Modification of biochar with Fe₃O₄ and humic acid-salt for removal of mercury from aqueous solutions: a review

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ABSTRACT
The application of magnetic biochar (MBC) has attracted significant attention due to its recyclability and adsorption capacity for Hg from aqueous solutions. However, its applicability is still inadequate, relying on poor selectivity. Some chemical substances could improve the sorption capacity of MBC. This review offers an advanced technological route to modify-MBC composition with significant adsorption volume toward Hg. Non-polluting humic acid-sodium salts (Ha-Na) were proposed to optimize Fe₃O₄-modified biochar (FBC), while the pyrolyzed substrate for the initial biochar (BC) production originated from any agricultural biomass material. The non-polluting Ha-Na can improve the FBC-specific surface area, the number and structure of pores, moderate the pH and adsorb Hg(II) from aqueous solutions. Further, the interaction of three simple projected equation mechanisms is proposed for BC, FBC, and Ha-Na. BC modified with the support of Fe₃O₄ and optimized by Ha-Na can be applied to improve Hg(II) adsorption, while insights and future investigations are suggested.

1. Introduction
Globally, mercury (Hg) is among the major pollutants, which, even at a low amount, lead to harmful effects on both human health and the environment [1]. Several studies have shown that geogenic and anthropogenic factors such as the industrial revolution and biomass burning increase the concentration of Hg in the environment. The determination of Hg in the environment has been previously estimated with various Hg analyzers. The electrochemical sensors, gas chromatography-triple quadrupole mass spectrometry, cold vapor integrated quartz crystal microbalance (CV-QCM), fluorescence and colorimetric, atomic absorption spectroscopy, and atomic fluorescence spectroscopy, among others, have all been reported to be accurate analytical methods for determining Hg ions [2].

Through fish and seafood consumption, bacteria can methylate Hg to methyl mercury (MeHg), which occurs primarily in human organisms [3]. However, marine food is the most frequent dietary source of MeHg globally. Current researchers from China show that rice (Oryza sativa), a daily food for billions of people, can be a fundamental source of MeHg in regions with a high level of inorganic Hg contaminants [4]. The estimated value of MeHg consumed by inhabitants from rice surpassed the international guidelines, which dedicate (94–96)%, and only 1–2% assimilated through fish [5]. Zhang et al. [6] observed that MeHg concentrations in rice grains could reach up to 569 µg/kg of total Hg, while 145 µg/kg was in MeHg form. According to Wu et al. [7] report, rice grown close to abandoned Hg-mining region contained levels of
>100 µg/kg in its edible portion, thus presenting a considerable health problem in the large population. Because of their growing rice crops in aqueous fields, China’s Guizhou and Shaanxi provinces were well known as MeHg bio-accumulative regions. In China, 4.2% of agricultural soil should be abandoned due to heavy metal pollution, while a high risk of 2.0% is associated with Hg pollution, according to the Environment Quality Standard for soil in China (GB15618-1995 II) [8].

The dominant source of Hg was mining, which led to environmental Hg contamination, and the biogeochemical cycle of Hg. There are plentiful Hg resources in China at the Wanshan Hg mining area, Guizhou, China, which is the core Hg production center [9]. Zhang et al. [10] reported that roughly 40% of the global anthropogenic emissions come from East and Southeast Asia, and around 75% of Hg emerges from China. When Hg is deposited in lakes, specific bacteria convert Hg to inorganic Hg(II) and MeHg naturally, allowing Hg(II) to saturate in the aquatic animals’ body tissues and humans with access to Hg(II) contaminated seafood. In addition, people have recently been exposed to Hg via rice ingestion grown around Hg(II) and MeHg contaminated mining sites [11]. Hg concentrations in many foods are less than 20 µg/kg, primarily in the inorganic forms [12]. Human exposure to Hg can result in endocrine effects, neurological disorders, kidney and liver damage, and impeding childhood growth [13].

Several papers reported biochar (BC) production [14,15] and chemical modification for toxic element treatment [16]. It is well shown that BCs alleviate toxic elements’ contamination in the aquatic environment [17]. The limitation of BC’s commercial application in wastewater treatment is the initial requirement for separation with centrifugation and filtration prior to application. Secondary pollution during these processes may emerge from the desorption of pollutants adsorbed on the BC, creating additional challenges. An effective technique to address these BC challenges in waste water treatment is the introduction of transition metals (Ni, Fe, Co, etc.) or their oxides into the matrices of BC to form magnetic BCs (MBC). It can rapidly and simply remove particle BC from aqueous solution and enhance the removal of organic pollutants and heavy metals from wastewater [18]. Feng et al. [19] showed magnetic MBC has future hope due to its magnetic separation properties. Notably, for Hg(II), researchers have concentrated their efforts on improving Hg(II) treatment techniques such as adsorption, ion exchange, coagulation, and chemical precipitation [20]. Adsorption drew the most attention among these techniques due to its low cost and environmental friendliness [21–24].

However, for this process, it is necessary to have efficient and cost-effective materials. In this regard, some adsorbents, including activated carbon, coal fly ash, natural zeolites, and synthetic zeolites, have been suggested for the adsorption of pollutants from aqueous solutions [25]. Undoubtedly, the most effective technique for Hg removal is adsorption [26].

Ma et al. [27] also showed adsorption as a highly productive technique for treating Hg aqueous polluted sites and Hg uptake transported by plants in aquatic environments.

Some countries are still meeting limitations in ecological complex and aqueous amendment techniques for Hg(II) contamination irrespective of the various previously proposed Hg treatment techniques; optimizing the treatment processes is necessary. The core aim of this literature is to propose a novel technology for Hg(II) removal in the aqua environment using humic acid-sodium salts (Ha-Na) to optimize Fe₂O₃ modified biochar (FBC). Humic substances are considered additives or modifiers because they contain phenolic (-OH) and carboxyl (-COOH) highly dense functional groups, as well as aldehyde (-CHO) and ketone (-C(O)C-) groups distributed over several cyclic, aliphatic, and aromatic chains. These highly dense functional groups support aqueous component interaction via hydrophobic interaction, electron donor-acceptor, and hydrogen bonding. Therefore, the Ha-Na optimized FBC could be outstanding for aqueous or soil remediation by alleviating the aqueous or soil’s chemical and physical properties. The Ha-Na optimized FBC has potential chemo-sorption properties as a sorbent to remove organic pollutants. Moreover, Ha-Na acts as a Hg(II) detaining agent to form (Ha-Na-Hg), owing to its ability to capture toxic heavy metals. FBC modified with Ha-Na can improve Hg(II) adsorption and aquatic soil remediation.

2. Biomass pyrolysis and synthesis of magnetic biochar

Biomass comes from animals and plants, and it is a renewable organic material. Biomass pyrolysis is a complex process, and it is operated in thermal conditions with no contact with oxygen. Giwa et al. [28] reported that BC, bio-oil, and gas could be obtained through pyrolysis. Mathematical modeling of the biomass pyrolysis process was well detailed in Kaczor et al. [29] study. Different elements [carbon, hydrogen, and oxygen] are removed as gases and volatiles, which causes a drop in the O/C and H/C atomic ratios and, in turn, a rise in aromaticity and carbon content, which improves the stability of the BC. Kan et al. [30] reported that based on the substrate, temperature range, and duration of the feedstock in reactor pyrolysis, it can be classified into three major classes: conventional/traditional, fast, and ultra-fast/flash pyrolysis. Meanwhile,
the relative distribution of products is dependent on the pyrolysis operating parameters and pyrolysis type as shown in Table 1.

Traditional pyrolysis is appropriate for agriculture because it produces a high BC yield at low temperatures (~350–400°C) [33]. The BC surface area obtained via traditional pyrolysis remains constant depending on the partial removal of volatiles from biomass. However, biomass BC from traditional/conventional pyrolysis (<500°C) constitutes smaller pore size, lower surface area, and more oxygen-containing functional groups, making it better suited to the elimination of inorganic contaminants [14,34]. As the pyrolysis temperature rises, the tendency for improved volatile removal gets stronger [35]. A higher pyrolysis temperature (>500°C) produces BC with a highly amenable surface area, bigger micropore volume, and stronger hydrophobicity, enhancing the produced BCs highly effective for the removal of organic pollutants [14]. Flash pyrolysis is executed at a high rate of heating with a very fine feed particle size (2 mm), within a very short residence time, with the core objectives of yielding bio-oil [36]. The char yield and attributes in terms of shape, surface chemistry, structure, and reactivity are significantly influenced by the temperature of the pyrolysis reactor. Surface functional groups’ hydrophilicity is degraded with the flash pyrolysis. Therefore, flash pyrolysis temperatures dramatically altered the morphology of the chars, resulting in the loss of the original biomass cell structure, sintering, and macropore development [37]. It is commonly acknowledged that the properties of the BC and the makeup of the target metals play a significant role in the adsorption ability of BC toward heavy metals. Due to its vast surface area, porous structure, and abundance of functional groups on its surface, such as phenolic, hydroxyl, and carboxyl groups, BC can be an efficient medium for the sorption of Hg and other heavy metals [14,38].

MBC can be synthesized by different methods such as impregnation, liquid phase precipitation, liquid phase reduction, and ball milling [18]. Impregnate pyrolysis leads to MBC fabrications, where it is controlled by saturating biomass with transition metal salt solution after the solvent has been successfully removed. Afterward, the desiccated residue is subjected to pyrolysis in a muffle furnace without oxygen or noble gas to produce MBC [39]. The liquid precipitation method needs to prepare BC first, then mix the BC with Fe⁴⁺/Fe²⁺ salt solution to form a suspension. After that, add NaOH solution drop-wise while stirring at room temperature, then precipitation occurs [40]. The liquid phase reduction technique for MBC production elucidates that Fe³⁺/Fe²⁺ salt is reduced into Fe⁰ by injecting a NaBH₄/KBH₄ solution into a mixture of BC and Fe⁴⁺/Fe²⁺ salt under nitrogen purging. Using this technique, a nanoscale zero-valent iron BC composite (BC-nZVI), which was evenly spread over the BC surface and showed no signs of aggregation, was established [40,41]. Large-scale MBC composites have frequently been created using the effective mechanical ball milling technique. At room temperature, these MBC samples were made in a planetary ball milling device with BC, iron or iron oxides, and agate jars. Higher exterior and internal specific surface areas and acidic surface functional groups were present in ball milling MBC samples, demonstrating remarkable adsorption capacity in eliminating heavy metals from aqueous solutions [42]. BC magnetization and pyrolysis co-occur, the adsorption rate, and the physicochemical characteristics of MBC can be enhanced by monitoring the pyrolysis operating parameters such as temperature, heating rate duration, and rare gases. For instance, Xin et al. [43] reported that MBC produced from corncob under 650°C offered 61.97 mg/g after biomass pretreatment with 0.5 FeCl₃ solutions. Furthermore, the pyrolysis temperature can also affect iron oxides (Fe₂O₃) formed in MBC. Xiaohong et al., (2017) have shown that pyrolysis temperature has a significant impact on the physicochemical properties of MBC and iron salts under the 600–900°C temperature range.

2.1. Assessment of magnetic biochar

BC from different biomass has gained much consideration as it shows an excellent adsorption rate for organic pollutants and toxic heavy metals in aqueous solution [44]. The pyrolysis process, where slow pyrolysis was proposed and operated under temperatures spanning from (300 to 600) °C, produces a high BC yield [45]. For instance, Akhil et al. [46] study showed BC as a superb contaminant remediation, but raw BC is inadequate; thus, BC physiochemical properties should be upgraded. According to Zhang et al. [47] study, dusted BC leads to the problem of separation from the environmental medium if applied, resulting in another pollution setback for utilization as an enormous scale adsorbent. In contrast to this, the transition metals with their oxides can be applied into the BC matrix for MBC production, which is separable after the

| Pyrolysis Process | Heating Rate (K/s) | Solid Residence Time (s) | Temperature (K) | Particle Size (mm) | Product Yield (%) |
|------------------|-------------------|--------------------------|-----------------|-------------------|------------------|
| Slow             | 0.1–1             | 450–550                  | 550–950         | 5–50              | Gas 35, Oil 30, Char 35 |
| Fast             | 10–200            | 0.5 – 10                 | 850–1250        | <1                | Gas 30, Oil 50, Char 20 |
| Flash            | >1000             | < 0.5                    | 1050–1300       | <0.2              | Gas 13, Oil 75, Char 12 |
adsorption operation [18]. M. Li et al. [48] and X. Li et al. [49] described that MBC can enhance the adsorption of U⁴⁺, Cd⁴⁺, Pb²⁺, Zn²⁺, Cu²⁺, Hg, methylene blue, tetracycline, pesticide, and phosphate from the aqueous environment. Moreover, Liu et al. [50] demonstrate specifically different applicable techniques for BC preparation.

According to previous studies, MBC has shown great attraction in many fields. For instance, it acts as a catalyst [10], heavy metal removal from aqueous solutions [51], environmental remediation [18], magnetic resonance [52], and energy storage [53]. Pinewood, corn cob, cottonwood, and chitosan have been transformed into MBC production, showing efficiency in many sectors [54]. Further, Q. Li et al. [55] discovered that magnetic particles in the (10–64.7) nm range of Fe₃O₄ achieve the highest magnetization level. Agri biomass (waste) is well known for manufacturing MBC. Furthermore, numerous inorganic salts have been used as magnetic species to produce MBC. For example, ferric chloride, manganese chloride, ferric sulfate, cobalt chloride, ferrous sulfate, nickel chloride, and ferrous chloride are respectively adsorb additive materials [56]. Additionally, to intensify adsorption volume, MBC can be modified with numerous metal salts such as lanthanum nitrate, zinc chloride, magnesium chloride, manganese nitrate, and cerium chloride. Besides, during the operating conditions to manufacture MBC, an organic conditioner (e.g. K₂FeO₄) was used to adsorb hexavalent chromium as an oxidative modifier. The potential of this organic group, and the formation of chemical bonds with organic pollutants, enhances the adsorption capacity and application range if utilized as additives in MBC production. The simple route for the synthesis of MBC with Fe₃O₄ is presented in Figure 1.

According to Yi et al. [18] in their studies, plant biomass wastes cover 80% of BC production, with a 43.93% heavy metal adsorption rate compared to other biomasses. After crushing the plant biomass waste, it is mixed with Fe₃O₄ for magnetization and then operated under fast pyrolysis to produce MBC. Fast pyrolysis can have a high biomass yield with an advanced absorption capacity-to-porosity ratio. It is symbolized by high surface area, functional groups, porous composition, and saturated mineral elements [57]. The increase in the operational temperature of the pyrolysis improves MBC’s porous structure. Xu et al. [58] examine how BC’s adsorption properties are affected by pyrolysis temperature range, corresponding to ammonium adsorption capacity. Moreover, Hu et al. [21] reported that the consequence of increasing pyrolysis temperature amplifies the carbonation of MBC. The pyrolysis temperature impacts the physicochemical properties of MBC; therefore, increasing the pyrolysis temperature in a medium-range can rise the MBC adsorption capacity. The BC modified from Eichhornia crassipes resulted in a high amount of hexavalent chromium adsorption, with an adsorption capacity of 82.2 mg/g under pH 2 from aqueous solutions [59]. Based on Hou et al. [60] MBC modification can also transfer a high number of amino acid groups on the BC surface, which helps in capturing heavy metals such as Pb²⁺, Cd²⁺ and MeHg.

### 2.2. Basic physicochemical characteristics of magnetic biochar

MBC’s physical and chemical properties immensely enhance its potential to adsorb heavy metals. MBC’s diverse structures are due to pyrolysis conditions, raw materials and modifier substances of BC pH, pore arrangements, surface area, functional group, elemental composition, and cation exchange volume. These physicochemical properties are briefly discussed in the subsection below.

#### 2.2.1. Surface area and functional groups of magnetic biochar

Yi et al. [18] showed agriculture waste as the best feedstock for MBC production. The MBC from agriculture can ingest alkaline earth metals, alkaline metals, Si, H, N, S, and P. For instance; China generates roughly 0.7 billion tons of agricultural waste a year [61]. Hence, scraped biomass materials are converted into BC through the pyrolysis process. The biomass pyrolysis process beneath 400°C offers insufficient removal of volatiles from biomass, and this does not affect the

![Figure 1](image-url). Simple route for the synthesis of magnetic biochar/FBC with Fe₃O₄ nano particles.
surface area of the BC much. Within the temperature range of 400°C up to 900°C, the BC surface area begins to rise as the microporous structure of BC is simultaneously formed. Fe₂O₃ encourages pore development, leading to excellent expansion of pore volume and surface area. Dou & Jiang [62] characterized the surface morphologies and surface areas of numerous BC, and the results indicated that modified BC has higher surface areas.

Considerably, BC chemical identification counts on the operating conditions and biomass variety. For example, pyrolytic temperature leads to the change of BC functional groups. The pyrolysis temperature range impacts the syngas-oil-BC products and the carbon/hydrogen/oxygen element ratio. Commonly, biomass hydrogen/carbon/oxygen ratio are 1.4–1.8 and 0.55–0.75, respectively [63]. During pyrolysis, the prime reactions are dehydrogenation, decarboxylation, and decarbonylation; simultaneously, these different reactions can affect the functional group of the BC. Numerous studies show that at high pyrolytic temperatures, the weak bond between carbon and hydrogen can collapse, resulting in the disappearance of functional groups and aliphatic structures. Carbohydrates, on the other hand, begin to produce carbonyl and carboxyl groups above 300°C. Furthermore, Montoya Sánchez & de Klerk [64] reported that increasing the temperature above 600°C results in the formation of a large number of aromatic rings in BC. The porous structures of MBC indicate gigantic adsorption and specific surface area. Besides, it offers a favorable abode for countless microorganisms that bio-adsorb toxic heavy metals. For instance, Epping et al. [65] reported that Escherichia coli cells were modified by a metallo-regulatory protein which presents huge affinity and refinement in connection with Hg using an ice nucleation protein anchor.

2.2.2. pH and surface charge

In addition, pH is an essential and critical constituent in removing heavy metals using MBC. Moreover, it affects the physicochemical characteristics of MBC in the aqueous phase. The heavy metal ion morphology plus the BC surface charge can be affected by pH value, which impacts the adsorption capacity of BC [66]. According to Regual & Sarmah [67] their study shows that MBC is stable and works efficiently within [4.5–8.5] pH range. Tomczyk et al. [68] contrasted many kinds of BC under a pyrolysis temperature range of 350 to 700 °C. This study reported that BC produced at a high temperature has a high pH than those made at a lower pyrolysis temperature. For example, M. Chen et al. [69] studied the adsorption of NH₄⁺ and physicochemical properties of MBC by acid. The p-N properties of BC were due to the rise of pH value to a peak at 5.0, and Cu²⁺ adsorption volume would increase. Nevertheless, by crossing the pH peak, adsorption capacity lessens marginally. Han et al. [70] studied the adsorption capacity of BC for polar and nonpolar contaminant removal by activating BC via FeCl₃ and AlCl₃ additions. According to the results, activated BC shows outstanding adsorption characteristics. Nguyen et al. [71] modified spent coffee grounds with Fe₂O₃ and pyrolyzed them at 700°C for tetracycline removal by persulfate existence. When the pH was in the middle of 2.0 and 4.5, the highest removal capacity of 96% was attained. In contrast, despite adsorption rising with increasing pH value, when the pH value goes beyond the peak, the adsorption quantity of the heavy metal anions starts to decrease.

Besides the existence of heavy metal ions, other ions synchronize in the aquatic environment, and the presence of those ions does not affect heavy metal adsorption volume. Liu et al. [72] show that the presence of K⁺, Mg²⁺, SO₄²⁻, Ca²⁺, and NO₃⁻ ions can diminish the efficiency of the BC adsorption towards heavy metal ions. Increasing the ionic concentration leads to a decrease in the amount of heavy metals adsorbed. Wang et al. [73] prepared engineered BC with KMnO₄ and pyrolyzed it under 600°C. Engineered BC has a higher surface area than pristine BC when prepared with KMnO₄ and pyrolyzed at 600°C for Cu²⁺, Cd²⁺, and Pb²⁺ adsorption. Several kinds of research have shown the impact of K⁺, Mg²⁺, Ca²⁺, and NH₄⁺, and Zhang et al. [74] reported the effect of those ions on Cd²⁺ and Pb²⁺ adsorption under the dosage of modified BC. Moreover, heavy metal ions have a significant impact on BC adsorptions. When the initial concentration of heavy metal ions is high, this leads to the powerful heavy metal adsorption by BC. Because of the lower ion concentration of heavy metals, adsorption occurs on the surface of BC [75]. Medha et al. [76] used MBC for the sorption of Cr⁶⁺ and Zn²⁺ and studied the ions’ initial concentration of Cr⁶⁺ and Zn²⁺ and their effects. Increasing the concentrations of the initial ions leads to increased MBC adsorption volume. The associated reason was that the super-saturated heavy metal ions strengthen impulsion to counter the mass transfer resistance in contaminated aquatic soil. Table 2 presents studies on the different heavy metal elements adsorbed by MBC from biomass materials.

3. Performance of sodium humate-modified magnetic biochar on Hg(II) removal

3.1. Assessment of sodium humate adsorption performance

Humate salt derivatives from lignite brown coal are enriched in phenolic and carboxylic alkaline groups and are aromatic; they offer suitable conditions for chemical reactions, biological activity, and physical improvement of soil and heavy metal aqueous solution
Table 2. Different heavy metal elements adsorbed by magnetic biochar from different biomass.

| Raw material      | Temperature range (°C) | After producing BC and magnetized BC, this study reported that hypochlorite addition leads to high removal of the Ti (I) ions under pH 6 to 9, where the adsorption volume of Ti (I) was 1123 mg/g. | Remark | Reference |
|-------------------|------------------------|-----------------------------------------------------------------------------------------------------------------|--------|-----------|
| Watermelon rinds  | 500                    | The chestnut shell was pyrolyzed, and magnetic gelatin formed. The gelatin microsphere increased the specific surface area of pristine BC for adsorption. Compared to the BC control (17.5 mg g⁻¹), the highest adsorption volume of the magnetized BC was 45.8 mg g⁻¹. |        | [78]      |
| Chestnut shell    | 450                    | The use of Kenaf with MBC offered a high amount of Cd²⁺ adsorption under pH 5 to 6, where BC supported by iron particles has a high affinity to Cd²⁺ and enhances pore volume and surface area. |        | [91]      |
| Kenf Fiber        | 500                    | The co-precipitation method produced MBC for chromium Cr⁶⁺ and Acid orange 7 (AO7) dye from water. MBC was reported to have high pollutant removal capacity. The adsorption volume was 80.96 mg g⁻¹ for Cr⁶⁺ and 110.27 mg g⁻¹ for AO7. |        | [79]      |
| Woodchips         | 450–700                | The 400–500°C pyrolysis temperature range for sewage sludge was the best temperature to produce good BC with high specific surface area and pore volume for Al³⁺ and Cu²⁺ adsorption from an aqueous medium. |        | [80]      |
| Sewage sludge     | 300–700                | After synthesizing BC, it was carbonized, magnetized, and sulfurized. A one-step heating process produced sulfurized MBC for Hg (II) adsorption from the aquatic medium under acid pH medium of 3.5–5. The adsorption capacity was 8.93 mg/g Hg(II). |        | [81]      |

at higher pH values, fulvic acid – soluble in water at all pH values; humin, which is the humic substance fraction insoluble in water, while hymeatomelic acid is the fraction of Ha, which is soluble in alcohol [83]. The characteristics and structure of humate substances depend on their origin and extraction conditions. However, on average, the properties of humate substances are remarkably similar. Notably, a core characteristic of the Ha-Na and humic substances are their adsorption ability to bind metal cations and sorb organic compounds. The humic substances are effective binders for polycyclic aromatic hydrocarbons, persistent organic pollutants, and other organic compounds [83,84]. Further, humic substances, such as Ha-Na, possess features of high-density functional groups that support aqueous component interaction via electron donor-acceptor, hydrogen bonding, and hydrophobic interaction.

BC is produced under a pyrolysis temperature of 600°C, improved with Ha-Na enhancing the adsorption of methylene blue [62]; consequently, the adsorption volume is enhanced. Ha-Na is a material not only reckoned with for detoxifying but also for its non-toxic characteristics. The degradation of harmful pollutants in water, detoxification of strychnine and heavy metals are the peculiar potencies. Further, merging sodium humate with humic acids (Ha) to produce the Ha-Na compound can result in multiple quantities of functional groups in MBC, leading to the increase of adsorption sites. The application of Ha-Na combined with lime was non-toxic and highly efficient as a depressant for arsenopyrite. The recovery of Zn concentrate was 92.21%, thus mitigating environmental pollution and optimize resource utilization [85]. The chemical adsorption of arsenopyrite with Ha-Na was through its Ca atoms and carboxyl groups, thus enhancing Ha-Na adsorption processes.

Other humate salts such as Potassium-Humate were applied in the phyto-stabilization of Fe and Cu²⁺ (546 ± 181 mg kg⁻¹ and 29.3 ± 7.5 mg kg⁻¹), showing profoundly higher adsorption concentration rates at the root, minimizing transportation of the metals to aerial parts of the plant, compared to the control [86]. The initial and final adsorption performance of Cu²⁺ was enhanced with Ha-Na with remarkable features of stability and recyclability [87]. Different metals’ adsorption performances with Ha-Na and different humate salts are summarily described in Table 3. Ha-Na is extracted from peat, lignite, and Leonardite, and it is completely soluble in water. Countless articles have described Ha-Na as the essential substance in several fields. Sun et al. [88] found that Ha-Na can enhance the SO₄ and SiC powder’s adsorption volume, and Y. Liu et al. [89] reported that the SiC adsorption volume was 2.368 mg/g with Ha-Na. Moreover, it appeared to be primarily used as a dietary supplement by developing egg quality, as an additive for biomass, and by

treatment [82]. The core difference between humate salts and humic acids (Ha) is that humate salts are the salt of Ha, while the Ha is a significant organic acid that arises as a constituent in soil. Notably, the Ha dissolves readily in water only at a high pH soil value, while humate salts are ionic compounds and are readily dissolve in water. There are three main fractions of humic substances; Ha, which is insoluble in water under strongly acidic conditions (pH <2) but soluble
Table 3. Performance of humate salts/sodium humate on different heavy metal adsorption.

| Metal types | Humate salts/sodium humate experiment | Effects and outcome | References |
|-------------|-------------------------------------|---------------------|------------|
| Cu\(^{2+}\) | Adsorption of Cu\(^{2+}\) from aqueous solution was conducted with the preparation of starch-g-poly(acrylamidocrylic acid)/sodium humate (St-g-PAA/SH) hydrogels. | The combination St-g-PAA polymeric networks with only 5% sodium humate enhanced both the initial and final adsorption capacity for Cu\(^{2+}\). | [87] |
| Arsenopyrite and Zn | Sodium humate salt (NaHA) and Lime (CaO) combined as depressant for arsopyrite pre-treated by CuSO\(_4\) for butyl xanthate. | The chemical adsorption of arsopyrite with Ha-Na was through its Ca atoms and carboxyl groups thus enhancing Ha-Na adsorption processes. The NaHA-CaO achieved Zn concentrate and Zn grade recovery of 92.21%, and 51.21%, respectively. | [85] |
| Fe and Cu\(^{2+}\) | The pot assay experiment was conducted with plants | Potassium-Humate showed higher adsorption concentrations rate at the root for Fe and Cu\(^{2+}\) (546 ± 181 mg kg\(^{-1}\) and 29.3 ± 7.5 mg kg\(^{-1}\)); reducing and averting transportation of the Fe and Cu\(^{2+}\) metals to aerial parts of the plant. | [86] |
| Heavy metal ions: Cu\(^{2+}\), and Co\(^{2+}\) | HA was obtained from brown coal with 2% NaOH (1.8 m/v) mixed intensively for 1 h at 25°C. Modification of the HA was conducted with bis (3-aminopropyl) amine. | The aim of the HA modification is to increase the sorption capacity. Maximum sorption percentages of modified HA achieved were 99.2% for Cu\(^{2+}\) and 90% for Co\(^{2+}\), respectively. The pH range 2–8, influenced the sorption characteristics. | [99] |
| Pb\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Ni\(^{2+}\) | Novel adsorbent was synthesized with Ha combined with magnetic nanoparticles (HA-O/Fe\(_3\)O\(_4\)) Chemical modification. | The HA-O/Fe3O4 unveiled rapid kinetic performance within (10 min). It presents reusability and recyclability effectiveness over 90% offering sustainability to absorb Pb\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Ni\(^{2+}\). HA increase the adsorption capacity of MB onto the BC from 8.62–11.03 mg/g and 10.79–16.21, for white clover and peanut shells residues, respectively. | [90] |

*Methylene blue (MB) biomass pyrolysis was conducted at 600°C and HA introduced to synthesized Ha-Na-modified BC.

*MB was mentioned because of its carcinogenic, non-biodegradable, toxicity, severe environmental challenges, and threats to human health safety. A trial to alleviate MB was previously reported with HA-BC.

3.2. Sodium humate-modified magnetic biochar and mechanism on Hg(II) removal

Progress for toxic heavy metals’ removal from aquatic environments is still challenging. Various research studies have shown contrasting techniques for BC modification and improved adsorption capacity for specific pollutants. Saeed et al. [91] used MBC modified by Kenaf Fiber with pristine for Cd\(^{2+}\) adsorption from an aqueous state. Several technologies amend BC by including engineered nanoparticles to increase the adsorption capacity of pollutants and improve soil properties. Servin et al. [92] investigated CeO\(_2\) nanoparticle-modified BC in the agricultural field. Irrespective, BC characterization manifested the capability to adsorb toxic heavy metals and methyl blue from the aqueous phase. BC modification with chemical substances is needed to enhance the affectivity of adsorption for specific contaminants. Chianese et al. [84] reported Ha as an environmental assurance for wastewater treatment and showed a high potential to sorb hydrophobic organic and cationic contaminants.

Moreover, Ha can also be applied in agriculture and has a positive impact by improving micro and macronutrient consumption and promoting root maturation [93]. The primary essential characteristics of the Ha constitute the organic-free radical concentration, hydroxyl group content, phenolic and carboxylic. The degrees of humification enhance the adsorption of pesticides and other xenobiotic organic substances [94]. Humic materials can detoxify water through the influence of bioavailability, binding, and transport of heavy metals. The detoxifying characteristics and kinetic features of the Hg reduction ions by humic materials are well studied by [95]. Therefore, according to the study results of Chakraborty et al. [96], Hg(II) can be reduced by humic substances in the aquatic system, with the presence of HNO\(_3\) and H\(_2\)SO\(_4\) individually, together with KMnO\(_4\), which could entrap not less than 95% of gaseous Hg.

Numerous experiments were conducted to promote different heavy metal removal techniques, but some studies reported that unamended BC adsorption volume is finite. It is essential to modify BC for advanced adsorption achievement. Several studies have suggested two procedures to modify BC in past studies. The first procedure is to modify biomass directly before pyrolysis operation, and the second procedure is the modification of BC after pyrolysis operation. Choudhary et al. [97] fabricated NaOH-modified BC, and the results showed maximum adsorption capacity toward Ni\(^{3+}\) and Cu\(^{2+}\), due to more oxygen-holding functional groups on the surface of BC. They reported that modified BC specific surface area was advanced more than BC, which is unmodified. Jizhou et al. [60] previously combined vermicompost with KMnO\(_4\) solution before pyrolysis, afterward it was utilized for Cd\(^{2+}\) removal from aqueous solution.

Additionally, Ha is present in a large quantity in the environment, and it can be extracted from peat and lignite. A precise portion of sodium hydroxide solution can remove Ha from роде coal, which is then separated and dried to get a concentrated Ha-Na by-product, which is a fertilizer and completely soluble in water.
Figure 2. The route for aqueous system mercury (II) removal by humic acid-sodium salt-modified biochar.

Please see Figure 2 for the proposed route of aquatic environment Hg(II) removal by Ha-Na-MBC.

The main factors influencing the adsorption performance of MBC include pyrolysis temperature, biomass and modifier, the dosage of adsorbent, pH value, reaction temperature, contact time, initial pollutant concentration, and competitive anion. Physiochemical characteristics have an impact on the BC capacity for heavy metal adsorption. Several researchers reported that the chemical properties of modified BC increase the specific surface area in heavy metal adsorption operations [22].

The possible formation mechanism equation for the performance of MBC or FBC modified with Ha-Na for Hg adsorption/treatment in aqueous solution can be simply represented in three stages as thus:

\[
\text{Fe}_2\text{O}_3 + \text{BC} \rightarrow \text{FBC} \quad (1)
\]

\[
\text{FBC} + \text{Ha} \rightarrow \text{Na} = \text{FBC} - \text{Ha} - \text{Na} \quad (2)
\]

\[
\text{FBC} - \text{Ha} - \text{Na} + \text{Hg}(\text{II}) = \text{FBC} - \text{Hg} - \text{Ha} - \text{Na} - \text{Hg} \quad (3)
\]

The introduction of transition metals or their oxides was initially suggested in equation (1), Fe$_2$O$_3$ was introduced into the matrices of BC to form FBC. The FBC will provide binding sites for Hg reduction via its skeletal carbon structures, and at the same time, Fe and its oxides will offer Hg ion immobilization. According to Liang et al. [98] the optimization of BC with Fe$_3$O$_4$ or transition metal oxides to form FBC proceeds via three stages as follows: stage 1 – ‘Hydrolysis, complexation, and reduction’, stage 2 – ‘Decomposition and dehydration’, stage 3 – ‘Decomposition and reduction’. In this review, the formation mechanism stipulates that MBC was further modified with Ha-Na to generate FBC-Ha-Na (2); the produced FBC-Ha-Na can be subjected to Hg adsorption or treatment in an aqueous medium to adsorb Hg concentration. The final projected reaction was FBC-Hg-Ha-Na-Hg (3); the Ha-Na and MBC will offer an attractive surface area to immobilize the Hg, offering low concentrations of Hg in the solution. Further illustrations of the FBC-Ha-Na mechanism performance are highlighted in pictorial form in Figure 3.

It is important to mention that FBC might have high stability with the leaching of low Fe concentrations. It is suggested that experiments be conducted to ascertain the stability and recyclability performance of the FBC and its optimization with Ha-Na, a biopolymer and an ecologically friendly material.

4. Insights and future perspectives

Numerous studies have enhanced BC’s physiochemical properties and performance capacity through...
magnetization and modification. The challenges associated with the optimization process still need to be redressed and further investigated. After the conversion, the Ha-Na impact and the optimum portion to modify FBC plus modification mechanism and functional group formation have to be examined. Hou et al. [60] reported that the functional group formation on the poly(amino acid) surface, such as sulfhydryl, amino, and carboxyl, enhances the adsorption of heavy metals like MeHg, Cd$^{2+}$ and Pb$^{2+}$. Humic substances can form complexes between heavy metal ions and Ha and also between metal ions and Ha: Cu, Zn, Mn, Fe, Au, Al, and Se, thus affecting their availability. Hence, the physiological effects of complexes prepared from Ha and targeted biogenic elements could be further examined, including Hg(II). Purification of water from heavy metal ions with the help of sorption processes using humic substances is quite promising. The associated reasons for the sorption enhancement are that humic substances are a mixture of high molecular substances with complex structures substituted by different functional groups and chemical structures. Humic substances can undergo chemical modification and provide the ability to form stable complexes with heavy metal cations [99]. The feasibility of this performance for FBC modified with Ha-Na for Hg(II) treatment in contaminated aqueous environments can be investigated at the lab scale.

The ability of FBC-Ha-Na to resist in an acidic medium while also being biocompatible and adsorbing Hg(II) must be investigated further. Investigating if FBC modified by Ha-Na could adsorb other beneficial minerals in the soil is crucial. The ecological impact of modified FBC with Ha-Na or with other Ha salts must be explored further, as modified BC existence on soil for an extended period might alter aqueous soil environmental functions and the maturation period, causing secondary contamination. For example, Hou et al. [60] reported the impact of the long-term application of BC on aqueous soil properties, such as the shift in pH, adequate nutrients, and microbial community structure. The inhibition of other heavy metal ions during the Hg(II) adsorption process has to be scrutinized, and the mutation of modified FBC with Ha-Na in the remediation of aqueous applications has to be further investigated.

There is a need to examine whether FBC modified by Ha-Na can adsorb more toxic heavy metals and other water organic pollutants. Dou & Jiang [62] showed that Ha-Na-BC prepared under 600°C pyrolysis temperatures promoted methylene blue removal from wastewater. This was influenced by the development of Ha-Na molecules and the increase in surface area in BC. The mechanism applied in Dou & Jiang [62] study can be investigated for the feasibility of Hg(II) adsorption and treatment in an aqueous environment. The Ha-Na modified BC had larger mesopore volumes than the raw BC, which greatly increased the adsorption capabilities. In the utilization of Ha-Na modified BC in waste water treatment for methylene blue, Dou & Jiang [62] stated that in the adsorption kinetic study, methylene blue sorption to Ha-Na-modified multiple mechanisms could dominate BC, and both intraparticle diffusion and film diffusion are the rate-limiting steps of the adsorption process. Study and investigation into the application of Ha-Na modified BC in waste water treatment for heavy metals, notably Hg(II) in the aqueous environment need to be intensified, and scientific literature is still limited. Ha-Na-BCs could therefore be a cost-effective adsorbent for the removal of Hg(II), methylene blue, and other heavy metals from wastewater. Different techniques to modify FBC to improve selectivity and soil remediation capacity must be intensively investigated. Other methods for Hg(II) remedial capacity in water, soil, and air with magnetic nanocomposites modified with Ha-Na should be investigated and efficacy compared with FBC-Ha-Na for industrial and commercial-scale purposes.

5. Conclusions

Different reports on Hg’s adsorbents and treatment techniques have shown great potential. Among the reports, BC, an adsorbent and a significant product of the pyrolysis process, showed efficacious adsorbent properties. Pyrolysis conditions and biomass types can seriously influence BC. Therefore, the report aims to optimize BC adsorbent performance for effective Hg(II) removal and treatment in the aqueous environment. Firstly, BC activation, magnetized by Fe$_3$O$_4$ to produce FBC, was proposed in this review. In the second stage, the FBC will be modified by Ha-Na to improve its specific surface area, pore structure, functional group, and selectivity towards heavy metal ions and Hg(III) adsorption. Ha-Na was suggested to modify FBC due to their pollution control efficacy in the aqueous environment and their adsorption capacity, ion exchange, and chelating characteristics. The proposed route needs further laboratory experimentation to confirm the novelty. Future research should look into the dosage of Ha-Na used to modify FBC as well as the toxicological effects, maturing period, stability, and recovery rate of the Ha-Na to optimize FBC for its applications in an aqueous environment. The in-situ experiments, economic, sustainability, adaptive, eco-friendly, and non-invasive analyses of the proposed route for BCs modified with Fe$_3$O$_4$ support and optimized by Ha-Na for Hg(II) removal in the aqueous environment should be conducted prior to commercial-scale application.

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