REVIEW ARTICLE



Interactions Between Biochar and Nano(Micro)Plastics in the Remediation of Aqueous Media

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Abstract

Plastic is a material that has become ubiquitous since entering the marketplace in the 1930s and 1940s; as a result, the presence of nano and microplastics (NMPs) are pervasive in natural environments affecting air, soil and water ecosystems. These NMPs are varied in size (categorised as either microplastics at 5 mm–1 μ m or nanoplastics at <1 μ m), shape and chemical composition. They represent a potential threat to aquatic life and human health through ingestion and inhalation. The toxicity of NMPs is attributed to chemical additives introduced during production and the absorbance of inorganic and organic chemical contaminants in environmental settings. This review is designed to discuss the use of biochar as a natural adsorbent for the remediation of water contaminated with NMPs. Biochar is a sustainable, affordable material which can remediate water and contribute to ecosystem restoration. Whilst it is well established as a material to sorb organic and inorganic contaminants, its use to remove NMPs is in its infancy and as such this review sets out to outline the mechanisms and modifications of biochar to remove NMPs from aqueous environments. Although removal mechanisms in laboratory settings are becoming clearer this review highlights that remediative studies need to be undertaken in conjunction with the systematic investigation of the effect of key environmental parameters on remediation and the use of environmentally aged NMPs. The future direction of this discipline also needs to incorporate field trials alongside laboratory work to develop a stronger understanding of the viability of biochar to remove NMPs from waterways.

Highlights

- Biochar is a viable option to treat NMP contaminated water.
- Essential biochar characteristics: zeta potential, SSA, texture and pore size.
- Future studies must consider environmental parameters in conjunction with biochar.
- Needs a blended laboratory and field study approach to study environmental parameters.
- Studies need to include interaction between biochar and naturally aged plastic.

Keywords Nanoplastic · Microplastic · Biochar · Remediation · Water · Emerging contaminant

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Introduction

Plastic is a material that came to mass market prominence in the 1930s and has been a ubiquitous presence both domestically and industrially ever since. After plastics entry into the marketplace, production has risen exponentially from a 1950s global production of plastic of around ~1.5 million tonnes to ~ 360 million tonnes in 2018 with estimates of current plastic production being as high as 400 million tonnes (Fig. 1) with a significant proportion of this being single use plastic (Okoffo et al. 2021; Chow et al. 2023). Approximately 60% of produced plastic is disposed of into the environment with up to 23 million tonnes of plastic waste entering waterways, a figure that is projected to increase to 53 million tonnes per annum by 2030 (Borrelle et al. 2020; Chow et al. 2023). This plastic waste can break down into smaller fragments becoming nano or microplastics (NMPs) with the potential for environmental and health consequences.

Microplastics (MPs) are defined by Frias and Nash (2019) as "synthetic solid particles or polymeric matrices, with regular or irregular shape and with size ranging from 1 μ m to 5 mm, of either primary or secondary manufacturing origin, which are insoluble in water." These plastics are classified as either primary plastics or secondary plastics. Primary NMPs are initially produced to < 5 mm and are predominantly used for textiles, medicines, and cosmetics such as facial and body scrubs (Cole et al. 2011; Browne 2015). Primary NMPs of this nature enter freshwater environments by being carried by wind or surface runoff, or due to the release of contaminated water from water treatment plants; this contamination is then often carried into coastal waters (Gall and Thompson 2015).

Secondary plastics are the result of the breakup and deterioration of larger plastic waste. In the environment such degradation may occur as a result of photodegradation, thermo-oxidative degradation, hydrolysis and/or biodegradation by microbes (Gazal and Gheewala 2020). The sources of these plastics are varied and have been seen to include trawler nets, pre-production plastic pellets and domestic waste; these larger plastics and are considered to comprise the bulk of plastic pollution seen environmentally (Eerkes-Medrano et al. 2015; Eriksen et al. 2013).

These materials have become a ubiquitous presence and are now ever present in our natural environment impacting air, soil, and water quality (Loganathan and Kizhakedathil 2023). As a result, the remediation of waterbodies to remove nano and micro plastics (NMPs) is a topic that has gathered attention in recent years with remediative processes and materials studied. Techniques to remove NMPs have included physical processes (e.g., filtration), chemical processes (e.g., advanced oxidation) and biological processes



Fig. 1 Global plastic production per year 1950 to 2018 (in million metric tons) (Okoffo et al. 2021)

(e.g., enzymatic digestion). However, whilst useful as part of a suite of measures, these processes all have limitations such as the requirement for long contact times, the inability to contend with the diverse nature of NMP waste or a lack of efficacy for smaller NMPs (Hidayaturrahman and Lee 2019; Park and Kim 2019). A material that has emerged as an option to remove NMPs from water is biochar. During this review, we will critically assess studies which discuss the use of biochar as a method of remediating NMPs of varying sizes, shapes, and charges from water. Biochar is a porous, carbon rich material that is the product of biomass pyrolysed under limited oxygen conditions at temperatures between 350 and 1000 °C (European Biochar Foundation 2016). It has attracted attention due to being low cost and sustainable in nature with several attributes including the ability to sequester carbon, with the potential to reduce net emissions of CO₂ by up to 1.8 Gt per annum; augment soil fertility through the retention of nutrients and immobilisation of heavy metals; and adsorb both organic and inorganic pollutants from aqueous environments (Woolf et al. 2010; Chen et al. 2018; Cairns et al. 2020; Wang et al. 2020; Qiu et al. 2021; Liu et al. 2023). Whilst there has been in-depth study of biochar relating to the sorption of inorganic and organic materials, study into the removal of NMPs from aquatic environments is still in its infancy. However, the mechanisms of both organic contaminant and inorganic contaminant removal from water by biochar are broadly understood and are relevant to NMP removal (Cairns et al. 2022a, b). The diversity of the environmental uses of biochar has been demonstrated through studies demonstrating the removal of inorganic and organic materials in variety of environmental or simulated environmental settings including road runoff (Cairns et al. 2021), stormwater (Kaya et al. 2022), drinking water (Eniola and Sizirici 2023), mine water (Cairns et al. 2022a; b) and industrial wastewater (Nyamunda et al. 2019). These results indicate that biochar could be used in a range of aquatic media to remove NMPs. Although there are still a number of gaps in the study of biochar to remove inorganic and organic pollutants (e.g., selectivity, novel modification, field studies and scaling up) as the use of biochar to remove NMPs is still in an early stage the opportunity for further study is significant. In order to more fully understand the interactions between biochar and NMPs, a multidisciplinary approach would be beneficial. Such an approach would thoroughly characterise environmentally found plastics in conjunction with the characterisation of biochar. Plastic shape, size, and chemical composition as well as the effects of environmental degradation of plastics are pertinent considerations to be reviewed in conjunction with water remediation by biochar to ensure studies are representative of true field scenarios. The purpose of this review paper is to highlight the variety of NMPs found environmentally, broadly outline their various characteristics, understand the viability of biochar as a sorbent for these materials and outline the direction future research in this area needs to consider.

Nanoplastics and Microplastics in the Environment

Chemical Composition of NMPs

NMPs are composed of natural and synthetic polymers. Over the last century, the understanding of polymers as long chain molecules bonded covalently has been cemented; this has led to the development of a variety of polymers that are in use today. Polymers have become ubiquitous being found in diverse everyday products from packaging to sporting goods (Odian 2004). A number of these synthetic polymers are found in environmental settings as NMPs; the polymer types that are most often produced and found environmentally include polyethylene (PE) which accounts for 29.6% of production, polypropylene (PS) which accounts for 7.1% of production, poly(vinyl chloride (PVC) which accounts for 10.4% of production, poly(ethylene terephthalate) (PET) which accounts for 6.9% of production and polyurethane (PU) which accounts for 7.4% of production (Gewert et al. 2015) (Fig. 2).

Physical Characterization: Shapes, Size and Colours

Since the term "microplastics" has been coined there has been great focus on the issue of plastic pollution resulting in a significant amount of novel research. However, despite the quantity of research a consensus on definition for nomenclature for size and shape are still missing. The effect of this is that the comparison of microplastic and nanoplastic proliferation, significance of localised contamination, and ecological impact is markedly more difficult between research hampering understanding and potential remediative solutions.

Shapes

Environmental plastics can be found in a variety of shapes and sizes (Teresa Rocha-Santos 2017). The shapes of NMPs have been described in several ways, most commonly: fibre, fibre bundles, fragments, spheres, pellets, films, and foams (Fig. 3) (Rochman et al. 2019). However, there is not a consistency in shape nomenclature, definition or parameter amongst the literature. Classification of microplastic shape can range from two to five categories of shape utilizing different terminology for equatable shapes such as sphere, bead, microbead, and pellet (Tong et al. 2020a; b; Zobkov et al. 2020; Sarkar et al. 2021; Sekudewicz et al. 2021). Such inconsistency makes comparative studies and remediative solutions more difficult, particularly with different microplastic NMP shapes being attributed with different affinities for sorption/removal (Hu et al. 2022). For secondary plastics shape is determined by the form of the primary plastic and the way in which the plastic has degraded to an NMP (e.g. photo, chemical, biological or abrasion) and the length of time the plastic has been subjected to the environmental parameters.

The shape of NMPs is recognized as a characteristic that enables a link between the NMP and the origin and pathway of the contamination as certain shapes of NMP are shed by specific products (Helm 2017; Rochman et al. 2019).

Fig. 2 Polymer types and structures alongside their percentage of demand in Europe (PE—polyethylene, PP—polypropylene, PS—polystyrene, PVC—poly(vinyl chloride), PET—poly(ethylene terephthalate), PU—polyurethane) (Gewert et al. 2015)





Fig. 3 Fibres with clean-cut ends (a) and fraying (b). Fibre bundles (c) are in a tightly wound mass that cannot be untangled. Fragments are rigid (d, e) and irregular (f). Spheres (g) are round with a smooth

There is the potential for this type of linkage to inform both addressing pollution at source and the deployment of the appropriate methods in the remediation of existing, and potentially ongoing, contamination. Examples of the linkages between NMP shape and primary plastic include NMP fibres being connected to the production of synthetic clothing, upholstery and carpets in Shanghai (Liu et al. 2019a; b) and NMPs which are cylindrical in nature being associated with contamination as a result of the release of industrial pellets (Rochman et al. 2019). The shapes of NMPs may also have a bearing on how easily the plastic can move in the environment with thin flat films being more prone to being transported atmospherically (Allen et al. 2019). Aligned to this the shape of the NMP can also affect the potential for increased sorption of toxic chemicals as NMPs with a larger ratio of surface area to volume have increased potential for the accumulation of harmful chemicals and subsequent ingestion by organisms (Rochman et al. 2019).

Colour

Whilst numerous colours have been described by studies the most prevalent are blue and red (Hidalgo-Ruz et al. 2012), however it should be noted that particularly dark, light, or transparent NMPs are likely to be understated when visual analysis is undertaken (Hartmann et al. 2019). Unlike shape, NMP colour is not necessarily useful to link the NMP with the origin or pathway of the contaminant; this is exacerbated by the fact that the colour of NMPs can change due to environmental weathering (Rochman et al. 2019). The loss of colour in this manner lessens the importance of visual assessment of NMPs and heightens the importance

surface. Pellets (**h**) are typically rounded or cylindrical. Films (**i**) are flat, thin, and malleable. Foams (**j**) are soft and compressible (Rochman et al. 2019)

of spectral and chemical analytical techniques. If studies to remove NMPs from water are to move toward the utilization of environmentally sourced plastic the loss of colour must be taken into consideration in terms of NMP quantification pre and post removal. The use of dyes, such as Nile Red, should be considered as a method of enabling more accurate quantification during studies (Hernandez et al. 2023).

Size

Plastics size is an important part of the definition and characterisation of plastics. The size of plastics found environmentally can be driven either by industrial production (primary plastics) or the degradation of larger primary plastics into secondary plastics of smaller size. Primary plastics are the by-products of particulate emissions created by industrial production (Laskar and Kumar 2019). Secondary plastics are larger plastic materials that continuously degrade as a



Fig. 4 Schematic diagram of plastic sources, degradation, entry to the food chain and human ingestion

result of weathering processes breaking down the larger particulate material into smaller fragments (Arthur et al. 2009). The weathering of plastics occurs because of various natural reactions including sunlight and thermal radiation, biodegradation, temperature fluctuation and physical abrasion (Fig. 4) (Zha et al. 2022).

Plastics of differing sizes have been attributed different nomenclature. However, as with the description of the shape of NMPs, there is a lack of consistency across the literature. Thompson et al. (2004) initially coined the term microplastic to describe microscopic pieces of plastic. This definition was updated by Arthur et al. (2009) who put forward 5 mm as a maximum threshold for microplastics. In 2018 Gigault et al. attempted to clearly define the size of nanoplastics as between 1 nm and 1 µm. Despite these attempts at clear nomenclature there is still no universal agreement on plastic size description. Studies often divide microplastics into several further categories, e.g. ≤ 0.5 mm, 0.5–1 mm, 1–2 mm, $2-5 \text{ mm or} < 25 \mu\text{m}, 25-50 \mu\text{m}, 50-100 \mu\text{m} \text{ and} > 100 \mu\text{m},$ with these categories differing noticeably between the literature. With research demonstrating that the particle size of plastics has a direct effect on removal efficiency such nomenclature is important (Ma et al. 2019). Although definitions of the size of plastics vary and the categorization within broader nomenclature is not consistent the terminology associated with the broad size categories of plastics is more constant with plastics > 25 mm known as macroplastics, between 25 and 5 mm known as mesoplastics, between 5 mm and 1 μ m known as microplastics and < 1 μ m known as nanoplastics (Fig. 5). The ongoing environmental degradation of plastics continually uncover fresh surfaces, enabling the movement of chemical additives to exposed sites with associated environmental and health consequences.

Micro-Plastics and Co-contaminants/ Additives of Concern

NMPs can contain chemicals substances from two broad sources: (i) chemical compounds (additives) introduced during the production of the plastic to improve the functionality (Hahladakis et al. 2018) and (ii) chemicals absorbed



Fig. 5 Definition of plastic size classes (author photo)

environmentally (Gazal and Gheewala 2020). These chemicals are a source of toxicity which can severely threaten ecosystems and human health (Hahladakis et al. 2018; Prata et al. 2019).

Additives are incorporated into plastics to improve aesthetics (colour and transparency) and to improve resistance to environmental factors such as UV, heat, mould and bacteria. Whilst these additives improve the functionality and aesthetics of the end product, they are often toxic, not chemically bound to the plastic polymer and can leach into the surrounding environment (Hahladakis et al. 2018; Prata et al. 2019). Lithner et al. (2011) ranked the most hazardous additives used in plastic production which included brominated flame retardants, phthalate plasticisers and lead heat stabilisers. These chemicals have been associated with developmental and neuro disorders, reproductive toxicity, cancer, and diabetes (Kim et al. 2014). The proportion of additives is not uniform across plastic types with different polymers requiring different proportions dependent on use (Akoueson et al. 2021). Up to 80% of the PVC in medical devices is comprised of phthalate, which can bind with molecular targets in the body causing hormone disruption, whereas only 10% of polypropylene is comprised of additives (Tickner et al. 2001; Mariana et al. 2016; Akoueson et al. 2021). The leaching of BPA from plastic is also highlighted as a concern to human health with exposure of between 0.2 and 20 ng mL⁻¹ being associated with adverse human health effects (Lang et al. 2008; Melzer et al. 2012). Upholstery, carpets and electronics are also sources of NMPs containing additives linked to health effects; the natural abrasion of these products release brominated flame-retardant additives forming household dust which is subsequently inhaled (Johnson-Restrepo and Kannan 2009).

Plastic also has the ability to absorb organic and inorganic chemicals in an environmental setting due to large surface area and hydrophobicity enabling NMPs to sorb and concentrate pollutants such as divalent metal ions, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and perfluorochemicals (e.g. perfluorooctanesulfonate and perfluorooctanesulfonamide) (Rochman et al. 2013; Wang et al. 2015; Allen et al. 2018; Tang et al. 2021; Tursi et al. 2022). Different plastics, with varied characteristics, have affinities with different contaminants. PVC, with a C-C backbone, has been seen to sorb polychlorinated biphenyls whereas PET, with a heteroatom backbone, has been seen to have a low sorption capability for polychlorinated biphenyls (Allen et al. 2018). The affinity of a given NMP with a given inorganic chemical has a direct consequence environmentally and to human health.

Implications for Human Health

Human exposure to NMPs occurs through a number of pathways most notably ingestion via transfer along the food chain, bottled water, tap water, and inhalation (Kumar et al. 2022). The uptake of plastic is generally asserted to have negative implications for human health due to the additives used in its production, plastic sorption of toxic contaminants, and the plastic acting as a scaffold for pathogenic microorganisms and parasites (Vethaak and Leslie 2016). However, despite this most studies do not fully explore the environmental interaction between NMPs and other contaminants, e.g. metals, and the resultant implications for human health. Exposure to NMPs in environmental settings has been discussed as having the potential for bioaccumulation and the attendant effects on the nervous system, kidneys, respiratory system, digestive system, and placenta (Fig. 6).

The presence of NMPs in marine species which form part of the food chain has been widely acknowledged, as has the presence of NMPs in tap and bottled water (Llorca et al. 2020; Cverenkárová et al. 2021; Muhib et al. 2023). It has been estimated that between 39,000 and 52,000 NMPs are ingested and up to 121,000 NMPs are inhaled per person each year (Cox et al. 2019). Inhalation occurs as a result of airborne NMPs from a variety of sources most notably household dust, industrial pollution, tyres and fibres from clothing (Johnson-Restrepo and Kannan 2009; Wright and Kelly 2017; Kumar et al. 2022).

The transport of airborne NMPs is heavily influenced by wind (speed and direction), altitude (with lower regions being more prone to higher concentrations) and seasonality with lower temperatures resulting in fewer airborne particles



Fig. 6 Potential health effects resulting from the bioaccumulation of NMPs and chemical contaminants in the human body **a** nervous system (Yin et al. 2022), **b** kidney system (Li et al. 2023a, b), **c** respiratory system (Jenner et al. 2022), **d** digestive and excretore system (Zhang et al. 2021) and **e** placenta (Ragusa et al. 2021)

(Facciolà et al. 2021). Indoor settings have also been seen to have a higher concentration of NMPs due to lower dilution volumes; indoor concentrations as high as 59.5 particles/ m³ have been recorded as opposed to outdoor concentrations in the same study and location which only reached 1.5 particles/m³ (Facciolà et al. 2021). The presence of additives and sorbed pollutants such as PAHs and PCBs ingested and inhaled as a result of NMPs have been considered to have carcinogenic and mutagenic effects on humans (Cverenkárová et al. 2021). It has been demonstrated that NMPs can cross human tissue membranes into the blood in a way analogous to drug delivery systems promoting uptake and distribution (Vethaak and Leslie 2016; Kumar et al. 2022). It is suggested that the penetration of cells by NMPs can have deleterious effects on human health such as cytotoxicity, DNA oxidative damage and genotoxicity (Kumar et al. 2022).

Whilst a number of these studies highlight the potential for NMPs to pose significant human health risks most do not present a direct connection between human ingestion of NMPs and resultant human health risk. Research does indicate that NMPs are likely to lead to human health risks through estimations of ingestion (Cox et al. 2019), animal (Rawle et al. 2022) and aquatic organism studies (Athey et al. 2020), and the presence of NMPs in drinking water (Mohan et al. 2023) but the effect of NMPs on human health is still contentious. Although there is a general consensus around the ubiquitous presence of microplastics environmentally some research refutes that their presence poses a risk to humans. Yang et al. (2019) modelled polystyrene behaviors through the study of mice and extrapolated the threshold concentrations required for such NMPs to effect human wellbeing to be \sim 7.7 g and therefore deleterious effects were considered unlikely to occur.

The potential for NMPs to negatively impact human health is well discussed but for this to be confirmed future studies need to focus on the direct connection between human exposure to NMPs and negative health effects. Particular attention needs to be given to the consequence of exposure to NMPs which have been part of a multi-contaminant system.

Removal and Treatment Technologies

The ubiquitous nature of plastic pollution aligned with its negative ecological and health effects necessitates the consideration of removal and treatment technologies. As NMPs are an emerging pollutant their removal has not traditionally been considered by wastewater treatment plants (WWTPs), in fact WWTPs are often acknowledged as a key source of NMP contamination (Altuğ and Erdoğan 2022). In order to address the remediation of waterways from NMPs new technologies must be developed and deployed. Currently the primary processes to remove or mitigate NMPs revolve around either physical, chemical, or biological processes.

Physical Processes

The key physical processes to remove NMPs from water primarily consist of sedimentation and filtration. In this context filtration is an overarching term which includes a number of techniques such as sieving, sand filters, screening and membrane filtration. These techniques can be effective at removing larger plastics, but many are less effective at removing smaller NMPs.

Sedimentation is often undertaken using the conventional activated sludge process (CASP). This treatment technique allows NMPs to adhere to suspended solids and be separated through settling (Bui et al. 2020). Although this is a widely used technique results are incredibly varied with reported removal percentages being between 40.7 and 91.7% (Liu et al. 2019a, b; Ngo et al. 2019). The type and shape of the NMP is a key factor in the efficacy of sedimentation with fibre removal being greater than other shapes of NMP (Khan et al. 2022; Torkashvand and Hasan-Zadeh 2022). Another consideration with sedimentation is the disposal of the resultant solid waste with high NMP concentration, which is often used for land treatment potentially allowing the NMPs to reenter aqueous environs (Alavian Petroody et al. 2021; Okoffo et al. 2021).

Sieving is a common filtration method that is deployed in the removal of NMPs. A stack of sieves is used to trap the NMPs with sieve sizes being reported between 400 and 45 µm. However, at this sieve sizing nano plastics are not removed (Carr et al. 2016). Sand filters have also been used as a removal technique with low associated costs and fast removal of NMPs (Khan et al. 2022). Studies indicate that whilst sand filters are effective with larger NMPs when NMPs are $< 65 \mu m$ there is the potential for them to pass through the sand filtration due to the porosity of the media (Hidayaturrahman and Lee 2019). Membrane technology is a further filtration method that is commonly implemented for the removal of organic contaminants (Dharupaneedi et al. 2019). Although membranes can be effective for microplastics larger than 10 µm they are less effective for NMP removal for particles smaller than 10 µm and often foul which reduces NMP removal efficacy as well as decreasing the removal of other target pollutants (Ma et al. 2019; Park and Park 2021).

Chemical Processes

The chemical processes involved in the removal or chemical degradation of NMPs are primarily coagulation and advanced oxidative processes. Traditionally coagulation and agglomeration are used in treatment plants to create larger particles through the addition of a coagulant, such as Fe or Al compounds, which are then removed via sedimentation. Charge neutralization, adsorption and sweep flocculation are the key mechanisms for NMP removal with the positive ions of the metal coagulant adsorbing onto the surface of the negatively charged NMP to form flocs (Xu et al. 2021). However, coagulation with Fe based coagulants have been seen to have a removal efficiency of less than 15% even where high concentrations of FeCl₃·6H₂O were used (Ma et al. 2019).

Advanced oxidation processes (AOP) have been undertaken in an attempt to rapidly alter the surface morphology of NMPs through degradation. The potential for AOP to move beyond degradation to decomposition has garnered interest. Photo-catalytic AOP is the method that is the most commercially implemented for contaminants whereby a hydroxide radical is produced which attacks and breaks down organic contaminants (Mihaela 2018). Laboratory based studies have been undertaken to review the effect of UV in the range of 254–300 nm on various plastics including PS, PE, PVC, and PET (Suhrhoff and Scholz-Böttcher 2016; Lin et al. 2020). UV exposure has been seen by these studies to result in changes in surface structural properties inducing the cleavage of chemical bonds with cracks, wrinkles and perturbances becoming evident.

Ozone has also been employed for AOPs to degrade NMPs due to it being such a strong oxidant. Ozonation has been seen to result in the formation of oxygenated functional groups and degradation of polymer chains for a number of plastics including PE, PP, and PET (Hidayaturrahman and Lee 2019). It is also used in conjunction with hydrogen peroxide to rapidly age and cause NMP degradation (Amelia et al. 2021; Gomes de Aragão Belé et al. 2021). The inclusion of hydrogen peroxide increases the rate of degradation beyond that of ozone and has been suggested as a pretreatment to biodegradation (Amelia et al. 2021).

Biological Processes

Plastic-degrading microorganism process is a further area of research for wastewater treatment (Ahmed et al. 2018; Ebrahimbabaie et al. 2022). Microorganisms have been proven to degrade plastics, indicating that microbial metabolic pathways of plastic depolymerization is an innovative recycling method to dispose of plastic waste. However, the length of time needed for the biodegradation of plastic waste can range from weeks to months, making the industrial scale deployment of biological process unrealistic. The reduction of the mass of PE in water by only 14.7% has been seen to take 60 days by a specifically isolated microbial consortium (Park and Kim 2019). Another factor hindering the use of biological processes is that the majority of plastics contain additives and components that can interfere with the biodegradation process. As a result, current biological systems cannot cope with the diverse nature of our plastic waste. However, this does potentially present an opportunity to develop and design new biological systems that can efficiently break down wide range of plastics to upcycle plastics into new materials with high value (Miri et al. 2022).

Biochar as a Remediation Material

A material that has emerged with the potential to remove NMPs from water is biochar; a porous carbonaceous material already used for the remediation of inorganic and organic contaminants from water. Biochar has the potential to overcome some of the issues encountered by current NMP removal techniques including the removal of nano as well as micro plastics demonstrating a point of difference with many physical techniques, proving to be effective in shorter timescales than biological processes and with greater removal efficiencies than chemical treatments such as coagulation.

Pristine Biochar

The use of biochar to remove NMPs from water has been studied in relation to both pristine (unmodified) biochar and modified biochar. When using pristine biochar in the removal of NMPs the two key variables which dictate the structure and characteristics of the biochar are pyrolysis temperature and feedstock. However, it is critical to consider these variables in conjunction with the chemical composition of the target plastics and the water chemistry of the environment which is to be remediated.

The effects of pyrolysis temperature were considered by Magid et al. (2021) on the adsorption of polystyrene NPs using biochar with a cornstalk feedstock. As temperatures increased from 500 to 700 °C and finally 900 °C specific surface area (SSA), hydrophobicity and aromaticity were also seen to increase and a change in zeta potential was observed. The increase in hydrophobicity and SSA alongside a reduced negative zeta potential with increasing temperatures was also observed by Hsieh et al. (2022) from 300 to 500 °C, Ganie et al. (2021) from 350 to 750 °C and Wang et al. (2020) from 400 to 700 °C. As pyrolysis temperatures increase there is an effect on the molar H/C ratio as the proportion of H reduces and the proportion of C increases. This ratio is generally accepted as an index for the degree of aromaticity and is critical to hydrophobic interactions and π - π interactions. As pyrolysis temperatures increased Magid et al. (2021) saw this change in H/C ratio in their corncob biochar which was attributed to the thermal conversion of organic matter into carbonated organic matter and the formation of structures containing aromatic rings. Hydrophobicity and aromaticity as a result of the change in H/C ratio were highlighted as major factors determining polystyrene NP adsorption (Magid et al. 2021). Hydrophobic functional groups, such as alkenes, have been seen to be more evident in biochar produced at higher pyrolysis temperatures resulting in greater NMP removal (Hsieh et al. 2022). Where hydrophobic sites are more readily accessible hydrophobic reactions promote the adsorption of non-polar compounds such as the NMPs (Cairns et al. 2022a, b; Zhu et al. 2022).

The zeta potential and point of zero charge (PZC) are also characteristics of the biochar that are commonly highlighted as critical to the sorption of NMPs. Biochar generally has a negative zeta potential value as a result of negative surface charge (Wang et al. 2020). However, as pyrolysis temperatures increase the zeta potential of the biochar becomes less negative, the PZC is at a higher pH and the sorption of NMPs increases (Ganie et al. 2021; Hsieh et al. 2022; Magid et al. 2021). Zeta potential is relevant in terms of electrostatic repulsion; if the charge of the NMP is negative, e.g. due to the presence of oxygenated functional groups such as carboxyl groups, then the more negative the charge of the biochar the more electrostatic repulsion will inhibit the sorption of the NMP by the biochar (Ganie et al. 2021). The strength of a repulsive zeta potential creates an energy barrier and the interaction between the biochar and the NMP must exceed the primary energy barrier for sorption to take place (Magid et al. 2021). In the study undertaken by Zhu et al. (2022) the initial zeta potentials of PSNPs and MBC were - 34.5 mV and 6 mV, respectively enabling the sorption of the NPs through electrostatic attraction as opposed to merely eliminating electrostatic repulsion. Ganie et al. (2021) also investigated the zeta potential of the NMP and a strong negative charge on the plastic was evident. The interaction between the zeta potential of the biochar and the NMP is essential to understand and illustrates the importance of adequate NMP characterisation alongside biochar characterisation. The experimental design of Wang et al. (2020) used microplastic particles that were 10 µm in size specifically to try and circumvent the effects of zeta potential and focus on SSA and pore system effects.

The increase of SSA is a well-documented consequence of increasing pyrolysis temperature (Cairns et al. 2022a, b). At higher pyrolysis temperatures amorphous carbon condenses to crystalline structures, an increase in pores can be observed and there is an increase in the amount of volatile compounds removed all of which contribute to such an increase in SSA (Chen et al. 2012; Wang et al. 2016; Zhang et al. 2013). In their study of biochar's removal of 10 μ m plastic spheres Wang et al. (2020) saw an increase in pyrolysis temperature led to the layers of the biochar becoming thinner with weaker components being removed leading to a high pore system. An increase in SSA and pore abundance was also seen by Ganie et al. (2021) with an increase in pyrolysis temperature leading to an increase in NP removal by sugarcane bagasse biochar. Here an increased pore volume alongside a higher surface area was deemed to be essential to induce optimal mechanical interlocking. Pyrolysis temperature increases leading to an increased surface area were also reported by Hseih et al. (2022) and Magid et al. (2021) where it was considered a major factor in the adsorption of NPs. However, the need to consider SSA in conjunction with pore size rather than a stand-alone characteristic is essential. An increase in SSA can be due to an increase in small pores often less than 10 nm (Ganie et al. 2021; Magid et al. 2021; Zhu et al. 2022). As a result of this pore size distribution, NMPs over 10 nm were too large to enter into all of the pores and cracks in the biochar preventing their removal from water. Although SSA is a useful indication of potential removal of NMPs, sorption is not necessarily proportional to SSA between NMPs and biochar (Ganie et al. 2021).

Whilst pyrolysis temperature is reported as essential to SSA and pore size distribution, feedstock has also been discussed in relation to pore shape and the effect of pore shape on NMP sorption. Woodchip, cellulose and lignin feedstocks have been seen to result in contrasting surface morphologies (Hsieh et al. 2022). SEM analysis demonstrated that lignin had a smooth surface with fractured edges, cellulose retained the original fibre structure and had wrinkled surfaces whereas woodchip preserved the contour of the original biomass with sponge like textures and curly flakes at the edge. Woodchip was seen to be more effective at trapping microplastics due to its irregular rough structure as opposed to the least effective feedstock, lignin, with its smooth surfaces. SEM also revealed that as pyrolysis temperatures increased surfaces became rougher indicating the importance of the combination of feedstock and pyrolysis temperature to NMP sorption. The large biochar pores seen as by BET analysis by Magid et al. (2021) were determined to be probably more dependent on plant materials and the structure of the biomass as opposed to pyrolysis temperatures. Feedstock and pyrolysis temperature were also highlighted as drivers of differences in morphology between biochar types by Wang et al. (2020). The microstructures of the biochar were categorised as 'rind', 'chip, 'loofah' and 'honeycomb'. These microstructures were seen to be important in how the microplastics were retained with three categories of retention being proposed as a result of these morphological categories: 'stuck', 'trapped' and 'entangled' (Fig. 7). Being stuck denoted microplastics being retained between gaps in the filter particles; this was associated with sand filters rather than biochar and was seen to be the least effective in terms of microplastic retention. Being trapped denoted the microplastics entering the pores of the biochar



Fig. 7 Microstructure and morphology of the pore system of biochar samples: 'Rind' in C300 (\mathbf{a} , \mathbf{b}), 'Chip' in C400 (\mathbf{c} , \mathbf{d}), 'Loofah' in C500 (\mathbf{e} , \mathbf{f}) and 'Honeycomb' in Hardwood (Wang et al. 2020)

and losing their mobility and was associated with the 'honeycomb' and 'loofah' microstructures. These microstructures were seen with hardwood biochar pyrolysed at higher temperatures rather than corn straw biochar and were seen where microplastic removal was most effective. Being entangled denoted microplastics being held in place by small biochar particles or 'chips' which wrap around the microplastics and was seen with corn straw biochar pyrolysed at lower temperatures resulting in less microplastic removal. Whilst discussing the morphology of the biochar and the importance to the retention of the microplastics Wang et al. (2020)

Table 1 Repres	entative studies or	n the use of bioch	ar and modified b	iochar to remove	various NMPs, ty	pe of study and r	emoval mechanisms			
Author	Feedstock/ modification	Pyrolysis temp	Polymer	Purchased/lab- oratory aged/ naturally aged polymer	MNP conc/volume	Adsorbent dosage	Adsorbent capacity/removal efficiency	Time	Laboratory study/field study	Removal mechanism(s)
Ganie et al. (2021)	Sugarcane bagasse	350 °C, 550 °C, & 750 °C	Negatively charged polystyrene latex beads (500 nm)	Purchased	10 mg/L, 10 mL	15 mg	24% (350 °C), 39% (550 °C), 99% (750 °C)	5 m	Laboratory	Pore retention and electro- static attraction
Hsich et al. (2022)	Lignin, cel- lulose, and woodchip	400 °C and 700 °C	Carboxylate polystyrene (1 µm)	Purchased	4 mg/L	0.3 g and 0.6 g (within sand column)	Woodchip at 700 °C and 0.6 g – 100%		Laboratory (using real river water and actual sewage water)	Trapping (pore filling)
Li et al. (2023a)	Pristine corncob and magnetised corncob	200 °C	Polyamide, pristine and aged. (<48, 48–58, 58–75, 75–125, and 125–180 μm)	Purchased, laboratory aged	10, 20, 40, 70, & 100 mg PA 30 mL	50 mg	Up to 97%	0.5, 1, 3, 6, 12, 18, 24, 48, 72, & 96 h	Laboratory	Complexation, hydrophobic interaction, and electrostatic interaction
Magid et al. (2021)	Corncob, oxidised	500 °C, 700 °C, and 900 °C	Polystyrene (50 nm)	Purchased	0.4 g/L, 10 mL	0.2 g		15, 30, 60, 120, 240, 480, 1500, 2160, 2880, and 4320 min	Laboratory	Pore filling, hydrophobic interaction, and hydrogen bonding
Shi et al. (2023a)	Magnetised	300 °C, 500 °C, & 700 °C	Amine polystyrene, carboxylate polystyrene (100 nm)	Purchased, laboratory aged	80 mg/L, 10 mL	10 mg	300 °C—43.67%, 500 °C—82.73% and 700 °C—57.02%	60 min	Laboratory	Hydrophobicity, electrostatic attraction, H-bonding for- mation and π - π conjunction
Shi et al. (2023b)	Rape straw CTAB modi- fied magnetic biochar	800 °C	Polysty- rene and carboxylate polystyrene	Purchased	20 mg/L, 250 mL	0.03 g	95.2% (polysty- rene) and 91.2% carboxylate-mod- ified polystyrene	60 min	Laboratory	Aggregation instead of adsorption

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Table 1 (continu	ued)									
Author	Feedstock/ modification	Pyrolysis temp	Polymer	Purchased/lab- oratory aged/ naturally aged polymer	MNP conc/volume	Adsorbent dosage	Adsorbent capacity/removal efficiency	Time	Laboratory study/field study	Removal mechanism(s)
Siipola et al. (2020)	Steam acti- vated pine and spruce bark	475 °C	Polyethylene microbeads (10 µm), cylindri- cal, smooth polyethyl- ene pieces (2–3 mm), & fleece shirt fibers	Purchased, clothing fibre (unaged)	2 g of each polymer	20 g	100% for the PE particles and nearly 100% for the fleece fibers, with only 1–4 fibers detected after elution. The majority of the spherical micro- bead MPs eluted rapidly within the first 2–14 fractions		Laboratory	Unknown
Singh et al. (2021)	Magnetised	550 °C and 850 °C	Carboxyl NP (1000 nm), amine NP (1000 nm), and carboxyl NP (30 nm)	Purchased	10 mg/L, 10 mL	5 mg	Maximum removal capaci- ties for NP1 (225.11 mg/g), and NP3 (206.46 mg/g) were obtained using FB-850, whereas FB-550 showed higher removal of NP2 (290.20 mg/g)		Laboratory	Surface compl- exation
Subair et al. (2024)	Banana peel	650 °C	Polystyrene ground and sieved to 75 µm, 150 µm, & 300 µm	Purchased, ground and sieved	0.05 g/L, 0.1 g/L, 0.15 g/L, and 0.2 g/L,	2	92.16%		Laboratory	Entanglement and entrapment in the porous system
Tong et al. (2020a; b)	Cellulose, Magnetised	400 °C	Carboxylate polystyrene (0.02 mm, 0.2 mm and 2 mm)	Purchased	4 mg/L, 3 PV			2 h	Laboratory	Surface rough- ness
Wang et al. (2020)	Cornstraw, hardwood	300 °C, 400 °C and 500 °C	Polystyrene (10 µm)	Purchased	1.6×108 (±0.2) parti- cle per L of solvent	70 mm length, 30 mm diam- eter	> 95%		Laboratory	Trapped & entangled (pore reten- tion)

Table 1 (contin	(pan									
Author	Feedstock/ modification	Pyrolysis temp	Polymer	Purchased/lab- oratory aged/ naturally aged polymer	MNP conc/volume	Adsorbent dosage	Adsorbent capacity/removal efficiency	Time	Laboratory study/field study	Removal mechanism(s)
Wang et al. (2021)	Sawdust, Mg/ Zn modified Magnetic	550 °C	Polystyrene (1 µm)	Purchased	100 mg/mL, 10 mL	10 mg	magnetic biochar 94.81%, Mg modified mag- netic biochar 98.75%, and Zn modified magnetic biochar 99.46%	5 h	Laboratory	Electrostatic interaction and chemical bond- ing interaction
Wang et al. (2022)	Peanut shells, magnetised	500 °C	Fluorescent polystyrene (1 µm)	Purchased	2 mg/L	0.5% of col- umn	92.36%		Laboratory	
Wu et al. (2023)	Magnetised rice straw	500 °C	Polystyrene (300 nm)	Purchased	1–100 mg/L	0.5 g/L	90.96%	5–180 min	Laboratory	Electrostatic attraction, sur- face complexa- tion, hydrogen bonding and π - π interac- tions
Zhu et al. (2022)	Functionalised corncob	650 °C	Polystyrene (100 nm)	Purchased	5, 10, 15, 20, 30, 40, and 50 mg/g	0.1, 0.2, 0.4, 0.6, 0.8, and 1 g/L	56.02 mg/g	24 h	Laboratory	

also recognised that the shape and surface properties of the microplastics in aquatic environments are likely to differ from the microspheres used in this column work, fibres have been demonstrated to be the most prevalent NMP shape as opposed to perfectly spherical plastics (Liu et al. 2019a, b). The influence of NMP shape on removal points to the importance of more robust NMP characterisation in such studies and the importance of using real-world microplastics.

Modified Biochar to Enhance Remediation

Whilst several studies review the efficacy of pristine biochar as a tool to remove NMPs, the majority of reports review the potential of modified biochar as a remediation tool (Table 1). Modifications that are deployed include activating biochar (e.g. through steam processes), magnetising biochar and oxidising biochar. These modifications are a further lever to enhance or change the structure and characteristics of pristine biochar, to be used alongside the previously discussed levers of feedstock and pyrolysis, to remove NMPs more effectively from aqueous environments.

Steam activation was a technique adopted by Siipola et al. (2020) to investigate the effects of increasing surface area and pore size of pine and spruce bark biochar. It has been seen to be effective in improving the sorption of organic and inorganic contaminants such as sulfamethazine, ibuprofen, and lead, in part as a result in the effect on surface morphology (Rajapaksha et al. 2015; Chakraborty et al. 2019; Kwak et al. 2019). Post steam activation pine bark had a relatively low surface area but a higher proportion of macro pores than spruce bark leading to superior microplastic removal by steam activated pine bark biochar (Siipola et al. 2020). This not only illustrates the importance once more of feedstock to the removal of microplastics but also the importance of pore size over surface area.

The most prevalent modification of biochar in the sorption of NMPs is the incorporation of metals into the biochar matrix, commonly known as magnetisation. This takes the form of loading the biochar with iron, which is sometimes combined with other metal such as magnesium or zinc (Wang et al. 2021; Wu et al. 2023). In terms of sorption the magnetising process is undertaken, in part, to move the charge of the biochar to become less negative and more positive, it also has the benefit of enabling the loaded biochar to be easily removed from water (Fig. 8). This change in charge is desirable to reduce the effect of electrostatic repulsion and increase electrostatic attraction of NMPs with a negative charge (e.g. as a result of the presence of functional groups on the plastic surface such as carboxyl). It also enables complexation between magnetised biochar and NMPs to take place and increases the surface roughness of the biochar improving the trapping of the NMPs by the biochar.



Fig. 8 The separation of magnetic biochar from solution. All three magnetic biochars were separated by magnet in three minutes under the action of a magnetic field which may facilitate separation and recovery of biochar post contaminant sorption. (Shi et al. 2023a, b)

There are five key methods of magnetising biochar (Yi et al. 2020): impregnation pyrolysis, co-precipitation, reductive co-deposition, hydrothermal carbonisation and 'other' which included the use of ball milling. Impregnation (Wang et al. 2021; Wu et al. 2023), co-precipitation (Li et al. 2023a, b; Tong et al. 2020a, b; Wang et al. 2022) and ball milling (Shi et al. 2023a) to date are the methods most commonly used in the magnetising of biochar to remove NMPs.

Magnetising biochar has the effect of moving the surface charge of the media from a more negative charge to a more positive charge. The difference between the charge of the pristine and magnetised biochar was illustrated by Wu et al. (2023) with the magnetised biochar still showing a positive charge at a solution pH of 6 as opposed to the pristine biochar which had a charge of ~ -20 mV at a pH of 6. As a result, one of the key benefits of magnetising biochar is the reduced importance of solution pH in sorption of NMPs (Singh et al. 2021); this has the effect of broadening the range of environmental pH that the magnetised biochar will be effective in. Singh et al. (2021) determined that changes in solution pH had minimal impact on NP removal once the material was magnetised. This indicated that mechanisms other than electrostatic attraction/repulsion were also relevant to sorption processes.

Spectroscopic analysis undertaken by Singh et al. (2021) pointed to the role of complexation of NPs with hydroxyl and carboxylate groups and π - π conjugation in the sorption. Post sorption, Wang et al. (2022) also cited the importance of the complexation reaction of the oxygen-containing functional groups on the surface of the biochar and resultant

increase in the removal of microplastics. The presence of the carboxyl group on aged plastics was seen by Li et al. (2023a, b) prior to sorption but these groups disappeared after sorption which was also argued to demonstrate complexation.

As with pristine biochar, surface roughness has been seen to be of importance in NMP removal. An increase in surface roughness as a result of the magnetising process was highlighted as a factor in the breakthrough percentage of 0.02 μ m NP particles decreasing from 68.5 to 0.5% with SEM images showing that the magnetisation process led to a change in surface morphology (Tong et al. 2020a, b). By calculating and comparing the DLVO interaction between plastic particles with pristine biochar and plastic particles with magnetised biochar Tong et al. (2020a, b) demonstrated that

Fig. 9 SEM images of BC (a) and metal impregnated biochar (MBC, Mg-MBC, and Zn-MBC) before and after MPs adsorption (b)–(g). The surface of Mg-MBC and Zn-MBC are much rougher than that of MBC, signifying higher trapping efficiency, which may lead to the adsorption equilibrium in a shorter time (Wang et al. 2021)



roughness significantly decreased the values of the energy barrier between plastics and the porous media resulting in greater deposition of plastic particles on the rougher surface. Similarly, Wang et al. (2022) contrasted the smooth tubular structure of the pristine biochar with the magnetised biochar that was rougher as a result of the formation of Fe₃O₄ surface crystals which was confirmed by surface nano-surface analysis as well as SEM (Fig. 9). This change in surface morphology was a factor in a Fe₃O₄ biochar/sand mix retaining 40.96% of polystyrene microplastics as opposed to a pristine biochar/sand mix only retaining 16.47% of polystyrene microplastics.

The effects of oxidising pristine biochar have also been studied with 5% of HNO_3/H_2SO_4 (Magid et al. 2021). Although this can be considered a modification, the oxidation was undertaken to simulate the long-term oxidative aging of biochar in the environment. Biochar ages naturally in the environment over time with processes such as oxidation significantly changing the characteristics of the biochar, e.g. the prevalence of oxygenated functional groups, with associated effects on biochar sorption of contaminants (Cross and Sohi 2013; de la Rosa et al. 2018). Oxidising biochar for the sorption of metals such as cadmium has been studied previously (Leyva-Ramos et al. 2005) using similar techniques deployed by Magid et al. (2021). During the oxidation process an increase in the proportion of O and N was demonstrated alongside a decrease in the proportion of C and H mainly as a result of the increase in oxidised functional groups, specifically hydroxyl functional groups, on the surface of the biochar. These hydroxyl functional groups were seen to play an essential role in the sorption of the NPs due to hydrogen bonding, which in turn was seen to diminish the importance of hydrophobic interaction.

Influence of Environmental Parameters on Biochar and Plastic Characteristics

The environmental parameters of a system heavily influence the efficacy of the removal of NMPs by biochar. Parameters such as pH, ionic strength, competitive ions, temperature, Natural organic matter (NOM), and flow are factors that should be considered to understand if biochar is a viable option to remediate NMPs in any given environmental setting.

The importance of solution pH in relation to zeta potential and PZC with the attendant effect on electrostatic repulsion/attraction is a fundamental part of the efficacy of biochar, particularly pristine biochar, in the removal NMPs from water. The effect of solution pH was recognised as a critical parameter to investigate the environmental applicability of biochar by Ganie et al. (2021). Their study assessed the sorption capacity of biochar at various pH and saw that biochar pyrolysed at 750 °C can remove NPs effectively at a solution pH < 7.5. Beyond this point a higher negative net charge is acquired by the sorbent and electrostatic repulsion negates removal. Magid et al. (2021), reviewed the effect of pH on NMP removal by varying the solution pH from 3 to 10. Maximum sorption by pristine biochar was seen at a pH of 5 with pH values lower than that leading to reduced protonation and therefore reduced electrostatic repulsion. Magnetisation of biochar has been seen to reduce the influence of environmental pH on sorption capacity by Shi et al. (2023a, b) and Li et al. (2023a, b) who did not see a reduction in adsorption until environmental pH reached~7, higher than a pH of ~5 where adsorption has been seen to decrease for pristine biochar (Ganie et al. 2021; Magid et al. 2021). Furthermore, when magnetised, drastic changes in zeta potential as a result of changing environmental pH have been shown to not be reflected in NMP sorption (Singh et al. 2021; Shi et al. 2023a).

It is the change in surface charge as a result of environmental pH which makes pH such an important factor in NMP removal. However, the charge of the biochar has to be considered in conjunction with the charge of the NMP to fully understand the effect of environmental pH. Magid et al. (2021) found the least effective pH value for polystyrene NP removal was ten due to the strength of the negative surface charge increasing on both the biochar and the NP causing repulsion. This finding highlights the obvious importance of the characteristics of plastic in terms of remediating plastic polluted waters. The majority of papers focus on the removal of neutral or negatively charged plastics where biochar is tailored, through pyrolysis temperatures and modifications, to target these NMPs. However, not all plastics are negatively charged. NMPs with varying charges have rarely been studied in unison, however Singh et al. (2021) undertook such a study of NMPs one of which was positively charged due to the presence of amine groups. The importance of the characteristics of NMP found and aged in natural environments is emphasized by Li et al. (2023a, b) and Shi et al. (2023a, b) who both simulate naturally 'aged' plastics by subjecting the pristine plastic to either a potassium persulfate $(K_2S_2O_8)$ solution or UV radiation. In both, laboratory synthesis of natural aging resulted in the forming of negatively charged oxygenated functional groups, such as carboxyl groups. Shi et al. (2023a, b) also evidenced an increase in the intensity of O/C post aging favouring hydrophilic interactions. Subjecting the microplastics to a potassium persulfate $(K_2S_2O_8)$ solution also led to erosion of the microplastics with visible signs of crack on the plastic surface and the creation of smaller particles of $< 1 \mu m$ due to chain scission (2023).

Ionic strength is a further environmental parameter that should be addressed in studies; as with environmental pH, ionic strength can affect key removal mechanisms and material characteristics such as zeta potential, plastic particle size and can cause competition for sorption sites (Li et al. 2023a, b; Tong et al. 2020a, b). Tong et al. (2020a, b) recognised that the increase of NaCl in solution decreased the negative zeta potential of nano and micro plastic particles sized between 0.002 and 2 µm. In turn this reduced DLVO interactions between NMPs and sorbent and increasing removal. This reduction in electrostatic repulsion under high ionic strength conditions (CaCl₂) was seen by Li et al. (2023a, b) to cause aggregation of microplastics with a size ranging from < 48 to 180 µm. The aggregation of these larger microplastics was seen to reduce removal as a result of steric hinderance. Competition for sorption sites between Ca²⁺ and microplastics was also posed as a possible reason for reduced plastic removal. These contrasting results further demonstrate the importance of plastic characteristics to understanding sorption mechanisms and the potential effect on sorption of environmental parameters. Ionic strength was also highlighted by Singh et al. (2021) as an important environmental parameter for sorption with a variety of real environmental samples namely freshwater, groundwater and tap water. The size and charge of the microplastics that Singh studied were 1000 nm carboxyl (negatively charged), 1000 nm amine (positively charged), and 30 nm carboxyl (negatively charged). For each of these NMPs an increase in ionic strength was seen to lead to aggregation and increased removal due to aggregates binding with available sites on the biochar with groundwater having the highest ionic strength and as a result the highest sorption.

Water flow in an environmental setting is also a consideration that studies rarely address but needs to be taken into account in the sorption of NMPs by biochar. Tong et al. (2020a, b) highlighted the effect of a rainstorm and attendant increase in flow would have on ionic strength with a dilution of the concentrations of ions that had been beneficial to sorption. This effect of an increase in flow due to rainstorms was also considered in terms of the potential release of biochar and plastic particles in a sand / biochar mix. Less than 1% of magnetised biochar was flushed out of the columns indicating that they are relatively stable even in simulated high environmental flow. In these high flows there was a release of the smallest NP studied $(0.2 \ \mu m)$ but magnetising the biochar reduced loss from 14.6% for a pristine sand/biochar mix to 7.5% for a magnetised biochar/sand mix. Flow was also a variable that Hseih et al. (2022) considered to effect sorption of microplastics by pristine biochar. An increase in flow from 0.37 to 14.66 mL/min saw microplastic retention double in columns with biochar but reduce in bare sand columns. However, Subair et al. (2024) found that an increase in flow from 3 to 9 mL/min moved removal efficiency of polystyrene microplastics between 75 and 150 µm by banana peel biochar from 100 to 91.53% due to the washing out of MPs immobilized by the biochar at higher flow rates. Differences in findings with such an important parameter, particularly in a field that is in its infancy, demonstrate the need for additional studies isolating this variable.

For some sorbents, such as cellulose aerogel or Fe-kaolin, reaction temperature can affect the diffusion rate of NMPs and their sorption capacity (Ali et al. 2023). However, where temperature has been reported as a variable in sorption by biochar, studies are not in agreement. In their study, using pristine unmodified biochar, Ganie et al. (2021) obtained maximum sorption capacities from the Langmuir isotherm model of 44.9 mg/g, 32.6 mg/g and 26.7 mg/g at 25 °C, 40 °C and 10 °C respectively. As temperatures increased the Gibbs free energy became more negative/enhanced spontaneity leading to enhanced removal. Using both Langmuir and Freundlich isotherms Wu et al. (2023) argued that the amount of adsorption increased with increasing temperature. This was attributed to an increase in reaction temperature leading to a rise in the proportion of activated molecules and diffusion rate of microplastics enabling their binding with sorption sites. However, when Shi et al. (2023a, b) investigated the influence of temperature on sorption at 15 °C, 25 °C and 35 °C using magnetised biochar the contribution of the different temperatures was deemed to be negligible. Similarly, Singh et al. (2021) deemed the contribution of temperature to be insignificant. Again, contradictions between studies such as this, particularly in a field that is in its infancy, necessitate further work in this area.

NOM also has the potential to affect the sorption of NMPs by biochar. NOM is a ubiquitous mix of organic compounds formed by the degradation of plant matter; when the fraction size of NOM enables it to pass through a 0.45 µm filter it is classified as dissolved organic matter (DOM) of which > 50% of mass is dissolved organic carbon (DOC) and 50-90% of the chemical make-up of DOM are humic substances (Al-Reasi et al. 2013). NOM can influence the removal performance of adsorbents as it can attach to either the surface of the sorbent or NMP (Ali et al. 2023). As a result of the ability of NOM to attach to the surfaces of sorbent and sorbate through electrostatic, hydrophobic, and π - π interactions the ability of biochar to remove plastics is reduced as NOM competes directly for sorption sites (Wang et al. 2021). The presence of DOC was also reported to be detrimental to the sorption of microplastics by biochar as a result of steric hindrances; aligned to this the presence of humic acid resulted in an abrupt fall in removal percentage (Ganie et al. 2021). The increase in humic acid led to an increase in negative zeta potential with the resultant increase in electrostatic repulsion and fall in sorption. Even at minor concentrations of humic acid (1 mg/L) the removal percentage of plastics was reduced by 55%. Singh et al. (2021) saw a similar increase in negative zeta potential as a result of DOM covering both the biochar and nano plastic through complexation to produce negatively charged surfaces. The

significance of this reduction in sorption was also to be different as a result of plastic type and charge.

Future Direction

Biochar has been established as a material capable of sequestering carbon, enhancing soil fertility and sorbing organic and inorganic contaminants from water. It also has the potential to remove NMPs from water, however, there is still the need to improve understanding of the interaction of biochar with NMPs in a natural setting focusing on key environmental parameters.

The importance and influence of environmental parameters on the efficacy of biochar as a sorbent for NMPs is apparent. More time needs to be spent on a blended approach between isolating and studying key parameters (such as temperature, flow and NOM) in a laboratory setting followed by field studies, which are currently scarce if not nonexistent. Current work that focuses heavily on laboratory studies is a key building block to advance the understanding of the interactions between biochar and NMPs which is in its infancy. However, these findings do not directly translate to the deployment of biochar in field conditions under a variety of environmental parameters. Work needs to be undertaken to systematically investigate the interplay of influential environmental parameters and study them in the presence of contaminants such as metals, pharmaceuticals, and hydrocarbons as well as NMPs. This will help the understanding of which environments are suitable for the deployment of biochar and what modifications could potentially be undertaken to widen the range of environments that deployment would be effective in. Field studies would also help tease out other barriers to effective use at scale such as DOM leading to "caking" resulting in the biochar surface pores and functional sites being blocked. An overlay of mechanisms and limiting factors of biochar over potential environmental systems where biochar could be deployed to validate viability is a critical step to successful deployment at scale.

For the progression from laboratory studies to field studies to be successful there must also be greater attention paid to the importance not just of the biochar but the interaction between biochar and naturally aged plastic subjected to natural parameters rather than laboratory made, pristine, spherical, functionalised plastics. The effects of natural aging on NMP morphology and chemical structure including size, shape and charge have been highlighted, as has the effect on these changes on other remediation techniques such as the use of membrane barriers (Hidalgo-Ruz et al. 2012; Helm 2017); studies incorporating NMP characteristics such as these for other remediation techniques can be used as a template to look toward multidisciplinary learning and progress the understanding of biochar as a remediator of plastics from water. Whilst these NMP characteristics are essential to the efficacy of biochar in the removal of NMPs, very few studies use either laboratory enhanced "naturally" aged plastics or plastics sourced from natural waters. This has the consequence of oversimplifying removal mechanisms. The shape, size and texture of biochar pores and plastics are recognised as being critical to interactions yet are rarely comprehensively studied as a result of the use of pristine, uniformly sized and shaped plastics in studies. In addition to plastic size, shape, and texture the added complexities of the interaction of plastics with other aqueous contaminants such as metals, microorganisms or toxins are not regularly considered. The combination of these contaminants is likely to influence removal mechanisms and the efficacy of biochar. Studies that use naturally aged plastics in a multi-contaminated system to review the true removal capability of biochar are required.

Finally, the regeneration of biochar and plastics needs to be investigated to ensure that the sustainable, circular economy benefits of biochar are realised. Where regeneration is considered at this stage in the study of the removal of NMPs by biochar, most work focuses on methods that are destructive to the plastics that have been removed from water. Thermal regeneration and chemical regeneration are the primary avenues cited whereby the plastic is either incinerated or deteriorates rendering the plastic unrecyclable, potentially producing gas pollutants or chemical waste. Further thought needs to be given to regeneration processes that allow both the biochar and plastic to be reused.

Conclusions

This paper highlights the potential for biochar to be used as a tool to remediate waterways effected by the increase in volume and variety of NMPs in environmental settings. The review of the literature outlined both the increasingly ubiquitous nature of NMPs seen environmentally, the sources of these materials and the potential hazards to human health and aqueous environments. In summary, we argue that although the study of biochar to remove NMPs is in its infancy, biochar is a viable option to treat NMP contaminated waterways. Pristine biochar can be used to remove NMPs from water, the efficacy of which is driven by feedstock and pyrolysis temperature. Feedstock and pyrolysis temperature drive (i) biochar zeta potential, which is an essential characteristic to consider when trying to negate the potential for electrostatic repulsion dependent on biochar charge, NMP charge and environmental pH (ii) surface area and pore size, which are critical characteristics of biochar for the removal of NMPs (iii) the texture of the biochar surface with woody feedstocks producing irregular, rough structures which are more effective at trapping microplastics. Biochar can also be modified to improve the efficacy of NMP removal from water. The primary modification that has been studied is magnetisation which takes the form of loading the biochar with iron, sometimes combined with other metals such as magnesium or zinc. This modification increases complexation with NMPs, makes the surface of the biochar rougher (with attendant improved NMP capture), but, most importantly, allows biochar to be deployed in a wider range of environmental pH due to a decrease in biochar negative zeta potential. Future studies also need to consider the environmental parameters of a system which heavily influence the efficacy of the removal of NMPs by biochar. Parameters such as pH, ionic strength, competitive ions, temperature, NOM and flow are factors that should be included in studies to determine whether biochar is a viable option to remediate NMPs in any given environmental setting. More time needs to be spent on a blended approach between isolating and studying key parameters (such as temperature, flow and NOM) in a laboratory setting followed by field studies, which are currently scarce if not nonexistent. For the progression from laboratory studies to field studies to be successful there must also be greater attention paid to the importance not just of the biochar but the interaction between biochar and naturally aged plastic subjected to natural parameters rather than laboratory made, pristine, spherical, functionalised plastics.

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Declarations

Conflict of interests The authors have no relevant financial or non-financial interests to disclose.

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