

Fe/Mn/N Tri-Doped Sawdust-Derived Biochar Nano-Adsorbents: A Systematic Review on the Recent Progress in Heavy Metal Removal from Contaminated Water

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Abstract

Heavy metal contamination of aquatic environments remains a major global environmental challenge due to rapid industrialization, mining, agricultural activities, and urban expansion. Toxic metals such as cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), copper (Cu), zinc (Zn), and mercury (Hg) are persistent, non-biodegradable, and bioaccumulative, posing significant ecological and public health risks. Conventional wastewater treatment technologies, including chemical precipitation, membrane filtration, ion exchange, and electrochemical methods, are constrained by high operational costs, sludge generation, membrane fouling, and limited efficiency in treating complex multi-metal systems. Consequently, adsorption has emerged as a sustainable and cost-effective alternative for heavy metal remediation. This review critically examines recent advances in Fe/Mn/N tri-doped sawdust-derived biochar nano-adsorbents for the removal of heavy metals from contaminated water systems. The review discusses the occurrence, sources, environmental impacts, and toxicity of heavy metals, as well as the principles and limitations of conventional treatment technologies. Particular emphasis is placed on the synthesis, physicochemical properties, characterization, and adsorption mechanisms of Fe/Mn/N tri-doped biochar, highlighting the synergistic roles of iron, manganese, and nitrogen in enhancing surface functionality, adsorption capacity, reaction kinetics, and selectivity. Recent developments in adsorption isotherms, kinetic and thermodynamic modelling, and advanced characterization techniques are also examined to provide insight into adsorption behaviour and mechanism. Furthermore, current research trends, empirical findings, existing knowledge gaps, and future perspectives for large-scale application are discussed. The review demonstrates that Fe/Mn/N tri-doped sawdust biochar represents a promising, environmentally friendly, and economically viable adsorbent capable of addressing the limitations of conventional treatment technologies. Future studies should prioritize pilot-scale investigations, regeneration and reusability assessments, and performance evaluation under real wastewater conditions to facilitate commercial implementation and support sustainable water resource management.

Keywords: Fe/Mn/N tri-doped biochar; sawdust-derived biochar; heavy metals; adsorption; nano-adsorbents; wastewater treatment; contaminated water; environmental remediation; adsorption kinetics; adsorption isotherms.

1.0. Introduction

The increasing demand for clean water, coupled with rapid industrialization, mining,

agricultural expansion, and urbanization, has resulted in the continuous discharge of heavy metals into aquatic environments. Heavy metals such as cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), copper (Cu), zinc (Zn), and mercury (Hg) are among the most hazardous pollutants because they are toxic, non-biodegradable, persistent, and capable of accumulating in living organisms, thereby posing significant risks to ecosystems and human health (Faiz *et al.*, 2024). Exposure to these metals has been associated with kidney damage, neurological disorders, carcinogenic effects, and disruption of essential biological processes (Pratush *et al.*, 2018). Conventional treatment methods, including chemical precipitation, membrane filtration, ion exchange, coagulation-flocculation, and electrochemical processes, have been widely applied for heavy metal removal. However, these technologies are often limited by high operational costs, excessive sludge generation, membrane fouling, and reduced efficiency in treating multi-metal wastewater systems (Qasem *et al.*, 2021). Consequently, adsorption has emerged as a simple, cost-effective, and environmentally sustainable alternative for wastewater treatment. Among various adsorbent materials, biochar has attracted considerable attention because of its high porosity, large surface area, and abundance of oxygen-containing functional groups that facilitate heavy metal removal through electrostatic attraction, ion exchange, surface complexation, and precipitation (Sajjadi *et al.*, 2019). Sawdust-derived biochar is particularly attractive due to its low cost, renewability, and widespread availability. Nevertheless, pristine biochar generally exhibits limited adsorption capacity, necessitating structural modification to improve its performance. Recent advances have demonstrated that doping biochar with iron (Fe), manganese (Mn), and nitrogen (N) significantly enhances its physicochemical properties and adsorption efficiency. Iron and manganese introduce additional active sites and redox-active centers, while nitrogen doping increases surface electron density and functional groups that strengthen metal adsorption (Ippolito *et al.*, 2020; Guo *et al.*, 2025). The synergistic combination of these dopants produces Fe/Mn/N tri-doped biochar with superior adsorption capacity, improved kinetics, and greater selectivity for multiple heavy metals (Liu *et al.*, 2024). This review therefore examines recent advances in Fe/Mn/N tri-doped sawdust biochar nano-adsorbents for the removal of heavy metals from contaminated water systems. It discusses heavy metal pollution, adsorption mechanisms, biochar modification strategies, characterization techniques, adsorption models, and current research trends while highlighting existing knowledge gaps and future prospects for developing sustainable wastewater treatment technologies.

2.0. Heavy Metals in Aquatic Systems

2.1 Overview

Heavy metal contamination has emerged as one of the most persistent environmental problems affecting freshwater and marine ecosystems worldwide. Unlike most organic pollutants that may undergo microbial or photochemical degradation, heavy metals are chemically stable, non-biodegradable, and capable of remaining in aquatic environments for prolonged periods (Faiz *et al.*, 2024). Their persistence allows continuous cycling between water, suspended particles, sediments, and aquatic organisms, resulting in long-term ecological degradation and increased human exposure through drinking water and the food chain (Ali *et al.*, 2019; Faiz *et al.*, 2024).

Recent global assessments indicate that heavy metal pollution continues to increase because of rapid industrialization, urban expansion, mining activities, petroleum exploration, agricultural intensification, and inadequate wastewater management, particularly in developing countries (UNEP, 2023; Faiz *et al.*, 2024). Aquatic environments act as the final sinks for most anthropogenic contaminants, receiving untreated or partially treated industrial effluents containing toxic metals. Once introduced into aquatic systems, these metals undergo

complex physicochemical transformations involving adsorption, desorption, oxidation, reduction, precipitation, dissolution, and complexation with organic and inorganic ligands, thereby influencing their environmental behaviour and toxicity (Briffa *et al.*, 2020).

The environmental significance of heavy metals is further amplified by their ability to bioaccumulate within aquatic organisms and biomagnify along food chains. Fish, shellfish, molluscs, aquatic plants, and benthic organisms accumulate metals at concentrations several orders of magnitude greater than those found in surrounding waters, increasing human exposure through dietary consumption (Jaishankar *et al.*, 2014). Numerous epidemiological studies have linked chronic heavy metal exposure to neurological disorders, kidney dysfunction, cardiovascular diseases, developmental abnormalities, endocrine disruption, reproductive impairment, immune suppression, and several forms of cancer (Pratish et al., 2018; Tchounwou *et al.*, 2012).

2.2 Sources of Heavy Metals in Aquatic Systems

Heavy metals originate from both natural (geogenic) and anthropogenic sources. Although weathering of rocks, volcanic activities, and atmospheric deposition contribute naturally occurring metals to surface waters, human activities now account for the overwhelming majority of heavy metal contamination worldwide (Ali *et al.*, 2019).

2.2.1 Natural Sources

Natural sources include: Weathering of metal-bearing rocks, volcanic eruptions, atmospheric deposition, soil erosion, forest fires, and geothermal activities

These natural processes generally contribute relatively low metal concentrations and constitute part of the Earth's natural geochemical cycle (Alloway, 2013).

2.2.2 Anthropogenic Sources

Human activities remain the dominant contributors to heavy metal pollution in aquatic environments. Major anthropogenic sources include mining operations, petroleum exploration and refining, electroplating industries, battery manufacturing, textile industries, leather processing, fertilizer production, pesticide application, municipal wastewater, electronic waste recycling, steel manufacturing, cement production, coal combustion, landfill leachates, and urban stormwater runoff (Qasem *et al.*, 2021).

Industrial effluents frequently contain mixtures of cadmium, chromium, lead, nickel, copper, zinc, mercury, arsenic, cobalt, manganese, and iron, making wastewater treatment considerably more complicated than single-metal systems because of competitive interactions among metal ions (Briffa *et al.*, 2020)



Figure 1: Sources of Heavy Metals

2.3 Environmental Fate and Transport

Following their release into aquatic environments, heavy metals rarely remain entirely dissolved. Instead, they partition continuously among dissolved phases, suspended particles, sediments, aquatic vegetation, microorganisms, and aquatic fauna (Sparks, 2003).

Their transport and environmental fate are governed by several physicochemical variables, including: Solution pH, temperature, oxidation-reduction potential, dissolved oxygen, organic matter concentration, salinity, water hardness, presence of competing ions, and microbial activity. Sediments function as long-term reservoirs because adsorption onto clay minerals, iron oxides, manganese oxides, and organic matter immobilizes many dissolved metals. However, environmental changes such as declining pH or altered redox conditions may remobilize these contaminants back into the water column, thereby creating secondary pollution sources years after the initial contamination event (Förstner & Wittmann, 2012).

2.4 Heavy Metal Speciation

The toxicity, mobility, and bioavailability of heavy metals depend primarily on their chemical speciation rather than their total concentration (Stumm & Morgan, 2012).

Chromium exists mainly in two oxidation states: trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}). Hexavalent chromium is considerably more toxic because it possesses greater solubility, mobility, and membrane permeability, enabling rapid cellular uptake and subsequent oxidative damage (Pratuseh *et al.*, 2018).

Mercury occurs as elemental mercury (Hg^0), inorganic mercury (Hg^{2+}), and organic mercury (particularly methylmercury). Methylmercury represents the most toxic form because of its exceptional ability to bioaccumulate and biomagnify through aquatic food webs (Tchounwou *et al.*, 2012). Similarly, lead, cadmium, nickel, copper, and zinc exist as free ions or inorganic and organic complexes depending on environmental conditions. Solution pH remains one of the most influential variables governing heavy metal mobility and adsorption behaviour (Alloway, 2013).

2.5 Bioaccumulation and Biomagnification

Heavy metals possess an exceptional capacity to accumulate within living organisms. Bioaccumulation refers to the gradual increase in contaminant concentration within an organism relative to its surrounding environment, whereas biomagnification describes the progressive increase in contaminant concentration across successive trophic levels (Jaishankar *et al.*, 2014).

A typical contamination pathway is illustrated as:

Water → Phytoplankton → Zooplankton → Small Fish → Large Fish → Humans

Consequently, predatory fish frequently contain the highest concentrations of mercury, lead, cadmium, and chromium, posing substantial health risks to populations dependent on aquatic food resources (Tchounwou *et al.*, 2012). Chronic dietary exposure has been associated with developmental disorders, neurological impairment, renal dysfunction, cardiovascular diseases, and increased cancer risk (Pratish et al., 2018).

2.6 Toxicological Effects of Major Heavy Metals

Heavy metals produce diverse toxicological effects depending on exposure duration, concentration, chemical form, and individual susceptibility (Tchounwou *et al.*, 2012).

Table 1: Health Effects of Heavy Metals

Heavy Metal	Major Sources	Principal Health Effects
Cadmium (Cd)	Mining, batteries, phosphate fertilizers	Kidney damage, osteoporosis, carcinogenicity
Chromium (Cr ⁶⁺)	Electroplating, leather tanning	Lung cancer, liver damage, respiratory disorders
Lead (Pb)	Batteries, paints, petroleum activities	Neurotoxicity, developmental disorders, anaemia
Mercury (Hg)	Gold mining, chlor-alkali industries	Neurotoxicity, developmental abnormalities
Nickel (Ni)	Electroplating, stainless steel industries	Dermatitis, respiratory disease, carcinogenicity
Copper (Cu)	Mining, plumbing systems	Liver damage, gastrointestinal disorders
Zinc (Zn)	Galvanizing industries, fertilizers	Gastrointestinal irritation, interference with copper metabolism

Although copper and zinc are essential trace elements, excessive exposure disrupts enzymatic activities, oxidative metabolism, and cellular homeostasis (Pratish *et al.*, 2018).

2.8 Implications for Environmental Remediation

The persistence, mobility, bioavailability, and toxicity of heavy metals underscore the urgent need for efficient remediation technologies capable of treating complex multi-metal wastewater systems (Qasem *et al.*, 2021). Conventional treatment methods often experience reduced performance under competitive adsorption conditions because multiple metal ions compete for available active sites. Consequently, increasing attention has been directed toward engineered adsorbents such as Fe/Mn/N tri-doped sawdust-derived biochar, which possess multiple adsorption mechanisms, abundant functional groups, enhanced surface heterogeneity, and improved selectivity for simultaneous removal of diverse heavy metals (Liu *et al.*, 2024; Guo *et al.*, 2025). These next-generation biochar materials represent a promising and sustainable solution for improving water quality and supporting global environmental protection initiatives.

3.0. Conventional Technologies for Heavy Metal Removal

3.1 Overview

The increasing occurrence of heavy metals in industrial wastewater has necessitated the development of efficient treatment technologies capable of reducing metal concentrations to environmentally acceptable limits before discharge into receiving water bodies. Over the past several decades, numerous conventional physicochemical and biological treatment techniques have been developed for heavy metal removal. These technologies include chemical precipitation, coagulation-flocculation, ion exchange, membrane filtration, electrochemical treatment, solvent extraction, flotation, phytoremediation, and biological remediation (Qasem, Mohammed, & Lawal, 2021). Although these methods have demonstrated varying degrees of success under controlled operating conditions, many suffer from significant economic, operational, and environmental limitations, particularly when treating wastewater containing multiple heavy metal contaminants.

Selection of an appropriate treatment technology depends on several factors, including the type and concentration of contaminants, wastewater characteristics, operational cost, energy requirement, sludge generation, treatment efficiency, ease of operation, and environmental sustainability (Fu & Wang, 2011). Consequently, researchers have increasingly focused on developing alternative technologies that are cost-effective, environmentally benign, and capable of treating complex wastewater matrices.

3.2 Chemical Precipitation

Chemical precipitation remains one of the oldest and most widely used technologies for heavy metal removal from industrial wastewater. The process involves converting dissolved metal ions into insoluble compounds through the addition of suitable chemical reagents, followed by sedimentation and filtration (Fu & Wang, 2011).

Hydroxide precipitation is the most common approach, where alkaline reagents such as sodium hydroxide (NaOH) or calcium hydroxide [Ca(OH)₂] are added to increase the solution pH, causing dissolved metals to precipitate as metal hydroxides. Other precipitation methods include sulfide precipitation, carbonate precipitation, and phosphate precipitation, depending on the specific wastewater characteristics (Qasem *et al.*, 2021).

Despite its simplicity and relatively low capital cost, chemical precipitation presents several drawbacks. Large volumes of hazardous sludge are generated during treatment, requiring further stabilization and disposal. In addition, incomplete precipitation may occur in wastewater containing complexing agents or multiple competing metal ions, thereby reducing overall treatment efficiency. The process is also highly sensitive to pH fluctuations, making continuous monitoring necessary (Fu & Wang, 2011).

3.3 Coagulation–Flocculation

Coagulation-flocculation is another conventional physicochemical treatment process widely employed for removing suspended solids, colloidal particles, and dissolved heavy metals from wastewater. During coagulation, chemical coagulants such as aluminium sulfate (alum), ferric chloride, ferric sulfate, or polyaluminium chloride destabilize negatively charged particles by neutralizing their surface charges. Subsequently, flocculation promotes aggregation of these destabilized particles into larger flocs that can easily settle under gravity (Bratby, 2016).

Although coagulation-flocculation can significantly reduce heavy metal concentrations, its efficiency depends strongly on wastewater chemistry, pH, coagulant dosage, mixing intensity, and hydraulic retention time. Furthermore, similar to chemical precipitation, this technology generates considerable quantities of sludge requiring proper handling and disposal. Excessive use of chemical coagulants may also increase treatment costs and

introduce secondary contaminants into treated water (Qasem *et al.*, 2021).

3.4 Ion Exchange Technology

Ion exchange is a highly efficient separation technique based on reversible exchange of ions between a solid resin and the surrounding aqueous solution. Synthetic cation exchange resins containing negatively charged functional groups selectively adsorb dissolved metal cations while simultaneously releasing less hazardous ions such as sodium or hydrogen into solution (Fu & Wang, 2011). Ion exchange systems achieve excellent removal efficiencies for dilute wastewater streams and are capable of recovering valuable metals for reuse. However, resin fouling by suspended solids, organic matter, or competing ions significantly reduces operational efficiency. Moreover, regeneration of exhausted resins requires concentrated chemical solutions that generate secondary waste streams. The relatively high cost of commercial ion exchange resins further limits widespread application in developing countries (Qasem *et al.*, 2021).

3.5 Membrane Filtration Technologies

Membrane-based separation technologies have become increasingly important for advanced wastewater treatment owing to their high separation efficiency and ability to remove dissolved contaminants without introducing additional chemicals. Common membrane processes include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and electrodialysis (Shannon *et al.*, 2008).

Reverse osmosis and nanofiltration are particularly effective for removing dissolved heavy metals because of their extremely small pore sizes, enabling rejection efficiencies exceeding 95% for many contaminants. Nevertheless, membrane systems are associated with several operational challenges, including membrane fouling, scaling, concentration polarization, high energy consumption, and frequent membrane replacement. These limitations substantially increase maintenance costs and reduce long-term economic viability, particularly in resource-limited settings (Qasem *et al.*, 2021).

3.6 Electrochemical Treatment Methods

Electrochemical technologies utilize electrical energy to facilitate removal of dissolved contaminants from wastewater through oxidation, reduction, coagulation, flotation, or electrodeposition mechanisms. Common electrochemical techniques include electrocoagulation, electroflotation, electrooxidation, and electrodialysis (Chen, 2004). Electrocoagulation has attracted considerable interest because sacrificial aluminium or iron electrodes continuously generate metal hydroxides capable of adsorbing and precipitating dissolved heavy metals. Electrochemical methods generally achieve rapid treatment with relatively small sludge volumes. However, high electricity consumption, electrode passivation, equipment corrosion, and operational complexity remain significant limitations for large-scale implementation (Chen, 2004).

3.7 Biological Treatment Technologies

Biological approaches employ microorganisms, algae, fungi, aquatic plants, or agricultural biomass for heavy metal removal through biosorption, bioaccumulation, biotransformation, and phytoremediation mechanisms (Volesky, 2007). Microbial cell walls contain numerous functional groups, including hydroxyl, amino, phosphate, and carboxyl groups, capable of binding dissolved metal ions through ion exchange and complexation reactions. Similarly, aquatic macrophytes accumulate substantial quantities of heavy metals within their tissues, making phytoremediation an environmentally friendly treatment option.

Despite their environmental advantages, biological methods generally require longer

treatment times, exhibit lower tolerance to high contaminant concentrations, and are highly sensitive to environmental conditions such as pH, temperature, nutrient availability, and dissolved oxygen (Ali *et al.*, 2019).

Furthermore, industrial effluents rarely contain individual heavy metals in isolation. Instead, multiple contaminants coexist and compete for treatment sites, reducing the efficiency of precipitation, ion exchange, and membrane processes. These challenges have stimulated increasing interest in adsorption-based technologies capable of simultaneously removing multiple heavy metals under diverse environmental conditions (Sajjadi, Chen, & Egiebor, 2019).

3.9 Transition towards Adsorption Technology

Among all available treatment technologies, adsorption has emerged as one of the most promising approaches because of its operational simplicity, high efficiency, minimal sludge generation, low energy demand, and adaptability to complex wastewater matrices (Qasem *et al.*, 2021). Recent developments in advanced adsorbent materials, particularly engineered biochar nanomaterials, have significantly improved adsorption capacity, selectivity, regeneration potential, and environmental sustainability. Consequently, adsorption using modified biochar has become a major focus of current environmental remediation research and represents a promising alternative to conventional wastewater treatment technologies.

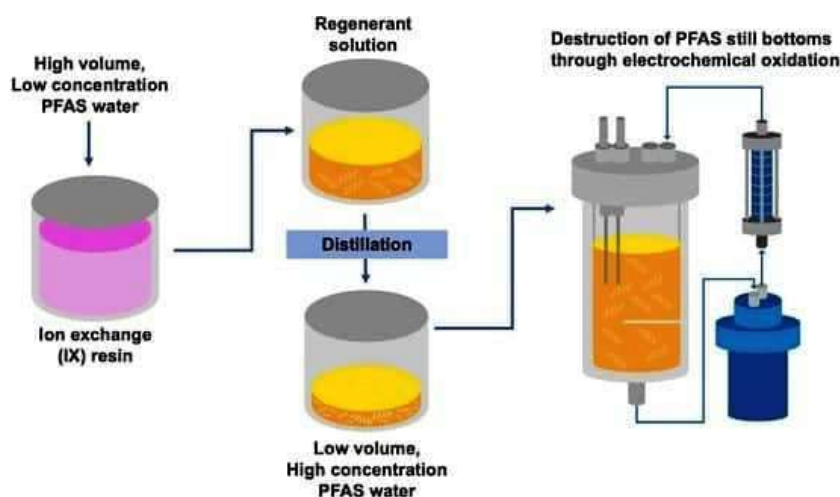


Figure 2: Infograph showing Efficiency vs Limitations of the conventional technologies

4.0. Adsorption Technology for Heavy Metal Removal

4.1 Introduction

Adsorption has become one of the most widely investigated technologies for the removal of heavy metals from contaminated water due to its high efficiency, operational simplicity, cost-effectiveness, and environmental sustainability. Unlike conventional physicochemical treatment methods that often generate large volumes of toxic sludge or require substantial energy input, adsorption involves the accumulation of dissolved contaminants onto the surface of a solid adsorbent through physical or chemical interactions (Qasem, Mohammed, & Lawal, 2021). Owing to these advantages, adsorption has emerged as one of the most promising approaches for treating industrial effluents containing multiple heavy metal ions.

In recent years, increasing environmental regulations and the need for sustainable wastewater treatment have accelerated research into advanced adsorbent materials capable of simultaneously removing several toxic metals under varying environmental conditions. Engineered biochar materials, activated carbons, zeolites, clay minerals, metal-organic frameworks, graphene-based composites, agricultural wastes, and nanomaterials have all

demonstrated considerable potential as adsorbents for heavy metal remediation (Sajjadi, Chen, & Egiebor, 2019; Liu *et al.*, 2024).

4.2 Fundamentals of Adsorption

Adsorption is a surface phenomenon in which atoms, ions, or molecules from a liquid or gaseous phase accumulate on the surface of a solid material known as the adsorbent. The substance being removed from solution is referred to as the adsorbate. The driving force for adsorption arises from attractive interactions between the adsorbate and the adsorbent surface, resulting in a reduction in the free energy of the system (Ruthven, 1984).

Most engineered biochar materials remove heavy metals predominantly through chemisorption mechanisms involving oxygen-containing and nitrogen-containing functional groups (Guo *et al.*, 2025).

4.2 Mechanisms of Heavy Metal Adsorption

Heavy metal adsorption is considerably more complex than simple physical attachment. Multiple mechanisms often operate simultaneously, with the dominant mechanism depending on adsorbent properties, solution chemistry, and the nature of the metal ions (Sajjadi *et al.*, 2019).

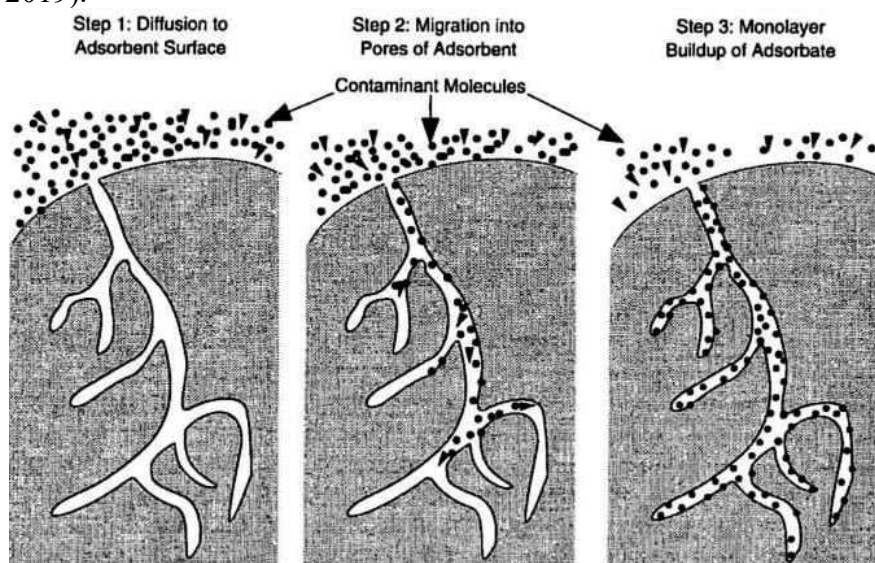


Figure 3: Diagrammatic representation of Mechanisms of Heavy Metal Adsorption

4.3.1 Electrostatic Attraction

Electrostatic attraction occurs between positively charged heavy metal ions and negatively charged functional groups present on the adsorbent surface.

Functional groups involved include: Carboxyl ($-\text{COOH}$), Hydroxyl ($-\text{OH}$), Phenolic groups, Nitrogen-containing groups

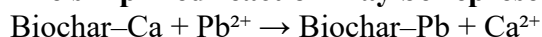
At solution pH values above the point of zero charge (pH_{pzc}), these functional groups become negatively charged, thereby attracting positively charged metal ions such as Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , and Hg^{2+} (Ippolito *et al.*, 2020).

4.3.2 Ion Exchange

Ion exchange is one of the dominant mechanisms responsible for heavy metal adsorption by biochar.

During adsorption, naturally occurring cations such as: H^+ , Na^+ , Ca^{2+} , Mg^{2+} and K^+ are exchanged with dissolved heavy metal ions.

The simplified reaction may be represented as:



Ion exchange contributes significantly to the high adsorption capacities observed for engineered biochars.

4.3.3 Surface Complexation

Surface complexation involves the formation of coordination bonds between metal ions and functional groups present on the adsorbent surface.

Important functional groups include: Hydroxyl groups, Carboxyl groups, Carbonyl groups, Amino groups, Pyridinic nitrogen and Pyrrolic nitrogen. These groups donate electron pairs to heavy metal ions, forming highly stable inner-sphere complexes that enhance adsorption strength (Guo *et al.*, 2025).

4.3.4 Chelation

Chelation is particularly important in nitrogen-doped biochars.

Nitrogen-containing functional groups coordinate strongly with transition metals such as: Cu, Ni, Cd, and Pb. The formation of stable chelate complexes significantly improves adsorption selectivity and increases adsorption capacity.

4.3.5 Surface Precipitation

Under favourable pH conditions, dissolved metal ions react with hydroxide, carbonate, phosphate, or oxide species present on the adsorbent surface to form insoluble precipitates.

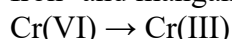
Examples include: $\text{Pb}^{2+} + \text{CO}_3^{2-} \rightarrow \text{PbCO}_3$ and $\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu}(\text{OH})_2$.

These precipitates become immobilized on the adsorbent surface, contributing substantially to overall metal removal efficiency (Ippolito *et al.*, 2020).

4.3.6 Redox Reactions

Some modified biochars contain redox-active components capable of changing the oxidation state of adsorbed contaminants.

Iron- and manganese-modified biochars facilitate oxidation-reduction reactions such as:



The reduced chromium species subsequently form stable complexes or precipitates with the adsorbent surface, greatly decreasing toxicity and mobility (Liu *et al.*, 2024).

4.3.7 Pore Filling

Highly porous adsorbents possess extensive networks of micro-, meso-, and macropores.

Heavy metal ions diffuse through these pores and become trapped within the internal pore structure.

Although pore filling alone contributes relatively little to heavy metal adsorption compared with chemisorption, it significantly increases overall adsorption capacity by exposing more active sites (Sajjadi *et al.*, 2019).

4.4 Factors Affecting Heavy Metal Adsorption

Adsorption performance depends on numerous operational and physicochemical factors.

4.4.1 Solution pH

Solution pH is widely regarded as the most influential operational parameter controlling adsorption performance.

4.4.2 Contact Time

Adsorption generally proceeds through three distinct stages:

1. Rapid external surface adsorption.
2. Gradual intraparticle diffusion.
3. Equilibrium stage.

Initially, abundant vacant adsorption sites permit rapid uptake. As these sites become occupied, adsorption gradually slows until equilibrium is attained (Wang & Guo, 2023).

4.4.3 Adsorbent Dosage

Increasing adsorbent dosage increases: Surface area, number of adsorption sites, and removal efficiency.

However, adsorption capacity expressed as mg/g may decrease at excessive dosages due to particle aggregation and underutilization of active sites (Foo & Hameed, 2010).

4.4.4 Initial Metal Concentration

Higher initial concentrations provide a stronger concentration gradient, increasing mass transfer rates during the early stages of adsorption.

Nevertheless, excessively high concentrations may rapidly saturate adsorption sites, resulting in lower percentage removal despite higher adsorption capacities (Qasem *et al.*, 2021).

4.4.5 Temperature

Temperature influences adsorption kinetics, equilibrium, and thermodynamics.

For exothermic adsorption processes, increasing temperature generally reduces adsorption efficiency, whereas endothermic systems exhibit improved adsorption at elevated temperatures (Sahmoune, 2019).

4.4.6 Competing Metal Ions

Real industrial wastewater usually contains mixtures of heavy metals rather than individual contaminants.

Competition among Pb^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} , and Cr species reduces adsorption efficiency because all ions compete for the same active binding sites (Liu *et al.*, 2024).

4.5 Advantages of Adsorption Technology

Compared with conventional treatment methods, adsorption offers numerous advantages: High removal efficiencies for trace contaminants, simultaneous removal of multiple heavy metals, low operational cost, minimal sludge generation, simple equipment design, easy process control, regeneration and reuse of adsorbents, applicability to both batch and continuous treatment systems, compatibility with renewable biomass-derived adsorbents, high environmental sustainability (Qasem *et al.*, 2021; Sajjadi *et al.*, 2019).

5.0. Biochar as An Adsorbent For Heavy Metal Remediation

5.1. Introduction

Biochar has emerged as one of the most promising adsorbent materials for environmental remediation owing to its unique physicochemical properties, environmental sustainability, and cost-effectiveness. It is a carbon-rich porous material produced through the thermochemical conversion of biomass under oxygen-limited conditions, a process commonly referred to as pyrolysis (Lehmann & Joseph, 2015). Although biochar was initially promoted for carbon sequestration and soil improvement, extensive research during the past decade has demonstrated its remarkable potential for wastewater treatment, particularly for the adsorption of heavy metals and organic contaminants (Sajjadi, Chen, & Egiebor, 2019).

The growing interest in biochar is largely driven by the need to develop environmentally friendly alternatives to expensive commercial adsorbents such as activated carbon. Agricultural residues, forestry wastes, municipal biomass, animal manure, and industrial lignocellulosic wastes are increasingly being converted into biochar, thereby transforming waste materials into high-value environmental remediation products (Tan *et al.*, 2015). This approach not only reduces waste disposal problems but also supports circular economy principles by promoting biomass valorization and sustainable resource utilization.

Biochar possesses a highly porous structure, abundant surface functional groups, relatively large specific surface area, and considerable chemical stability, making it suitable for removing various inorganic and organic pollutants from aqueous systems. These characteristics have positioned biochar as one of the most extensively investigated adsorbents for treating contaminated water and wastewater (Ippolito *et al.*, 2020).

5.2 Production of Biochar

Biochar is primarily produced through pyrolysis, a thermochemical process involving the decomposition of biomass under oxygen-deficient conditions. During pyrolysis, volatile compounds are released while carbon-rich solid residues are formed. The characteristics of the resulting biochar depend largely on the feedstock type and pyrolysis conditions, including temperature, heating rate, residence time, and atmospheric environment (Lehmann & Joseph, 2015).

5.3 Physicochemical Properties of Biochar

The adsorption performance of biochar is largely determined by its physicochemical properties. Important characteristics include specific surface area, pore volume, pore size distribution, surface functional groups, elemental composition, ash content, aromaticity, pH, cation exchange capacity, and surface charge (Tan *et al.*, 2015).

5.4 Factors Influencing Biochar Properties

Several factors determine the adsorption performance of biochar.

5.4.1 Feedstock Type

The chemical composition of biomass strongly influences the characteristics of the resulting biochar. Lignocellulosic materials such as sawdust, rice husk, bamboo, coconut shell, and corn stalk generally produce biochars with high carbon contents and well-developed pore structures (Tan *et al.*, 2015).

Animal manures, sewage sludge, and agricultural residues often produce biochars with higher mineral contents, greater ash percentages, and increased alkalinity, which may enhance adsorption of certain heavy metals through precipitation mechanisms (Ippolito *et al.*, 2020).

5.4.2 Pyrolysis Temperature

Temperature is considered one of the most important parameters governing biochar quality. Increasing pyrolysis temperature generally increases aromaticity, carbon content, pore development, and specific surface area while reducing volatile matter and oxygen-containing functional groups (Lehmann & Joseph, 2015).

Biochars produced between 500 and 700 °C frequently demonstrate superior adsorption performance because they combine extensive pore development with sufficient structural stability (Sajjadi *et al.*, 2019).

5.4.3 Heating Rate and Residence Time

Heating rate and residence time influence pore formation, carbonization efficiency, and surface chemistry. Slow heating combined with adequate residence time promotes gradual

decomposition of biomass components and facilitates formation of stable porous carbon structures suitable for adsorption applications (Tan *et al.*, 2015).

5.5 Mechanisms of Heavy Metal Removal by Biochar

Heavy metal adsorption by biochar is governed by several simultaneous mechanisms.

Ion Exchange: Exchangeable cations naturally present within the biochar matrix, including Ca^{2+} , Mg^{2+} , Na^{+} , and K^{+} , are replaced by dissolved heavy metal ions, resulting in contaminant immobilization.

Surface Complexation: Hydroxyl, carboxyl, carbonyl, and amino functional groups coordinate directly with dissolved metal ions to form stable inner-sphere complexes. Surface complexation is particularly important for Pb^{2+} , Cu^{2+} , Cd^{2+} , and Ni^{2+} adsorption (Ippolito *et al.*, 2020).

Electrostatic Attraction: Negatively charged functional groups attract positively charged heavy metal ions through Coulombic interactions, especially at solution pH values above the point of zero charge.

Mineral Precipitation: Mineral constituents present within biochar may react with dissolved metals to form insoluble hydroxides, carbonates, phosphates, or oxides, thereby enhancing overall removal efficiency.

Physical Adsorption: Heavy metals may also become physically retained within the porous biochar matrix through pore filling and Van der Waals interactions, although this mechanism generally contributes less than chemisorption processes.

5.6 Advantages of Biochar Compared with Conventional Adsorbents

Biochar possesses several advantages over commercially available activated carbon and synthetic adsorbents.

These include: Low production cost due to the use of abundant agricultural and forestry wastes, renewable and environmentally sustainable feedstocks, high adsorption efficiency for diverse contaminants, relatively simple production technology, minimal environmental footprint, potential for regeneration and reuse, simultaneous removal of multiple contaminants.

Carbon sequestration benefits that contribute to climate change mitigation (Lehmann & Joseph, 2015; Ippolito *et al.*, 2020).

Because of these advantages, biochar has become an attractive material for wastewater treatment, particularly in developing countries where access to expensive treatment technologies may be limited.

6.0. Sawdust-Derived Biochar as A Sustainable Adsorbent for Heavy Metal Remediation

6.1 Introduction

Sawdust is one of the most abundant lignocellulosic wastes generated worldwide through timber processing, furniture manufacturing, sawmilling, plywood production, and wood-based industries. Millions of tonnes of sawdust are produced annually, particularly in developing countries where wood remains a major construction and energy resource (Tan *et al.*, 2015). Traditionally, sawdust has been disposed of through open burning, indiscriminate dumping, or landfilling, practices that contribute to environmental pollution, greenhouse gas

emissions, and inefficient utilization of biomass resources. Consequently, the conversion of sawdust into biochar has attracted considerable attention as an environmentally sustainable strategy for waste valorization and environmental remediation (Lehmann & Joseph, 2015).

Sawdust-derived biochar has emerged as a promising adsorbent because of its abundance, renewability, low production cost, and favourable physicochemical properties. The lignocellulosic composition of sawdust promotes the formation of porous carbon structures with abundant oxygen-containing functional groups following pyrolysis, making it suitable for adsorption of heavy metals from contaminated water (Sajjadi, Chen, & Egiebor, 2019). Compared with many agricultural residues, sawdust generally possesses relatively high lignin content, resulting in biochars with improved structural stability and greater aromatic carbon content (Tan *et al.*, 2015).

6.2 Chemical Composition of Sawdust

The physicochemical characteristics of sawdust-derived biochar are largely influenced by the chemical composition of the parent biomass. Sawdust consists primarily of cellulose, hemicellulose, lignin, extractives, and small quantities of mineral ash. These components undergo thermal decomposition during pyrolysis, producing biochar with unique structural and chemical properties (Lehmann & Joseph, 2015).

Typical lignocellulosic composition includes:

Component	Typical Percentage (%)
Cellulose	40–50
Hemicellulose	20–35
Lignin	20–30
Extractives	2–8
Ash	<5

Cellulose contributes to the formation of microporous carbon structures during pyrolysis, whereas hemicellulose decomposes at relatively low temperatures to generate volatile compounds. Lignin decomposes more gradually and is largely responsible for the development of aromatic carbon frameworks that impart structural rigidity and thermal stability to biochar (Tan *et al.*, 2015).

The relatively high carbon content and low ash content of sawdust distinguish it from other biomass feedstocks such as sewage sludge or animal manure, making it particularly attractive for producing high-quality biochar suitable for adsorption applications (Sajjadi *et al.*, 2019).

6.3 Production of Sawdust-Derived Biochar

The production of sawdust biochar involves several sequential processes, each influencing the final properties of the adsorbent. Initially, freshly collected sawdust is washed thoroughly with deionized water to remove adhering soil particles, bark fragments, oils, and other impurities. The material is subsequently dried under controlled conditions to reduce moisture content before size reduction through grinding and sieving to obtain a uniform particle size distribution. Pyrolysis is then carried out under oxygen-limited conditions, typically at temperatures between 400 and 700 °C. During this process, volatile organic compounds are released while carbon-rich porous structures are formed (Lehmann & Joseph, 2015). The resulting biochar is allowed to cool under inert conditions, washed to remove residual ash and soluble salts, dried, and stored in airtight containers before characterization and adsorption studies. Pyrolysis temperature strongly influences the quality of sawdust biochar. Low temperatures generally preserve larger quantities of oxygen-containing functional groups but produce lower surface areas. Conversely, higher temperatures enhance pore development,

aromaticity, and specific surface area while reducing the abundance of polar surface functional groups (Sajjadi *et al.*, 2019). Consequently, pyrolysis temperatures between 500 and 600 °C are widely regarded as optimal for producing biochars with balanced physicochemical properties suitable for heavy metal adsorption.

6.4 Physicochemical Properties of Sawdust Biochar

Sawdust-derived biochar possesses several characteristics that make it suitable for wastewater treatment. One of its most important features is its porous architecture, which provides numerous adsorption sites for dissolved contaminants. The interconnected network of micro-, meso-, and macropores facilitates rapid diffusion of metal ions from solution to internal adsorption sites, thereby improving adsorption efficiency (Tan *et al.*, 2015).

In addition to porosity, sawdust biochar contains various oxygen-containing functional groups, including hydroxyl (-OH), carboxyl (-COOH), carbonyl (C=O), and phenolic groups. These functional groups participate in ion exchange, electrostatic attraction, hydrogen bonding, and surface complexation with heavy metal ions.

The alkaline nature of many sawdust biochars also contributes to their adsorption performance by increasing solution pH during treatment, thereby enhancing precipitation and adsorption of certain heavy metals such as lead, copper, cadmium, and zinc (Ippolito *et al.*, 2020).

6.5 Mechanisms of Heavy Metal Removal by Sawdust Biochar

The removal of heavy metals by sawdust-derived biochar occurs through multiple interacting mechanisms rather than a single adsorption process. These mechanisms often operate simultaneously depending on the physicochemical properties of both the adsorbent and the contaminated water. Ion exchange represents one of the primary mechanisms, whereby naturally occurring cations such as calcium, potassium, magnesium, and sodium are exchanged with dissolved heavy metal ions present in solution. Surface complexation also contributes significantly, with oxygen-containing functional groups forming stable coordination complexes with metal ions such as Pb^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , and Zn^{2+} .

Electrostatic attraction becomes increasingly important at pH values above the point of zero charge, where negatively charged surface functional groups attract positively charged heavy metal ions. Additionally, pore filling within the highly porous carbon matrix facilitates physical retention of contaminants, while mineral precipitation contributes to immobilization of certain metals under alkaline conditions.

6.6 Modification Strategies for Sawdust Biochar

Numerous modification techniques have been developed to improve the adsorption performance of sawdust-derived biochar. These modifications aim to increase surface area, introduce additional functional groups, improve pore development, enhance surface charge, and create new adsorption mechanisms.

Common modification approaches include:

Physical activation, involving steam or carbon dioxide treatment to enlarge pore structures.

Chemical activation, using activating agents such as potassium hydroxide (KOH), phosphoric acid (H_3PO_4), or zinc chloride ($ZnCl_2$) to increase surface area and porosity.

Acid or alkali modification, which alters surface chemistry and introduces oxygen-containing functional groups.

Metal impregnation, whereby transition metals such as iron (Fe), manganese (Mn), magnesium (Mg), calcium (Ca), or aluminium (Al) are incorporated into the biochar matrix to create additional adsorption sites and improve redox activity.

Heteroatom doping, particularly with nitrogen, sulfur, or phosphorus, to increase electron density, enhance basicity, and strengthen adsorption through coordination interactions (Guo *et al.*, 2025). Among these approaches, simultaneous incorporation of iron, manganese, and nitrogen has recently emerged as one of the most effective strategies because it integrates multiple adsorption mechanisms within a single engineered adsorbent.

6.7 Applications of Sawdust Biochar in Water Treatment

Sawdust-derived biochar has been successfully applied for the removal of a wide variety of contaminants from aqueous systems. These include heavy metals such as cadmium, chromium, copper, mercury, lead, nickel, and zinc, as well as organic pollutants including dyes, pesticides, pharmaceuticals, phenolic compounds, and petroleum hydrocarbons.

Recent studies have demonstrated that modified sawdust biochars consistently outperform unmodified biochars due to their greater adsorption capacities, improved selectivity, and faster adsorption kinetics. These findings highlight the importance of continued material engineering aimed at enhancing the physicochemical properties of biomass-derived adsorbents (Liu *et al.*, 2024). Overall, sawdust-derived biochar represents an environmentally sustainable and economically viable platform for developing next-generation adsorbents capable of addressing increasingly complex wastewater treatment challenges. The subsequent evolution of this technology has led to the development of nano-biochar, in which particle size reduction and nanoscale engineering further improve adsorption efficiency, surface reactivity, and contaminant removal performance.

7.0. Nano-Biochar Technology

Nano-biochar represents an advanced generation of biochar materials engineered at the nanoscale to improve adsorption efficiency and contaminant removal from water. It is produced by reducing conventional biochar particles to nanometer dimensions through mechanical milling, chemical activation, ultrasonication, or other nanotechnology-based approaches. The reduction in particle size significantly increases the surface area, pore accessibility, and density of active adsorption sites, making nano-biochar more efficient than conventional biochar for heavy metal remediation (Sajjadi, Chen, & Egiebor, 2019).

Compared with bulk biochar, nano-biochar exhibits superior physicochemical properties, including higher porosity, improved surface functionality, enhanced dispersibility in aqueous solutions, and faster adsorption kinetics. These characteristics facilitate rapid interaction between the adsorbent surface and dissolved heavy metal ions, thereby increasing adsorption capacity and reducing equilibrium time (Ippolito *et al.*, 2020).

Nano-biochar removes heavy metals through multiple mechanisms such as electrostatic attraction, ion exchange, surface complexation, pore filling, and redox reactions. The abundance of nanoscale pores and functional groups allows simultaneous adsorption of several heavy metals, making nano-biochar particularly suitable for treating complex industrial wastewater containing multiple contaminants (Liu *et al.*, 2024).

Despite its excellent adsorption performance, large-scale application of nano-biochar remains constrained by challenges including particle aggregation, recovery after treatment, and production costs. Consequently, recent research has focused on surface modification and heteroatom doping to improve stability, reusability, and selectivity. These developments have paved the way for the emergence of metal-modified nano-biochars, particularly iron- and manganese-modified biochars, which exhibit even greater adsorption efficiencies.

8.0. Metal-Modified Biochar

Metal modification has become one of the most effective strategies for enhancing the adsorption performance of biochar. The incorporation of transition metals introduces

additional active adsorption sites, improves surface chemistry, and promotes redox reactions that facilitate heavy metal removal from contaminated water (Ippolito *et al.*, 2020).

Iron (Fe)-modified biochar is among the most extensively studied engineered adsorbents. Iron oxides and hydroxides deposited on the biochar surface provide abundant coordination sites for heavy metal ions through inner-sphere complexation. In addition, iron-containing phases promote oxidation-reduction reactions that convert certain toxic metals into less mobile forms, thereby improving removal efficiency.

Similarly, manganese (Mn)-modified biochar enhances adsorption by introducing manganese oxides that possess high oxidation potential and strong affinity for various heavy metals. Manganese oxides also facilitate catalytic oxidation reactions and improve adsorption selectivity, particularly for lead, cadmium, chromium, and mercury (Liu *et al.*, 2024).

The simultaneous incorporation of multiple metal species further enhances adsorption through synergistic interactions. Multi-metal modification increases surface heterogeneity, enlarges pore structures, and creates diverse binding sites capable of removing several contaminants simultaneously. These engineered materials generally outperform pristine and single-metal-modified biochars in terms of adsorption capacity, kinetics, and stability.

Metal-modified biochars have therefore emerged as promising adsorbents for industrial wastewater treatment, especially where multiple heavy metals coexist. Nevertheless, incorporating non-metal heteroatoms such as nitrogen can further improve adsorption by modifying the electronic structure of the biochar surface.

9.0. Nitrogen-Doped Biochar

Nitrogen doping has emerged as one of the most effective approaches for improving the adsorption performance of biochar. The incorporation of nitrogen atoms into the carbon matrix modifies the electronic structure of biochar, increases surface basicity, and introduces additional functional groups that enhance the interaction between the adsorbent and heavy metal ions (Guo *et al.*, 2025).

Nitrogen is commonly introduced during biochar synthesis using nitrogen-rich precursors such as urea, melamine, ammonia, or amino compounds. During pyrolysis, these compounds become integrated into the carbon framework, forming nitrogen-containing functional groups including pyridinic-N, pyrrolic-N, graphitic-N, and oxidized nitrogen species. These functional groups serve as active adsorption sites for heavy metals through coordination bonding, electrostatic attraction, and surface complexation (Guo *et al.*, 2025).

Nitrogen doping also improves the physicochemical properties of biochar by increasing electron density, enhancing electrical conductivity, and promoting greater surface polarity. Consequently, nitrogen-doped biochar generally exhibits higher adsorption capacities, faster adsorption kinetics, and greater stability than undoped biochar. In multi-metal systems, these characteristics improve adsorption selectivity and reduce competition among metal ions for available binding sites (Liu *et al.*, 2024).

Several studies have demonstrated that nitrogen-doped biochar achieves superior removal efficiencies for cadmium, lead, chromium, copper, nickel, zinc, and mercury due to the increased abundance of active nitrogen-containing functional groups. Furthermore, nitrogen doping enhances regeneration efficiency, allowing the adsorbent to retain much of its adsorption capacity after repeated adsorption-desorption cycles (Guo *et al.*, 2025).

Although nitrogen doping significantly improves adsorption performance, combining nitrogen with transition metals such as iron and manganese provides even greater enhancement through synergistic interactions. This has led to the development of Fe/Mn/N tri-doped biochar, one of the most promising engineered adsorbents for multi-metal wastewater treatment.

10.0. Fe/Mn/N TRI-Doped Sawdust Biochar

Fe/Mn/N tri-doped sawdust biochar represents a new generation of engineered nano-adsorbents designed to overcome the limitations of pristine and single-doped biochars. By simultaneously incorporating iron (Fe), manganese (Mn), and nitrogen (N) into the biochar matrix, the material integrates multiple adsorption mechanisms that significantly improve heavy metal removal from contaminated water (Liu *et al.*, 2024).

Iron contributes by forming iron oxides and hydroxides that provide strong coordination sites for heavy metal ions through inner-sphere complexation. These iron phases also facilitate oxidation-reduction reactions that reduce the mobility and toxicity of certain contaminants. Manganese introduces additional redox-active sites, enhances catalytic oxidation, and increases adsorption affinity toward metals such as lead, cadmium, chromium, and mercury (Ippolito *et al.*, 2020). Nitrogen complements these effects by increasing electron density, improving surface basicity, and introducing nitrogen-containing functional groups that strengthen electrostatic attraction and coordination with dissolved metal ions. The combined action of Fe, Mn, and N creates a highly heterogeneous surface with abundant active sites capable of simultaneously removing multiple heavy metals from solution (Guo *et al.*, 2025).

The enhanced adsorption performance of Fe/Mn/N tri-doped biochar is attributed to several synergistic mechanisms, including electrostatic attraction, ion exchange, surface complexation, pore filling, precipitation, and redox reactions. These mechanisms enable efficient removal of heavy metals even in complex wastewater systems where several contaminants compete for adsorption sites (Liu *et al.*, 2024).

Compared with pristine sawdust biochar, Fe/Mn/N tri-doped biochar exhibits significantly higher adsorption capacity, faster equilibrium time, improved thermal stability, greater structural integrity, and better regeneration potential. These characteristics make it a promising low-cost and environmentally sustainable adsorbent for treating industrial wastewater, mining effluents, produced water, and other multi-metal contaminated aquatic systems. Despite these advantages, further research is still required to optimize large-scale synthesis, evaluate long-term stability, investigate regeneration under continuous operation, and assess performance under real wastewater conditions. Addressing these challenges will facilitate the practical application of Fe/Mn/N tri-doped biochar in commercial water treatment systems.

The adsorption behaviour of this advanced adsorbent is commonly interpreted using adsorption isotherm, kinetic, and thermodynamic models, which provide valuable insights into the mechanisms governing contaminant removal.

11.0. Adsorption Models

Adsorption models are essential tools for understanding the interaction between adsorbents and adsorbates during wastewater treatment. They provide valuable information on adsorption mechanisms, surface characteristics, adsorption capacity, reaction rates, and the thermodynamic feasibility of the adsorption process. In studies involving Fe/Mn/N tri-doped sawdust biochar, adsorption behaviour is commonly interpreted using equilibrium isotherms, kinetic models, and thermodynamic parameters (Wang & Guo, 2023).

11.1 Adsorption Isotherm Models

Adsorption isotherms describe the relationship between the quantity of heavy metals adsorbed by the adsorbent and their equilibrium concentration in solution at constant temperature. These models help determine adsorption capacity and provide insight into the nature of the adsorbent surface.

Numerous studies have reported that heavy metal adsorption onto modified biochars is better described by the Freundlich model because of the heterogeneous distribution of adsorption

sites created during chemical modification and doping (Sajjadi *et al.*, 2019).

11.2 Adsorption Kinetic Models

Adsorption kinetics describe the rate at which heavy metal ions are transferred from solution to the adsorbent surface and provide insight into the controlling adsorption mechanisms.

11.3 Adsorption Thermodynamics

Thermodynamic analysis provides important information regarding the spontaneity, energy changes, and feasibility of adsorption processes. The principal thermodynamic parameters evaluated include Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) (Sahmoune, 2019). Negative values of Gibbs free energy indicate that adsorption occurs spontaneously without external energy input. Negative enthalpy values suggest that adsorption is exothermic, while positive entropy values imply increased randomness at the solid–solution interface during adsorption. Thermodynamic studies on engineered biochars have consistently demonstrated that adsorption of heavy metals is generally spontaneous and energetically favourable under optimum operating conditions. These findings support the practical application of Fe/Mn/N tri-doped biochar for wastewater treatment.

12.0. Characterization Techniques

Characterization techniques are fundamental for evaluating the structural, morphological, chemical, and thermal properties of engineered biochar before and after adsorption. They provide evidence of successful modification and help explain adsorption mechanisms through changes in surface chemistry and material structure (Sajjadi *et al.*, 2019).

The most commonly employed techniques include:

12.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is used to identify surface functional groups responsible for heavy metal adsorption. Characteristic absorption bands corresponding to hydroxyl (-OH), carbonyl (C=O), carboxyl (-COOH), and nitrogen-containing groups provide evidence of successful chemical modification. Changes in peak positions and intensities after adsorption indicate the involvement of these functional groups in metal binding (Guo *et al.*, 2025).

12.2 Scanning Electron Microscopy (SEM)

SEM provides detailed images of the surface morphology of biochar. It reveals pore development, surface roughness, particle distribution, and structural changes resulting from doping and adsorption. Modified biochars typically exhibit more porous and heterogeneous surfaces than pristine biochars, which contributes to improved adsorption performance (Ippolito *et al.*, 2020).

12.3 Differential Scanning Calorimetry (DSC)

DSC evaluates the thermal behaviour and stability of biochar materials by measuring heat flow associated with temperature changes. Improved thermal stability after Fe/Mn/N doping indicates stronger structural integrity and enhanced suitability for repeated adsorption applications.

12.4 X-ray Fluorescence (XRF)

XRF is employed to determine the elemental composition of biochar. It confirms the successful incorporation of iron and manganese into the biochar matrix and provides quantitative information on elemental distribution, thereby verifying the effectiveness of the doping process.

12.5 X-ray Diffraction (XRD)

XRD is used to determine the crystalline phases present in modified biochar. It identifies mineral phases such as iron oxides and manganese oxides formed during synthesis and provides evidence of structural changes resulting from pyrolysis and chemical modification (Liu *et al.*, 2024).

12.6 Brunauer–Emmett–Teller (BET) Surface Area Analysis

BET analysis determines the specific surface area, pore volume, and pore size distribution of biochar. Higher BET surface areas generally correlate with improved adsorption capacity because they provide more accessible adsorption sites for heavy metal ions.

12.7 X-ray Photoelectron Spectroscopy (XPS)

XPS provides detailed information on the chemical states of elements present on the biochar surface. It is particularly useful for confirming nitrogen doping, identifying oxidation states of iron and manganese, and investigating adsorption mechanisms through changes in surface chemical composition.

12.8 Zeta Potential Analysis

Zeta potential measurements evaluate the surface charge characteristics of biochar over a range of pH values. Surface charge strongly influences electrostatic interactions between the adsorbent and dissolved heavy metal ions, making zeta potential an important parameter for understanding pH-dependent adsorption behaviour.

Collectively, these characterization techniques provide comprehensive evidence of successful modification of sawdust-derived biochar and explain the improved adsorption performance observed following Fe/Mn/N tri-doping. The available structural and chemical information also forms the basis for interpreting adsorption mechanisms and evaluating the practical applicability of engineered biochar for wastewater treatment.

13.0. Empirical Review and Research Gap

13.1 Empirical Review

The application of engineered biochar for heavy metal remediation has received increasing attention over the past decade due to its excellent adsorption performance, environmental sustainability, and economic feasibility. Numerous studies have demonstrated that chemical modification and heteroatom doping significantly improve the adsorption capacity of biochar by increasing surface area, pore volume, and the abundance of active functional groups.

Sajjadi, Chen, and Egiebor (2019) comprehensively reviewed biochar-based adsorbents for wastewater treatment and reported that adsorption efficiency depends largely on feedstock type, pyrolysis conditions, and post-synthesis modification. Their study showed that engineered biochars generally outperform pristine biochars because modification introduces additional adsorption sites and enhances surface reactivity. The authors further observed that adsorption mechanisms involve ion exchange, electrostatic attraction, pore filling, precipitation, and surface complexation acting simultaneously.

Ippolito *et al.* (2020) investigated iron-modified biochar for heavy metal remediation and reported substantial improvements in adsorption efficiency compared with unmodified biochar. According to their findings, iron oxides deposited on the biochar surface enhanced adsorption through inner-sphere complexation and redox reactions. Their study further demonstrated that iron modification significantly increased the removal efficiencies of lead, cadmium, arsenic, and chromium from contaminated water.

Nitrogen doping has also been extensively investigated as an effective strategy for enhancing adsorption performance. Guo *et al.* (2025) reported that nitrogen-containing functional

groups such as pyridinic-N, pyrrolic-N, and graphitic-N improve electron density and surface basicity, thereby increasing adsorption affinity toward positively charged heavy metal ions. Their findings indicated that nitrogen-doped biochar consistently exhibited higher adsorption capacities and faster adsorption kinetics than undoped biochar.

Similarly, Liu *et al.* (2024) evaluated multi-doped biochar systems and concluded that simultaneous incorporation of transition metals and heteroatoms produces synergistic improvements in adsorption performance. Their study demonstrated that Fe/Mn/N co-doped biochar exhibited superior adsorption capacity for multi-metal wastewater compared with single-metal-modified adsorbents. The enhanced performance was attributed to the coexistence of multiple adsorption mechanisms, including electrostatic attraction, ion exchange, coordination bonding, and redox reactions.

Several researchers have also investigated adsorption kinetics and equilibrium behaviour of engineered biochars. Wang and Guo (2023) reported that adsorption of heavy metals by modified biochars generally follows the pseudo-second-order kinetic model, indicating chemisorption as the dominant rate-controlling mechanism. Furthermore, equilibrium data were better described by the Freundlich isotherm than the Langmuir model, suggesting multilayer adsorption on heterogeneous surfaces.

Thermodynamic investigations have consistently demonstrated that adsorption of heavy metals onto modified biochars is spontaneous and exothermic. Sahmoune (2019) reported negative Gibbs free energy (ΔG°) and enthalpy (ΔH°) values for several adsorption systems, confirming the feasibility of engineered biochar for wastewater treatment under ambient environmental conditions.

Collectively, these empirical studies demonstrate that surface engineering significantly enhances biochar performance and supports the development of multifunctional adsorbents capable of efficiently removing multiple heavy metals from contaminated water.

13.2 Research Gap

Despite the considerable progress achieved in biochar engineering, important knowledge gaps remain.

First, most published studies have focused on the adsorption of individual heavy metals under single-contaminant laboratory conditions. In contrast, industrial wastewater and produced water commonly contain several heavy metals simultaneously, resulting in competitive adsorption that significantly influences removal efficiency (Liu *et al.*, 2024).

Second, the majority of existing research has concentrated on pristine biochar or biochar modified with only one dopant, particularly iron or nitrogen. Comparatively few studies have investigated the synergistic effects of simultaneously incorporating iron, manganese, and nitrogen into sawdust-derived biochar.

Third, limited information exists regarding the adsorption behaviour of Fe/Mn/N tri-doped biochar under varying operational conditions such as pH, temperature, adsorbent dosage, and contact time. Likewise, comprehensive evaluations involving adsorption kinetics, equilibrium isotherms, and thermodynamic behaviour remain relatively scarce.

Furthermore, although laboratory-scale studies have reported encouraging adsorption efficiencies, relatively few investigations have addressed regeneration, reuse, long-term stability, continuous-flow treatment systems, and pilot-scale implementation. These limitations hinder the translation of engineered biochar technologies from laboratory research to full-scale industrial wastewater treatment.

Therefore, further research is required to optimize synthesis conditions, evaluate long-term performance under real wastewater conditions, investigate regeneration strategies, and assess the economic feasibility of large-scale production. Addressing these gaps will facilitate the commercialization of Fe/Mn/N tri-doped sawdust biochar as a sustainable and cost-effective

adsorbent for environmental remediation.

14.0. Conclusion

Heavy metal contamination remains one of the most serious environmental challenges affecting global water resources due to the persistence, toxicity, and bioaccumulative nature of metals such as cadmium, chromium, lead, nickel, copper, zinc, and mercury. Conventional treatment technologies, although effective in certain applications, are constrained by high operational costs, sludge generation, membrane fouling, and limited efficiency in complex multi-metal wastewater systems.

This review has demonstrated that adsorption continues to be one of the most effective and environmentally sustainable approaches for heavy metal remediation. Among available adsorbents, sawdust-derived biochar offers significant advantages because of its abundance, renewability, low production cost, and environmentally friendly nature. However, the relatively limited adsorption capacity of pristine biochar has stimulated extensive research into chemical modification and heteroatom doping.

Recent advances in nanotechnology and material engineering have resulted in the development of Fe/Mn/N tri-doped sawdust biochar, which integrates the beneficial properties of iron, manganese, and nitrogen within a single adsorbent. The synergistic interaction among these dopants substantially improves surface chemistry, pore structure, adsorption capacity, reaction kinetics, and adsorption selectivity. Characterization techniques such as FTIR, SEM, XRF, XRD, BET, DSC, XPS, and zeta potential analysis consistently confirm the successful modification of biochar and explain the mechanisms responsible for enhanced heavy metal removal.

Current empirical evidence indicates that Fe/Mn/N tri-doped biochar effectively removes multiple heavy metals through complementary mechanisms including ion exchange, electrostatic attraction, surface complexation, precipitation, pore filling, and redox reactions. Adsorption behaviour is generally best described by the Freundlich isotherm and pseudo-second-order kinetic model, while thermodynamic analyses indicate spontaneous and exothermic adsorption processes.

Overall, Fe/Mn/N tri-doped sawdust biochar represents a highly promising next-generation adsorbent capable of providing sustainable, low-cost, and efficient treatment of complex heavy metal-contaminated wastewater. Future research should prioritize pilot-scale applications, regeneration studies, continuous-flow systems, life-cycle assessment, and commercialization strategies to facilitate widespread implementation of this technology in industrial and municipal wastewater treatment.

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