unmodified biochar for polystyrene MPs. This improved capacity was due to the presence of hydroxyl functional groups representing the increased adsorption capacity. The performance of biochar in the capturing of MPs indeed varies according to its environmental conditions. Kumar et al. (2023) noted that dissolved organic matter, nutrient content, and pH levels would hinder MPs' adsorption by biochar. On the contrary, increase in temperature levels in aquatic systems have shown to facilitate the adsorptions of MPs by biochar. The above findings reaffirm the importance of modulating biochar modification methods and application strategies to specific environmental conditions and target pollutants. Biochar is a sustainable and economically cost-effective measure towards reducing the pollution load of MPs in the aquatic environment. The targeted modifications to optimize biochar in its physicochemical properties can translate to high adsorption efficiency for MPs, which in turn contributes toward safeguarding aquatic ecosystems and human health. Further inquiry into how biochar performs under different environmental conditions for an extensive period of time could add value to the scalability of development programs for real-life applications. Table 1 shows a summary of notable research assessing the efficacy of biochars in taking out MPs from the aquatic ecosystem.

Mechanism of MPs adsorption by biochar

The adsorption of MPs onto biochar involves multiple physicochemical interactions, influenced by the surface properties of both the biochar and the MPs. Since MPs are typically non-ionic, ion exchange is not a primary mechanism unless MPs coexist with charged contaminants (e.g., heavy metals or organic pollutants). The dominant adsorption mechanisms include (Figure 6) (Abdoul Magid et al., 2021;

Table 1. Representative research on biochar's ability to remove microplastics from aquatic environments

Raw materials	Pyrolysis temperature	Adsorbate	Results	References
Cellulose	400 °C	MP	Biochar reduced the transit and increased the deposition of plastic particles.	(Kumar et al., 2023)
Livestock manure	500 °C	PHA-MPs	Biochar enhanced the biodegradation of PHA MPs, increasing the degradation rate to between 22% and 31%.	(Tong et al., 2020b)
Prosopis juliflora	550 °C and 850 °C	MPs	Biochar produced at both temperatures demonstrated effective removal of microplastics, with an adsorption capacity exceeding 200 mg/g	(Wang et al., 2021a)
Pine and spruce bark	475 °C and 800 °C	Polyethylene (PE)	The steam-activated biochar proved to be an outstanding adsorbent for the removal of MPs.	(Sun et al., 2022)
Sawdust	550 °C	Polystyrene	The modified biochar demonstrated a high efficiency in removing MPs, achieving a removal rate of more than 94.8%.	(Siipola et al., 2020)
Cellulose	400 °C	Polystyrene	The addition of biochar impedes the transport of MPs particles	(Wang et al., 2021b)
Sugarcane bagasse	350 °C, 550 °C and 750 °C	Polystyrene	Biochar produced at 750 °C achieved a significantly higher MPs removal rate (exceeding 99%) compared to biochar prepared at lower temperatures	(Ganie et al., 2021)
Corn straw, hardwood	300 °C, 400 °C and 500 °C	MPs	Biochar derived from corn straw and hardwood at 500 °C exhibited greater capacity for removing and immobilizing MPs compared to biochar produced at lower temperatures	(Brennecke et al., 2016)

Peng et al., 2022; Ji et al., 2024):

Electrostatic Attraction

Biochar surfaces may carry charged functional groups ($-COO^-$, $-NH_3^+$, $-O^-$) that attract oppositely charged MPs. For example:

• Negatively charged biochar (e.g., oxidized biochar):

Biochar–COO^-+MP^+→Biochar–COO⋯MP^+ (1)

• Positively charged biochar (e.g., amine-modified biochar):

Biochar–NH_3^++MP^-→Biochar–NH_3⋯MP^- (2)

Surface Complexation

Chemical bonding occurs between biochar's functional groups (–OH, –COOH) and MPs, particularly when modified with metal oxides (e.g., Fe_3O_4, MgO):

Biochar–OH+MP–surface→Biochar–O–MP+H^+ (3)

Biochar–COOH+MP–OH→Biochar–COO–MP+H_2O (4)

Hydrogen Bonding

Polar functional groups on biochar (–OH, –COOH, $-NH_2$) form hydrogen bonds with polar MPs (e.g., polyamide, PET):

Biochar–OH⋯O=MP (5)

Biochar–COOH⋯H–MP (6)

Hydrophobic Interactions

Non-polar regions of biochar (e.g., graphitic domains) interact with hydrophobic MPs (e.g., polyethylene (PE), polypropylene (PP)):

Biochar–(C_nH_{2n+1})+MP–$(CH_2–CH_2)_n$→Van der Waals adsorption (7)

π-π Electron Donor-Acceptor (EDA) Interactions

Aromatic structures in biochar interact with π-electron-rich MPs (e.g., polystyrene (PS)):

Biochar–(C_6H_6)+MP–(C_6H_5)→π-π stacking (8)

Pore Filling

MPs are physically trapped within biochar's porous structure when pore sizes match MP dimensions:

MP (size *d*)+Biochar pore (size *d*)→Entrapment (9)

Intra-Particle Diffusion

MPs diffuse into biochar's internal pores and are retained:

MP (surface)→MP (internal pores) (10)

Chemical modification of biochar is, therefore, one way to increase adsorption efficiency because of more adsorption sites that are abundant and diverse. This, in turn, enhances the mechanisms which are important for the capture of MPs, including electrostatic attraction, hydrogen bonding, and surface complexation. For instance, chemical modification with introduction of functional groups, such as hydroxyl, carboxyl, or amine groups, to enhance the binding affinity of biochar for MPs. Meanwhile, physical modification mainly focuses on changing the microporous structure and surface area of biochar which, in turn, modifies pore-filling and intra-particle diffusion mechanisms. These changes in structure, therefore, would allow for physical trapping of microplastics (MPs) within biochar pores and increase its adsorption capacity. The choice of modification method-whether chemical or physical-has a direct bearing on the dominant adsorption mechanism (Wang et al., 2023). For example, biochar modified with metal oxides or salts demonstrates strong electrostatic interactions and surface complexation, while ball-milled biochar might rely more on pore-filling and intra-particle diffusion owing to increased surface area and porosity. To conclude, adsorption of microplastics onto biochar material is multi-layered and complex in nature and operates collectively via physical and chemical means. Tailoring biochar properties through appropriate modification can lead to improvement in its adsorptive properties. Further research effort now needs to be directed toward the optimization of these approaches and their application to real-world conditions in the quest for a solution to the increase in microplastic pollution challenge (Ashiq et al., 2019; Masinga et al., 2022).

In view of this, Table 2 offers a comparative view of different important mechanisms related to the biochar removal processes. This summary provides an overarching view of the key processes related to biochar and its effectiveness as a remediation agent.

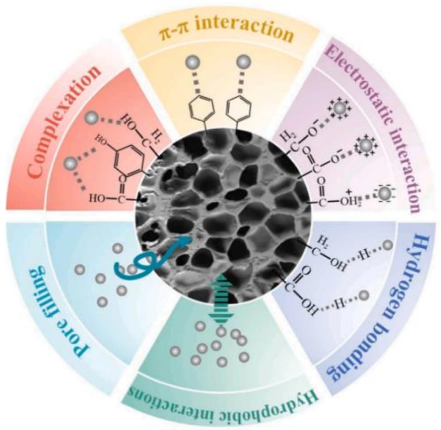

Fig 6. Mechanisms underlying the adsorption of MPs by biochar (Ji et al., 2024).

Table 2. A comparative overview of key mechanisms for MP removal by biochar and its modified forms

Adsorbents	Electrostatic interaction	Surface complexation	Hydrogen bonding	Hydrophobic interactions	π-π EDA interactions	Pore filling and intra-particle diffusion	References
Modified magnetic biochar	√	√					Wang et al., 2021a
Iron-modified biochar	√			√	√		Singh et al. 2021
Oxidize corncob biochar			√	√		√	Abdoul Magid et al. 2021
Magnetic rice biochar	√		√		√		Wu et al. 2023
Magnetic corncob Biochar	√	√		√			Li et al. 2023
Mesoporous biochar	√	√					Zhu et al. 2022
Biochar 750	√						Ganie et al. 2021

Statistical Comparison of Biochar Performance Across Studies

While existing research has demonstrated the efficacy of metal-modified biochar in MP removal, systematic statistical comparisons between studies remain limited. Below is a synthesized analysis of key findings, supported by statistical techniques where available, and recommendations for future work. Zhang et al. (2023) reported removal efficiencies of 96.24% (FeBC) and 84.77% (Fe-ZnBC) for polystyrene microplastics (PS-MPs), with one-way ANOVA confirming significant differences ($P < 0.05$). This highlights FeBC's superior performance over Fe-Zn and Fe-Mg modifications. Wang et al. (2021a) achieved 95% removal using biochar sand filters, but no direct statistical comparison with Zhang et al.'s results was conducted. A two-sample t-test or ANOVA could determine if these differences are significant. Singh et al. (2021) and Tiwari et al. (2020) corroborated Zhang et al.'s kinetic (pseudo-second-order, $R^2 = 0.9979$) and pH-dependent trends ($P < 0.05$ for reduced efficiency at pH 9–11), suggesting chemisorption and electrostatic repulsion as dominant mechanisms. Most studies statistically analyze their own data (e.g., ANOVA for pH effects) but lack meta-analyses that compare results across studies (e.g., FeBC vs. biochar sand filters). Additionally, variability in experimental conditions-such as MP type and water matrix-leads to inconsistent metrics, complicating direct statistical comparisons. Fe-loaded biochar (FeBC) demonstrated removal efficiencies of 72.39% in tap water (TW) and 78.33% in lake water (LW) (Zhang et al., 2023). However, to date, no studies have evaluated these conditions using other biochar types, such as those employed in Wang et al. (2021a). Competitive adsorption effects have been observed whereby dissolved organic matter (measured as COD) significantly reduces adsorption efficiency, with a strong negative correlation ($r < -0.9$) reported by Yao et al. (2023). However, this effect has not yet been statistically compared across other interference studies, such as those by Kumar et al. (2023), limiting comprehensive understanding of competitive adsorption impacts under varying conditions. To model removal efficiency, datasets from multiple studies (e.g., Zhang et al., 2023; Wang et al., 2021a; Ganie et al., 2021) should be integrated to evaluate the influence of key factors including biochar type (such as Fe-loaded biochar, MgO-biochar), pyrolysis temperature, and water matrix composition (e.g., tap water, lake water, synthetic wastewater). This combined dataset approach enables the development of robust predictive models that account for variations in biochar properties and environmental conditions, facilitating a comprehensive understanding of removal performance across diverse scenarios. In summary, while biochar's potential for MP remediation is statistically validated at the individual study level, advancing the field requires coordinated efforts to harmonize data and apply advanced statistical frameworks for cross-study validation. This will bridge the gap between lab-scale findings and scalable, real-world applications.

Challenges and Research Gaps

Though metal-modified biochar holds considerable promise for environmental remediation, grandfathering thorough investigations in case of critical challenges remains imperative for optimizing their practical deployment. Challenges appear normalized across technical, environmental, and economic parameters that face serious challenges before they can be translated to large-scale applications. Major technical and economic challenges exist in scalability. Current production methods are effective at lab scale but require substantial optimization for large-scale industrial applications in order to develop efficient metal incorporation techniques, standardize production protocols, and set quality control measures that would ensure consistent outcome characteristic across large production volumes.

Long-term stability is, however, the core area of concern that needs to be placed under extensive investigation. Such aspects include mechanical integrity while in service for prolonged periods, loss of metal components during long exposure to different environmental conditions, maintenance of adsorption-capacity over multiple cycles of treatment, susceptibility of the material to regeneration, post-regeneration costs, and the entire lifecycle of the material.

However, there also needs to be a clear assessment of possible environmental impacts because of using metal-modified biochar. Some key aspects are how metals leach under different environmental conditions, the bioaccumulation potential in aquatic environments, the effect on soil microbial populations when added as fertilizers, long-term retention time of metals in the environment, and the possibility of secondary contamination. Although metal-modified biochar is considered promising for practical applications, there is a considerable challenge for such applications due to the complex nature of the wastewater matrix in agriculture. Some of these challenges are competition between different contaminants for adsorption sites, interference due to dissolved organic matters and inorganic ions, variations with pH and ionic strength conditions, selective adsorption efficiency under complex contaminants, and formation of surface precipitates that limit the adsorption capacity.

These challenges include the development of improved modification approaches, installing comprehensive quality control measures, establishing complete environmental monitoring protocols, devising efficient regeneration and disposal strategies, and designing an application-specific optimization. These challenges can be met by integrated research efforts between materials science, environmental engineering, and ecological assessment to poise the sustainable and beneficial employment of metal-modified biochar for environmental applications. Successful resolution of these challenges will create an efficient future application of metal-modified biochar for environment remediation, especially the one involved in treating agricultural wastewater. A feasible solution to this problem necessitates balance with regard to the associated technological optimization of the material as well as more general environmental consequences of its implementation in real-world scenarios.

Future Perspectives and Recommendations

The development of metal-modified biochar technology requires thorough research programs on several critical considerations for a more realistic adoption and environmental sustainability. In the upcoming research avenues, both fundamental material development and applied technological aspects should be considered to address existing limitations and optimize performance traits.

(1) Optimization of metal modification techniques is hailed as a primary research concern, investigating novel combinations

of metals and new modification modes is emphasized. This includes the consideration of other metal precursors, more efficient methods of incorporation, and understanding the interactions between different metal species. All this research work aims to improve the adsorption capability, selectivity, and operating efficiency of the material at low costs.

(2) A comprehensive life cycle assessment is vital to assess the environmental footprints of metal-modified biochar through various phases from production, use, and disposal. The assessment should include energy consumption, resource use, emissions generation, and the related environmental impact across the whole value chain. Understanding these factors is key in achieving environmentally sound production and application protocols.

(3) The incorporation of metal-modified biochar within the scope of existing treatment technologies holds promise for system optimization. The research should, therefore, move towards integrated treatment strategies that combine biochar-based technologies with conventional physical, chemical, and biological processes. Such integration is likely to enhance overall treatment efficiency by addressing the limitations of individual technologies.

(4) Field-scale investigations encapsulating broader variations in environmental conditions are required to corroborate laboratory findings and assess actual performance. The studies would consider objective assessment of treatment efficiencies, operational constraints, maintenance needs, and long-term stability in real-world agricultural/industrial scenarios; all of which would duly inform ALL the practical implementation considerations and scaling-up.

(5) Economic feasibility analysis remains a key area of research, inclusive of detailed cost-benefit analysis concerning the execution of metal-modified biochar. Its considerations would include production cost, in addition to operational cost, maintenance needs, while one of the advantages accrues to resource recovery and/or mitigation of environmental impacts. Knowledge of such an economic footprint would play an important part in increasing farmer and wastewater treatment facility uptake.

(6) Seamless coordination of research across all these areas will be required for the successful development and application of metal-modified biochar technologies. This integrated approach will thus underpin the development of robust, efficient, and economically viable solutions to agricultural wastewater treatment, while also providing guarantees for environmental sustainability and practical applicability. These research initiatives, therefore, will provide a big technological push in framing the technology and overcoming the immediate technological shortcomings.

Anticipating into the future, the field of technology pertaining to metal-modified biochar will evolve and will go along with interdisciplinary collaboration as well as technological innovation. The development of research in such areas is likely to refine further and adapt the design of this technology for effective implementation in the future towards wide-ranging applications for environmental remediation. Eventually, this technology will contribute to the improvement of wastewater treatment in both the agricultural and industrial sectors towards a more sustainable and effective strategy.

Conclusion

This review comprehensively addressed the current state of biochar-based composites for environmental remediation, focusing on their synthesis methods, structural modifications, and pollutant removal efficiencies. Key modification strategies—such as metal impregnation, hydrothermal treatment, and ball milling—demonstrably enhance biochar's physicochemical properties, including porosity, surface area, and functional group availability. Notably, modified biochars have been reported to achieve adsorption capacities that are 2 to 5 times higher than unmodified counterparts. For example, Fe-modified biochar demonstrated Pb(II) adsorption of 123.4 mg/g compared to ~30–50 mg/g for typical pristine biochar. Similarly, dye adsorption increased from ~70 mg/g to over 200 mg/g with MgO modification. These performance improvements exceed those of many conventional sorbents like activated carbon under similar conditions, while maintaining cost-effectiveness and environmental sustainability. The significance of these findings lies in the scalable, low-cost nature of biochar production from agricultural waste and its customization potential for target pollutants. These advancements support the transition from lab-scale demonstrations to field-scale applications. Future research should emphasize life-cycle assessments, regeneration studies, and pilot-scale deployment to establish the feasibility and longevity of biochar-based remediation systems in diverse environmental contexts.

Abbreviation List

Abbreviation	Full Term
BC	Biochar
MBC	Modified Biochar
CNT	Carbon Nanotube
GO	Graphene Oxide
AC	Activated Carbon
FTIR	Fourier-Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction
BET	Brunauer–Emmett–Teller
TGA	Thermogravimetric Analysis
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
MB	Methylene Blue
Pb(II), Cd(II),	Lead, Cadmium ions

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