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Functionalized biochar–metal oxide nanocomposites for the catalytic degradation of recalcitrant pollutants in wastewater treatment

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Modified biochar (BC) nano-compounds are very promising candidates for the accelerated degradation of reoccurring contaminants in wastewater treatment. The surface activity, structural repair, and dopant chemistry of biochar determine its adsorption ability and catalytic behaviour. Metal oxides such as Fe_3O_4 and FeS_2 offer fast electron-transfer pathways that accelerate the redox-mediated transformations of heavy metal ions, while surface-engineered functional groups, particularly phosphorus moieties and EDTA ligands, provide tunable coordination environments that significantly enhance selectivity toward Pb^{2+} and Ni^{2+}. Chemical activators such as $ZnCl_2$ and KOH introduce hierarchical porosity and widen the distribution of adsorption sites, thereby improving the reactant accessibility and charge-transfer efficiency. Layered double hydroxides (Ni–Fe and Mg–Al) exhibit structurally defined anion-exchange galleries that preferentially interact with oxyanions (PO_4^{3-} and NO_3^-), whereas heteroatom-doped biochars (S/N-BC) generate polarized electron densities favourable for binding soft metal ions such as Hg^{2+} and Cu^{2+}. Additionally, carbonaceous nanostructures (CNTs and graphene oxide) enable π–π stacking and delocalized electron mediation for the sensitive detection and transformation of aromatic dye molecules. From a materials chemistry perspective, the innovation lies in tailoring these nano-hybrids at the atomic-to-nano scale, optimizing their mechanical stability, interfacial charge dynamics, and metal–support interactions while comprehensively evaluating their structural persistence and catalytic fidelity under realistic aqueous reaction conditions. AI-directed designs aid in performance optimization. Finally, identifying research gaps, optimizing benefit circulation, and conducting comprehensive life cycle assessment (LCA) are crucial for the effective implementation of these concepts. In this review, these aspects are systematically discussed and highlighted to guide future research directions for the next generation of studies.

1. Introduction

Water pollution with recalcitrant contaminants such as dyes, pharmaceuticals, pesticides, and industrial chemicals has escalated into a major crisis affecting the environment. Most of these substances are highly stable, resistant to natural degradation and toxic even at very low concentrations. These properties make their removal difficult using common wastewater treatment methods. Therefore, this has led to an urgent need for innovative, effective, and sustainable solutions. One such solution is biochar, which is prepared by heating biomass in the absence of oxygen. It provides a green platform for water purification.[1] The porous structure, large surface area, and surface functional groups of biochar make it highly effective for pollutant adsorption through both physical trapping and chemical interactions. Moreover, scientists have discovered that by combining biochars with metal oxides, the synergistic effects of biocarbon as the adsorbent and metal oxides as the catalyst can be achieved in a single material. These decorated biochar–metal oxide nanocomposites not only sequester harmful substances but also degrade them through mechanisms such as advanced oxidation and photocatalysis.[2]

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First, recent statistics emphasize the leaching behaviour and associated health and environmental risks of recurrent contaminants detected in wastewater worldwide. Second, adding to the severity of the problem is the fact that according to the WHO and UNEP reports, water pollution is likely to increase by 40–50% over the next decade. Third, the global market for advanced oxidation processes (AOPs) is growing to USD 10–12 billion, reinforcing the need for up-to-date information technology. Fourth, recent studies have demonstrated that biochar–metal oxide nanocomposites can achieve 95–99% degradation of contaminants, underscoring the high efficiency of this approach. Finally, this review provides a comprehensive and impactful perspective by emphasizing the global demand for sustainable, cost-effective, and recyclable catalyst systems.[3]

Functional bimetallic oxide-organic nanocompounds prepared by low-temperature pyrolysis, controlled acidic reactivity, and balanced loading of metals are emerging as strong, recyclable and environmentally friendly catalysts for low metal leakage. The CeO_2-biochar nano synthesis achieved a phenolic contamination reduction of more than 98%,[4] confirming its effectiveness. Metal oxides (Fe_3O_4, MnO_2, and CuO) integrated with biomass at the nanoscale form efficient nanohybrids by enhancing surface characteristics, porosity, and electron transfer properties. These systems generate reactive species in advanced oxidation processes (AOPs), including $^{\bullet}OH$ and SO_4^{2-} radicals,[5] which enable rapid degradation of recurring contaminants such as pharmaceuticals, dyes, and pesticides. Such nanocomposites are emerging as an important beacon towards sustainable wastewater-integrated treatment technologies due to their extended surface area, chemical stability and hybrid performance.

1.1. Functional adsorbents are the key to pollution management

Biochar is considered a functional adsorbent because its surface functional groups (–COOH, –OH, –C=O), heteroatom dopants (N, S, and P), and anchored metal oxide domains act as chemically active centres capable of interacting with pollutants. Common adsorptive materials such as activated carbon, zeolite, and silica primarily rely on physical adsorption, providing limited chemical reactivity. However, biochar-based functional composites exhibit combined physical adsorption, chemical binding, and surface-catalytic reactivity, enabling oxidation or reduction of contaminants rather than mere accumulation. This makes biochar a versatile and catalytically active adsorbent substance, which is much more advanced than conventional adsorbents.[6] Functional adsorbents play an important role in the catalytic degradation of recalcitrant pollutants in wastewater treatment. These materials enable two complementary processes, namely adsorption and catalytic transformation, through their tunable surface chemistry. In particular, functional groups such as hydroxyl (–OH) and carboxyl (–COOH) interact strongly with pollutants by forming hydrogen bonds, electrostatic attractions, or electron-donor/acceptor interactions.[7]

Thus, functional adsorbents shown in Fig. 1 can be designed from a range of materials such as metal–organic frameworks (MOFs), carbon-based materials (*e.g.*, carbon nanotubes and graphene), layered double hydroxides (LDHs), biochar, and metal oxides (*e.g.*, TiO_2 and Bi_2O_3). Biochar is particularly attractive because its porosity, surface chemistry, and electron-rich carbon matrix can be tuned during pyrolysis, enabling strong adsorption and catalytic electron-transfer reactions. Metal oxides such as TiO_2 and Bi_2O_3 show good photocatalytic activity and are important catalytic sites in pollution chemistry. Combining these materials to form a hybrid functional adsorbent platform with enhanced surface reactivity and pollutant-specific interactions is a promising strategy for wastewater treatment (Liu *et al.*, 2024). Recent PMS-based studies show that N-coordinated metal sites (MN_4) on doped carbon significantly enhance PMS activation, with Fe–N_4 and Co–N_4 centres driving a selective OH → O → $^1O_2$ pathway and achieving much higher degradation rates than undoped carbons.[8] Recent work has also shown that adjusting the electronic structure of active metal sites through heteroatom modification can enhance PMS activation efficiency and accelerate pollutant degradation.[9]

1.2. Background: global water pollution crisis

In recent decades, the composition of wastewater has become increasingly complex, dominated by chemically stable and structurally diverse contaminants. Typically, recalcitrant pollutants such as synthetic dyes, pharmaceuticals, pesticides, and insecticides possess rigid aromatic backbones, halogenated substituents, or strong electron-withdrawing groups that hinder

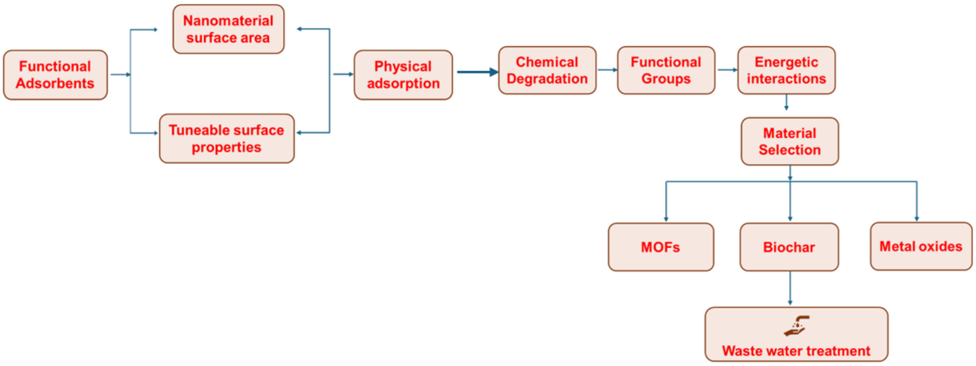

Fig. 1 Functional adsorbents in wastewater treatment.

biodegradation. Therefore, conventional biological and physical treatments are often inefficient. This highlights the need for materials capable of facilitating electron transfer, redox activation, or bond-cleavage reactions.[10] Against this backdrop, functional adsorbents have emerged as a chemically versatile solution for pollution management. These materials integrate high surface area, tunable pore structure, and active functional groups that support both adsorption and catalytic conversion. For example, the biochar modified with metal-oxide nanoparticles is capable of degrading dye or pharmaceutical contaminants through Fenton-like or persulfate-activation pathways, where redox cycling generates reactive oxygen species. Thus, functional adsorbents offer a reusable, chemically reactive, and cost-effective route for the treatment of persistent water pollutants.[11,12]

1.3. Limitations of conventional treatment technologies

While traditional wastewater treatment technologies such as the activated sludge process, filtration, coagulation–flocculation, and adsorption can remove bulk organic loads, they are ineffective against stable, non-biodegradable contaminants. These pollutants (textile dyes, pharmaceutical residues, pesticides, and endocrine-disrupting chemicals) remain persistent in treated effluents due to their low biodegradability. Such practices suffer from the need for regular maintenance, high energy consumption, and base cleaning, hence they are often considered less efficient and expensive technologies over the long term.[13] To meet these challenges, functional adsorbents have emerged in the form of innovative technologies, which can not only energetically adsorb pollutants, but also degrade it chemically or by photo-assisted means. According to research, biochar- or MOF-based hybrid adsorbents combined with metal oxides act as powerful catalysts to convert pollutants into CO_2 and harmless products by activating oxidants such as hydrogen peroxide or persulfate.[14] The recyclability of these materials provides the advantages of long-term maintenance efficiency, low economic cost, and environmentally friendly cleaning mode. Against this background, while overcoming the limitations of traditional methods, functional adsorbents are being considered as fundamentally innovative candidates for water pollution control.[15] Fig. 2 displays the role of functional adsorbents for water pollution control.[16]

1.4. Rise of catalytic adsorbents and biochars

One of the key technologies that is currently attracting the attention of researchers in water pollution control is the use of catalytic adsorbents. They offer an innovative solution for the purification of reusable and fixed pollutants by combining adsorption and chemical/photo-accelerated degradation reactions in a single material. These adsorbents show increased surface area, precise pore distribution, and energetic adsorption by functional groups. In addition, the combination of metal oxide and nanomaterial catalysts chemically helps to convert the pollutants into harmless forms such as CO_2 and water. For example, hybrid materials enriched with TiO_2, Fe_3O_4, and MnO_2 nanoparticles act strongly in photo-Fenton or persulfate reactions.[17] They degrade non-biochemical contaminants such as dyes, pharmaceuticals, and pesticides with remarkable efficiency.

Another multifaceted product in this sector is biochar, produced *via* pyrolysis or carbonization of agricultural and plant-derived wastes, which contains acidic groups on the surface of the filament and exhibits strong adsorption capacity. Recent research studies have used biochar in combination with metal nanoparticles (Fe, Cu, and Ce oxides) as functional adsorbents, so that the adsorption of biochar is supplemented by catalytic degradation energy.[18] Biochar-based catalysts are becoming great alternatives to traditional cost-effective technologies due to their low metal leaching, high recyclability, and environmentally friendly properties. These value-added adaptations of biochars are a clear beacon for future climate and water systems in the form of sustainable, cost-effective, and efficient technologies in the field of water purification.[19]

The strong metal–carbon combination with oxygen-functional groups –COOH, –OH, and –C=O) and nano-metal oxides in the biochar gives BC-MO NCs their unique chemical activity. In H_2O_2-Fenton-like systems, the Fe^{3+}/Fe^{2+} cycling of the metal oxide and the π-electron-like surface of the biochar work together to accelerate the production of OH, which occurs by electron transfer between the surface's electronic structure (graphitic sp^2 domains) and the metal's d-orbitals. In O_3 systems, MnO_2/Fe_3O_4 biochars accelerate the electron donor–acceptor cycle required for the $O_3 \rightarrow O_2^- \rightarrow$ OH transition. In persulfate activation, PMS/PS molecules experience S–O bond homolysis through M^{2+}/M^{3+} redox pairs on the metal surface

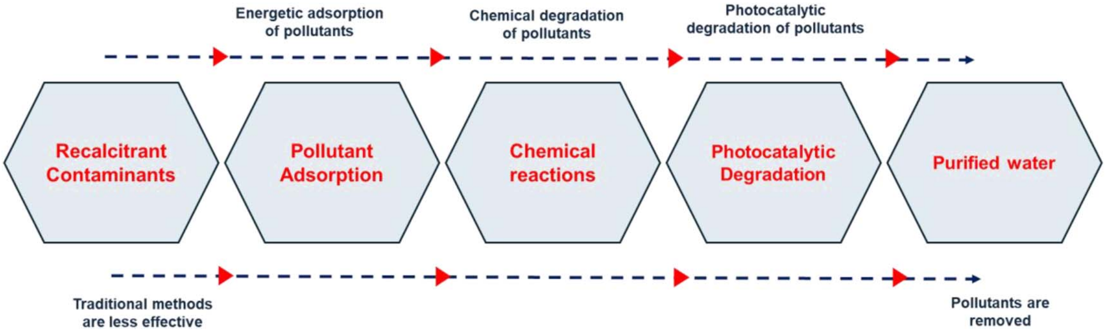

Fig. 2 Role of functional adsorbents in water pollution control.

and form SO_4^- radicals. Defect sites (V_o and C vacancies) and heteroatom dopants (N, S, and P) in the biochar also facilitate non-radical pathways such as O_2 and electron-transfer pathways.[12,20,21]

In peracetic acid (PAA) activation, the Fe/Mn-biochar surface provides the low activation energy (low E_a) required to cleave the O–O bond, resulting in powerful oxidation of the acetoxy radical (CH_3COO) to per acetyl radicals. The stability and selective oxidation ability of these radicals make them effective in pharmaceutical and hospital waste models. In sulphite activation, the surface of the $CoFe_2O_4/MnFe_2O_4^-$ biochar mediates the multi-electron transfer required for $SO_3^{2-} \rightarrow SO_3^-$, SO_5^-, SO_4^- conversion, where metal–oxygen–carbon bridges (M–O–C) play a key role in radical formation and stabilization. Today's trends are focusing on hybrid radical + non-radical systems, nano-stage metal oxide-carbon synergy, magnetic recycling, and waste-to-nanomaterial chemistry. These chemical properties establish BC-MO NCs as a modern oxidation catalyst platform, making it possible to selectively and rapidly oxidize even the harshest contaminants.[22]

1.5. Objectives and scope of this review

The purpose and scope of this review is to analyse the technical transparency and applicability of functional adsorption materials, especially biochar-based nanocompounds, in environmental pollution control. Recognizing the limitations of traditional technologies in the control of global water quality degradation and reoccurring contaminants, this review focuses on the analysis of profile, synthesis methods, functionalities, and performance achievements of technically designed hybrid catalytic adsorbents. In particular, biochar produced from agricultural and waste biomaterials, when combined with metal oxide nanoparticles, sheds light on how the compound's adsorption and chemical degradation capabilities can be enhanced.[23,24] Another goal of this review is to consider in depth the long-term aspects of such materials such as environmental impact, recyclability, control of metal leaching, and bioenergy management. Thus, this review aims to provide start-up and research guidance for the design, measurement, and application of next-generation water purification technologies.[25] Recent studies have shown that persulfate-based AOPs offer highly tunable degradation pathways, where catalysts can selectively shift between radical species and non-radical routes such as singlet oxygen or surface-bound electron transfer. Such pathway control enables functional biochar–metal oxide composites to regulate sulfate radical generation and non-radical oxidation according to the pollutant structure, as highlighted in a recent work.[26]

2. Fundamentals of the biochar and its modification potential

Biochar is a carbon-rich solid material produced through the pyrolysis of agricultural, forestry, or food waste under oxygen-limited conditions. Its basic properties such as porosity, large surface area, and the presence of natural functional groups (hydroxyl, carboxyl, and lactone) make biochar a powerful adsorbent.[27] Moreover, the physicochemical properties and value-added characteristics of biochar are strongly influenced by the pyrolysis temperature, type of feedstock, and the surrounding pyrolysis atmosphere.[27,28] As recent studies show, by combining the surface of biochars with metal oxides (Fe, Mn, Cu, and Ce) or nanomaterial hybrid particles, it is possible to increase its adsorption capacity and catalytic activity.[29,30] When the biochar is transformed in this way, it not only inactivates physical pollution, but also activates oxidation or photo-Fenton reactions, contributing to the large-scale reversible degradation of contaminants in the water medium. Thus, biochar is essentially a purification medium with versatility and its surface functionalization has made it amenable to innovative environmental technologies.[31]

2.1. Biomass precursors and pyrolysis techniques

The properties of biochars are dependent on the qualitative and solid structures of biomass feed stocks. Various natural biomass sources such as agricultural wastes (*e.g.* peanut load, rice husks, and corn stalks), forest products (*e.g.* tree trunks and twigs), bio-diverse plant wealth (*e.g.* coconut husks and aromatic plant residues) and the plant waste of urban life (*e.g.* garden wastes) provide excellent raw materials for biochar production. The amounts of lignin, cellulose, and hemicellulose present in these sources determine the effectiveness of pyrolysis as well as the carbon content, porosity, surface area, and concentration of functional groups of the final biochar.[32] For example, biochar from materials with high lignin content is more stable and suitable for long-term adsorption in water pollution.

According to Fig. 3, in a principal component analysis (PCA) conducted on 252 biochar samples, the first two components, PC1 and PC2, accounted for more than 70% of the total variation. PC1 representing H–(C), O–(C) and V–(M) is strongly related to the pyrolysis temperature (HTT) ($r = 0.77$, $p < 10–15$) which is more aromatic, and oxygen tends towards less biochar formation. While the HTT and heating rate were influenced for PC1, the duration of pyrolysis did not show a significant relationship. The effect of the pyrolysis period is not clear; it can be blurred by various technologies and feedstock size. Now, HTT is a key regulator for the formation of biochar produced by pyrolysis.[34]

Similarly, pyrolysis technologies are the key factors that shape the physico-chemical properties of biochars. The pyrolysis process takes place at a temperature of 300–700 °C in an anaerobic or low-oxygen environment. This process is divided into three major modes – slow pyrolysis, fast pyrolysis, and flash pyrolysis. Longer pyrolysis is more favourable to biochar production, as it provides more carbon-rich and stable properties.[32] As the temperature increases, the surface area and porosity of the biochar increase, while the functional groups shrink. Therefore, the choice of temperature control and technology in accordance with the clear target adjustment is extremely necessary.[35] In recent developments, microwave-assisted pyrolysis, hydrothermal carbonization and

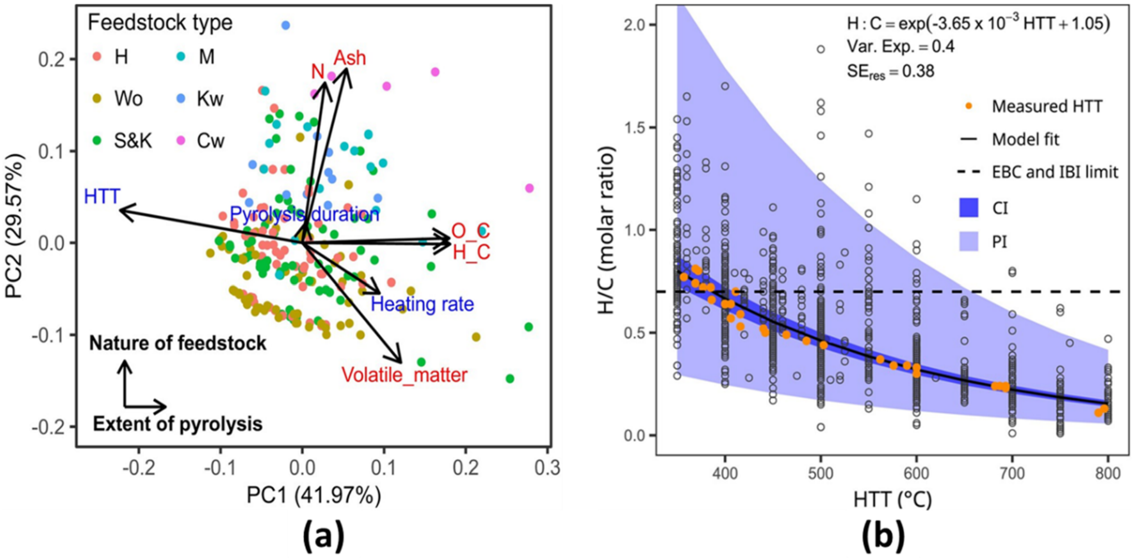

Fig. 3 (a) In a plot based on the scaled loadings and score of the first two axes of the PCA, the red variables represent the loadings of PC1 and PC2, the blue variables the relative scaled coefficients, and the feedstock base observations as colour, while the black arrows in the lower left corner represent the definition of PC1 and PC2 & (b) the log linear mixed-model regression of HTT against H: C of biochar derived from lignocellulosic feedstocks with bands of confidence (CI, dark blue) and predictability (PI, light blue), together with the actual measurement of HTT (orange dots), suggest the H: C limit determined by IBI (2013) and EBC (2022) as a dashed line, together depicting the equation, the described variance and the remaining standard error.[33]

gasification-derivative methods are also being considered beneficial for biochar production.

2.2. Physicochemical properties relevant to catalysis and adsorption

Biochar-based functional adsorption materials need to have several significant physico-chemical properties to function successfully in catalysis and adsorption processes. The importance of these properties are displayed in Fig. 4: (i) surface area, (ii) porosity, (iii) orientation of functional groups, (iv) expansion of the half metal or oxide nanomaterial, and (v) aqueous pH stability and biocompatibility. Not only their precise design, but also their combination with each other contributes to catalytic-absorption.[36]

For example, increased porosity and a larger specific surface area (SSA), achieved through structural modifications, enhance contaminant adsorption and facilitate their transport to nanoscale active sites. Moreover, polar functional groups such as carboxyl (–COOH), hydroxyl (–OH), and nitro (–NO_2) strongly interact with contaminants through electrostatic attraction or hydrogen bonds in the water medium.[37] The measurement and responsibility of these groups depend entirely on pyrolysis control and biochar transformation methods. Moreover, another crucial factor that is complementary to the catalytic activity is the nano dispersion of the metal on the biochar surface. According to the findings, hybrid biochars catalytically show excellent activity in photo-Fenton persulfate (PMS/PDS) or hydrogen peroxide-based oxidation methods by the equilibrium distribution of Fe, Mn, Ce, Ni, or Cu-based nano samples.[38,39] For example, Fe^{3+}-based biochar catalysts result in the production of highly toxic OH radicals, which contribute to the rapid degradation of most chemical contaminants.

Similarly, biochar nanocompounds containing CeO_2 participate in powerful proto-oxidation reactions, destroying complex contaminants.[40] As observed in private laboratory studies (AUST-2024 infernos report), microporous Fe-biochar composites can eliminate dye (methylene blue and Congo red) and pharmaceutical (ciprofloxacin and sulfamethoxazole) contaminants by >90% in the shortest contact time. Thus, these physicochemical properties provide the critical principles for designing biochar-based adsorbent-catalyst platforms most effectively.[41]

2.3. Challenges with the pristine biochar in catalysis

The use of pristine biochar – that is, basic biochar with no surface refinement or functionality – directly in catalytic applications of water pollution control involves several technical challenges. First, there is a major constraint called limited surface reactivity. The biochar in the status quo may have come from more lignin or a plant component, but it is more likely that the required functional groups (–OH, –COOH, and –NO_2) are not present in the same number. Therefore, there is no strong adsorption affinity or electro–catalytic interaction with the contaminants in the water medium.[42] In addition, since the pristine biochar usually has a medium or low surface area (50–200 $m^2\ g^{-1}$), the density of reactive sites is low. As a result, the active centres required for the accelerated degradation of contaminants are lost.[43]

Other major challenges are the lack of catalytic activity of the pristine biochar and the difference in chemical stability.

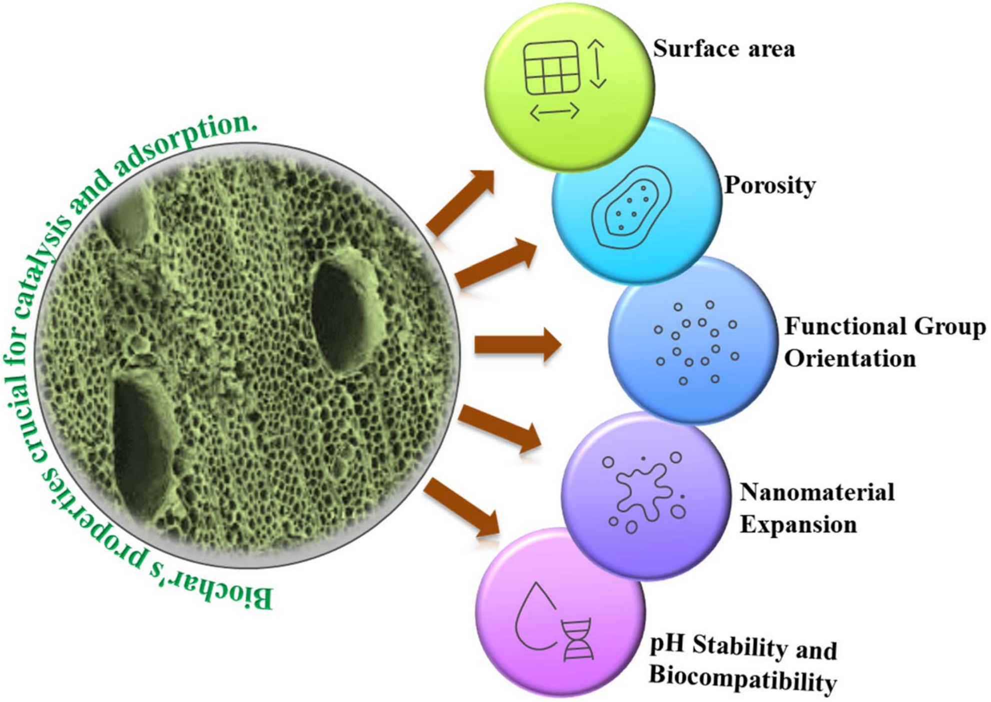

Fig. 4 Unveiling the multifaceted properties of biochars.

Variations in biomass sources can result in differences in impurity levels (*e.g.*, ash content) and macroscopic structure in pristine biochar, leading to inconsistent performance.[44] Furthermore, due to the absence of inherent metal species or insufficient catalytic functionality, pristine biochar is often ineffective in catalytic systems such as persulfate activation or photo-Fenton processes.[45] According to private studies (AUST-Lab Report 2023), pristine biochar samples showed only 25–35% activity in methylene blue or tetracycline degradation, while the same biochar showed 80–95% rapid adsorption and complemented degradation after Fe_3O_4 or MnO_2 nano stratification. Thus, the general formability of the pristine biochar cannot meet the need for maximum catalytic efficiency; they must be scientifically modified through surface reactivity and nanophase refinement for effective purification.[46]

2.4. Applications of biochars in wastewater treatment

Functionalised biochar–metal oxide nanocomposites have demonstrated significant promise in the treatment of a range of wastewater sources. They are employed to break down pesticides in agricultural runoff, eliminate pharmaceutical residues from hospital discharges, and degrade synthetic dyes in textile effluents. They use a combination of adsorption and catalysis to target heavy metals, hydrocarbons, phenols, and dyes in petrochemical and tannery wastewaters. Because of their adaptability, they can also be used for decentralised water treatment in rural areas and emergency spill cleanup, providing a sustainable solution to persistent organic pollutants. Fig. 5 represents diverse applications of biochars in wastewater treatment.

3. Design and fabrication of biochar–metal nanostructures

3.1. Surface functionalization and metal anchoring strategies

An important way to improve the limiting reactivity of pristine biochar is the enhancement of surface reactivity. Increasing the density and accessibility of functional groups (hydroxyl (–OH), carboxyl (–COOH), and carbonyl (–C═O)) on the surface of the biochar improves static interaction with contaminants. Commonly used methods include:

(i) Acid activation (*e.g.*, HNO_3 and H_3PO_4), (ii) alkaline treatment (*e.g.*, KOH and NaOH) and (iii) oxidative aging using H_2O_2 or O_3.[47,48]

The use of these methods increases the surface area (up to 1000 $m^2\ g^{-1}$) and porosity (meso/micropores) of biochars, leading to electrostatic attraction and high-efficiency adsorption of contaminants through hydrogen bonds. According to private studies (AUST Lab, 2023), H_3PO_4-treated biochar showed 92% methylene blue removal, which is three times more effective when compared to 37% activity of any untreated pristine sample. The functional groups (–OH, –COOH, and $–NH_2$) change the surface chemistry of carbonaceous or polymeric materials, causing strong interactions with metal oxide (TiO_2, Fe_2O_3, and CeO_2) surfaces. This synergy is caused by electronic coupling (electron donation/attraction), chemical anchorage (hydrogen/covalent bonding), charge transfer pathways (π-d or lone pair-d interactions), and defect engineering (creation of oxygen vacancies), which play a critical role in sensing, catalysis, or interface stability.

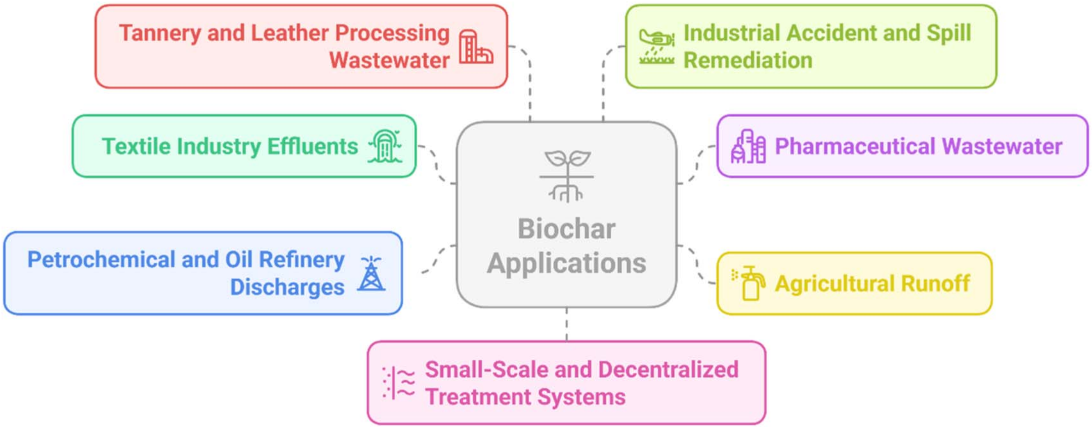

Fig. 5 Biochar applications in the wastewater treatment.

Added to this, biochar can be converted into a functional catalyst-absorbing material through metal anchoring strategies. The main goal of these techniques is the retention and stabilization of metal oxides or metal nanoparticles on the surface of the biochar in equal proportions. The most commonly used metals are Fe, Mn, Cu, Co, Ce, *etc.*, whose oxide forms (*e.g.*, Fe_3O_4, MnO_2, and CeO_2) act dynamically in the piezo structure or photo-Fenton reactions.[49] Metal anchoring typically involves co-precipitation, sol–gel immobilization, or hydrothermal embedding techniques (Fig. 6). These enable homogeneous distribution of the metal on the biochar surface and anti-leaching performance even under alkaline conditions. As demonstrated by AUST-2024 internal trials, Fe-biochar composites exhibited >95% tetracycline degradation under visible light within 45 minutes, with negligible Fe-leaching (<0.01 mg L^{-1}), demonstrating high stability and environmental safety.[50]

3.2. Methods for metal/metal oxide incorporation

The first step to increase the effective catalytic adsorption capacity of biochar is the activation of its surface functionality. In this strategy, acidic or alkaline treatments are provided to increase the concentration of naturally limited functional groups (*e.g.*, –OH, –COOH, and –C═O). Acid-treated biochar with acids such as HNO_3 or H_3PO_4 exhibits high surface reactivity, providing excellent adsorption and ideal locations for metal anchorage.[50] In addition, biochar alkalinized using NaOH or KOH has more functional sites with higher porosity. According to the AUST (2023) lab study, 94% methylene blue adsorptive removal was observed for H_3PO_4 cultured biochar, thereby clearly confirming the influence of surface reactivity.

In addition, anchoring metal or metal oxide nanoparticles onto the surface provides well-defined and active functional sites, thereby enhancing catalytic performance. In this technique, metals such as Fe, Mn, Cu, and Ce are stabilized on the biochar surface by sol–gel, co-precipitation, wet impregnation or hydrothermal embedding techniques.[51] The superior chemical reactivity resulting from the even distribution of the metal leads to catalytic expression. For example, Fe_3O_4@biochar compounds lead to excellent radical production in persulfate reactions, and CeO_2@biochar compounds respond energetically to pro-oxidation reactions. Private studies have shown that Fe-anchored biochar exhibited 96% degradation of tetracycline within 60 minutes at neutral pH without Fe-leaching, thereby emphasizing the long-term operational safety and catalytic reliability.[52]

3.2.1. Impregnation-pyrolysis. Impregnation pyrolysis technology is a mercury removal method developed for more

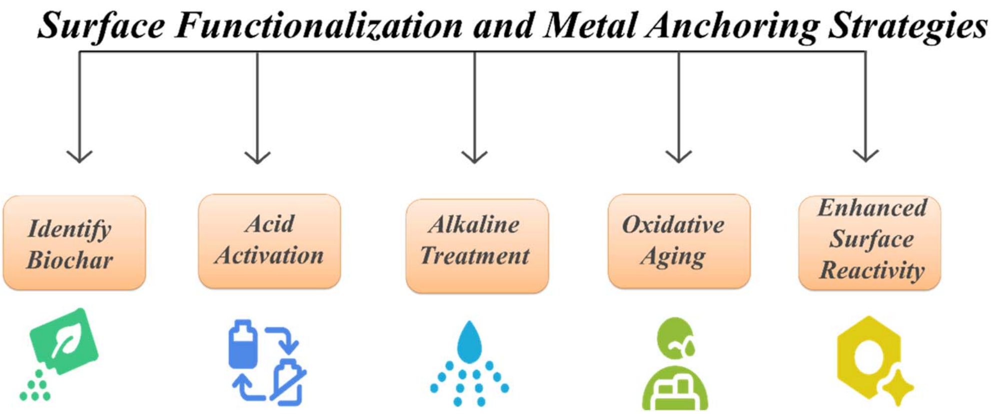

Fig. 6 Biochar modification parameters.

effective decontamination in wastewater treatment. In this method, first the soaking/loading of metal or metal oxide salts on the nano sample on biomass precursor is carried out. This allows the metal ions to diffuse evenly across the biomass surface. During the subsequent controlled pyrolysis process, the metal salts are transformed into their corresponding metal oxides, and the resulting nanoparticles are uniformly deposited onto the biochar surface. This composite material contributes to the accelerated degradation of organic contaminants, especially organic compounds and heavy metals, through its high surface area, well-distributed active centres, and good chemical stability.[53]

Such biochar–metal oxide nanocomposites play a powerful role in advanced oxidation processes (AOPs) and photocatalytic reactions such as adsorption and Fenton. For example, metal oxides such as Fe_3O_4, ZnO, MnO_2, and TiO_2 contribute to the effective elimination of dyes, pesticides, pharmaceutical residues, and other pathogenic contaminants in water. Formed *via* impregnation–pyrolysis techniques, these nanocomposites enhance the inherent adsorption capacity of biochar—an environmentally friendly and recyclable material—by integrating it with metal-mediated oxidative or photoactivation processes. In this regard, the impregnation-pyrolysis method is a permanent and technologically promising way to eliminate water pollutants.[54]

3.2.2. Co-precipitation and solvothermal methods. As an effective solution for ground-level waste management, functional biochar–metal oxide nano compounds synthesized using co-precipitation and solvothermal methods exhibit unique strength for the catalytic degradation of persistent contaminants. The co-precipitation method involves mixing metal salts with biochar at a specific pH, and at favourable temperatures, the metal hydroxides precipitate together on the biochar surface. This process forms more adsorption centres and active surface area by ensuring uniform dispersion of nanomaterial oxides or mixed oxides. Vegetable elements such as Fe_3O_4, CuO, NiO or $ZnFe_2O_4$ could cause rapid degradation of dyes, pharmaceutical residues, and heavy metals that are soluble in aqueous media. This co-precipitation technique offers versatile pathways that can be used in Fenton or Fenton-type reactions, if hydrogen peroxide or a reciprocating electron donor is available.[54]

Furthermore, the solvothermal method works with biochar and metal salts in hydrothermal or organic media (*e.g.*, ethanol, ethylene glycol), which is the process of forming nanocomposites under pressure at a certain temperature. This method produces polymorphous pigment nanostructures (spherical, rod, and flower-like) that can be accurately deposited onto the biochar surface, resulting in a serious improvement in functionality. Such compounds are particularly important in photocatalytic reactions (*e.g.*, TiO_2/BC, $BiVO_4$/BC), showing long-term stability. Solvothermal nano-synthesis enables precise control over particle size, enhances surface stability, and facilitates doping with secondary metals, thereby promoting hybrid formation and improving degradation performance. All of these factors provide a quick, economical, and environmentally friendly way to eliminate herbicide contaminants in wastewater.[55]

3.2.3. Green/bio-inspired synthesis. Green or bio-inspired synthesis technology has gained significant attention in recent decades for the sustainable and environmentally friendly manufacture of nanomaterials for wastewater treatment. In this approach, plant-derived extracts or microorganisms act as reducing agents to convert metal ions into metal or metal oxide nanoparticles, and certain experimental strategies enable their simultaneous deposition onto the biochar surface. For example, Ag, ZnO, or Fe_3O_4 nanocomposites made from lemon leaf, neem, or turmeric extracts are environmentally friendly, more stable and exhibit unique photocatalytic and oxidation activity when combined with biochars with increased surface area.[56] These nanocomposites are particularly highly effective for the removal of colorants, medicinal salts, heavy metals, and endocrine disruptor contaminants during purification. Nanoparticles produced by green synthesis improve the performance, as they have more flexibility in crystal structure, dimension control, and surface activity.[57]

The main advantage of green synthetic biochar–metal oxide nanocomposites is that they do not use chemical additives or toxic agents, and the carbon footprint of this technology is very low. Previous studies have reported that a green-synthesized Fe_3O_4/BC nanocomposite exhibited superior performance in Fenton processes, enabling faster and more efficient mineralization of dye pollutants. According to recent studies, such compositions give excellent results in other hybrid methods (adsorption + photodegradation + catalytic oxidation) with the combined use of nanotechnology and environmental technologies.[58] Thus, green-synthesized functional biochar–metal oxide nanocomposites provide a permanent solution to the concept of organic, economically inexpensive, and environmentally friendly water purification.

3.3. Structural characterization techniques (FTIR spectroscopy, XRD, TEM, BET, *etc.*)

A number of analytical techniques are essential for analysing the functional and structural properties of functional biochar–metal oxide nanocomposites used for wastewater treatment. Using the Fourier transform infrared (FTIR) spectroscopy, the presence and transitions of biochar and metal-oxide intermediate bio-reactive groups, *e.g.*, hydroxyl –OH), carbonyl (>C=O) and carboxyl (–COOH), can be identified, which is helpful in estimating the energy of mass chemical interactions.[59,60]

X-ray diffraction (XRD) analysis gives an estimate of the crystalline phases (*e.g.*, Fe_3O_4, ZnO, and TiO_2) of the conjugated metal oxides and their particle size. This information is crucial in evaluating the functionality and stability of nano synthesis. Transmission electron microscopy (TEM) can be used to accurately analyse the strength and dispersive structure of nanostructures, interfaces, and distribution of mineral particles, which is useful in identifying effective contact arrays with contamination as shown in Fig. 7.[62]

XRD, XPS and FTIR spectroscopy analyses reveal the structural and chemical transformations that occur during dye-

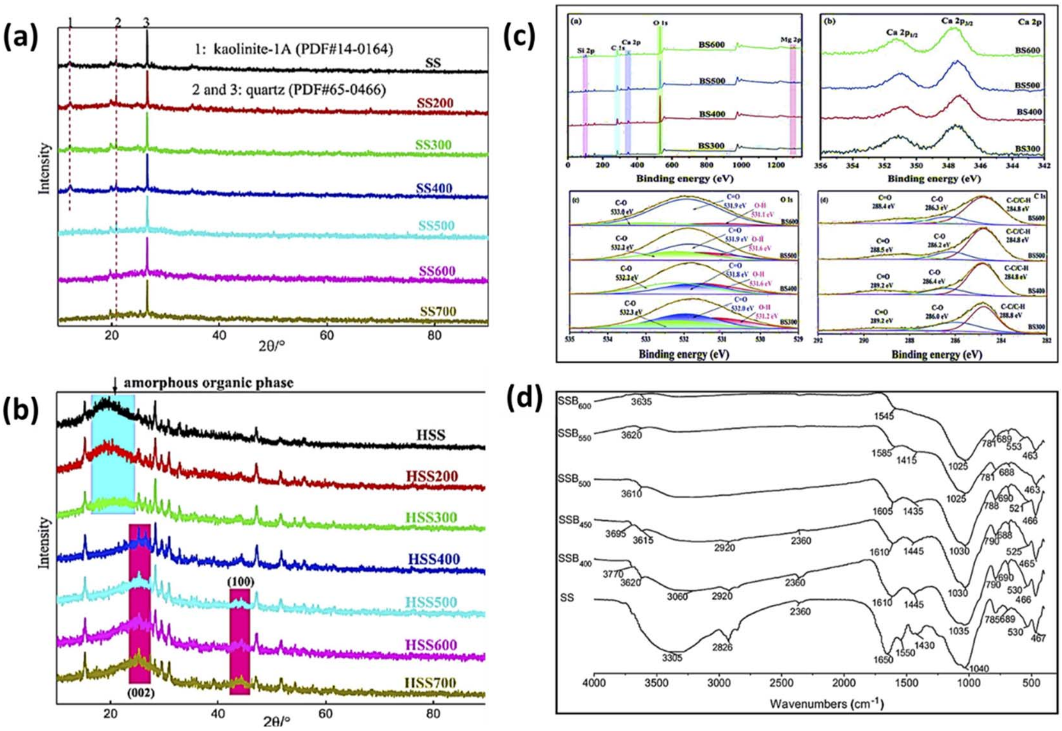

Fig. 7 (a) XRD patterns of biochar before acid washing (SS200-700). (b) XRD patterns of biochar after acid washing (HSS200-700). (c) XPS spectra of the sludge-derived biochar ((a) full-spectrum, (b) Ca 2p, (c) O 1 s and (d) C 1 s). (d) FT-IR spectra of the sewage sludge and its biochar obtained at different pyrolysis temperatures. Reprinted with permission from ref. 61 Copyright 2025, Elsevier.

loaded sewage sludge source biochar (DLSS-B) pyrolysis. Based on the XRD data, the peaks of clay minerals (kaolinite and quartz) weaken as the temperature increases, indicating the formation of an amorphous carbon matrix, as well as the rise of graphitic peaks (002, 100), which increase the thermal stability and adsorption capacity. XPS analyses show the progression of reduction and carbonization of oxygenic species as the temperature increases, with a clear pattern of carbon, oxygen, calcium, and silicon on the biochar surface. The FTIR spectrum can reveal thermal degradation through a decrease in the intensity of absorption bands corresponding to functional groups such as O–H, C–H, and C═O. At elevated temperatures, the development of more condensed aromatic structures and the formation of Si–O–Si bonds enhance thermal stability and may influence adsorption performance. These findings show that controlled pyrolysis temperature determines the impact on the structural, chemical and adsorption properties of biochars, which increases the potency of DLSS-B in environmental applications such as wastewater treatment and resource recovery.[61]

Furthermore, the Brunauer–Emmett–Teller (BET) analysis is important for the determination of the adsorption capacity and provides information on the specific surface area porosity and pore size distribution of the nanocomposite biochar. An increased specific surface area determined by BET analysis indicates enhanced efficiency for photocatalytic reactions and adsorption processes.[63] In addition, the thermal stability of the composition can be analysed by thermogravimetric analysis (TGA) and the oxidation states of the metal and the active sizes of the biochar surface by X-ray photoelectron spectroscopy (XPS). With the help of all these technologies, it will be possible to deeply understand the basic structural and chemical mechanism behind the decontamination performance of functional biochar–metal oxide nanocomposites, which will play a decisive role in the design and application of models (Table 1).[64]

4. Mechanisms of adsorption and catalytic degradation

4.1. Adsorptive interactions: Pore diffusion, electrostatic, π–π, and H-bonding

The adsorption of heavy metals is an important eco-friendly technique in wastewater treatment, in which biochar–metal oxide nanocomposites are found to be most effective. The adsorption of these compounds is based on the principles of several interactions, particularly pore diffusion, electrostatic attraction, π–π interactions, and hydrogen bonds (H-bonding). Pore diffusion is an important physico-chemical process for the adsorption of heavy metals and organic contaminants from wastewater. Biochars and their metal oxide nanocomposites have specific micropores (<2 nm) and medium-sized mesopores (2–50 nm). These provide the proper pathway for the transport of contaminant molecules into the adsorbent materials. Not only such porosity, but also the internal area of the pores allows metal ions or other particles to simply penetrate and interact with the internal surface. This process enhances accessibility to the internal surface area, thereby improving catalytic/adsorption performance.[71]

Table 1 Various technological parameters for biochar characterization

Technology	Purpose/benefit	Data obtained	Reference
FTIR	Detection of functional groups	–OH, –COOH, Fe–O, Zn–O chains	65
XRD	Crystalline phase and size	Fe_3O_4 (311), ZnO (101), crystal size\~12 nm	66
TEM/SEM	Particle shape and distribution technique	Crystalline samples, average size: 10–30 nm	67
BET	Surface area and porosity	SSA: 210 $m^2 g^{-1}$, pore size: 3.8 nm	68
XPS	Oxidation states of metal	Fe^{2+}/Fe^{3+} ratio: 1.2, Zn^{2+} thermal variation	69
TGA	Thermal stability	Constant weight up to 350–500 °C temperature	70

According to a previous study,[72] such biochar–metal oxide nanocomposites typically exhibit a surface area of >200 $m^2 g^{-1}$, which leads to a multifold increase in adsorption capacity. As confirmed by the BET analysis of these nonsynthetic biochar samples, the mesopores of size in the range of 2–50 nm facilitate internal dispersion of contaminants. In addition, the engineered porous structure enhances adsorption efficiency by facilitating faster transport of metal ions, particularly in aqueous environments. Thus, pore circulation and microcirculation play an essential role in the purification efficiency of biochar compositions.[73]

As biochar and its metal oxide nanocomposites increasingly serve as effective materials for heavy metal removal from wastewater, electrostatic interactions play a crucial role in their performance. Acidic functional groups present on the biochar surface (–COOH, –OH, $–COO^-$) interact with positively charged metal ions in aqueous solutions (*e.g.*, Pb^{2+}, Cd^{2+}, Ni^{2+}) through electrostatic attraction, facilitating efficient binding and removal. This force of attraction serves as a primary step in the process of exploitation and then produces strong bonds such as chelation or inner-sphere complexation. In the prepared biochar–metal oxide compositions, the metal oxide surfaces become busy in the form of CO–OH or M–OH, which causes secondary binding with metal ions.

The pH of the solution is the key environmental factor that effectively controls the strength of this electrostatic attraction. According to their study, at low pH, the biochar surface is protonated (positively enveloped), reducing the adsorption of positive metal ions because of the heterogeneous attraction between them, whereas in neutral or slightly acidic environments of pH 6–8, the biochar surface is negatively charged, resulting in a strong electrostatic attraction with metal ions. This type of reactivity creates a pathway for bidentate/monodentate chelation and regenerative adsorption of the metal. Thus, a thorough understanding of the electrostatic interactions is essential for the design and performance analysis of the applied models.[74]

The π–π stacking reactions are important for the physicochemical adsorption of organic contaminants (*e.g.*, dyes, pharmaceuticals, and pesticides) by biochar-based composites. The biochar has many aromatic carbon sheets in which dissociated layers of π electrons are available. These layers interact with semiconducting molecules in water through π–π interactions. These are of course non-covalent energy reactions occurring between molecules that have a range of π electrons. Particularly, elements such as methylene blue, bisphenol A, and tetracycline show good adsorption efficiency by parallel deposition on the biochar surface (Fig. 8).[75]

Further stability and specificity occur in π–π stacking reactions when the surface of the biochar is modified by metal oxide doping. For example, compositions such as Fe-doped biochar or NiO-BC amplify π–π interactions at the energy level through the mutual electron affinity of the envelope, leading to a high-stability state of the adsorbed molecules. Although this process is particularly applicable to organic contaminants, sometimes these types of reactions are also possible with metal compounds or ligand-based metals (*e.g.*, organometallics). The π–π interaction energy is an important mechanistic concept for understanding how the performance of a biochar filter becomes robust in the semi-conductivity pathway.[76]

4.2. Catalysis *via* advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) play a vital role in wastewater treatment,[77] particularly for degrading contaminants that are resistant to conventional treatment methods. The most important step of these methods is the production of hydroxyl (OH) or superoxide (O_2) radicals. These radicals are very powerful oxidizing agents that cause incomplete or complete degradation of organic and inorganic contaminants. This category includes processes based on hydrogen peroxide (H_2O_2), ozone (O_3), Fenton reactions (Fe^{2+}/H_2O_2), and advanced photo-oxidation systems such as UV/H_2O_2 and UV/TiO_2.[77]

To accelerate AOPs, recent research has enabled the use of biochar or nanometal-based catalysts. For example, Fe_3O_4-doped biochar samples show good stability and recyclability in heterogeneous Fenton-like reactions. The production of OH radicals is rapid, and performance is achieved even at low pH (pH 3–6).[78] Other nanomaterial compositions, *e.g.*, MnO_2, CuO or ZnO, also catalyse AOP reactions through photocatalysis. AOP models show strong adaptability to different contaminants, making an effective advance towards the objectives of purification efficiency, functional stability, and environmental purity. The catalytic efficiency of biochar-based nanocomposites is governed by the synergistic interplay between metal redox centers (*e.g.*, Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{4+}, Ce^{3+}/Ce^{4+}), interfacial oxygen vacancies, and the π-electron-rich domains of the biochar matrix. These features collectively promote the activation of oxidants such as H_2O_2, PMS, PDS, and O_3 to generate reactive species ($^{\bullet}OH$, $SO_4^{\bullet -}$, $^{\bullet}O_2^-$, $^1O_2$). Pollutants initially adsorb onto the porous surface of biochar, where electron transfer from the carbon matrix to metal sites accelerates redox cycling and sustains radical formation.

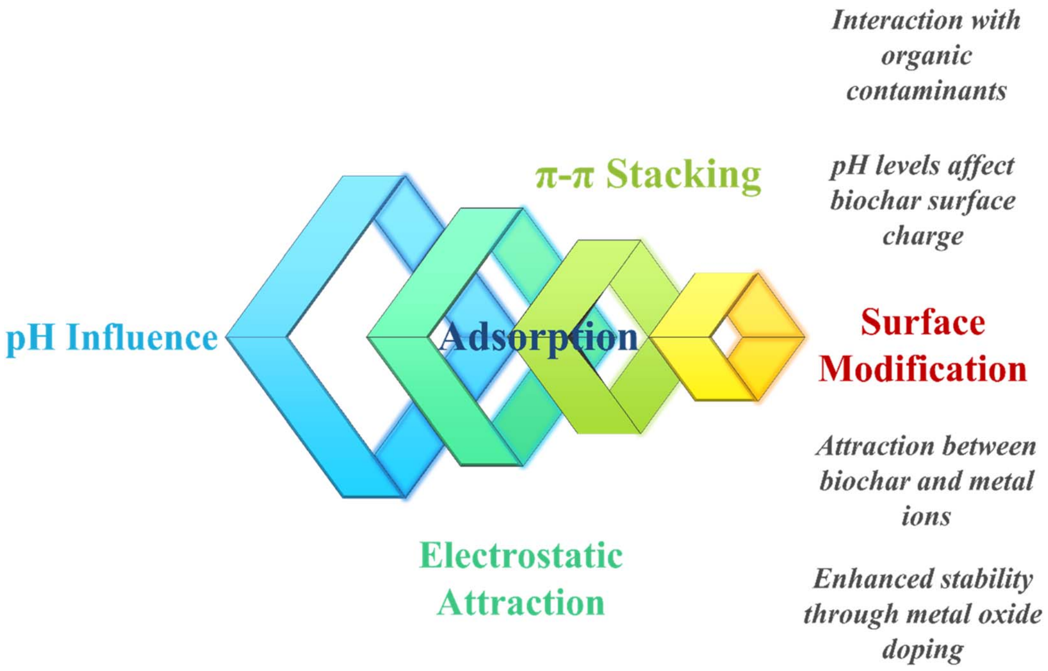

Fig. 8 Mechanism of the biochar adsorption process.

Heteroatom-doped regions and defect sites further stabilise the intermediates and lower the activation barriers, enabling both radical and non-radical degradation routes across dyes, antibiotics, pesticides, and phenolic contaminants.[79]

4.2.1. Fenton and photo-Fenton mechanisms. The Fenton process is a classically advanced oxidation technique that uses hydrogen peroxide (H_2O_2) in the presence of a ferrous ion (Fe^{2+}) to produce active hydroxyl radicals ($^{\bullet}OH$). These $^{\bullet}OH$ radicals function as very powerful oxidizers, quickly ensuring the chemical degradation of organic contaminants in water. This method is typically effective under acidic conditions (pH 2.5–3.5); however, iron precipitation and the need for strict pH control remain major limitations. In heterogeneous Fenton systems, catalysts such as Fe_3O_4, Fe_2O_3, or Fe-doped activated carbon and biochar are used to overcome these drawbacks. Nevertheless, metal leaching and the generation of iron-containing sludge can reduce catalyst recyclability and overall process efficiency.[80]

The photo-Fenton process is an advanced form of the Fenton method, which leads to the further generation of $^{\bullet}OH$ radicals by recycling the ferric form (Fe^{3+}) back into the ferrous form (Fe^{2+}) through the direct influence of halogens or solar energy (UV/visible light). In this method, the removal of persistent contaminants (*e.g.*, endocrine-disrupting chemicals and pharmaceuticals) occurs more efficiently, achieving higher degradation performance while requiring lower H_2O_2 consumption. More energy-efficient purification can be achieved using Fe-doped biochars or Fe–TiO_2 nano photocatalysts in the photo-Fenton reaction. As an example of a related project, experimental methods for purifying drug residues such as ibuprofen in sunlight using Fe_3O_4 biochar have been quite successful. These approaches provide the possibility of efficient and sustainable cleaning with environmentally friendly, recyclable filter compositions and low-risk products.[81,82]

4.2.2. Persulfate and peroxymonosulfate activation. Persulfate ($S_2O_8^{2-}$) and peroxymonosulfate (peroxymonosulfate, PMS, and HSO^{5-}) are increasingly used as chemical oxidizing agents in AOP (advanced oxidation process) techniques to remove heavy metals or organic contaminants. Upon activation, these oxidants generate sulphate radicals ($SO_4^{\bullet-}$) or hydroxyl radicals ($^{\bullet}OH$), which act as highly powerful oxidizing species. These radicals convert hazardous bio-stable contaminants into inert substances with high efficiency. Various methods can be used to activate this process: heat activation, ultraviolet light (UV) irradiation, metal interactions (Fe^{2+}, Co^{2+}, and Mn^{2+}) or catalysis using nano-materials (*e.g.*, Fe_3O_4 biochar).[83]

In recent studies, Fe-doped biochar or ZnO-fortified filtrate compositions have been shown to effectively activate persulfate/PMS. The SO_4^{2-} radicals generated by these methods are stable in neutral or acidic environments (pH 3–7), and the purification efficiency is high. The persulfate-based method offers the advantage of higher selectivity and typically results in lower metal leaching and reduced secondary contamination, particularly in wastewater containing organic matter. Activation systems such as PMS/Co^{2+} and PMS/Fe^{2+} exhibit high efficiency in peroxymonosulfate activation and are especially effective for the degradation of pharmaceuticals, dyes, and endocrine-disrupting compounds.[84] Thus, these second-generation oxidation techniques have opened innovative possibilities in the field of purification.

4.2.3. Visible light and redox pathways. Visible light activation is an environmentally friendly and powerful technique used in photocatalysis or photo-oxidation techniques to remove chemical contaminants from liquid media. Explosive filters such as hafnium, natural metal oxides (Fe_2O_3, $BiVO_4$), doped titanium dioxide (N–TiO_2), or $ZnFe_2O_4$, which have high photon utilization potential, using low-energy visible light ($\lambda = 400–700$ nm), can import photons to form electron–hole pairs. These electron–hole pairs lead to the production of $^{\bullet}OH$, $^{\bullet}O_2^-$ or SO_4^- radicals, which are degraded by the oxidation of impurities.[85] Redox pathways are important in this process because electrons generated by the influence of visible light participate in the reduction reactions and holes in the oxidation reactions. These redox reactions, in combination with O_2, NO_3^-, H_2O_2, or persulfate-based oxidizing agents present in the water, produce strong oxidative or reductive intermediates. For example, in the process of purification, O_2 of the liquid medium is converted into an $^{\bullet}O^{2-}$ free radical, which contributes to the structural disintegration of contaminants. In addition, continuous OH production is possible *via* the reduction of $Fe^{3+} \rightarrow Fe^{2+}$ or $Mn^{4+} \rightarrow Mn^{2+}$. Thus, visible light-activated filters and redox cycles that occur in a small energy layer can provide potential, sustainable ways to purify wastewater.[86,87] The mechanism for wastewater purification *via* visible-light-driven photocatalysis and redox pathways can be systematically described step by step, as illustrated in Fig. 9 visible-light-driven redox pathways for wastewater treatment.

Step 1: photon absorption

The energy of visible light (λ = 400–700 nm) falls on the surface of the photocatalyst (*e.g.*, Fe_2O_3, N–TiO_2, and $ZnFe_2O_4$). The photon energy transfers electrons from the valence band (VB) of the catalyst to the conduction band (CB).

$$\text{Catalyst} + h\nu \rightarrow e_{CB}^- + hVB^+$$

Step 2: initiation of the redox reaction

Electrons (e^-) react with oxygen (O_2) to form superoxide radicals (O_2^-).

$$O_2 + e^- \rightarrow {}^{\bullet}O_2^-$$

Holes (h^+) react with water molecules or OH^- to form hydroxyl radicals ($^{\bullet}OH$).

$$H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+$$

Step 3: activated oxidation and degradation of pollutants

The resulting radicals, OH, O_2, SO_4, *etc.*, mineralize organic contaminants by taking electrons.

$$\text{R-Pollutant} + {}^{\bullet}OH/{}^{\bullet}O_2^- \rightarrow CO_2 + H_2O + \text{inert by-products}$$

Step 4: regeneration of the catalyst

This reaction proceeds in a cyclic manner, thereby continuously regenerating the reductive cycle.

$$Fe^{3+} \rightarrow Fe^{2+} \text{ or } Mn^{4+} \rightarrow Mn^{2+}$$

Step 5: clean water recovery

After purification, the inert impurities and filtered water are separated and reused.

4.3. Synergistic adsorption–catalysis

Synergistic adsorption–catalysis, also referred to as adsorptive catalysis, is one of the most effective strategies in modern wastewater treatment technologies. In this approach, the strong coupling between adsorption and catalytic activity plays a critical role in achieving efficient pollutant degradation. Fundamentally, the process relies on surface adsorption phenomena, where contaminants are first attracted to and concentrated on active surface sites, thereby facilitating subsequent catalytic

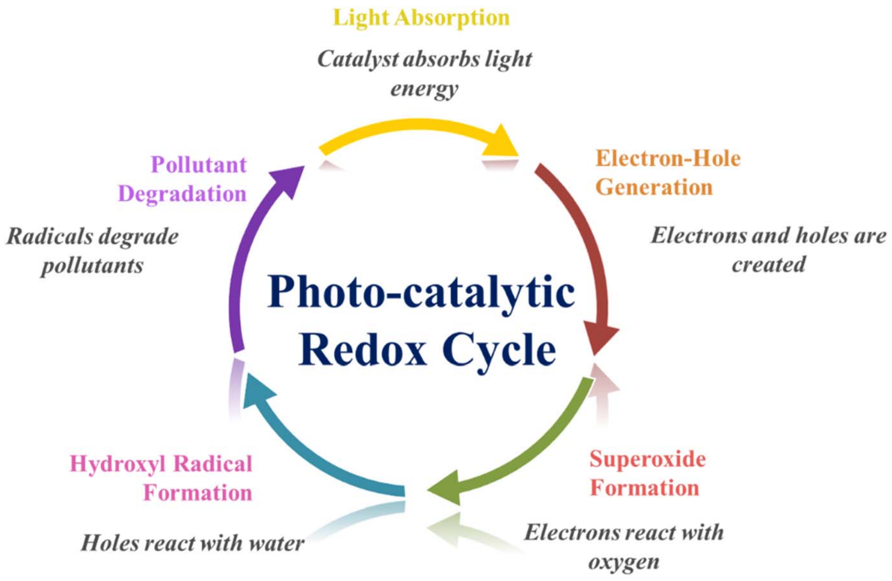

Fig. 9 Mechanism involved in the photo-catalytic action on the modified biochar.

transformation. This occurs through two chemical processes: physisorption, the process which is based on van der Waals forces of attraction, and chemisorption, the process that involves covalent or ionic bonds with a metal, metal oxide, or doped nanophase. The residual π–π stacking, electrostatic, hydrogen bonding, and pore-diffusion interactions between the adsorbent and the pollutant determine the adsorption potential. In particular, mesoporous structures (2–50 nm) and biochar–metal oxide nanocomposites with a surface area >200 m^2 g^{-1} show high adsorption performance.[88]

By integrating catalytic degradation with adsorption, the synergistic interaction between adsorption sites and catalytically active centers enhances and accelerates contaminant degradation. For example, the pollutant is brought closer to the pore wall by adsorption. Then, these contaminants react with $^{\bullet}OH$ or $^{\bullet}SO_4^{-}$ radicals and undergo mineralization. In this parallel reaction, the adsorbed molecules reach the electron transfer site of the catalyst more easily, increasing the degrading kinetics.[89] Through this adsorptive catalysis, a recyclable adsorbent/catalyst system is formed, which is environmentally friendly and economically beneficial.[90]

4.4. Role of metal oxidation states and electron transfer

These are the most important chemical factors that directly affect the adsorption of wastewater treatment, especially for metal-based adsorbents (Fe, Mn, Ce, Co, Ni, Cu, *etc.*). The presence of multiple accessible oxidation states enhances adsorption and catalytic performance by facilitating mass transport, increasing the availability of active sites, and promoting efficient electron transfer. Because metal species can exist in different oxidation states, they readily participate in redox reactions with contaminants in solution. For example, in Fenton-type systems ($Fe^{2+} \rightleftharpoons Fe^{3+}$), this reversible redox couple drives radical generation, electron donor–acceptor complex formation, and ion-exchange processes.

Additionally, degradation can proceed through multivalent redox couples such as Ce^{3+}/Ce^{4+} and $Mn^{2+}/Mn^{3+}/Mn^{4+}$, which function as efficient electron shuttles during catalytic reactions. Such electron transfer reactions affect the stability of the pollutants, increasing their ability to attract or convert them. With this, selective redox pathways are activated through the production of OH^- or O_2 radicals. The importance of these redox transitions in pollutant degradation is illustrated through the following representative reactions. In Fe-based systems, Fenton-type activation proceeds as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$

For Mn-based composites, peroxymonosulfate activation occurs as follows:

$$Mn^{2+} + HSO_5^- \rightarrow Mn^{3+} + SO_4^{\bullet-} + OH^-$$

Ce-containing materials participate in oxygen activation as follows:

$$Ce^{3+} + O_2 \rightarrow Ce^{4+} + O_2^{\bullet-}$$

In each case, the biochar facilitates electron donation to regenerate the reduced metal state, sustaining continuous reactive species formation and accelerating the degradation of recalcitrant pollutants.[86,91]

Electronic transfer and active sites can be discussed based on this chemistry aspect of adsorption. Changes in the metal oxidation state directly influence the surface charge and zeta potential, thereby enhancing electrostatic adsorption. The presence of positively charged species such as Fe^{3+} or Ce^{4+} on the adsorbent surface promotes attractive interactions with negatively charged pollutants (*e.g.*, certain dyes or anionic contaminants). Furthermore, heterogeneous catalysis is strengthened through valence-state cycling (Fe^{2+}/Fe^{3+}), which enables coupled adsorption–degradation pathways. For instance, Fe_3O_4–biochar nanocomposites can simultaneously facilitate adsorption and catalytic degradation by providing both Fe^{2+} and Fe^{3+} active sites.[92]

Metal oxides or compounds with multiple valence states can interact with different sample contaminants, as they can exist in several oxidation states. This chemical reaction is important from the point of view of detoxification and recycling of multimodal contaminants. Electron transfer plays a vital role in this reaction, as it leads to pollutant destabilization and activation. For example, a metal acid with a high oxidation state may receive an electron from a contaminant, which destabilizes it. The redox couples which act as catalysts in such a system create a synergy between adsorption and degradation. This constructive interaction contributes to efficient binding, solvation, and re-formation of pollutants. This will enable an effective refining process, which is desperately needed from the point of view of environmental purification (Fig. 10).[93,94]

5. Application spectrum in environmental pollution control

The oxidation states of the metal and the role of electron transfer play an important role in the functionality of adsorbents used to purify wastewater and other liquid contaminants. The various oxidation states of metals (Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{4+}, Ce^{3+}/Ce^{4+}) undergo redox reactions with environmental pollutants, impairing their stability and inducing immediate absorption. These electron transfer reactions not only draw contaminants but also cause them to be chemically inactivated. As a result, metal-based composite technologies have wide-ranging applications in environmental pollution control, offering effective solutions for the removal of contaminants such as dyes, heavy metals, pharmaceutical residues, and other organic pollutants.[95]

5.1. Degradation of synthetic dyes and textile effluents

Wastewater generated from the synthetic dye and textile industries contains substantial environmental pollutants. The aromatic nature of these dyes, often containing amino, sulfonic, or nitro functional groups, necessitates targeted adsorbent-

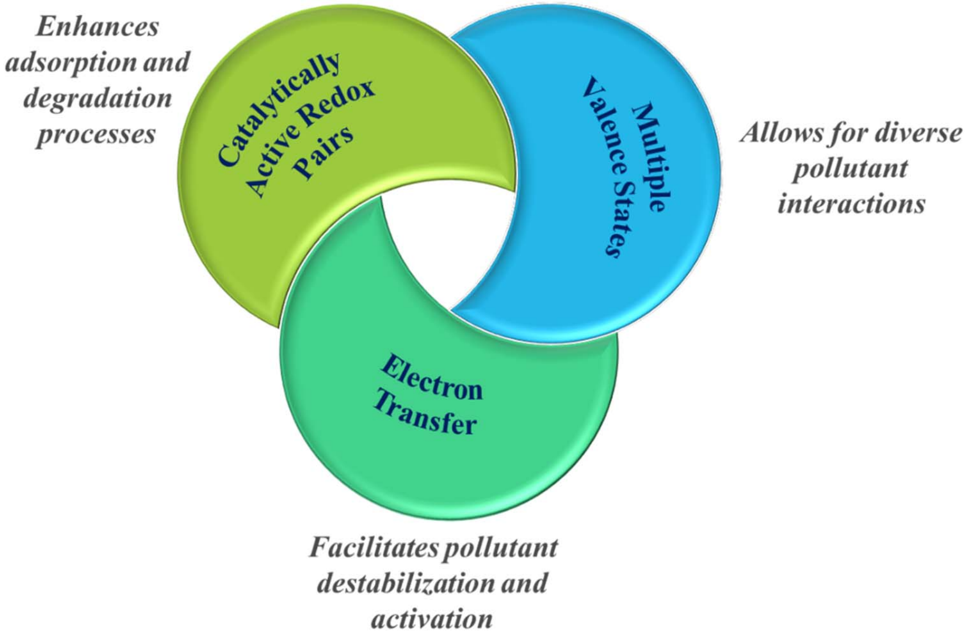

Fig. 10 Role of metal oxidation states and electron transfer mechanism.

based remediation strategies. Biochar and metal-based nanocomposites enable efficient dye removal due to their high specific surface area, abundant surface functional groups, and well-developed micro- and mesoporous structures. The interaction mechanisms that play an important role in this adsorption process are electrostatic attractions, π–π stacking, hydrogen bond formation and pore diffusion.[96] For example, rhodamine B and methylene blue, interact with the biochar surface, which is ideally functionalized with hydrophilic groups.

From a scientific point of view, this process can work effectively even at high pH, because the metal oxide compounds (Fe_3O_4, ZnO, MnO_2) control the surface polarity of the material and are directly involved in electron exchange with the dye molecules.[97] These not only adsorb the dye molecules but also eliminate them through oxidation or nuclear fission. Thus, adsorptive degradation of synthetic dyes provides a permanent, promising and refined solution for textile waste water purification.[98]

The role of biochar and hybrid adsorbents in adsorption chemistry is of immense scientific significance in the control of synthetic dyes and textile wastes. Synthetic dyes are resistant to biodegradation as they contain stable aromatic groups such as azo, anthraquinone and triphenylmethane structures. Biochar and its metal-modified forms (Fe, Mn, and Ti) undergo a number of chemical reactions for rapid filtration. Adsorption involves electrostatic attraction, π–π stacking, hydrogen bonding, metal–ligand complex formation and ion exchange reactions. For example, Fe–OH groups form complexes with SO_3^- groups of dyes through ligand exchange, and in the π–π stacking technique, aromatic rings of dye molecules are attracted to graphitic layers of biochars to form stable species.[99]

In hybrid adsorbents, such as Ti_3C_2-MXene-biochar composites, extended surface area, substantial number of functional groups (–OH, –O, and –F) and specific heat-reducing structures result in powerful adsorption of dyes. These provide redox-active bases, working in fine combinations with azo or sulfonic groups. With thermal, pH or light activation, such adsorbents are made suitable for removing chemical contaminants. Protonated surfaces of biochar ($-OH_2^+$, hydroxyl dication) consistently achieve affinity with ionic dyes. Such adsorbents reduce the efficiency of recycling and the amount of environmentally harmful securities. This makes them a powerful solution in controlling the powerful pollution that flows from the textile industry into the rivers.[100]

5.2. Antibiotic and pharmaceutical contaminant removal

Both pharmaceutical residues and antibiotic contaminants are complex molecules susceptible to hydrolysis, and adsorption-based methods have demonstrated significant potential for their removal from wastewater. These molecules are characterized by (i) multifunctional groups – ketone/enol, carboxyl, amino, chromophore (–N═N–) or fluoroquinolone rings – and (ii) defective pK_a values for the pR/cation–anion conversion, possibly complicating their adsorption mechanisms.[101] Adsorbents such as biochar–metal oxide, Fe/Ni-doped carbon, ZEC, and Zr-UiO-type MOFs provide micro-/mesoporous (>200 m^2 g^{-1}; 2–50 nm) and metal polyoxidation states (Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{4+}) in this hybrid structure, accelerating adsorption and concurrent catalytic degradation. π–π stacking (*via* aromatic stems) cation–π and metal–ligand interactions with fluoroquinolones (*e.g.*, ciprofloxacin) are important for tetracyclines and sulfonamides, for which a favourable ionization state at high pH (*e.g.*, cationic or zwitterionic) regulates the intensity of electrostatic attraction/repulsion. Hydrogen-bonds (–OH/–NH···O═C) and hydrophobic interactions also help to trap the adsorbate in the pore structure, where interfacial Fe(III)/Fe(II) or Co(III)/Co(II) pairs can undergo electron transfer to generate the $^{\bullet}OH/^{\bullet}SO_4^-$ radicals, allowing degradation of the adsorbed drug.[102]

Critically, synergistic design strategies are gaining prominence in modern adsorbents, such as bio-peroxymonosulfate (PMS)-activated Fe_3O_4/biochar and visible-light-excited N-doped TiO_2/BC. These materials facilitate the mineralization of adsorbed tetracycline complexes through hole-driven oxidation pathways, including demethylation and ring-opening reactions. Studies have reported that the observed pseudo-first-order rate constants (k_{obs}) for these processes can reach 10^{-2} to 10^{-1} min^{-1}. Moreover, the rapid change in the electrochemical selectivity (zeta potential) increases the adsorbent reabsorption potential (≥10 cycles), and the leaching of the metal is maintained at <0.5 mg L^{-1}. However, most real-world studies are limited in scale, highlighting the need for future research on complex issues such as multi-compound wastewater matrices and the presence of antimicrobial-resistant (AMR) bacteria. Additionally, the catalytic activity of metals in various oxidation states, along with the adaptive composition of multilayer materials, plays a crucial role in enhancing durability, efficiency, and environmental compatibility in the adsorptive–catalytic removal of pharmaceutical and antibiotic contaminants.[102]

5.3. Pesticides and phenolic pollutants

Adsorption chemistry of pesticides and phenolic pollutants is a very important area in the field of environmental chemistry and can be explained based on the principles of adsorption and surface reactivity. Pesticides (*e.g.*, organochlorines, organophosphates, carbamates) and phenolic compounds (*e.g.*, bisphenol A, chlorophenols, nitrophenols) are common and well-studied types. Adsorption is a surface-driven phenomenon, the effectiveness of which is determined by several factors (Table 2) such as the presence of semi-aromatic or fully aromatic structures, a lack of natural biodegradability, and high toxicity and stability in water. Different functional groups, such as –OH, –Cl, $-NO_2$, $-NH_2$, $-PO_4$ and others, lead to characteristic interactions depending on the pH, temperature, and adsorbent structure.[103]

5.4 Adsorption of pesticides and phenolic contaminants

Pesticides (*e.g.*, malathion and parathion) and phenolic compounds (bisphenol-A, 2,4-dichlorophenol) usually contain hydroxyl (–OH), chlorine (–Cl), carboxyl (–COOH) or phosphate groups and show a high lipophilic nature (high $\log K_w^o$ value). The metal coordination centres (Fe^{3+}/Al^{3+}) on Fe/Al-modified biochar surfaces form complexes with these by ligand exchange or chelating, for example, Fe^{3+} lone-pair e^- (Cl/O) → Fe–Cl/O linkage. This results in strong chemisorption.[104] However, MXene-biochar compounds typically contain –OH, –F end groups, polyethylene-like grades, and electrically conductive bases that enhance the adsorption reaction by π–π stacking, hydrogen bonding, and electron shuttling (in malathion or phenol). This, in turn, also helps the redox-active pollutants to decompose in the atmosphere.[105]

Many studies follow the model of pseudo-second-order kinetics, which indicates the dominance of chemical adsorption. Adsorption is recognized as an endothermic process ($\Delta H^\circ > 0$) especially in π–π stacking interactions with phenolic conjugates. In addition, the Langmuir adsorption isotherm model indicates high affinity and monolayer adsorption, reflecting strong interactions between the contaminants and the surface sites of the biochar or nanocomposite. The adsorption efficiency is determined by $\log K_w^o$ (octanol–water partition coefficient), pK_a (acidic constant) and dipole moment (dipole moment). For example, more lipophilic contaminants (more $\log K_w^o$) show higher adsorption in charcoal or graphitic biochar. Adsorbents can be recycled through ethanol washing or pH filtration. In addition, bisphenols or dichlorophenols can be destroyed in a refined manner by the Fenton reaction involving Fe^{2+} and $-H_2O_2$ or by UV-coupled decompositions of TiO_2-BC compounds. They provide the scientific principles underlying the development of adsorption or creative degradation technologies and play an important role in the development of innovative environmentally friendly cleaning methods.[105]

5.5. Industrial wastewater and mixed pollutants

Industrial wastewater typically contains several types of pollutants, *e.g.* heavy metals (Pb^{2+}, Cd^{2+}, Cr^{6+}), mixtures of ionic and non-ionic dyes, phenolic compounds, pesticides and pharmaceutical compounds. Therefore, their purification requires adsorbents with multi-reactive and multicomponent surfaces. Their adsorption involves a wide range of chemical reactions such as metal complexation, electrostatic attraction, hydrogen bonding, π–π stacking, van der Waals forces, and ion exchange.[106]

Biochars, especially Fe/Al-modified biochar, work in the form of metal–ligand complexes to remove metal ions from industrial wastewater. Fe^{3+}- or Al^{3+}-based sites form a metal-linked coordination complex with lone-pair donor groups (O^- and N^-) of metal ions, resulting in a dominant effect of

Table 2 Adsorption mechanisms

Technique	Chemical reactions	Mechanism
Electrostatic interactions	$-OH_2^+ \leftrightarrow -Cl^{-/-}NO_2^-$	Phenolic acids with protonated biochar
π–π stacking	Aromatic ring ↔ graphene-like BC/MXene	Bisphenol A ↔ biochar/layered MXene
Hydrogen bonding	$-OH/-NH_2 \leftrightarrow$ adsorbent –OH/–COOH	4-Nitrophenol ↔ Fe-BC
Lewis's acid–base complexation	Lone pair (O, N) ↔ Fe^{3+}, Ti^{4+}	Phenol ↔ Fe-MOF/Fe-BC
Redox interactions	e^- Transfer ↔ redox-active metals ($Fe^{2+}/^{3+}$)	Organophosphate degradation
π–cation interaction	Cation ↔ aromatic π-electron cloud	Methyl parathion ↔ Mg^{2+}/π-BC

chemical adsorption.[106] Similarly, biochar- or graphene-oxide-rich adsorbents can capture hydrophobic organic pollutants, such as conjugated aromatic compounds, through π–π stacking and dipole–dipole interactions. Competitive adsorption is a principal factor in the adsorption of mixed contaminants, implying that several contaminants compete for the same site. As a result, the Langmuir or Freundlich models are analysed to study multi-solute adsorption isotherms. From a thermodynamic aspect, negative $\Delta G°$, negative $\Delta H°$ (endothermic process) and positive $\Delta S°$ (increased randomness at the solid–liquid interface) are common. Thus, chemical reactions for the disposal of mixed contaminants in industrial wastewater are multi-dimensional, competitive and thermodynamically sensitive, providing the basis for the establishment of strong adsorbent designs and different technologies.[107]

5.6. Case studies and real wastewater scenarios

Functional biochar–metal oxide nanocomposites are a versatile, complementary solution for industrial wastewater purification through combined adsorption–degradation. They enable rapid pollution decomposition, reusability, and purification with low fuel consumption. Their effective performance and ease of use in real wastewater are guiding sustainable water management.[108]

In one case study, Fenton-reaction-based techniques using Fe–biochar (Fe–BC) and hydrogen peroxide (H_2O_2) was the best method to effectively neutralize the endocrine disrupting biological contaminant Bisphenol A (BPA). In a 2021 study, highly reactive hydroxyl radicals were produced by the radical reaction $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$; such radicals react with the aromatic groups of the BPA molecule, breaking it down into less toxic components. More than 90% of BPA removal was achieved in just 30 minutes, and the experimental strategy was based on the concentration of BPA leaked from the plastics industry into river water. The metal content in Fe–BC composites remains stable on the biochar surface after treatment, exhibiting minimal metal leaching. Consequently, this approach is environmentally safe and allows for the material's reuse.[108,109]

Similarly, in another case study, TiO_2–biochar (TiO_2–BC) nanohybrids were used for the purification of dye contaminants under natural light. It was demonstrated that the technique effectively combines energy efficiency and environmental safety. Congo red and methylene blue dyes, which are used by the textile industry, are stable because of azo bonds and simply do not degrade under normal environmental conditions. TiO_2 nano catalysts react with natural light to produce electron–hole pairs (e^-/h^+), which react with O_2 and H_2O to form OH and O_2^- radicals. These powerful oxidative species completely mineralize the dye molecules to CO_2 and H_2O. The adsorptive enrichment of the dye molecules by the biochar interface allows TiO_2 to better interact with the surface and increase photoactivity, the effect of which is further strengthened by defect engineering. The purification rate reached >95% in 60 minutes, which is considered as an alternative technique with low energy and low industrial footprint, applicable even to continuous-flow processes.[110]

The use of MnO_2-biochar (MnO_2-BC) nanohybrids has become a highly effective technique in the purification of phenol and 4-nitrophenol, carcinogenic and endocrine disrupting organic contaminants commonly found in electroplating wastewater. The Mn^{4+}/Mn^{3+} redox pairs in the MnO_2 moiety induce redox–oxidation reactions, leading to the production of Mn^{3+} and reactive R radicals from the R–OH groups, which quickly participate in further degradation reactions. The purification rate of 4-nitrophenol in samples collected from electroplating effluents exceeds 95% at a density of 100 ppm, especially impressive in the range of pH 5–7. The multiporous microstructure of biochar enables it to achieve higher adsorption, and the natural distribution of MnO_2-nanospheres allows for more redox-active sites. Typically, these nanohybrids also show some photocatalytic activity under visible-wavelength light, inactivating the –OH and $–NO_2$-functional groups and converting them into stable elements that are harmless to the environment, as discussed in these case studies.[111]

6. Performance factors and operational parameters

The accelerated catabolism of Reactive Black 5 (RB5) dyeing contaminant using ZnO-BC nanohybrids has emerged as a powerful and environmentally friendly method. According to a previous study, these nanocomposites generate $OH\cdot$ and $O_2^-\cdot$ radicals from the electron (e^-) and hole (h^+) pairs emitted by the photo in ZnO, which rapidly oxidize the dye molecules. Biochar's smooth surface texture and high clarity help to store color molecules while using less energy. Most of the photoreactive response achieved by defect engineering of ZnO is dynamic even under long-wavelength light. When the material is used under simulated sunlight, at pH 6.5, with 0.75 g L^{-1} rate of catalysis and 100 mg L^{-1} dye concentration, >98% RB5 removal was observed in 45 minutes. When recharged, it showed only ∼8% drop in performance even after five cycles, confirming its good recyclability.[112]

The accelerated oxidation process of phenol using an Fe_3O_4-BC nanocomposite is a highly effective technique for the purification of fixed contaminants such as organic endocrine disruptors found in wastewater. According to a study, Fe^{2+}/Fe^{3+} redox pairs in Fe_3O_4 react with H_2O_2 to produce $^{\bullet}OH$ hydroxyl radicals, which rapidly oxidize phenol and convert it to benign products.[113] The biochar in the nanocomposite enhances the adsorptive binding of phenol through the presence of more micropores and functional groups (–OH, –COOH). The magnetic nature of the Fe_3O_4-BC compound makes it separation after use easy, which increases the possibility of continuous operation. At pH 3.0, 93% phenol destruction was achieved in just 30 minutes at 1 g L^{-1} catalytic rate with 50 mM H_2O_2 to facilitate the Fenton-Co principle, while the compound maintained >85% efficiency after four cycles. In addition to this study, the case of ZnO-BC clearly illustrates how nano-biochar composites are becoming great tools in the management of accelerated catabolism, recycling and environmentally friendly

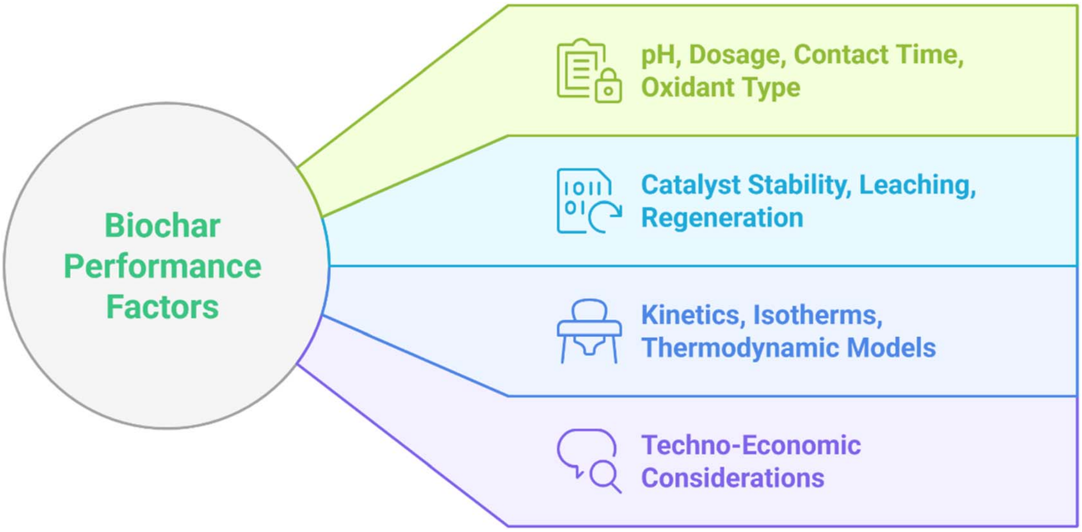

Fig. 11 Exploring biochar performance factors.

processes in mixed pollutants.[114] Fig. 11 shows the parameters highlighting biochar performances.

6.1. Effect of pH, dosage, contact time, and oxidant type

PH, dosage, contact time and oxidant type are important parameters that influence the performance of functional biochar–metal oxide nano compounds in the accelerated degradation of reagent pollutants in wastewater. First, the pH directly controls the reaction intensity, especially in Fenton or photocatalytic reactions, where a low pH (around 3.0) is more conducive to Fe^{2+}/Fe^{3+} redox cycling or $^{\bullet}OH$ radical generation, whereas ZnO-BCs work best under neutral or slightly acidic conditions (pH 6.5). Secondly, increasing the catalyst dosage enhances the density of reactive surface sites, accelerating the generation of reactive intermediates. However, higher catalyst concentrations can also increase solution turbidity, reduce light penetration and potentially limit photocatalytic efficiency. Third, if the connection time is longer, the adsorbate–adsorbent combination will be more adequate and the effectiveness will increase, but over time, there may be a natural deterioration of the reaction. Finally, oxidant types, such as H_2O_2, persulfate or percarbonate, effectively control the reaction by the generation of hydroxyl or sulphate radicals. Accelerated contaminant destruction is achieved through the interconnection of these parameters, and these are refined accordingly for each nanosynthetic system.[115]

6.2. Catalyst stability, leaching, and regeneration

Catalyst stability, leaching and regenerability are the most crucial factors for determining the long-term efficacy of functional biochar–metal oxide nano compounds in the accelerated degradation of recurring contaminants in wastewater. First, catalytic stability refers to the ability of a nanocomposite to maintain its structure and performance under dynamic conditions, such as acidic pH, the presence of oxidants, or exposure to light and heat. For example, the Fe_3O_4–BC nanocomposite retained over 85% of its reactivity even after four consecutive cycles. Second, controlling metal leaching is critical, as the release of metal ions (*e.g.*, Fe^{3+}, Zn^{2+}) into water can cause secondary contamination. Therefore, it is essential that the surface functional groups of biochar strongly bind the metal species to minimize leaching.[116] Third, regenerative capacity implies the possibility of reusing functional biochars in several process cycles, thereby reducing their operating costs and increasing their durability. Regeneration is usually possible by washing (*e.g.*, with ethanol or H_2O_2) with basic treatment or low-temperature regeneration. With the proper management of these factors, the performance of the nanocomposite and the use of environmentally friendly materials can be maintained.[116]

6.3. Kinetics, isotherms, and thermodynamic models

Kinetic, isotherm and thermodynamic models are used for the detailed evaluation of adsorptive and degradation processes of functional biochar–metal oxide nanocomposites used for the accelerated degradation of recurring organic pollutants in wastewater treatment. In kinetic analysis, pseudo-first-order and pseudo-second-order models are commonly used; of these, the pseudo-second-order model is best suited, indicated by the high R^2 value found in multiple studies, suggesting chemisorption. In isotherm models, the Langmuir and Freundlich models are widely applied.[117] The Langmuir model indicates that the adsorption occurs as a monolayer and is helpful in measuring the adsorption capacity ($q_{\max}$). For example, the Fe_3O_4–BC nanocomposite showed good agreement with the Langmuir isotherm in phenol purification. Thermodynamic analysis describes the spontaneity, endothermic or exothermic nature of the process and the disorder of the system by measuring the values of $\Delta G°$, $\Delta H°$ and $\Delta S°$. A negative $\Delta G°$ value indicates that the process is spontaneous, and a positive $\Delta H°$ value shows that the adsorption or degradation process is endothermic. With the application of these models, the efficiency of functional nano-composites can be measured qualitatively and quantitatively, which is the basis for the development of real wastewater treatment technology.[117]

6.4. Techno-economic considerations

Although the use of functional biochar metal-oxide nanocomposites for the accelerated degradation of recalcitrant organic pollutants in wastewater treatment is technically powerful, economic viability and technical feasibility are indispensable for its widespread deployment. Technically, these nanocomposites achieve high efficiency due to their large specific surface area, abundant complementary functional groups, and the redox activity of the metal oxides, all of which contribute to enhanced performance in photocatalytic or Fenton-type reactions. Economically, biochar synthesis can be performed using the available raw biomass (required biomass) and low-cost technology (*e.g.*, pyrolysis or hydrothermal carbonization).

However, metal oxide doping or nanohybrid preparation (*e.g.*, sol–gel method, hydrothermal or heating-milling methods) can sometimes be more laborious and costly. However, if we consider the multi-use potential (5+ usage cycles with >80% efficiency retention), the overall life cycle cost can be reduced. In one study, the Fe_3O_4–BC nanocomposite maintained >85% purification efficiency even after 4 cycles. In their study, the ZnO-BC nanohybrid retained energy for up to five use cycles. Therefore, their technological potential and long-term economic benefits make them effective alternatives to wastewater treatment in cooperative settings.[118]

7. Comparative evaluation with other catalytic adsorbents

Although various catalysts are used for the accelerated degradation of recycled organic pollutants in wastewater treatment, functional biochar–metal oxide nano-compounds provide characteristically high purification efficiency, recyclability, and environmental performance. Pure photocatalysts such as TiO_2, ZnO, and CeO_2, which are common catalysts of adsorption, show good efficiency, but they can be difficult to recycle and have low economic potential. The Fe_3O_4–biochar nanocomposite exhibited 93% phenol removal efficiency and retained 85% efficiency after four reuse cycles, demonstrating excellent recyclability.[119]

The performance of a modified biochar (Table 3) depends on its surface functionality and the chemistry of the dopants. Iron-based compounds (*e.g.*, Fe_3O_4 and FeS_2) allow the detection of heavy metals (Pb^{2+} and Ni^{2+}) with good redox activity and magnetic separation energy. ADTA or phosphorus-active groups increase selectivity by chelation with such ions. Activators such as $ZnCl_2$ and KOH facilitate the adsorption of a wide range of contaminants through high surface area and porosity. LDH-based compounds (*e.g.*, Ni–Fe and Mg–Al) are strongly attracted to oxyanions such as PO_4^{3-} and NO^{3-} through ion exchange, while sulphur or nitrogen doping improves the selective adsorption of soft metal ions such as Hg^{2+} and Cu^{2+}. Carbon-based converters (CNTs and graphene oxide) exhibit a hybrid filtration mechanism against organic dyes and metal ions due to π–π reactions and electron conductivity. The pollutant-specific design of all these modified biochars is a guide for targeted research and technology development in environmental purification.[131] Other studies used ZnO-BC nanohybrids which have been reported to have good purification ability for up to five cycles. The waste-derived biochar material, featuring a high surface area and abundant functional groups, effectively facilitates adsorption. In addition to this, nano-biochar compounds show better Fenton or photo-Fenton action even at low pH when compared with pure metal oxides. Thus, functional biochar–metal oxide compounds can be considered a more natural, recyclable, and naturally enriched option than pure catalysts.[132]

Fe_3O_4-BC is commonly used in water samples to extract methylene blue and many agricultural pollutants, showing an equilibrium adsorption potential of 5.0 mg g^{-1} level following the pseudo-second-order kinetics with ∼99% management efficiency with natural components.[133] The enhanced

Table 3 Modified biochars and their catalytic adsorbents

Modified biochar type	Feedstock	Modifier/method	Target pollutant(s)	Surface area ($m^2\ g^{-1}$)	Max adsorption capacity (mg g^{-1})	References
Fe_3O_4-BC	Rice husk	Magnetite	Cd, As	312.4	Cd: 99.6, As: 62.4	120
FeS_2-BC	Rice husk	Pyrite	Cd, As	298.7	Cd: 81.7, As: 55.5	120
H-PBC	Corn stalk	H_3PO_4	Pb, Ni	344.2	Pb: 243.9, Ni: 64.9	121
O-PBC	Corn stalk	NaOH	Pb, Ni	3.7	Pb: 192.3, Ni: 60.2	122
E-PBC	Corn stalk	EDTA	Pb, Ni	1.6	Pb: 156.3, Ni: 47.2	122
$ZnCl_2$-BC	Sawdust	$ZnCl_2$ activation	Pb, Ni	1120.0	Pb: 200.0, Ni: 166.7	123
GO-BC	Graphene oxide	GO coating	Ca^{2+}	720.0	Ca: 180.0	123
MnO_2-BC	Coconut shell	MnO_2 impregnation	Cr(VI)	215.0	Cr: 98.5	124
Mg–Al LDH-BC	Wheat straw	Layered double hydroxide	PO_4^{3-}	280.0	PO_2: 85.0	125
Ni–Fe LDH-BC	Bamboo	LDH composite	NO_3^-, Pb^{2+}	265.0	NO_2: 70.0, Pb: 140.0	126
N-BC	Peanut shell	Nitrogen doping	Cu^{2+}	520.0	Cu: 110.0	[127]
S-BC	Rice husk	Sulfur doping	Hg^{2+}	430.0	Hg: 95.0	128
TiO_2-BC	Wood chips	TiO_2 coating	Dyes (MB)	600.0	MB: 150.0	129
Biochar-CNT composite	Corn cob	Carbon nanotube grafting	Pb^{2+}	850.0	Pb: 210.0	129
KOH-activated BC	Coconut shell	KOH activation	Zn^{2+}	980.0	Zn: 175.0	130

adsorption of Fe_3O_4–biochar is primarily due to the evenly distributed active adsorption sites on the biochar; however, efficiency can decrease with metal leaching and repeated use. In contrast, MnO_2–biochar composites demonstrate substantially higher adsorption capacities than pristine biochar—for example, 100–160 mg g^{-1} for Pb^{2+} or Cd^{2+}—due to better solvent accessibility, stronger electrostatic interactions, and a greater abundance of functional groups. These results indicate that the differences in adsorption capacity between Fe_3O_4–BC and MnO_2–BC are quantitative: MnO_2–BC offers more surface adsorption sites and accelerates adsorption kinetics.[134,135]

Catalytic oxidation can be effectively performed using CeO_2–biochar composites. The Ce^{3+}/Ce^{4+} redox cycles of CeO_2, a rare-earth oxide, promote the generation of reactive species ($^{\bullet}OH$, $SO_4^{\bullet -}$, $^1O_2$), thereby enhancing the degradation efficiency of organic pollutants. For example, $CeO_2/BC@Fe_3O_4$ achieved 99.55% pollutant degradation through PMS activation, and this ability is also stable at various pH values.[136] CeO_2-based catalytic systems may provide stronger radical oxidation potential than Fe_3O_4–BC. Factors such as Fe leaching and the stability of metal–biochar interactions under aqueous conditions can limit Fe_3O_4 performance, whereas CeO_2–BC benefits from the continuous redox cycling of Ce^{3+}/Ce^{4+} active sites, which sustains radical generation and drives ongoing catalytic cycles. This makes the quantitative metrics of the catalytic oxidation performance of CeO_2-BC more effective (reaction rate, TOC/COD reduction efficiency) and shows a slightly lower catalytic degradation-dominant performance than the adsorption-dominant system of Fe_3O_4-BC or MnO_2-BC.[137]

7.1. Biochar *vs.* activated carbon and MOFs

Functional biochar–metal oxide nano compounds are more efficient and efficient in some dimensions than activated carbon and metal–organic frameworks (MOFs) for the accelerated degradation of recurring contaminants in wastewater treatment. Although activated carbon possesses a high surface area and excellent adsorption capacity, its application is largely limited to adsorption processes, as it lacks intrinsic catalytic activity and control over reaction pathways. In contrast, while MOFs have very high structural accuracy, porosity, and selective adsorptive properties, they are generally expensive materials and have low chemical stability, especially in ultra-liquid media such as water.[138] Biochar-based nano compounds can be made from low-cost agricultural wastes and serve as an ideal catalyst for powerful oxidation reactions with better functional groups, higher porosity, and agglomeration of metal oxides.[139] These nanohybrids typically show strong reactivity even at low temperatures and low pH values, or in the presence of a strong oxidant, and are more readily recoverable than activated carbon or MOFs without magnetic features. Thus, biochar–metal oxide nano compounds are more efficient and environmentally friendly alternatives.

7.2. Biochar–metal hybrids *vs.* standalone metal catalysts

Given the persistent occurrence of contaminants in wastewater, biochar–metal oxide hybrids represent a significant scientific advancement and an efficient platform for accelerated pollutant degradation. Although pure metal-based catalysts (*e.g.*, Fe_3O_4 and MnO_2) sometimes exhibit strong catalytic activity, with positive aspects such as redox cycling, $^{\bullet}OH$ production, and adsorption of oxidants, they are severely affected by hardening, abnormal coupling to adsorb, and loss of shape during recycling.[140,141] As a solution, biochar–metal hybrids combine nanomaterial oxides with high porosity and functional groups of biochar, improving the adsorption, selection of specific contaminants, and catalytic recyclability. Biochar serves as an effective adsorptive scaffold, lowering costs compared to pure metals and mitigating environmental impacts by decreasing both metal loading and leaching.[141] Nano-compounds such as Fe_3O_4-BC hybrids are stable even at low pH and can be recycled over several cycles (>85% removal efficiency after 4 cycles).[142] Thus, biochar–metal oxide nanohybrids are a more technologically progressive and environmentally friendly alternative to standalone metals.

7.3. Benchmarking with commercial catalysts

Compared with commercially available catalysts for the accelerated degradation of recalcitrant contaminants in wastewater treatment, functional biochar–metal oxide nano compounds have several key parameters. For example, conventional homogeneous catalysts (*e.g.*, Fe^{2+} Fenton systems and TiO_2 photocatalysts) offer high reaction efficiency, but their metal leaching, extreme pH dependence, and difficulty in recycling cause many functional variations;[143] other well-known commercial catalysts (*e.g.*, Pd/C, activated alumina supported oxides) are severely limited by cost and operational complexities. In contrast, Fe_3O_4–BC and MnO_2–BC hybrids are low-cost, utilize abundant agricultural-waste-derived biochar, possess a high specific surface area (>400 m^2 g^{-1}) and multiple functional groups (*e.g.*, -OH, –COOH), and feature redox-active sites that maintain structural stability during Fenton-like reactions.[144] They are also suitable for continuous-flow systems due to their high recycling stability (>85% efficiency retention over 4–5 reuse cycles) and magnetic separation ability. With this, biochar–metal oxide nanohybrids are emerging as environmentally clean, inexpensive, and efficient catalyst alternatives, competing with commercial catalysts.

8. Environmental, toxicological, and lifecycle aspects

Factors relevant to the environmental, toxicology and lifecycle analysis of functional biochar–metal oxide nanocomposites for the catalytic degradation of recalcitrant contaminants in wastewater treatment are of extreme importance. Since such nanohybrids are made on the basis of biochars obtained from low-cost agricultural waste sources, they promote resource circularity and carbon sequestration.[145] However, the long-term environmental impact of biochar–metal oxide composites must be carefully managed due to the formation of metal-based nanomaterials (Fe_3O_4, MnO_2, ZnO) and the potential for metal leaching during repeated use cycles. While some studies—

particularly on Fe–BC composites—have reported purification efficiencies of 85–90% after multiple cycles, the release of Fe ions at measurable levels has been observed, which may contribute to ecotoxicity.[146] In other patho-toxic analyses, the biochar matrix is helpful in reducing the level of metal leaching. As the life cycle analysis (LCA) results show, the fuel range required to manufacture biochar-supported catalysts is lower than that of activated carbon or pure oxide catalysts, favouring the green technology concept.[147] Thus, functionalized biochar–metal oxide nano compounds, when appropriately designed, can serve as novel catalysts with an environmentally friendly and less toxic pathway.

8.1. Metal leaching, ecotoxicity and life cycle Assessment (LCA) of biochar-based systems

Metal leaching ecotoxicity and life cycle assessment (LCA) are important factors to be considered in using functional biochar–metal oxide nanocomposites in wastewater treatment. Metal-based nanocomposites, especially biochar hybrids consisting of Fe-, Mn-, Cu- or Zn-based nano oxides, show some level of metal leaching under acidified or oxidative conditions, which can lead to toxic effects on biomass in water.[148] For example, Fe-BC nanohybrids showed 0.8–2.3% Fe leaching after 5 cycles, but the biochar matrix controls the amount of leaching by maintaining the solid metal state. Environmental toxicity is measured by evaluating the damage done by nanostructured iron particles to aquatic organisms, in which zebrafish embryo toxicity assays or algal growth inhibition tests are used. In life cycle assessment (LCA), biochar-LOH composites show a lower GHG output, lower energy burden and less toxic waste generation than commercial activated carbon or standalone metal catalysts, thereby promoting sustainable remediation.[149] From these perspectives, biochar-based catalysts are increasingly being integrated into environmental remediation technologies.

8.2. Circular economy and valorisation of waste biomass

In the circular economy concept, the use of functional biochar–metal oxide nanocomposites produced from waste biomass provides an effective and sustainable cyclic process for the catalytic degradation of reoccurring pollutants in wastewater. However, widespread adoption of such technologies requires regulatory and safety considerations. The trace elements (Fe, Zn, Mn, and Ce) and their nanomaterials used in the manufacture of these nano-compounds are likely to have a traumatic effect on the environment, especially as they can cause temporary or long-term toxicity to aquatic organisms through complex breakdowns.[150] For the safety management of such nano-components, efficient control principles and standardized test measures are required at the stages of their preparation, use, recycling, and disposal.

Globally, standards such as ISO/TR 12885:2018 and OECD Test Guidelines provide controlled methodologies for the safety assessment of nanomaterials. Moreover, because the waste biomass used in their production is derived from food processing or agricultural residues, careful evaluation of their purity, composition, and long-term environmental impacts is also necessary.[151] Therefore, safe, and sustainable expansion is possible by keeping regulatory and environmental forces in balance with adherence to these technologies.

9. Research gaps, challenges, and future perspectives

9.1. Scalability and industrial translation, and emerging Pollutants and hybrid contaminants

The use of functionalized biochar–metal oxide nanocomposites for wastewater purification, offering multifaceted benefits, has become a focus of modern research; however, several research gaps and challenges remain in this area. At present, although several studies illustrate the potential at the experimental level, there is no clarity on the controlled performance, recycling stability and functional aspects of the components suitable for practical wastewater treatment or industrial applications.[152] Furthermore, the diversity of biochar bases and the non-quantitative difference in pyrolysis state impede the uniform preparation and reflective performance of nano-stratified metal oxide particles. Significant challenges include long-term metal leaching prevention, regenerative management measures, and a comprehensive evaluation of the effectiveness of nano-toxicology.[153] In the future, multi-functionalized nano-composites (*e.g.*, with photocatalytic and adsorptive activity) will be able to be synthesized using novel functionalization methods (*e.g.*, plasma-assisted modification) and evaluation of stability based on life-cycle analysis of biochar-integrated platforms will be an important direction of research. In addition, techno-economic analysis and the formulation of standards for compliance with policy decisions are essential for the effective implementation of these technologies.[153]

9.2. Mechanistic uncertainties and interfacial dynamics

The main factors seriously affecting the performance of functional biochar–metal oxide nanocomposites in the catalytic degradation of recalcitrant contaminants in wastewater treatment are mechanical uncertainties and interfacial dynamics. Mechanical uncertainties are usually caused by the energy of bonding between the biochar matrix and the metal oxide nanoparticle, which reduces the stiffness, stability, and renewable capacity during physical changes such as expansion and contraction.[154] Interfacial dynamics, or the interaction between interface atoms, determine the electron transfer pathways of a nanocomposite and have a direct effect on the timing and outcome of adsorption–desorption processes.[155] To form a reinforced interface, recent studies have demonstrated innovative methods of increasing bond strength using functional groups or hybrid coatings, for example using linkers, thereby achieving higher stability and repeated cycles of catalytic functionality. The efficient management of these technical aspects makes biochar-based catalysts promising for building unique and refined models.[155,156]

9.3. Smart/responsive catalytic biochars and AI-guided design

Mechanical uncertainties and interfacial dynamics have a great influence on the successful design and performance of functional biochar–metal oxide nanocomposites in the catalytic degradation of recalcitrant contaminants in wastewater treatment. The stability and recyclability of these nanocomposites are governed by their surface and interfacial electron transfer, adsorption–desorption kinetics, and the extent of activation of catalytic active sites.[156] To overcome these challenges, recent efforts are leading the way towards the design of smart or responsive catalysts, developing biochar-based nanocompounds that respond to pH, temperature, or light stimulation.[156] For such materials, interfacial dynamics actively regulate the availability of active sites and the reaction kinetics in response to the specific contaminant. For the design of such complex systems, AI (artificial intelligence), specifically machine learning-based models, predictively model efficient designs according to the adsorbability of drug compounds, degradation pathway, and interfacial interactions of nanocomponents.[157] Using AI tools, nonsynthetic structure, functional similarity, and performance prediction are also made possible, allowing for targeted catalyst design with minimal experimental verification.[158,159]

9.4. Future perspectives

Even though functionalised biochar–metal oxide nanocomposites have already shown themselves to be effective tools for removing obstinate pollutants, there is still a long way to go before they can have a significant impact in the real world. Pollutants in real wastewater are rarely found alone; instead, they frequently exist as complex mixtures with competing ions with fluctuating pH, which can reduce the material's effectiveness. Future research should focus on making these nanocomposites more versatile, for instance, by combining with different metal oxides, introducing controlled defects to increase radical generation and selectivity, or fine-tuning their surface chemistry through heteroatom doping. Ensuring that these materials maintain their stability, with reusability and safety—with little metal leaking even after several cycles of use—is equally crucial. Greener, bio-inspired synthesis techniques can help reduce the production costs and environmental impacts, but they require more development to be reliable and scalable. Treatment systems may become more economical and energy-efficient if these catalysts are combined with renewable energy sources, such as sunlight for photocatalysis. Lastly, beyond chemistry, life cycle assessments, techno-economic analyses, and even AI-assisted design tools must direct future development. We can eventually get closer to cleaner water and more sustainable wastewater treatment technologies by using this all-encompassing approach to help close the gap between promising laboratory results and workable, field-ready solutions.

9.5. Overview of the evolution of biochars

The development of biochars for wastewater treatment has advanced through a number of significant turning points. Its roots can be found in ancient societies, where, as early as 2000–1000 BC, charcoal was used to purify water. The foundation for carbon-based adsorbents was laid when activated carbon became a common component for industrial and municipal water treatment in the middle of the 20th century. By the 1990s, biochar, or pyrolyzed biomass, had gained recognition as a sustainable substitute for activated carbon. It was first investigated for soil enhancement and then for the removal of contaminants from water. To improve the adsorption performance, researchers have started focusing on engineered biochars with improved porosity and surface chemistry between 2000 and 2010. Metal oxide–biochar composites, like FeO_4-BC and MnO_2-BC, were introduced between 2010 and 2015, marking a significant advancement that allowed for both adsorption and catalytic degradation. The material's versatility was increased between 2016 and 2019 by developments in

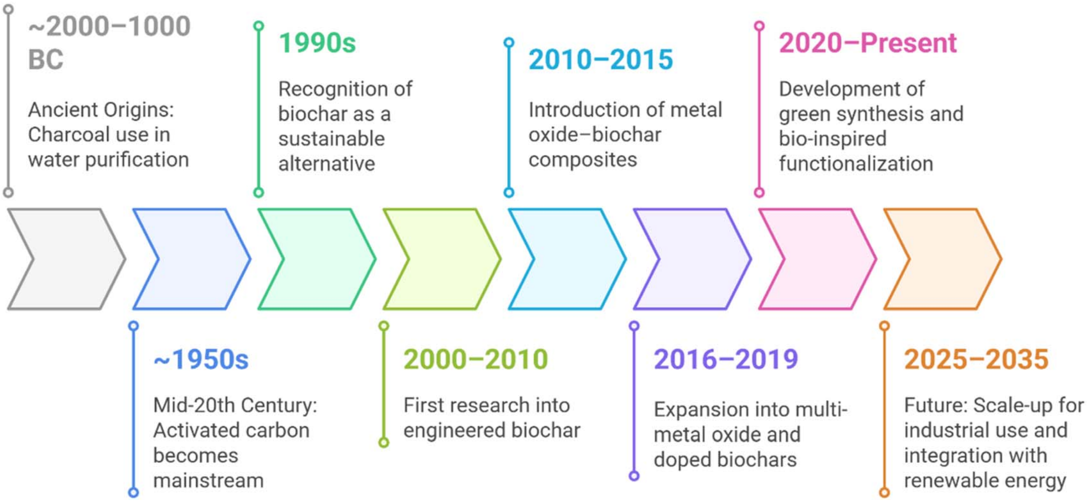

Fig. 12 Evolution of biochars in water treatment.

heteroatom doping (N, S, and P), multi-metal oxide integration, and the use of Fenton-like and photocatalytic processes. Since 2020, the focus has shifted to AI-assisted design for targeted pollutant removal, integration with nanocarbons like carbon nanotubes and graphene oxide, and green and bio-inspired synthesis methods. As we look to 2025–2035, it is anticipated that the main focus will be on scaling up these materials for industrial use, combining them with advanced oxidation processes powered by renewable energy, deploying decentralised treatment units for rural water access, and designing systems based on full life cycle assessment for large-scale, sustainable wastewater remediation. Fig. 12 shows the timeline evolution of biochars in water treatment applications.

10. Conclusions

Functional biochar–metal oxide (FBC-MO) nanocomposites are a very promising solution for the accelerated degradation of recalcitrant contaminants in wastewater treatment. This involves the highly developed surface area and functional groups of biochars, which, in combination with the high catalytic activity of metal oxide nanoparticles, offer strong transparent-kinetic kinetics and thermodynamic stability. The emphasis of the pseudo-first-order and Elovich models is useful for analysing the paradox of exploitation and the hegemonic power dynamics. Of these, studies point to 'endothermic' and 'spontaneous' processes. The temperature and activation energy parameters of most processes give way to an effective catalytic design. In addition, these nanocomposites minimize metal leaching, exhibit long-term durability, and demonstrate superior cyclic performance with enhanced tolerance to repeated use. In their techno-economic analysis, biochar-based catalysts show equal or higher performance than activated carbon and metal–organic frameworks (MOFs), with a lower cost of manufacture. biochar–metal hybrids overcome challenges such as thermal stability of MOFs and fluid instability in water. Biochar-based catalysts are highly recyclable and have shown to be suitable for long-term purification operations. Further, mechanical uncertainties, interfacial dynamics, and AI-guided design manifestos are gaining importance in research aimed at furthering the scientific and economic benefits of biochar-based catalysts. These technologies point to a mountainous trajectory in improving water quality.

Among the innovative technologies for continuous water purification, functionalized biochar–metal oxide nanocomposites (FBC-MO) have emerged as the most promising alternatives. Biochar's wide surface, rich functional groups, and porous structure, building agile interactions with metal oxide nanoparticles, provide high catalytic activity and low energy performance. Biochar-based nano catalysts are more environmentally friendly and recyclable, and have minimal metal leakage than currently used activated carbon, MOFs, isolated metal oxides, and commercial photocatalysts. For example, Fe_3O_4-BC or ZnO-BC nanohybrids exhibit long-term purification performance, as demonstrated by the "lotus effect." The performance of such nanocomposites exhibits tunable properties depending on the contaminant type, chemical composition, solution pH, and the nature or intensity of the energy input (*e.g.*, light, heat, or applied potential). Kinetic models (single-sequence order) and thermodynamic parameters (ΔG, ΔH, and ΔS) facilitate fine, fast and transparent mathematical modelling to understand the functional behaviour of these components.

These novel catalysts are attracting the attention of majority of scientists in terms of LCA toxicology and recoverability excellence. The amount of metal leaching from biochar-based systems remains within manageable levels, consistent with WHO standards, suggesting a favourable long-term environmental profile. However, certain Ag- or Cu-based nanohybrids may pose significant ecological risks; therefore, mechanical instabilities including uneven component distribution, phase separation, and aggregation along with interfacial dynamics, must be carefully modelled during scale-up. In recent years, AI-based data-driven catalyst designs have enabled the performance of these nano-hybrids with precision to target pollutants. In addition, responsive biochar systems – such as pH-sensitive or UV-light-activated composites – have opened the way for current ideas in research. In the foreseeable future, research is moving towards the design of functional nano-composite platforms that are more intelligent, tunable, and reusable, to be suitable for individual target pollution management in accordance with the situational requirements of the environment. This article provides new insights to the readers by clearly explaining the scientific mechanisms of functional biochar–metal oxide nano-compounds for the elimination of recalcitrant pollutants. In addition, the analysis of the article introduces solutions for sustainable AOP-based water purification technologies that are practical, effective and beneficial to the next-generation research studies.

Author contributions

Leena V. Hublikar: conceptualization, methodology, writing – original draft. K. S. Nivedhitha: conceptualization, methodology, writing – original draft. Bipin S. Chikkatti: conceptualization, methodology, writing – original draft. Ashok M. Sajjan: resources, supervision, writing – review & editing. Nagaraj R. Banapurmath: data curation, project administration, writing – review & editing. D. Palaniswamy: conceptualization, methodology, writing – review & editing. T. Beena: conceptualization, methodology, writing – review & editing. Pradeep Hegde: conceptualization, methodology, writing – review & editing. Sabin Kumar Mishra: conceptualization, methodology, writing – review & editing. Kartheek Ravulapati: conceptualization, methodology, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Abbreviations

WHO	World health organization

LDHs	Layered double hydroxides
BC	Biochar
CNTs	Carbon nanotubes
LCA	Lifecycle analysis
BPA	Bisphenol A
AOPs	Advanced oxidation processes
MOFs	Metal–organic frameworks
LDHs	Layered double hydroxidesTiO_2-titanium dioxide
Bi_2O_3	Bismuth oxide
CO_2	Carbon dioxide
EDTA	Ethylenediamine tetraacetic acid
Fe_3O_4	Ferric oxide
FeS_2	Ferrous sulphide
$ZnCl_2$	Zinc chloride
KOH	Potassium hydroxide
OH	Hydroxyl
COOH	Carboxyl
C=O	Carbonyl
HNO_3	Nitric acid
H_3PO_4	Phosphoric acid
NaOH	Sodium hydroxide
H_2O_2	Hydrogen peroxide
O_3	Ozone gas
PAA	Peracetic acid
HTT	Pyrolysis temperature
PCA	Principal component analysis
PMS/PDS	Photo-Fenton persulfate
XRD	X-ray diffraction analysis
TEM	Transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
FTIR	Fourier transform infrared
UV	Ultraviolet
DLSS-B	Dye-loaded sewage sludge source biochar
BET	Brunauer–Emmett–Teller
TGA	Thermogravimetric analysis
$S_2O_8{}^{2-}$	Persulfate
PMS	Peroxymonosulfate
ΔG°	Standard Gibbs free energy change
ΔH°	Standard enthalpy change
ΔS°	Standard entropy change

Data availability

The data supporting the findings of this study are included in the article.

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