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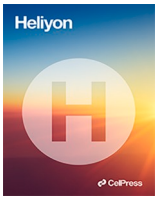

Review article

Adsorptive removal of toxic heavy metals from wastewater using water hyacinth and its biochar: A review

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ABSTRACT

Heavy metal contamination in aquatic ecosystems worsens due to rapid industrial expansion. Biochar, an efficient and economical adsorbent, has attracted much interest in environmental science, particularly in removing heavy metals (HMs). The paper covers basic details on biochar, its preparation, and potential chemical and inorganic modifications. Possible adsorption mechanisms of HMs on biochar, which include electrostatic attraction, ion exchange, surface complexation, chemical precipitation, and hydrogen bonding, are also discussed. These mechanisms are affected by the type of biochar used and the species of HMs present. Research findings suggest that while biochar effectively removes HMs, modifications to the carbon-rich hybrid can enhance surface properties such as surface area, pore size, functional groups, etc., and magnetic properties in a few cases, making them more efficient in HM removal. The choice of feedstock materials is one of the key parameters influencing the sorption capacity of biochars. This review aims to investigate the use of various forms of water hyacinth (WH), including aquatic plants, biomass, biochar, and modified biochar, as effective adsorbents for removing HMs from aqueous solutions and industrial effluents through a comparative analysis of their adsorption processes. However, further studies on the diverse effects of functional groups of modified biochar on HMs adsorption are necessary for future research.

1. Introduction

Water, the source of life, is intimately involved in every aspect of our daily lives and is a crucial element for almost every living organism on the planet [1]. In its various forms, water plays an irreplaceable role in sustaining the balance of ecosystems. While water makes up around two-thirds of the Earth's surface, merely 2.5 % is freshwater and suitable for human consumption [2,3]. These limited water resources are threatened by pollution. Along with the growing population, agricultural and industrial sectors are expanding rapidly, releasing a massive amount of contaminated wastewater [4]. Around 380 trillion liters of wastewater are produced annually worldwide. However, only 24 % of this is treated before being dumped in rivers or utilized again in agriculture [5,6]. Every day, more than 60,000 m^3 of toxic waste from various industries and factories enters the canals and rivers of Dhaka [7]. The World Health Organization (WHO) reports that roughly 700 million individuals in 43 different nations are presently struggling with water scarcity, and projections suggest that by 2025, most people on the planet (almost two-thirds) will live in areas with insufficient access to water [8].

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Heavy metals (HMs) are a common pollutant that is difficult to remove. Various HMs in industrial effluent threaten human well-being and the environment [9]. These HMs usually reach the environment from several sources, including petroleum combustion, power plants, electronics, batteries, pharmaceuticals, chemicals, plastics and paper mills, automobile exhaust, agrochemicals, mining, and inappropriate waste disposals [10–12]. Direct release of these hazardous HMs pollutes the primary water sources. It may even enter the food chain, causing extensive damage to aquatic fauna and flora and disrupting ecological balance [13,14]. HMs show non-biodegradable properties [15], a high water-borne dispersal capacity [16], and an inclination to accumulate within living organisms such as fish, plants, animals, and human tissue [17,18]. Some HMs such as As, Cd, Pb, and Hg are included in the list of top 10 chemicals of concern published by WHO [19]. Water- and soil-based HMs come into the food chain via plants, animals, and the human body. For example, *Cd comes from fertilizers* (Triple Super Phosphate, Ammonium Phosphate Sulfate, etc.*), Pb* and *Cr mostly from industrial, electronic, and medical wastes, and* As and Hg from polluted water [20]. In Bangladesh, most fruits [21], vegetables [22], freshwater fishes [23,24], and drinking water samples [25,26] near industry have all been found to contain HMs above the WHO's maximum allowable limits. Toxic HMs have several acute and chronic effects on body organs [27]. Exposure to even trace amounts of hazardous HMs over an extended duration can cause severe and often fatal illnesses like cancer. Additionally, it can lead to detrimental effects on the neurological, skeletal, gastrointestinal, and integumentary systems [28].

Researchers have recently aimed to develop environmentally friendly, inexpensive, and suitable methods to remove HM contaminants from wastewater. Conventionally, a sequence of treatment methods have been employed to eliminate HMs from aqueous solutions, including chemical precipitation [29], membrane separation [30], ion exchange [31], evaporation [32], reduction [33], adsorption [34], reverse osmosis [35], and so on [36,37]. However, most methods mentioned above are expensive, high energy consuming, non-selective, use toxic chemicals, and could be more effective when applied on a large scale [38]. Adsorption is acknowledged as the most dependable and promising approach due to its notable effectiveness, simple design, user-friendly nature, good reusability, and cost-effectiveness [39]. Widely used adsorption materials are activated carbon, clay minerals, carbon nanotubes, sewage sludge ash, zeolites, biochar, etc. [40].

Biochar is currently utilized for wastewater treatment, particularly in removing HM pollutants from water. It stands out among other available adsorbents due to its cost-effectiveness, large-scale applicability, environmental advantages, and high sorption capacity [41]. Various carbonaceous organic sources, such as agricultural waste and residues, municipal and industrial byproducts, and activated sludge, serve as feedstock of biochar [42]. The adsorption characteristics vary among materials derived from different raw sources. Selecting economical and eco-friendly raw materials is crucial for preparing efficient adsorbents with distinct adsorption properties.

Water hyacinth (WH), *Eichhornia crassipes*, is a fast-growing, inexpensive, and sustainable source of biomass and biochar [43,44]. WH biomass has been used as an effective adsorbent to remove HMs and other nanoparticles due to its high percentages of cellulose (35 %) and hemicellulose (30 %) with low percentage of lignin (10 %) content [45,46]. The hydroxyl (−OH), amino ($-NH_2$), and carboxyl (C=O) groups found in cellulose allow for the cation exchange that facilitates the adsorption of various HMs [19]. Fig. 1 illustrates the distribution of published articles on WH's application in removing HMs from wastewater. The search for articles on HMs removal by adsorbents derived from WH till 2023 involved initial keywords such as "water hyacinth," "heavy metals," "adsorption," and "wastewater treatment." Variations of HMs' names (e.g., Arsenic, Chromium, Lead, etc.) were utilized in place of the keyword "heavy metals." Statistical data were obtained from the Web of Science database as of November 14, 2023.

WH, a member of the pontederiaceae family, is an aquatic plant that proliferates in every freshwater environment. Originating in the American tropics, it has invaded various tropical and subtropical regions, including Asia, Australia, Europe, and North America [47,48]. The International Union for Conservation of Nature (IUCN) has listed WH among the top 100 invasive plants that pose a significant threat to global biodiversity [49]. When WHs grow densely on the water's surface, they can block sunlight, impeding the growth of aquatic plants and reducing the overall photosynthetic activity in the water [50]. Additionally, they obstruct irrigation, river navigation, waterways, and hydropower systems. Enormous sums are spent annually worldwide on the selective removal of these aquatic weeds [51]. Hence, converting WH into biochar for HM-contaminated water treatment could be a promising approach to

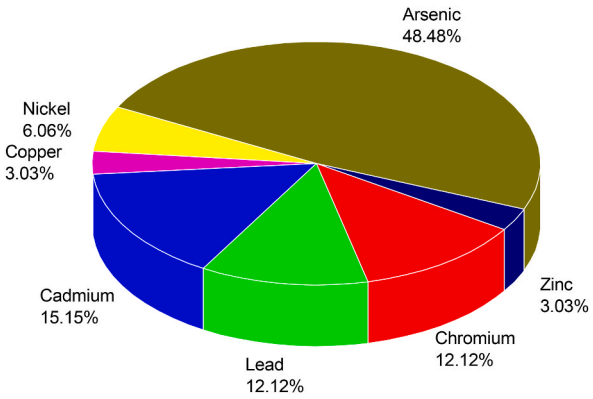

Fig. 1. Pie chart represents the percentage of articles published on HM removal using water hyacinth till November 14, 2023 (Web of Science database).

removing HM ions from water and managing this troublesome invasive species.

This paper addresses a research gap by conducting a comparative study of various forms of WH, including aquatic plants, biomass, biochar, and modified biochar for HM remediation. By focusing on the latest advancements in sorption processes, the study aims to demonstrate the potential of these WH forms as sustainable and economically viable options for long-term HM remediation in aquatic environments. The key areas covered: (1) diverse methods for biochar preparation and activation, (2) the corresponding mechanisms involved in removing HMs from wastewater, and (3) recent developments in HM remediation from industrial wastewater and aqueous solutions, with a specific focus on WH in its various forms.

2. Biochar

Biochar is a carbon-riched substance derived from carbonaceous biomass by pyrolysis under oxygen-limited conditions [47]. The main biochar component is carbon (C), which makes up about 70 % of its composition. The remaining percentage includes hydrogen (H_2), nitrogen (N_2), oxygen (O_2), sulfur (S), ash, etc. [48]. Biochar has been frequently used to remove HM pollutants from wastewater because of its large surface area, excellent porosity, presence of function groups containing oxygen, low preparation cost, and ease of modification [49].

2.1. Preparation of biochar

The European Biochar Certificate (EBC) provided a framework for promoting the sustainable production of biochar in Europe, addressing critical aspects such as feedstock selection, pyrolysis conditions, quality assurance, environmental impact, and certification [50]. The EBC emphasized using sustainable biomass feedstock for biochar production, including agricultural residues, forestry waste, and organic byproducts. The guidelines outlined parameters for pyrolysis, including temperature, heating rate, and treatment time. It also recommended that pyrolysis be carried out under controlled conditions to maximize biochar yield, quality, and stability while minimizing emissions of harmful gasses.

An ideal precursor for biochar should be abundant, sustainable, high in carbon, low in ash, free of hazardous compounds, and readily available to ensure a consistent supply. Cost-effectiveness is also crucial to ensure the economic viability of biochar production. Diverse forms of biomass are employed as a source material of biochar. Biochar can originate from crop and food residues, industrial, municipal, and even medical waste [51,52]. Carbon-rich feedstock, including bamboo, groundnut husk, rice husk, tree bark, wood chips, grass, palm bark, corn and rice straw mill waste, sewage sludge, paper sludge, etc., are currently used commercially [53]. Waste management has also been achieved by efficiently using biochar produced from industrial and municipal wastes [51]. It is reported that several variables affect the qualities of biochar, such as the type of source material used, the thermochemical conversion method, and the biochar production temperature [54].

Preparing biochar typically involves pyrolysis. Depending on the specific operating conditions, there are three basic pyrolysis processes: slow, fast, and flash. Table 1 details the corresponding operational parameters and the total yield for each type of pyrolysis.

The pyrolysis process begins with dried biomass placed into a furnace after a moisture-reducing pre-drying phase. Moisture evaporation is the initial step, which is crucial for starting carbonization. Subsequently, in the 370–400 °C degasification phase, efficient removal of volatile components like H_2, N_2, CO, and CO_2 occurs, although this phase consumes about 40 % of the energy yield. Elemental carbon is concentrated after degasification through high-temperature treatment (400 – 650 °C), which also breaks and rearranges chemical bonds to produce new functional groups and eliminates fibrous structure [55]. Finally, cooling brings the processed material to ambient temperature, rendering it ready for use. Fig. 2 illustrates the steps of the carbonization or pyrolysis process. Pyrolysis is integral for converting biomass into valuable products, including biochar and biofuels.

The pyrolysis temperature plays a crucial role in enhancing the removal capacity of HMs by improving porous structures, surface area, and C/O ratio of biochar [56]. By releasing gasses and clearing out the first blockages in the material's pores, biomasses are broken down through high-temperature pyrolysis. With the formation of additional pores, channels, or amorphous carbon structures, the material's specific surface area is significantly increased, which is advantageous for uses like filtration, catalysis, and adsorption [57]. In a study, Liu et al. [58] showed that a higher pyrolysis temperature led to more pores with generally smaller hole diameters and rough surfaces (Fig. 3).

2.2. Activation of biochar

Achieving high-performance outcomes with pristine biochar in practical applications poses a challenge because of insufficient surface functionality, limited pore characteristics, and low surface area. However, pristine biochar exhibits limited attraction to

Table 1
Overall yield of different pyrolysis depending on the operating conditions [3].

Operating conditions	Time (s)	Temperature (K)	Heating rate (K/s)	Overall yield (%)		
				Biochar	Bio-oil	Biogas
Conventional Pyrolysis	450 – 550	550 – 950	0.1 – 10	35	30	35
Fast pyrolysis	0.5 – 1.0	850 – 1250	10 – 200	50 – 70	10 – 30	15–20
Flash pyrolysis	<0.5	1050 – 1300	<1000	60	40	5–15

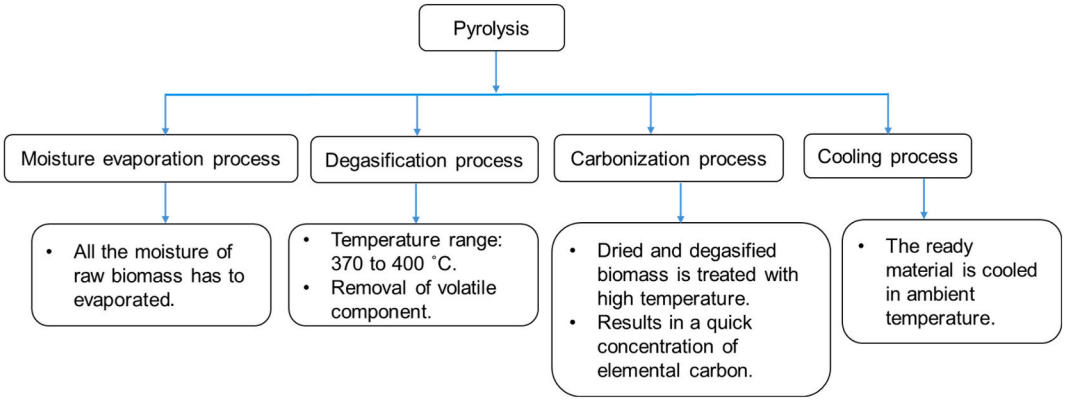

Fig. 2. Steps of carbonization/pyrolysis process.

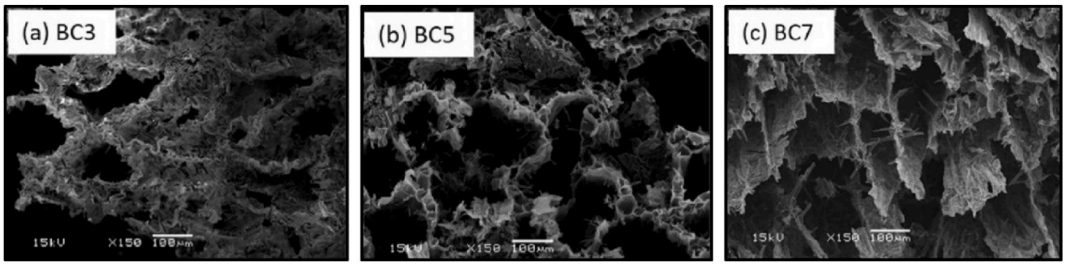

Fig. 3. SEM images of WH biochar pyrolysis at (a) 300 °C, (b) 500 °C, and (c) 700 °C [58].

anionic substances due to delocalized π electrons on its surface [59]. Through activation, various functional groups are added to the surface of biochar to enhance its adsorbent properties [60]. Two activation methods, physical and chemical, were used to improve the properties of biochar. The steps of the biochar activation process are shown in Fig. 4.

2.2.1. *Physical activation*

Biochar undergoes physical activation at temperatures up to 900 °C. Steam activation creates pores and enhances surface area, pore volume, and acid functional groups while reducing aromaticity and polarity. However, Gas purging (CO_2 activation) improves biochar's surface area, pore volume, and activated sites. The interaction forms a microporous structure by converting carbon to carbon monoxide [61].

2.2.2. *Chemical activation*

The technique most frequently used to activate biochar is chemical activation. Chemical activation methods primarily involve acid and alkaline activation. *Acidic modification* serves a dual purpose: It eliminates undesirable metallic impurities from biochar and introduces acidic functional groups that significantly modify its physical and chemical characteristics. Frequently used acidic agents are

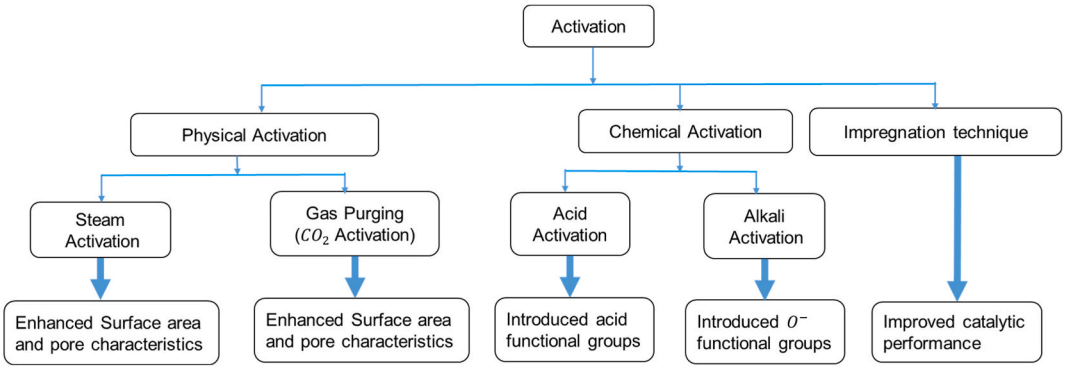

Fig. 4. Biochar activation steps.

H_2SO_4, HNO_3, HCl, etc. [62]. *Alkaline activation*, employing agents like NaOH or KOH, aims to introduce potential functional groups on the modified biochar and enhance the surface area and porosity [63]. Zahedifar et al. [64] introduced HNO_3 to enhance C=O and −COOH groups and then modified the surface of date leaf-derived biochar with $–NH_2$ and −COOH groups using N, N′ -Dicyclohexylcarbodiimid (DCC), and ethylenediamine. To incorporate the −COOH functional group onto the biochar surface, Zhou et al. [65] conducted functional modification of biochar using iminodiacetic acid (MBCI). Modifying the biochars with NH_3 and HNO_3 increased −OH and −COOH functional groups [66]. Phosphorus-containing groups were incorporated onto the biochar surface using reagents such as ammonium dihydrogen phosphate, ammonium polyphosphate, and phosphoric acid [67]. Table 2 outlines the impact of chemical activation on biochar.

2.2.3. Incorporation of inorganic (metal-oxide) modifiers

Integrating inorganic modifiers, including metal oxides, can enhance HM adsorption efficiency in biochar. This incorporation improves surface area, functional groups, and active sites [70].

Metal oxides loaded onto biochar have been demonstrated to enhance the removal efficiency of HMs through various mechanisms significantly. Composite materials consisting of biochar and metal oxides display unique properties arising from the interactions between the two components, offering advantages from both [71]. Metal oxides are dispersed throughout the carbon matrix, which increases the surface area and provides a significant number of HM adsorption active sites through chemical bonding processes like surface complexation and chemical precipitation [72]. Moreover, metal oxides introduce additional functional groups that enable ion exchange and electrostatic attraction, thereby enhancing the adsorption capacity of biochar. The low affinity of pristine biochar for anionic contaminants is often caused by its negative surface charge [73]. However, modifying biochar with positively charged metal oxides can effectively alter its surface properties, increasing its affinity for these impurities. Furthermore, modification with metal oxides can introduce magnetic activity, facilitating the recovery of contaminants from aqueous solutions. For instance, adding magnetite (Fe_3O_4) to the composite material improves its magnetic characteristics and speeds up the separation process [74].

Zinc oxide (ZnO) is a highly effective adsorbent for anionic species in wastewater, attributed to its non-toxicity, high surface area, thermal stability, porous structure, and strong adsorption capacity [75–77]. ZnO nanoparticles can reduce Cr (VI) to Cr (III) by acting as a photo-catalyst. In a study, Yu et al. [78] presented the utilization of biochar/ZnO composites for Cr(VI) adsorption, determining that an optimal configuration involves 30 wt% of ZnO, resulting in a removal efficiency of 95 %. However, they observed a decrease in the removal percentage of Cr(VI) with additional loading of ZnO. This could be attributed to the reduction in total surface area and the blockage of pores in the biochar. Li et al. [79] fabricated nano ZnO/ZnS-biochar using a slow pyrolysis process from corn stover. The modified biochar exhibited enhanced surface area and pore volume, demonstrating a solid sorption capacity for Pb(II), Cu(II), and Cr (VI). This implied that introducing zinc salt during the synthesis catalytically facilitated the development of a porous structure.

Luo et al. [80] employed TiO_2/biochar to effectively eliminate Cd(II) and As(V) from water. Adding TiO_2 into the carbon matrix increased specific surface area and pore volume. However, the average pore size was reduced due to pore filling. The sorption mechanism of modified biochar was governed by ion exchange and complexation processes. In a study, Zhang et al. [81] showed that loading MnO_2 on WH biochar enhanced HM ions (Cu, Cd, Pb, and Zn) adsorption. The abundant surface Mn-OH groups of MnO_2--loaded biochar result in high adsorption capacities. Surface complexation was the dominant mechanism for HM ion immobilization. In another study, MnO_2-loaded biochar (MBR) prepared from aerobically composted swine manure exhibited enhanced surface characteristics and excellent adsorption capacity for Pb (268.0 mg/g) and Cd (45.8 mg/g) compared to unmodified biochar [82]. The optimal removal efficiency was pH-dependent, peaking at 0.2 g/L MBR dosage, and ion exchange was used to remove metal ions. Li et al. [83] fabricated a new hybrid adsorbent called HFO-BC by impregnating hydrous ferric oxide within biochar pores. This adsorbent showed excellent performance against HMs like Cd (II) and Cu (II), with maximum sorption capacities of 29.9 mg/g and 34.1 mg/g, respectively. HFO-BC demonstrated effective anti-interference for Cd (II) and Cu (II) removal in high Ca (II) and Mg (II) concentrations due to specific inner-sphere complexation with HFO. A biochar/iron oxide composite was synthesized by Navarathna et al. [84], enabling facile removal and regeneration in stirred tank batch treatments. Based on the Sips isotherm, the composite demonstrated an adsorption capacity of 5.49 mg/g for As (III). Additionally, redox reactions facilitated the conversion of portions of As (III) to less toxic As (V) during adsorption on Fe_3O_4.

2.2.4. Incorporation of organic modifiers

Adding organic materials to biochar can enhance HM adsorption from aqueous solutions through several mechanisms. Organic materials can effectively increase the surface area of the composites [85,86]. Additionally, organic materials often contain functional groups such as −COOH, −OH, and $−NH_2$, which can form complexes with HM ions, improving their adsorption affinity [87]. They can

Table 2
Impact of chemical activation on biochar.

Feedstock	Modifier	Functional groups	Ref.
Date leaves	HNO_3	C=O and −COOH	[64]
	DCC and ethylenediamine	$−NH_2$, and −COOH	
Palm fiber	Iminodiacetic acid	−COOH	[65]
Wheat straw	KOH, HNO_3 and NH_3	−OH, −COOH and C−N	[66]
Peanut shells	Ammonium dihydrogen phosphate, ammonium polyphosphate, and phosphoric acid	Phosphorus-containing groups	[67]
Coconut shells	HNO_3 and NH_3	−OH, −COOH	[68]
Forest Residue	NaOH and H_3PO_4	Phosphorus-containing groups	[69]

also introduce reactive sites on the biochar surface, leading to enhanced chemical interactions with HM ions. This may include redox reactions or surface complexation, which can facilitate the removal of heavy metals from aqueous solutions [88].

Chitosan is a natural organic polymer extracted from chitin in the exoskeletons of crustaceans like shrimp, crabs, and lobster [89]. It is widely used in composite materials to remove HM ions from water. The presence of $-NH_2$, C=O, and −OH functional groups in chitosan creates active sites that effectively bind with metal ions, facilitating their removal from water through adsorption [90]. Chitosan-modified magnetic loofah biochar was developed for the effective removal of Cr(VI) and Cu(II) [91]. While the biochar derived from loofah exhibited enhanced pore structure and surface area, its HM adsorption rate was relatively low (Fig. 5) [91]. However, by incorporating 40 wt% chitosan into the magnetic biochar, the composite demonstrated significantly improved adsorption capacities of 30.14 mg/g for Cr(VI) and 54.68 mg/g for Cu(II). The chitosan modification introduced −COOH onto the composite surface is crucial in efficiently removing HMs. Table 3 outlines the impacts of various modified biochars on the adsorption of HMs in contaminated water.

3. Adsorption mechanism of biochar

It is essential to understand its adsorption mechanisms to optimize the utilization of biochar in water treatment processes. HMs and biochar interact through various adsorption mechanisms that depend on several factors, including the specific pollutants, the pore size of biochar, chemical bonds between the sorbate and the sorbent, etc. [93]. Electrostatic attraction, ion exchange, surface complexation, chemical precipitation, and hydrogen bonding constitute the fundamental mechanisms involved in the adsorption of HMs on biochar [94]. The adsorption mechanisms of HM ions by biochar are illustrated in Fig. 6. Biochar typically exhibits a mixed distribution of macro and micro-pores throughout its matrix. This pore structure contributes to a high surface area-to-volume ratio, providing sufficient sites for adsorption of HMs.

Additionally, HMs can penetrate the internal pore structure of biochar via physical adsorption, where they are held by various binding sites, such as functional groups on the biochar surface or within the pore network [95]. HM ions form surface complexes with functional groups on the biochar surface, such as −COOH and −OH groups [96]. Before and after adsorption, the functional groups on the biochar surface may change due to complexation with HM ions. Oxygen-containing functional groups on biochar can undergo ion exchange with HM ions [97]. In this process, metal ions replace hydrogen ions (H^+) associated with these functional groups.

The pH at the point of zero charge (pH_{zpc}) is a crucial parameter in understanding the surface charge properties of the sorbent material, such as biochar. At a pH above the pH_{zpc}, the surface of the sorbent becomes negatively charged due to the deprotonation of functional groups on the biochar surface. This deprotonation leads to an increase in negative charge density on the biochar. Therefore, the positively charged HM ions (Zn^{2+} and Pb^{2+}) have a stronger electrostatic attraction to the negatively charged adsorbent surface, leading to their strong adsorption onto the sorbent surface. Conversely, when the pH is below the pH_{zpc}, the surface of the sorbent

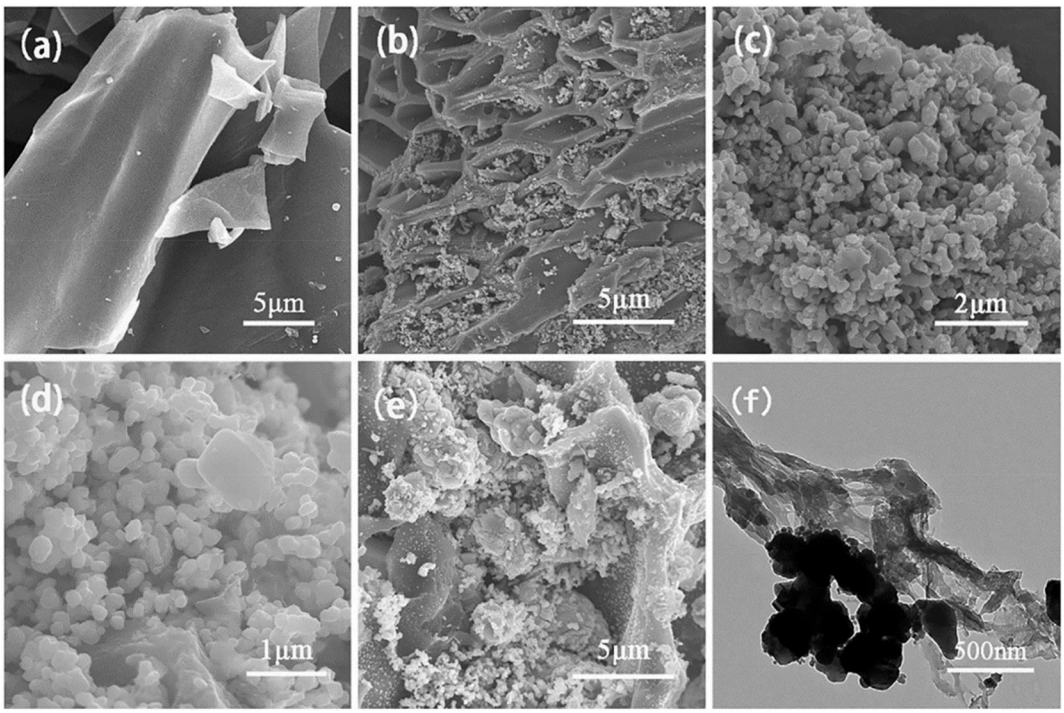

Fig. 5. SEM images of (a) loofah biochar; (b), (c), and (d) SEM images of magnetic loofah biochar at different magnifications; (e) SEM image of 40 wt%-Chitosan-magnetic biochar composite; and (f) TEM image of 40 wt%- Chitosan-magnetic biochar composite [91].

Table 3
Impacts of organic and inorganic modification of biochars on the adsorption of HMs from contaminated water.

Feedstock	Modifier	Heavy metals	Initial concentration of HM ions (mg/l)	Optimum dosage (g/l)	Surface Area (m^2/g)	Max. Adsorption capacity (mg/g)	Max. Removal efficiency (%)	Ref.
Water hyacinth	ZnO	Cr (VI)	100	4	469.6	23.75	95	[78]
Corn stover	ZnO/ZnS	Cr (VI)	400	2	397.4	24.5	21.3	[79]
		Cu (II)				91	39	
		Pb (II)				136	35	
Corn cobs	TiO_2	Cd (II)	300	1	450.4	72.5	70	[80]
Water hyacinth	MnO_2	Cd (II)	100	500	120.2	232.5	~ 30	[81]
		Cu (II)				248.9	~ 100	
		Zn (II)				239.4	~ 70	
		Pb (II)				249.2	~ 100	
Swine manure	MnO_2	Pb (II)	210	0.2	70.9	268	–	[82]
		Cd (II)	100			45.8	–	
Peanut shell	Hydrous ferric oxide	Cd (II)	50	0.2	–	29.9	~ 100	[83]
		Cu (II)				34.1	~ 100	
Wood	Fe_3O_4	As (III)	10	2	320	5.49	68	[84]
Loofah	Chitosan	Cr (VI)	40	0.5	104.91	30.14	37.67	[91]
		Cu (II)				54.68	68.35	
Rice husk	Polyethyleneimine	Cr (VI)	100	1	–	435.7	~ 100	[92]

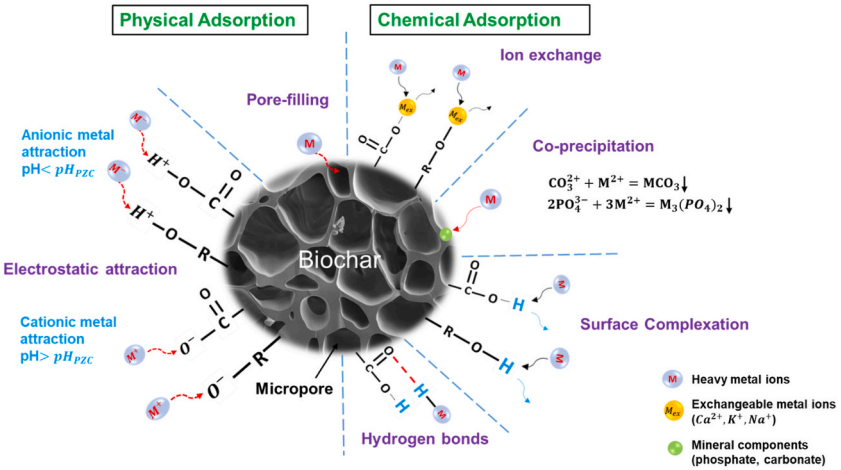

Fig. 6. Schematic diagram of adsorption mechanisms of HM ions by biochar.

becomes positively charged due to the protonation of functional groups on the biochar surface. This protonation leads to an increase in positive charge density on the sorbent surface. The positively charged adsorbent surface and the negatively charged HM ions ($HCrO^{4-}$, $Cr_2O_7^{2-}$) may be more electrostatically attracted to one another under such circumstances.

The adsorption mechanisms for As (V) on peanut shell biochars involve surface complexation and electrostatic interactions supported by pH studies, modeling, FTIR, and XPS analyses. Functional groups like C=O, −OH, −C−H, and C=C−C play crucial roles in surface complexation and electrostatic interactions during As(V) adsorption from aqueous solution [98]. In another study, Cai et al. [99] reported that at low pH values (2.0 − 4.0), Cr (VI) exists primarily as oxygen-containing anions, mainly $HCrO^{4-}$ and Cr_2O^{7-}. Meanwhile, amino groups and certain oxygen-containing groups such as −OH and −COOH on the biochar surface can protonate at low pH, creating sites with a positive charge ($-NH^{3+}$, $-OH^{2+}$, and $-COOH^{2+}$). This results in the biochar surface acquiring positive charges. Consequently, Cr (VI) can readily bind to the electropositive surface through electrostatic interactions and form complexes with the surface groups. Sattar et al. [98] reported that the adsorption of As (III) or As (V) onto the biochar made from peanut shells involved an ion exchange mechanism that the −OH groups enhanced.

The incorporation of ZnO into biochar enhanced the surface characteristic of the composites, enhancing its positive surface charge and improving its attraction to anionic species [100]. The increased adsorption of HMs by the ZnO/biochar composite is attributed to the photocatalytic properties of ZnO by promoting the reduction of Cr (VI) to Cr (III) [101]. Furthermore, the presence of zinc chromium oxide hydrate ($CrH_4O_6Zn_2$) suggests the occurrence of precipitation between Cr ions and ZnO [78]. The combination of MnO_2 and biochar also demonstrated a solid ability to adsorb HM ions. Introducing MnO_2 resulted in a considerable increase in the composite's specific surface area and pore volume. Biochar/MnO_2 composite formed complexation with HM ions [81]. According to Shang et al. [102], the functional groups on the surface of the composite may be necessary for the Cr(VI) adsorption mechanism onto biochar/graphene oxide composite. They postulated that complexation and electrostatic attraction would be the mechanisms of Cr (VI) ion adsorption by the composite.

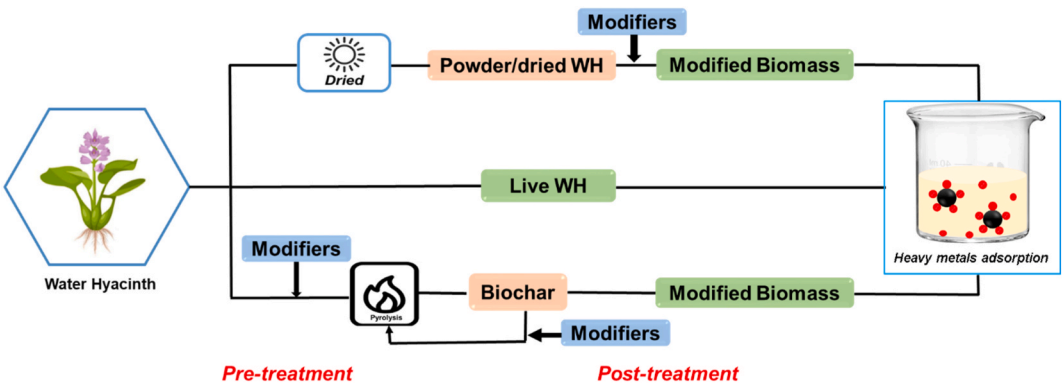

Fig. 7. A schematic illustration of the adsorption processes of HMs using several forms of adsorbents derived from WH.

4. Water hyacinth for the removal of heavy metals

The effective adsorption of HMs by WH biomass and its biochar is attributed to a distinctive combination of features, including abundant functional groups, a large surface area, high cation exchange capacity, natural affinity for HMs, biochemical composition, low cost, rapid growth, and sustainability. Activation processes are employed to enhance biochar's adsorption capacity. These processes involve pretreating the biomass before or after post-treating the biochar after pyrolysis with modifiers like acids, bases, or nanoparticles. Fig. 7 schematically illustrates the adsorption processes of HMs using various forms of adsorbents derived from WH.

4.1. Live water hyacinth

In recent decades, increased attention has been directed toward researching how specific aquatic plants can eliminate HM ions from aquatic ecosystems [103,104]. Studies on phytoremediation using live sorbents are increasingly focusing on aquatic plants because of their capacity to absorb HMs from their environment. Due to its remarkable affinity and ability to accumulate HMs, WH is a biomarker introduced into wetlands for phytoremediation in water systems. With rapid growth, high biomass production, effective absorption of HMs and other pollutants, low operating costs, and renewability, it is a suitable option for wastewater treatment in both industrial and domestic sources [105]. The highest absorption of HMs occurs in the roots of WH, with the order of metal uptake in different organs being roots > leaves > stem [106]. In a study, Gupta et al. [106] investigated the capacity of WH to absorb Cr(VI) from an aqueous solution. They found that, over 16 days, 99 % of Cr(VI) was removed at a WH concentration of 5 mg/l. Mishra et al. [107] tested WH to assess its potential in removing five HMs (Fe, Cu, Cd, Cr, Zn). The findings revealed that WH could absorb various HMs, with removal efficiency ranging from 77 % to 95 % within 12 days. This remarkable capacity can be attributed to WH's extensive biomass, fibrous roots, and broad leaves, enabling it to uptake higher concentrations of HMs. WH exhibits limited Cr mobility compared to other HMs because of barriers or the absence of appropriate transport mechanisms for moving Cr from the roots to the shoots. Zheng et al. [108] demonstrated that WH roots are a biosorbent material with a significant affinity and substantial capacity for Cu(II) adsorption. In a separate investigation, Zheng et al. [109]examined how WH roots interact with Cu(II) and Cd(II) in aqueous solution, studying their behavior in both single-metal and mixed-metal conditions. The roots showed a stronger attraction to Cu(II) than Cd(II), which significantly slowed down the sorption of Cd(II) in binary solution (Fig. 8) [109]. The release of both protons and cations like Ca^{2+} and Mg^{2+} during metal sorption, along with the higher affinity of Cu(II) compared to Cd(II), supported the concept that ionic exchange played a vital role in the HM adsorption process. Findings of some studies where living WH plants were used to remove HM ions from aqueous solutions and industrial effluent are displayed in Table 4.

Zhu et al. [111] highlight the capacity of WH in phytoremediation for six HMs [As(V), Cd(II), Cr(VI), Cu(II), Ni(II), and Se(VI)]. WH exhibited maximum accumulation for Cd and Cr in controlled environments, moderate levels for Se and Cu, and lower accumulation for As and Ni. The plant demonstrated efficient bioconcentration factor (BCF) of these HMs when exposed to low concentrations, particularly for Cd, Cr, and Cu, making it a promising choice for phytoremediation of wastewater polluted with these elements. Table 5 represents the accumulation rate and BCF of HMs by WH plants.

4.2. Dried and powdered water hyacinth

Dried plant biomass is inexpensive and practical for removing HM ions from industrial wastewater. Dried biomass offers handling, transportation, and conservation benefits over living systems. The biomass is typically dried and powdered to increase the surface area and adsorption sites. Various functional groups in non-living biomass, including –OH, -COOH, C=O, etc., play a crucial role in binding HMs [113].

Phaenark et al. [113] investigated the potential applications of dried WH as a biosorbent for HM ions such as Pb and Cd. They found that while the removal efficiency of Pb and Cd decreased with higher initial metal solution concentrations, it increased with greater

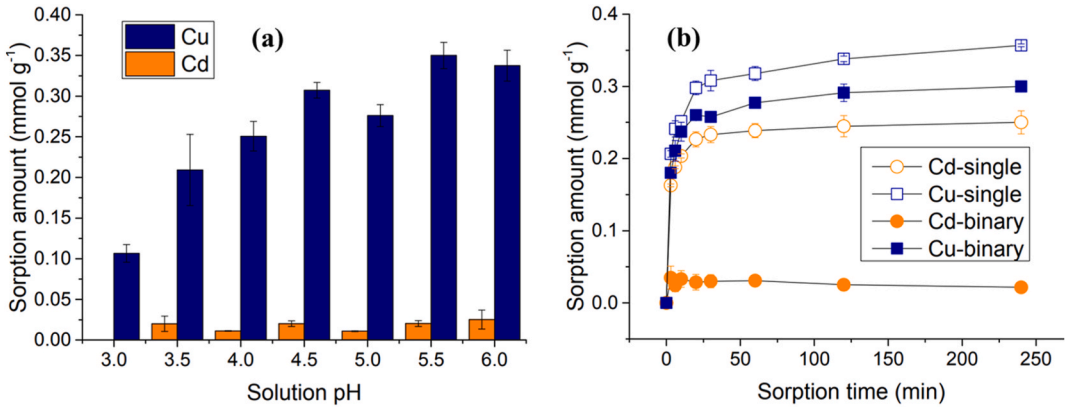

Fig. 8. Cu and Cd sorption levels in (a) binary-metal environment at varying pH, (b) single and binary system over time [109].

Table 4
Adsorption of HMs from aqueous solutions and industrial effluents by live water hyacinth.

Adsorbent	Heavy metal	Initial concentration of HM ions (mg/l)	Adsorption time (hr.)	Max. Adsorption capacity (mg/g)	Max. Removal efficiency (%)	Ref.
WH	Cr	5	384	2.36	99	[106]
WH	Fe	1	288	8.6	86	[107]
	Cu			9.5	95	
	Cd			8.1	81	
	Cr			8.5	85	
	Zn			9.2	92	
WH roots	Cu	30	1	22.7	38	[108]
WH	Pb	30	12	4.45	99	[110]

Table 5
Rate of HMs accumulation and bioconcentration factor (BCF) by water hyacinth plants.

Adsorbent	Heavy metal	Initial concentration of HM ions (mg/l)	Adsorption time (day)	Max. bioconcentration factor (BCF)	HM accumulation rate (mg/kg.day)	Ref.
WH roots	Cr	0.1	1	1823	0.53	[111]
	Cd			2150	1.85	
	Cu			595	1.15	
WH roots	Cd	4	8	622.3	255.5	[112]
	Zn	40	4	788.9	1423	

biomass doses, with a notable removal of about 94 % of Pb and 86 % of Cd occurring within the first 45 min of contact time. In a parallel study, Ibrahim et al. [114] revealed that the WH plant's root and shoot exhibited nearly the same removal efficiencies, reaching 75 % for Cd and over 90 % for Pb. The presence of −COOH groups, confirmed by FTIR, indicated that hydrogen bonds formed by these reactive functional groups played a crucial role in the removal process. Dried WH was used to remove Zn(II) and Cd(II) from both single and binary-metal solutions [115]. Accumulation factors for both HMs were higher in the roots and upper parts when tested individually rather than as a mixture. Zn(II) displayed higher root accumulation than Cd(II), which had a three-fold greater root uptake than the upper parts. In the case of Zn(II), root uptake was approximately four to six times higher than in the upper parts. This indicated Cd (II) exhibited quicker mobility from the root to the top than Zn (II). Hemalatha et al. [116] investigated various components of dried WH for removing Zn and Cr from wastewater in the electroplating industry. SEM micrographs of leaves, stems, and roots of WH are shown in Fig. 9 [116]. Their findings indicated that the biosorbent derived from the plant's roots achieved a maximum Zn removal rate of 98.9 %, while the stem-based biosorbent exhibited a maximum Cr removal rate of 96.4 %. Vargas et al. [117] used cellulose nanofibers (CNF) and crystalline nanocellulose (CNC) extracted from WH by acid hydrolysis method to remove Pb(II) efficiently from

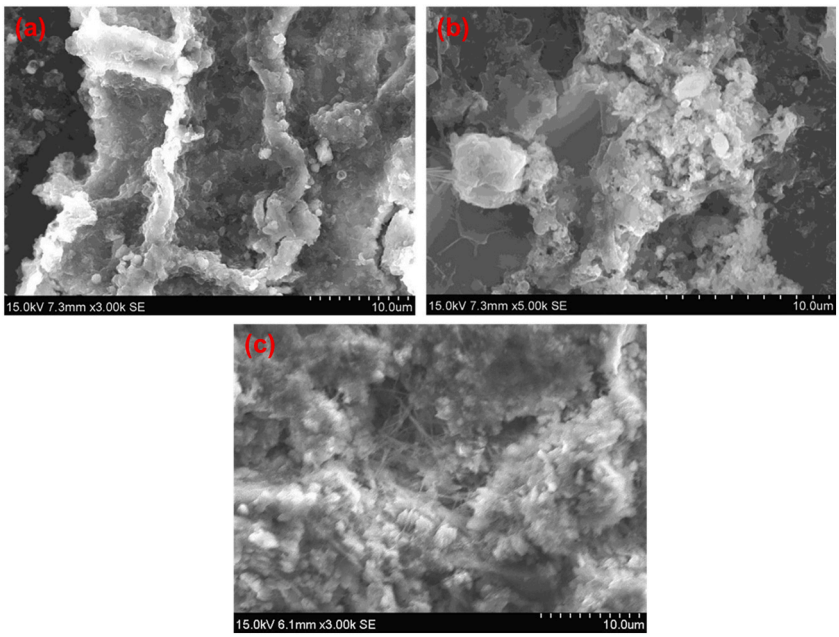

Fig. 9. SEM micrographs of (a) leaves, (b) stem, and (c) roots of WH [116].

aqueous solution. Maximum adsorption capacities (Q_{max}) of CNC and CNF at different temperatures were examined, and it was found that Q_{max} for CNC and CNF at 45 °C was 30.36 and 87.10 mg/g, respectively. It was reported that the structural properties of the nano-cellulose depend mainly on the sources of cellulose.

Dried WH root was chemically modified with HNO_3 to enhance its adsorption capacity. This led to a maximum Cr (VI) removal efficiency of 95.43 % at pH 3.0 and a metal concentration of 10.0 mg/l after a 2h contact period [118]. The adsorbent exhibited a maximum adsorption capacity of 1.28 mg/g at a metal concentration of 5.0 mg/l. In a study, Zubir et al. [119] introduced a composite of WH and chitosan bentonite in a 3:1 ratio for removing Pb (II). They achieved a Pb (II) adsorption capacity of 2.50 mg/g, which was better than the individual adsorption capacities of Chitosan-Bentonite (1.87 mg/g) and WH (1.22 mg/g). The presence of −OH) and −NH groups in the Chitosan-bentonite significantly contributed to the effective adsorption of Pb (II). Taye et al. [120] investigated the use of a biopolymer composite (WH/graphene oxide/chitosan/polyvinyl alcohol) containing WH to improve the adsorption capability of Cr (VI). At pH 1.0 and 330 min of contact time, they reached the maximum adsorption capacity of 202.59 mg/g. The high adsorption capacity of the composite is attributed to the incorporation of functional groups containing oxygen. (−OH and C=O). The increase of adsorption capacity from 84.02 to 99.03 mg/g with a change in adsorption temperature from 25 °C to 55 °C suggests that adsorption is more favorable at higher temperatures. Moreover, the synthetic material demonstrated a reuse efficiency of over 65 % for five consecutive cycles. Table 6 presents information collected from an analysis of published research articles focused on dried WH and its application in removing HMs from water solutions.

4.3. Biochar derived from water hyacinth

Biochar made from WH has shown promise in the adsorption of HMs from various wastewater sources. Due to its advantages in resource recycling and waste management, the conversion of WH into biochar is gaining popularity. Biochar has more mineral ash and functional groups than activated carbon, rendering it a powerful adsorbent for various toxic HMs [125]. Additionally, different chemical and physical changes have been investigated to increase the adsorption capacity of biochar [126]. The findings of related studies demonstrate that biochar modification can significantly enhance its adsorption ability.

In a study, Zhang et al. [127] investigated the efficiency of WH-biochar (WHB) pyrolyzed within the temperature range of 250 − 550 °C for removing Cd from aqueous solutions. The findings revealed that biochar pyrolyzed at 450 °C (WHB 450) exhibited rapid Cd sorption compared to alternative temperatures, reaching a maximum Cd sorption capacity of 70.3 mg/g. The mechanisms responsible for Cd sorption by WHB 450 involved ion exchange, followed by surface complexation, Cd precipitation, and the formation of Cd−Cπ bonding. In a similar investigation by Li et al. [128], WHB produced at lower temperatures exhibited better Cd sorption capacities. WHB pyrolyzed at 300 °C exhibited a higher Cd sorption capacity than WHB pyrolyzed at 500 °C despite having a smaller specific surface area. This suggests that factors other than surface area affected Cd sorption. Lower temperature-produced biochars tended to have a high concentration of functional groups that contained oxygen, including −COOH and −OH. The maximum Cd adsorption capacities were 49.8, 36.9, and 25.8 mg/g for WHB pyrolyzed at 300, 500, and 700 °C, respectively. Although all adsorbents achieved

Table 6
Adsorption of HMs from aqueous solutions by dried water hyacinth.

Adsorbent	Heavy metals	pH	Initial concentration of HM ions (mg/l)	Optimum dosage (g/l)	Adsorption time (min)	Max. Adsorption capacity (mg/g)	Max. Removal efficiency (%)	Ref.
CNC (WH)	Pb (II)	6	125	8	180	30.36	–	[117]
CNF (WH)	Pb (II)					87.10	–	
Dried WH	Pb	6	20	4 %(w/v)	45	2.9	94	[113]
	Cd		2	2 %(w/v)		2.86	86	
Dried WH roots	Pb	5	50	5	60	9.2	92	[114]
	Cd					8.08	80.8	
Dried WH shoots	Pb	5	50	5	60	9.5	95	
	Cd					8.6	86	
Dried WH roots	Cd (II)	7	2.5	–	16 days	–	82.2	[115]
	Zn (II)		6	–		–	89	
Dried WH shoots	Cr	5	55	1	30	54.82	99.69	[116]
	Zn	11	170		40	167.45	98.5	
Dried WH roots	Cr	5	55	1	30	52.22	94.54	
	Zn	11	170		40	168.2	98.94	
Dried WH leaves	Cr	5	55	1	30	53	96.36	
	Zn	11	170		40	165.24	97.2	
WH/GO/CS/PVA	Cr (VI)	1	100	3	330	202.59	80	[120]
WH/chitosan	Pb (II)	–	50	–	5	2.5	–	[121]
Dried WH roots/HNO_3	Cr (VI)	3	10	14	120	1.28	95.43	[118]
Dried WH/NaOH	Ni	6.6	3500	3	240	293.8	25.2	[122]
	Cu	4.6	4000		300	276.3	20.7	
Dried WH/citric acid	Ni	7.5	300	0.65	300	59.64	13	[123]
	Cu	6		0.5	180	77.98	12.99	
	Cr	5		0.4	120	96.89	12.91	
Dried WH roots/sodium tripolyphosphate	Cr (VI)	8	1000	18	120	7.7	13.86	[124]

over 90 % Cd removal efficiency, WHB 700 exhibited the highest efficiency at 99.2 %. Ding et al. [129] investigated the adsorption of Pb (II) and Cd (II) on WHB generated at three temperature levels (300 °C, 450 °C, and 600 °C).

WHB 450 displayed the highest HM adsorption capacity compared to WHB 300 and WHB 600, with Pb (II) showing more significant adsorption than Cd (II). Analysis of FTIR spectra before and after Cd (II) and Pb (II) adsorption revealed that the adsorption mechanism primarily depends on biochar functional groups, evidenced by peak introductions and shifts. Due to its large surface area, nano-sized WHB shows a greater affinity for HMs. Nano-WHB demonstrated outstanding removal efficiencies, achieving 99.8 % for Cd and 98.8 % for Cr, compared to approximately 85 % for conventional WHB, as reported by Fathy et al. [130]. WHB has also shown promise for the removal of HMs from industry effluents. Approximately 99 % of the Cr (III) was removed from the discharge effluents of a tannery industry in Jashore, Bangladesh, using WHB, as reported by Hashem et al. [131].

Zhou et al. [132] optimized the WHB preparation parameters (heating duration, treatment temperature, and heating rate) using the response surface method (RSM). Their model predicted a Pb(II) adsorption capacity of 24.95 mg/g, nearly identical to the actual experimental value of 24.94 mg/g, resulting in a minimal error of just 0.02 % (Fig. 10). This optimization required a heating time, treatment temperature, and a heating rate of 2.65 h, 433 °C, and 19.96 °C/min, respectively. The effect of ionic strength (Na^+) was found to be low. In contrast, the adsorption of Uranium (U(VI)) is significantly influenced by the pH level study conducted by Xu et al. [133] on WHB. Moreover, there was a stronger agreement between the Langmuir isotherm and the experimental value (R^2 = 0.995–0.998). Furthermore, kinetic analyses revealed that the experimental value fit well with the PSO model, suggesting that chemical adsorption was predominant in the adsorption process. Biochar generated from biomass without pretreatment typically exhibits limited adsorption capacity [134,135]. To enhance its adsorption capabilities by increasing functional group content, various activation methods like chemical modifications (acid and alkali treatment), oxidation, and surface loading of nanomaterials have been employed [136,137]. Shang et al. [102]enhanced the Cr(VI) removal efficiency by coating WHB with graphene oxide (GO). The maximum Cr(VI) removal efficiency for WHB-GO reached 95.6 %, whereas WHB achieved 72.3 %. This improvement in removal efficiency was due to the incorporation of GO molecules, which expanded the surface area and introduced additional functional groups (C–H and C–O stretching vibration, stretching of C–O–C) to the adsorbent. Yu et al. [78] improved Cr(VI) removal efficiency to 80 % by modifying WHB with ZnO nanoparticles compared to the untreated biochar. The successful distribution of ZnO nanoparticles with a particle size of 13–60 nm on WHB is depicted in Fig. 11 [78].

The reduction in Cr(VI) removal percentage occurred when the ZnO loading exceeded 30 wt% due to decreased surface area and pore blockage of the WHB. They also explored the influence of pyrolysis temperature on Cr (VI) removal efficiency. A rise in Cr(VI) removal from 14.7 % to 51.2 % was observed as the carbonization temperature increased from 500 to 750 °C, which was followed by a sharp decline to 25.6 % at higher temperatures (>750 °C), attributed to variations in specific surface areas and pore volume of the biochar.

A significant change in the surface properties (specific surface area and pore volume) of WHB after the incorporation of zero-valent iron and chitosan was reported by Chen et al. [138]. Furthermore, the activated biochar exhibited new peaks of the N–O stretching vibration and increased −OH groups, which promote Cr (VI) removal from water. Improvement of the surface areas of WHB after the incorporation of Fe was also confirmed by other experiments [139,140]. H_3PO_4 activation of WHB resulted in a broad porous surface with irregular pores. Additionally, a substantial quantity of oxygen-containing functional groups was generated on the surface of WHB, facilitating the binding of Pb(II) through strong chemisorptive bonds or ion exchange [141]. Using the chelating ligand

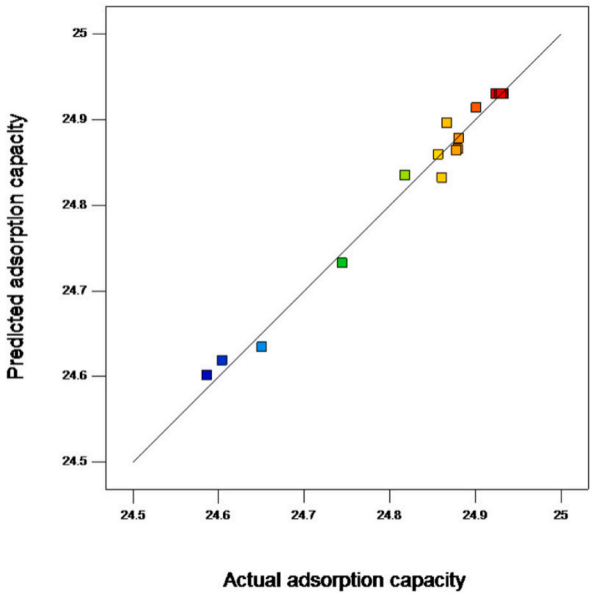

Fig. 10. Correlation between the experimental and predicted data [132].

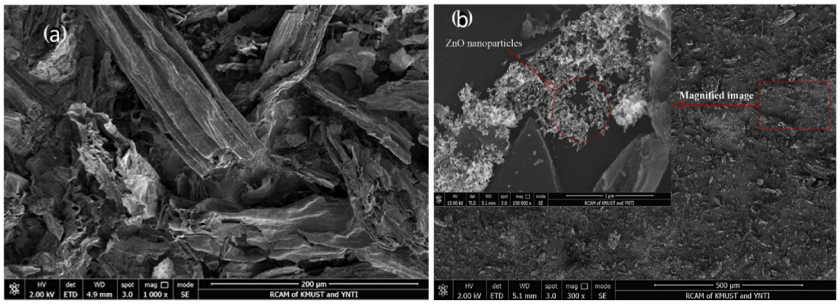

Fig. 11. SEM images of (a) WHB and (b) WHB/ZnO with 30 wt% ZnO loaded [78].

2-aminothiazole in the chemical modification of WHB induced a more disordered pore structure than the pristine biochar. This indicates a strong chemical bonding between the biochar surface and the chelating ligand, providing additional active sites that contribute to the increased uptake of Pb and Hg [142].

Separating powdered biochar from an aqueous solution through subsequent filtration or centrifugal processes poses challenges in practical applications. Modifying biochar with magnetic materials can alter surface properties and prove advantageous for facilitating convenient liquid-solid separation from the aqueous solution after the adsorption process [143–145]. The magnetic modification of the biochar led to an increase in surface area, but there was a significant reduction in pore size. This is attributed to the blocking some pores by iron oxide particles [58]. For magnetically modified biochar, HMs were removed from aqueous solutions through electrostatic interaction, ion exchange, reduction, complexation, and π-π interaction [146]. Several experiments showed that magnetic WHB exhibits a stronger attraction to Cu and Zn than Ni in individual and mixed solutions [147,148]. This phenomenon can be attributed to variations in the ionic radii of these metals, which is explained by ion exchange theory and the interactions between hard and soft acids and bases [149,150]. Details regarding removing HMs from contaminated water by pristine and modified biochar based on published articles are represented in Table 7.

In summary, the modification methods applied particularly influence the removal efficiency and adsorption capacity of WHB. Modified WHB exhibits considerable potential in wastewater treatment, displaying a significant affinity for toxic HM ions. Surface modification generates potential oxygen-containing functional groups on the WHB surface, promoting the binding of HMs through strong chemisorptive bonds.

4.4. Application of biochar in industrial wastewater treatment

In many countries, industrial wastewater discharge remains one of the primary causes of water pollution [157]. HMs such as Pb, Hg, Cd, Cr, etc., are common contaminants from various manufacturing processes in industrial wastewater. Tannery wastewater is often regarded as the most challenging industrial wastewater to remediate due to its high concentration of hazardous compounds [158]. A potential way to reduce environmental pollution and encourage sustainable practices across various industries is using biochar in industrial effluent treatment [159–161].

The possibility of using biochar activated with 85 % phosphoric acid as an adsorbent to remove.

Cr (VI) from tannery effluent was examined by Parameswari et al. [162]. Batch adsorption studies showed that the activated biochar reached a Cr (VI) biosorption ranging from 70.05 % to 88.75 % in the first cycle under ideal conditions (pH = 2, 1 % biosorbent dose: 1 %, reaction time: 35h). In their research, Gajendiran et al. [163] explored a sustainable approach to address tannery wastewater concerns through the application of different treatment combinations. These included modified WH biochar with KOH and biomass from *B. cereus* and *A. flavus*. The study found that KOH-modified WH biochar with *B. cereus* and *A. favus* significantly reduced various HMs in tannery wastewater. The efficiency of WH shoot powders in removing Cr (VI) and Cu (II) from the discharge effluents of a tannery factory in Jashore, Bangladesh, was examined by Saibur et al. [164]. In 180 min, the maximum amount of Cr (VI) removed from the effluent was 87.50 %, while the maximum amount of Cu (II) removed was 83.35 % after 120 min. Sarkar et al. [165] experimented with a similar nature and reported that the WH shoot powder had an adsorbent capacity of 98.83 % and 99.59 % for Cr and Cu ions, respectively, in a tannery effluents located at Hazaribagh, Dhaka, Bangladesh. Table 8 illustrates the use of biochar and biomass in treating industrial wastewater.

Integrating biochar into wastewater treatment holds promise but requires thorough long-term sustainability assessments to evaluate its viability. Here are several vital points to consider:

1. Assessments should consider the environmental effects of using much biochar to treat wastewater. This entails assessing its impact on greenhouse gas emissions, water quality, and the general health of the ecosystem.
2. Consider resource use, energy consumption, and waste generation when evaluating the sustainability of biochar production.
3. Assess the viability of using biochar-based wastewater treatment systems on a large scale from an economic perspective. This entails evaluating the expenses related to the production of biochar, the installation, upkeep, and operation of the system.
4. To determine the long-term efficacy and performance of biochar-based wastewater treatment systems.
5. Rigorous monitoring and assessment should be carried out over an extended duration.

Table 7
Adsorption of HMs from aqueous solutions and industrial effluents by WHB.

Adsorbent	Heavy metal	Pyrolysis temperature (°C)	pH	Initial concentration of HM ions (mg/l)	Optimum dosage (g/l)	Surface Area (m^2/g)	Max. Adsorption capacity (mg/g)	Max. Removal efficiency (%)	Ref.
WHB	Cd	450	–	50	5	–	70.3	~ 100	[127]
WHB	Cd	300	5	10	1	3.5	49.8	>90	[128]
		500		15		6.7	36.9	>90	
		700		20		175.4	25.8	99.2	
WHB	Cd	450	5	100	2	51.2	74.99	–	[129]
	Pb						128.95	–	
WHB	Cd	500	5	5	20	–	1.28	97.4	[130]
	Cr					–	0.98	98.4	
	Ni					–	0.47	98.8	
WHB	Cr (III)	500	8.2	3190.1	57	–	–	99	[131]
WHB	Pb (II)	400	5.5	50	2	9.595	195.24	–	[132]
WHB	U (VI)	400	6	30	0.2	50.54	138.57	–	[133]
WHB/ferric/ ferrous sulfate	Cd (II)	700	6	150	2	94.9	45.8	61.06	[58]
WHB/ZnO	Cr (VI)	700	7	100	4	469.6	43.48	95	[78]
WHB/26.3 % MnO_2	Cd (II)	450	4.5	150	0.5	120.2	232.5	~30	[81]
	Cu (II)						248.9	~100	
	Zn (II)						239.4	~70	
	Pb (II)						249.2	~100	
WHB/GO	Cr (VI)	300	2	100	2	25.89	150.02	–	[102]
WHB/ferric/ ferrous chloride	As	250	5.3	100	5	69	7.41	~ 100	[126]
WHB/Fe/ Chitosan	Cr (VI)	400	2	50	1	833.10	82.2	97.34	[138]
WHB/Fe	Cr (VI)	600	5.5	20	2	60.24	18.78	96	[139]
WHB/Fe	Cd (II)	350	7	2	1	–	56.62	–	[140]
WHB/45 % H_3PO_4	Pb (II)	450	6	50	1	423.6	118.8	90.1	[141]
WHB/amine/ thiol groups	Pb (II)	327	5.5	50	1	–	310.9	~ 100	[142]
	Hg (II)						252.5	~ 100	
WHB/$FeCl_3$	Cr (VI)	700	2	100	0.5	2097.50	202.61	–	[146]
WHB/$FeCl_3$/Co $(NO_3)_2$	Cu	400	4–5	50	10	101.4	18.3	80.6	[147]
	Zn						10.1	81.6	
	Ni						7.33	61.5	
WHB/$FeCl_3$/ Chitosan	Cu	400	7	200	–	–	38.46	–	[148]
	Ni						0.48	–	
Sulphonated WHB	Zn	500	3	100	6.25	–	16.37	~ 100	[151]
	Ni		5	1000		–	20.41	12.75	
WHB/Al/Zn	Pb (II)	600	6	50	–	112.146	227.13	–	[152]
WHB/37 % phosphoric acid	Cr	500	2	100	15	203.83	6.03	90.4	[153]
WHB/melamine thiourea	Pb (II)	277–327	5.5	50	1	452.62	237.4	68	[154]
	Hg (II)						292.6	97	
	Cd (II)						97.9	45	
WHB/cobalt sulfate	Pb	550	7	200	3	192	67.815	95	[155]
WHB/ferric/ ferrous chloride	Zn (II)	450	6	20	1.2	1038.48	9.42	79.6	[156]
	Cu (II)						3.53	92	

6. It is essential to align compatibility, scalability, and potential benefits with other treatment technologies.

Optimizing overall efficiency and long-term sustainability assessments, which also help address obstacles and promote sustainable solutions, can help decide upon the potential of biochar in wastewater treatment.

5. Conclusions

This paper has dealt with removing HMs from aqueous solutions and industrial effluents using adsorbents based on various forms of WH ranging from aquatic plants to biomass and biochar. In practice, removing HMs with inexpensive materials is promising. WH, rich in cellulose and hemicellulose, has a great structure, porous features, and potential functional groups. It is an affordable and sustainable source of biomass and biochar. The review reveals that the efficiency of using WH biochar for removing HMs from aqueous

Table 8
Application of biomass and biochar in treating industrial wastewater.

Adsorbent	Feedstock	Sample	Location	Heavy metal	Max. Removal efficiency (%)	Ref.
Biochar +85 % phosphoric acid	WH	Tannery wastewater	India	Cr	88.75	[162]
10 g of biochar + 10 mL of *B. cereus* and 10 g of *A. flavus* biomass	WH	Tannery wastewater	Tiruppur, Tamil Nadu, India	Cr	54.75	[163]
				Cd	49.52	
				Pb	30.5	
				As	17.53	
				Co	29.07	
				Cu	14.75	
				Fe	5	
				Zn	27.27	
				Mn	9.2	
Biomass	WH shoots	Tannery wastewater	Jashore, Bangladesh	Cr (VI)	87.5	[164]
				Cu (II)	83.35	
Biomass	WH shoots	Tannery wastewater	Hazaribagh Bangladesh	Cr (VI)	98.83	[165]
				Cu (II)	99.59	
Biochar	Algal	Textile industry wastewater	Pakistan	Cr (VI)	97.88	[166]
nMnO-modified biochar	Wood	Tannery wastewater	India	Cr (VI)	96.9	[167]

solutions varies among studied adsorbents. The modification/activation of the biochar gives the composite materials new properties or a noticeable improvement in their current properties, which are desired in wastewater purification processes. Different adsorption mechanisms that interact with HMs and biochar depend on various factors such as the particular pollutants, the pore size of the biochar, the chemical bonds between the sorbent and the sorbate, the pH of the solution, and the pyrolysis and modification techniques carried out. The results, as demonstrated, highlight the versatility of various forms of WH adsorbents as a simple and environmentally friendly platform for wastewater treatment.

Furthermore, it contributes significantly to mitigating and controlling invasive species like WH. Despite the substantial progress presented in this paper, the potential applications of WH and its biochar are likely still in progress, indicating a vast and promising avenue for future exploration. Future studies should focus on enhancing the efficiency and scalability of WH-based sorption processes, investigating novel modification techniques to improve adsorption capacities, and assessing the feasibility of large-scale implementation in real-world settings.

Data availability statement

Data will be made available on request.

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Additional information

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CRediT authorship contribution statement

M. Hedayet Ullah: Writing – original draft, Conceptualization. **Mohammad Jellur Rahman:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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