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The Enhancement of Heavy Metal Adsorption from Wastewaters: Nano-Modifications, Biochar, Biomass Modification, Modifications by Metal Ions and Technique Using Organic-Inorganic Polymers

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Abstract

One way to get carbon-rich biochar (BC) is to thermally decompose agricultural solid waste in an oxygen-limited environment. Due to the various functional groups and its porous structure, it has been considered as a potential and low-cost metal contaminated water treatment sorbent. The surface of BC can be modified with the introduction of nanomaterials to make new biochar nanohybrids (BNHs), which can enhance the sorption and removal ability of the biochar for heavy metals (HMs). One of the physicochemical properties that can be acquired by loading the nanomaterials onto the biochar surface is the adsorption capacity of HM. It is done by altering the functional group profile, and active site availability on the BC surface. The main study interest is the impact of varying raw materials and pyrolysis conditions on key biochar physicochemical properties that enhance heavy metal immobilization. These properties are aromatic structure, cation exchange capacity. Care is taken in the reduction of hazardous Cr6+ and the oxidation of mobile As3+ in the six redox reactions and physical adsorption, precipitation, ion exchange, and direct remediation processes. In addition to direct interactions, the benefits of biochar to the soil environment include improving physicochemical properties, enhancing soil microbiological activity, promoting growth, and enhancing soil carbon sequestration. Soil remediation is not only for metals, soil biochar also improves soil physicochemical properties (e.g., CEC, porosity) and has a role in reducing the mobility of metals in eroding soils and carbon sequestration. This paper aims to emphasize the possibility of utilizing biochar as an affordable option to conventional remediation approaches. It can immobilise metals, enhance soil

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quality, and decrease the carbon emissions simultaneously. Although biochar has great potential in HM pollution remediation, it has not been extensively applied yet and may not be able to solve all the problems encountered in actual environmental remediation. Biochar is being integrated with other remediation technologies, such as phytoremediation and microbial remediation, as a key strategy to address these limitations. Thiol (-SH), amino (-NH2), or phosphate (-PO4 3−) engineered biochars could be exploited to selectively bind specific metal combinations like Cd2+/Pb2+ or As3+/Cr6+ and are worthy of further studies. The accuracy and efficiency of remediation can be improved with this method. Furthermore, complicated polluted locations may find hope in the creation of multi-functional biochars with the ability to adsorb, undergo redox alteration, and support microbes all at once. Beyond material design, one of the most important roles to help make the transition between small-scale research in the lab and the larger-scale applications is important. While useful mechanistic insights are provided, most of the studies that were analysed in this publication which may not capture the complexities of the real world. Although some field-scale trials have been reported, there are inherent limitations in the use of biochar on a large scale due to its variability in soil properties, profile contamination and concerns about the long-term stability of the product. For possible application in practical situations, several issues need to be considered such as accessibility of feedstocks, processing methods, transportation logistics and how to apply it. All of these have an impact on the scaling, performance and durability of the biochar-based solution. It is very urgent to conduct (LCA) to economic benefits associated with biochar. Future studies should address the issues encountered in the operations, analyse the long-term performance, and create implementation frameworks within contexts to bridge the real-world implementations. Future research should investigate secondary effects like desorption of pollutants, release of nanoparticles, and the toxic effects on the ecosystem to ensure the safety of the ecosystem in the long run. This study describes the processes of preparing the various HM ions based on nano biochar hybrids depending on the type of modifying agent to remove various HM ions from wastewaters.

Keywords: Heavy Metal, Wastewaters, Biochar, Biomass Modification, Technique

Introduction

With the increasing concern about pollution of the water sources from natural and man-made industrial effluents, a growing number of countries are concerned about the contamination of the water sources. The removal of heavy metals (HMs) in contaminated streams is a key issue and has a critical impact on plants and animals' growth and metabolism. HM are metals with high density (>5 g/cm3) and biological toxicity. Thus, it is necessary to conduct the HM decontamination of the wastewaters. There are several possible techniques for removing HM from industrial wastewaters such as adsorption, electrochemical treatment, and biological treatment. The adsorption process is especially advantageous for removing HM ions (due to its simplicity and cost-effectiveness). The capacity of several adsorbents to remove heavy metal pollutants has been studied [1, 2]. However, the use of the agricultural byproducts for HM adsorption might be a win–win thought. Agricultural wastes be the sustainable and low-cost HM adsorption substrates. Agricultural waste not only includes all waste products, but anything left over from agricultural production that does not provide a direct economic value to the farmer.6 However, given the high organic content, agricultural wastes can be used to enhance soil. Biochar is a solid agricultural waste and can be produced by thermochemical technologies like biomass pyrolysis and flash carbonisation. It has a high carbon content. Researchers are keen to investigate biochar as a soil amendment to boost crop yields while reducing nutrient leaching, greenhouse gas (GHG) emissions, and the use of fertilisers [3-5]. The biosorption capacity of biochar is very high, owing to its porous structure and functional groups. To remove lead and cadmium from polluted calcareous soil, biochar made from sewage sludge can be utilised. The capacity of biochar to remove heavy metals (HM ions) from wastewaters has been the subject of many studies and is seen as a potential waste management solution for the removal of Cd, Pb, Ni, As, Hg and Cr from biochar produced from different feedstocks such as rice husk, pine wood, wood bark, and cotton wood.

Multiple mechanisms are involved in the process of heavy metal adsorption from wastewaters using biochar. These involve electrostatic forces between the metal and the functional surface of the cation exchange of metals with alkaline metals on the surface of the biochar, precipitation of the metal, reduction of the metal and subsequent sorption, and complexation of the metal with functional groups and π electron-rich domains on the biochar. The type of sorption mechanisms is strongly dependent on the feedstocks, biochar production process and the metal to be removed. Various physical and chemical characteristics of biochar affect its ability to remove metals, which is dependent on the type of feedstock used, pyrolytic processes, and the circumstances. However, biochar is not always able to hold sorption capacity because the pyrolysis process is carried out at high temperature which causes the surface of the biochar to lose active functional groups. The adsorption capacity of pure biochar is limited, and can be improved by modifying the biochar, as shown. Thermal disposal of biomass and the use of carbonaceous adsorbents are both impacted by the need to increase the HM adsorption capacity from wastewaters. The adsorption capacity of biochar can be improved if its functions (surface area, functional groups, etc.) are improved [6, 7]. However, it was remarked in the published studies that the biochar particle size is much larger than 50 mm, which is considered as nanobiochar. The researchers also found that particle size did not affect the adsorption of heavy metals from wastewaters and polluted soils. Nanobiochars are highly potential as HM adsorbents, but the low production yields are a huge challenge. A variety of approaches have been taken to enhance the functionality of BC, such as BC modification. Biochar can be treated with an alkali solution to activate it and mineral such as haematite (γ-$Fe2O3$) and reductant to enhance the sorption of biochar. Generally, the adsorption capability of the modified biochar is greater than that of the raw biochar. An encouraging method is to improve the ability of biochar to remove pollutants from its surface by modifying it with nanoparticles. As a result of their higher surface-to-volume ratio, nanomaterials improve the catalytic degrading ability, surface active sites, pore size and functional groups of biochar. In order to lessen the impact of toxins and pollutants, nano-remediation makes use of the unique qualities of nanomaterials, which allow them to undergo chemical reduction as well as catalytic reactions. The researchers discovered that the sorption capacity could be raised by adding ZnS nanocrystals to biochar, which is about ten times higher than that of unmodified biochar [8-10]. Thus, a Biochar-ZnS nanocomposite was developed. However, Zhang et al. investigated the possibility of using MnO2 loaded biochar for better removal of HM ions from water. The integrated goals like waste management, removal of HMs and carbon sequestration are promising targets for the modification of biochar with nanomaterials. Cleaning up polluted sites is not only important, but ensuring sustainability in the process is the holy grail. Thus, nano-remediation utilising nanomaterials derived from agri-waste has the potential to be a fruitful approach to managing and controlling HM contamination.38 Several assessments have already looked into the possibility of using engineered or modified biochars for wastewater treatment [11]. The removal of HM from wastewaters can be done through physical activation via nitrogen, carbon dioxide and steam, or chemical activation via acid, alkali and oxidising reagents. To remove inorganic and organic contaminants, Weidner et al. and Zhao et al. described in detail how to modify BC with metal oxides. In their reviews, no additional agent that modifies was mentioned. Metal sorption mechanisms based on functionalisation of BC via oxidation, nitroenation, and sulfuration, as well as on various surface functional groups of BC are presented. The use of nanocomposites for HM detoxification of wastewaters was investigated, taking into consideration the advantages of nanotechnology in the current world. In their study, Ho et al. concentrated on methods like as coprecipitation, carbothermal reduction, and pyrolysis to create nanoscale BC with metal supports. Detailed explanations of how BC sorbs metals, including a quick comment on nanomodifying BC to make it even more effective. For the purpose of removing HMs, other inorganic metals, and organic contaminants from wastewaters, the following materials are prepared: magnetic BC, nanometal oxide/hydroxide-BC, and BC coated with functional nanoparticles [12, 13]. However, no thorough literature survey has been found that involves detailed outlooks into the method used to prepare BNHs using various organic and inorganic functional components. Hence, the aim of this study is to fill this gap of information by presenting a detailed study of the various recently published biochar-assisted nanomaterial manufacturing processes. They are based on the nature of the components that are added to BC to deplete the different HM ions from wastewaters. Also, the mechanisms of different modifying agents, organic and inorganic polymers, metal precursors and biomass feedstock have been discussed.

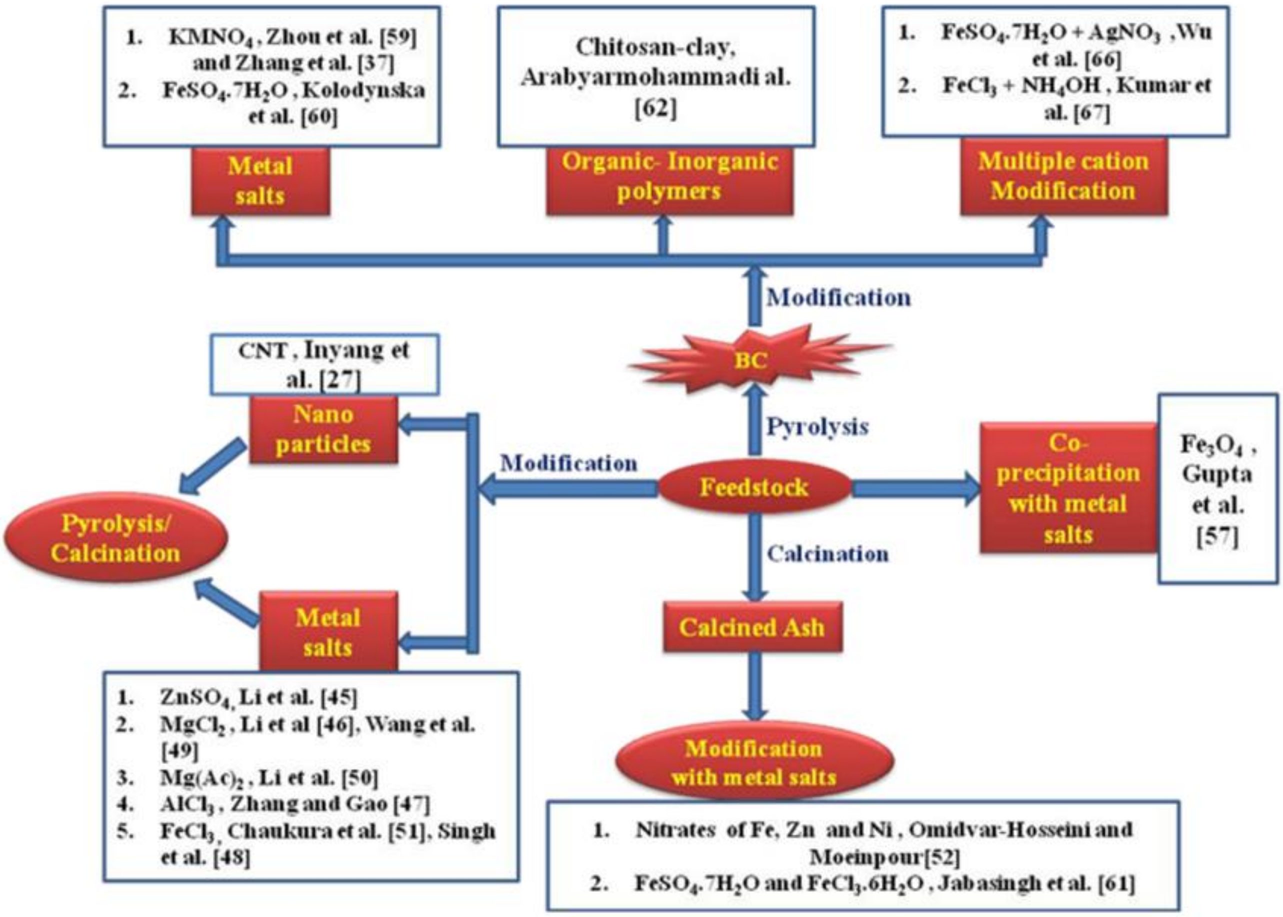

Figure 1. Different modification techniques of biomass and BC.

Methods of preparing Biochar Nanohybrids

In order to improve biochar's ability to remove organic-inorganic contaminants, a lot of research has focused on finding ways to combine the benefits of porous biochar with the distinct physical characteristics of nanomaterials. There are two possible ways to functionalize biochar to be usable for a range of applications, by incorporating nanoparticles. A one-step solution is changing the biomass to use in the preparation of BC, calcination and coprecipitation. In these changes, BC/biomass could be treated on the surface with nanoparticles, organic-inorganic polymers (which can generate BNHs) and a variety of metal precursors (such as metal oxides, chlorides, sulphides, sulphates, and nitrates).

Biomass Modification

Before pyrolysis or calcination can be used to biomass, the raw material must undergo pretreatment, which entails modifying it. This process is energy efficient because biomass is simultaneously pyrolysed with the metal precursors.

Modifications by Metal Ions, Sulphur and Chloride

A promising approach to the development of BNHs that have an improved sorption capability is biomass coated with metal salts during catalytic pyrolysis. Water based solutions of $ZnSO_4$, $MgCl_2$, $Mg(Ac)_2$, $AlCl_3$ and $FeCl_3$ are commonly used for impregnation. Pyrolysis treatment is a process of heating the biomass at high temperatures that can convert biomass with high content of metal ions into BNHs or nanocomposites. Increased surface area and high porosity characteristics of the nano counterparts lead these nanocomposites to have better adsorption ability. For instance, Li et al., suggested pyrolysis of maize stover biomass contaminated with zinc to obtain the nano ZnO/ZnS modified biochar, which showed improved porosity structure compared to the original biochar (BET = 102.9 m2/g and TPPV = 0.20 cm3/g). Similarly, Li et al. pyrolyzed biomass with the inclusion of banana, cassava, corn, camellia nutshell and taro straw to make five different biochars with different Mg loading. SEM analysis of the resultant product revealed the presence of spherical to irregularly shaped Mg particles such as $Mg_2(OH)_3Cl·4H_2O$ and MgO that could have been responsible for ion exchange and other processes on the biochar surface [14-17]. After impregnating Loblolly pine (Pinus taeda) biochar with $MnCl_2·H_2O$ and then subjecting it to pyrolysis at 600 °C, MnO-loaded biochar was produced, which had 6.7% less carbon than the original biochar.49 On the other hand, the BET study showed that the surface area doubled because the pore volume increased by about seven times. A MgO hybrid carbonaceous composite was prepared using sugar cane leaf waste using the same method. With the SEM-EDX study, we are certain that there are Mg compounds in the composite surface. Hybridisation with magnesium oxide improved the production of the carbon sponge composite similar to nanotubes.

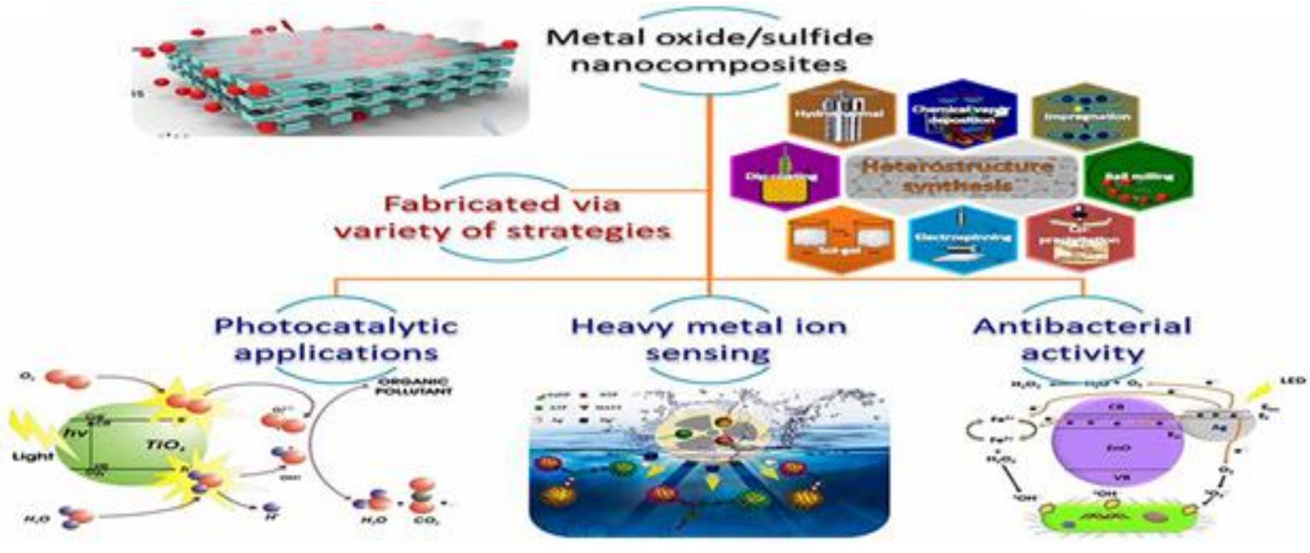

Figure 1. Synthesis of metal oxides/sulfides-based nanocomposites

Nanoparticle Modification (Biochar Modification)

CNT is a fine-grained structure with a large surface area, so there is a need to enhance their adsorption properties to functionalise BC. To make a CNT−biochar nanocomposite, Inyang et al. used a CNT suspension that had been ultrasonicated. Biomass of milled hickory chip and sugar cane bagasse were individually mixed into CNT suspension and then the mixture was pyrolyzed to produce CNT−biochar nanocomposites. Biochar is a by-product of the organic pyrolysis process. Thermolysis is a process of decomposing an organic compound by heating at high temperatures under the absence of oxygen. Pyrolysis can be described as conventional, rapid and flash pyrolysis with different heat parameters used. Biochar generated by high-temperature technology (HTT) is a suitable material for BNHs due to its large surface area and high porosity and it can be loaded with functional ingredients or metals with high accuracy and efficiency on its surface [18, 19]. However, novel and beneficial properties are provided by the hybridisation of BC with functional components loaded on BNHs, showcasing the synergistic effect of both components.

The Chemical Changes Caused by Metal Oxides, Sulphates and Nitrates

The most common method to obtain BNHs is to perform surface chemistry modification of BC using metal precursors. The surface characteristics of BC are improved and its catalytic and magnetic activity are enhanced when metallic species are included into its carbon matrix. It is not unusual to observe the inorganic analogue sticking to the surface of the BC in aqueous solution. A coprecipitation method has been used by many researchers to load various inorganic oxides in biochar from a variety of feedstocks. MnO_2 nanospheres (size: 30 nm) were found on the surface of the NMBCs through the use of the coprecipitation technique that generated a more porous surface for the MnO_2-biochar composite. In the same way, water hyacinth BCs were reported in the literature as being loaded with MnO_2 as channeled nanosheets covering their entire surface. In another study, a solution of $NaBH_4$ was used to prepare magnetic nanobiochar that was coated with uniformly distributed zerovalent iron via the coprecipitation method. $FeSO_4$ was used as the catalyst of this process. The formation of Fe and charcoal bonds was further verified from the FTIR peaks of the absorption bands at approximately 680 cm^{-1}. Recently, researchers have been tuning into the process of calcining biomass to form biochar and composites from biochar. Heating inorganic materials to a point where they become more crystallinity and free of surface contaminants and volatile components is called calcination [20]. A sugar cane bagasse-Fe_3O_4 composite was successfully prepared by coprecipitation of bagasse residue with $FeSO_4·7H_2O$ and $FeCl_3·6H_2O$ in ammonia solution and calcination. Structures of the modified bagasse that were either spherical or rod-shaped were detected in the product by transmission electron microscopy (TEM). The effect of the interaction between bagasse and the Fe−OH bond in their hybrid was validated by shifting the position of the bagasse peak from 897 cm−1 to 874.6 cm−1. The Fe3O4 bands of vibration were also observed in the bagasse-Fe3O4 composite IR spectra. A magnetic nanoparticle of Ni0.5Zn0.5Fe2O4 sol−gel had been prepared by mixing the metal nitrates with calcined ash of Acacia nilotica seed shells in an aqueous solution. BNHs were prepared by calcining this sol−gel.

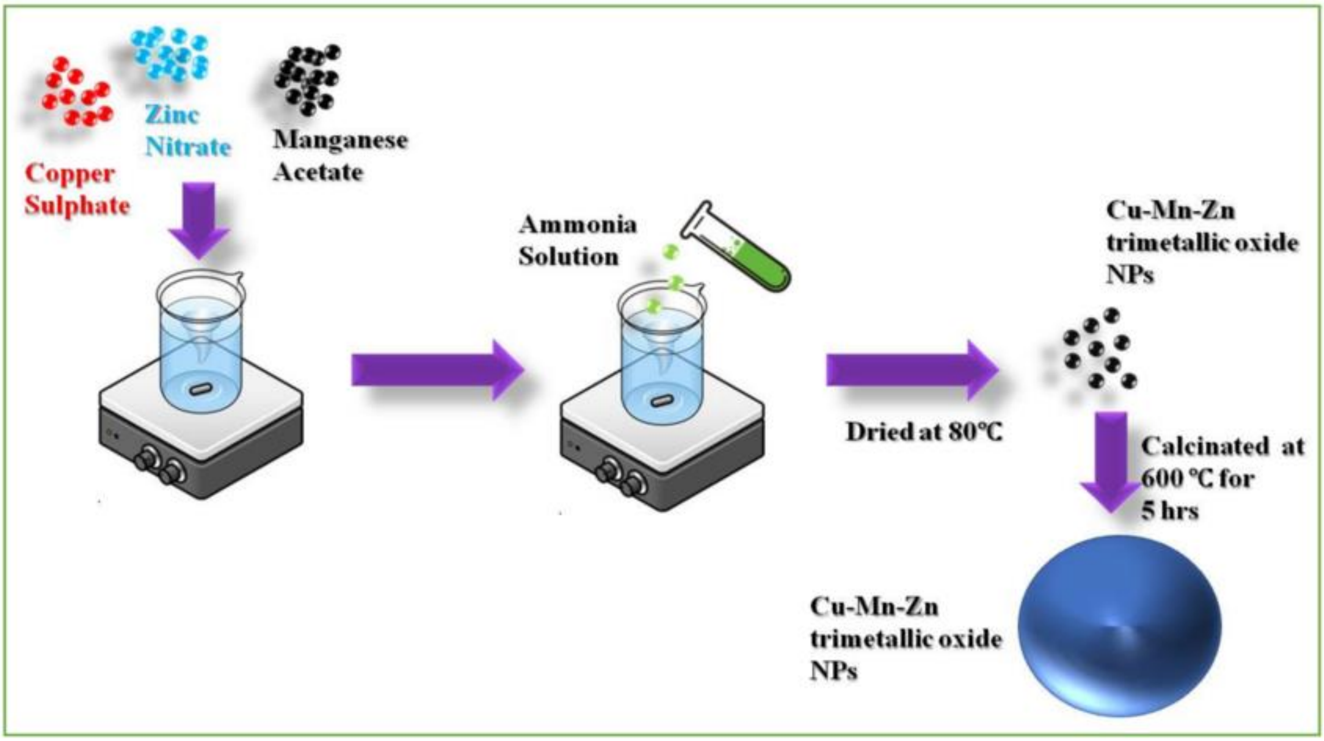

Figure 2. Synthesis of Cu-Zn-Mn mixed trimetal oxide nanoparticles (NPs).

A **Modification Technique Using Organic-Inorganic Polymers Was Employed**

Another way for modifying is to immobilise an organic or inorganic polymer into a carbon. The immobilization of organic or inorganic polymer into carbon is another modification method applied in BNH development. This implies the formation of an effective composite material with increased porosity and interface chemistry with heavy metal contaminants, transforming the BC into an effective one. This implies the formation of an effective composite material with increased porosity and interface chemistry with heavy metal contaminants, thus transforming the BC into an effective one. Nevertheless, there is a dearth of material about the organic-inorganic alteration of BC. Nanobiocomposite of the bark chips modified with chitosan and clay by mixing the aqueous solutions of biochar, chitosan-clay with acetic acid (2% v/v). Since chitosan has the ability to be biocompatible, eco-friendly, and appropriate for biocomposite manufacture, it was selected by the researchers. The layered structure and exchangeable hydrated cations of nanoclay is the main reason for its popularity as a polymer additive for the improvement of physical properties of polymers such as chitosan, which has been attributed to the presence of amino groups. Although BNHs demonstrated better adsorption properties, it is expected that a multiple cation salt can enhance the adsorption by providing the biochar with a dual adsorption mechanism. In their study, Wu et al. discovered that biochar could be used to facilitate Ag/Fe nanoparticles [21, 22]. They used FeSO4·7H2O to mix with biochar in the presence of NaBH4 to create a discontinuous layer of Ag. Then they added AgNO3 to the mixture, stirring vigorously.

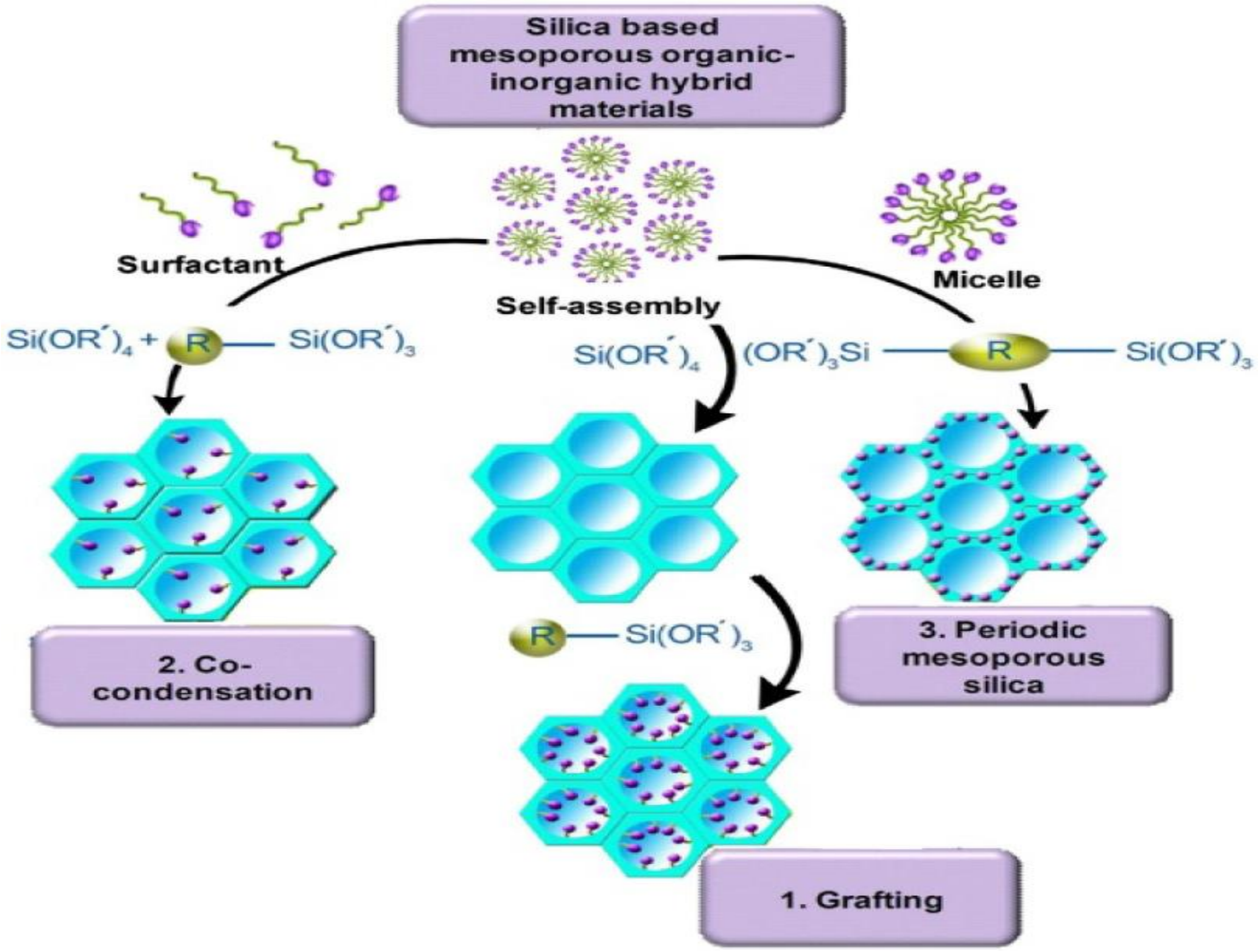

Figure 3. Organic-inorganic hybrid mesoporous silica can be synthesized by different approaches: Using grafts, in situ grafting or co-condensation, and periodic mesoporous silica.

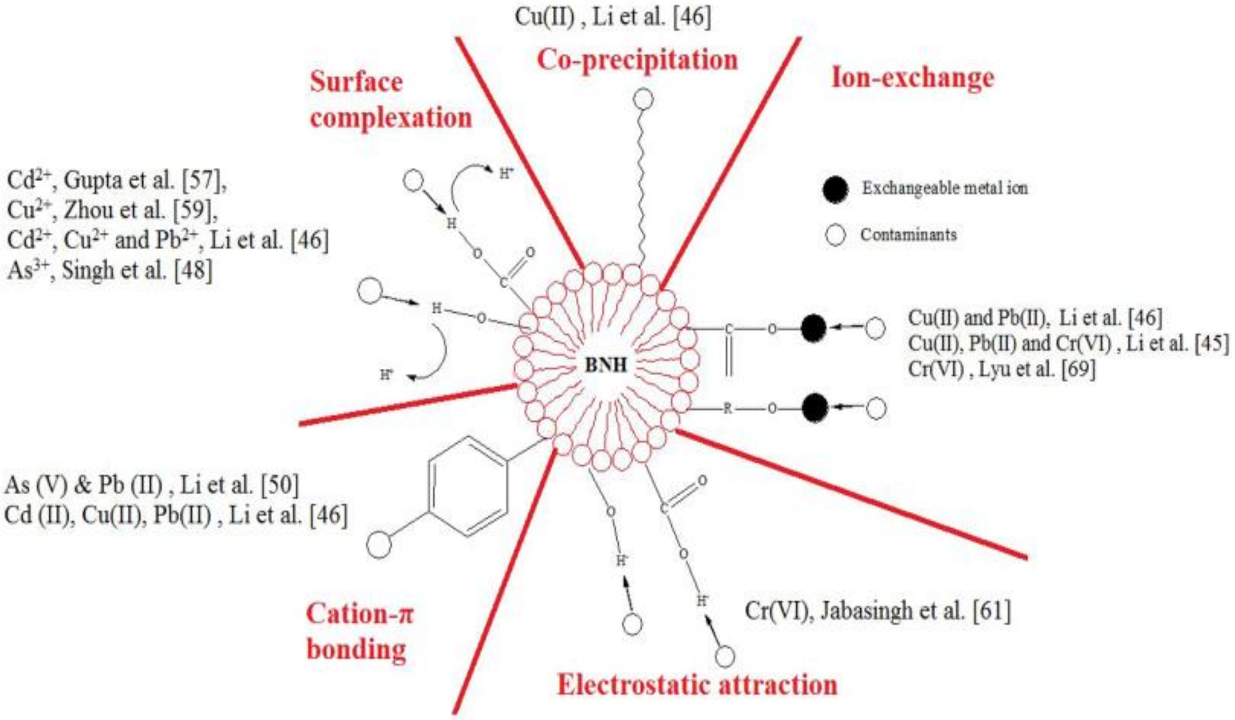

Figure 4. Various heavy metal adsorption processes on BNH surfaces.

The Use of Used Ingredients from Food Crops in The Production of BNHs (Bulk of Households) Heavy Metals.

It was encouraging to find some evidence that the filter properties of nano modified biochar (BC) derived from agricultural byproducts could remove HM ions tested the adsorption capacity of Cu^{2+} ions in wastewater using a hybrid of biochar and nano MnO_2 and found that the adsorption rate of the hybrid material was 142.02 mg/g, which is much higher than that of the pure nano MnO_2 and biochar (93.91 mg/g). It was also demonstrated that the amount of adsorption increased with the increase in pH value than pHZPC, the competition for the surface of the adsorbent between Cu^{2+} ions and a large number of H^+ ions occurred. Additionally, the adsorption capacity for both H^+ and Cu^{2+} ions was reduced due to electrostatic repulsion between the cations generated by the large positive charge. The binding energies at 934.7 eV that were seen in the XPS spectra were determined to be Cu 2p3/2. The Cu^{2+} ions were detected as CuO (28.87%), $Cu(C_2H_3O_2)_2$ (24.07%) and $Cu(OH)_2$ (16.51%) on the adsorbent surface. The peaks of the metal adsorbed adsorbent showed that the band appeared at lower wavenumbers than the FTIR spectrum before the adsorption of Cu^{2+}, indicating that the adsorbent complexed with Cu^{2+} in the surface of the adsorbent. The change in the peak at 1504 cm^{-1} wavenumbers indicated the creation of COO−Cu, whereas the peaks at 1385 and 511 cm^{-1} wavenumbers are caused by the −OH deformation vibrations of hydrated MnO_2 on the surface of NMBCs that generate Mn−O−Cu. Successful discussion of the sorption mechanisms of magnetic micro Fe_2O_3 modified sugar cane bagasse for the removal of Cr^{6+} ions from wastewater has already taken place. The best adsorption time was still 180 minutes even at low concentration of Cr^{6+} and high percentage of removal was observed. A higher adsorption of Cr^{6+} was observed with the increase in the concentration of the adsorbent for the metal solution of 1 ppm (150 mL). Besides, the adsorption capacity remained constant even if the amount of the adsorbent was considerably increased. The adsorption of Cr^{6+} was found to increase from pH 3 to pH 5 and not change at pH > 5.0. The strong positive charge of the adsorbent surface led to an easier binding of the additional Cr^{6+} ions (as CrO_4^{2-} ions) at any pH lower than the adsorbent surface pHpzc (5.8). The electrostatic forces of repulsion caused a decrease in the ability of surfaces to adsorb when the pH was above 5.8. The HM percent removal increased from 15.31% to 71.29% when the pH of the solution was changed from 3.0 to 5.0. The primary reason for the effective adsorption of Cr^{6+} ion is due to their metal−ligand complexation. Another mechanism that was suggested is the transport of the Cr^{6+} ion from the solution to a surface of the adsorbent and then the diffusion of the Cr^{6+} ion into the pores of the surface. In another study, positively charged Cd(II), Co(II), Zn(II) and Pb(II) ions were found to be attracted to the negatively charged groups on the surface of zerovalent iron modified biochar. The adsorption process was found to be Exothermic Physical Adsorption process, which is favourable at low temperature. This adsorption process began to increase as the contact time increased because there were many active sites on the surface, but it eventually became level off. When pH is 2, the acidic sites on the sorbent surface were occupied by H^+ ions that affected metal ion binding and decreased the efficiency of all metal ions' uptake [23, 24]. The highest adsorption was obtained at pH 5 but it increased with pH. Li et al.48 used six straw feedstocks to produce Mg-loaded biochars and studied the adsorption capability of these biochars for different heavy metals, considering their pH value. Adsorption was not effective at low pH. The adsorption of Cd(II), Cu(II) and Pb(II) by all biochars increased rapidly with the increase in pH. After the metal adsorption, the pH values increased as a result of the excess of hydroxyl ions in the solution. When the pH of the biochar surface was increased, causing the biochar to be negatively charged, the metal ions were more easily attracted to the surface for adsorption. The biochar was found to be highly capable of loading a large amount of Mg^{2+} ions in the complexes, and is subjected to strong ion exchange, as shown by the shifting of FTIR peaks of different groups. The XRD pattern and SEM-EDS images confirmed the decreased magnesium amount and increased metal amount that occurred in some of the compounds (such as $Pb_3(CO_3)_2(OH)_2$, $CdCO_3$, $Cu(OH)_2 \cdot NO_3$, $Cu_2Cl(OH)_3$, etc.), which confirmed the adsorption through the ion exchange mechanism. According to the Langmuir model, a mixture of AlOOH and cottonwood biochar was able to adsorb more As(V) from water than Al_2O_3 alone, but it was on par with activated Al_2O_3. The Langmuir model showed that MgO hybridised biochar had an outstanding adsorption capacity of 157 mg/g for As(V) and 103 mg/g for Pb(II), respectively, in another investigation [25-27]. As the pH of the solution rose, the adsorption capacity of Pb(II) rose and As(V) fell. The FT-IR, XRD and XPS results confirmed the formation of $MgHAsO_4$, $Mg(H_2AsO_4)_2$ crystals of the nanocomposite, which further confirmed the adsorption of As(II). The C $\pi-\pi^*$ transition was responsible for the adsorption of Pb(II) in the Pb−carboxylate interaction. The XPS spectra showed the characteristic peaks of the $H_2AsO_4^{-1}$ and $HAsO_4^{2-}$, AsO_4^{3-} and Pb 4f, thus confirming the adsorption of two metals. As(V) ions at pH 3–7 exist in the form of $H_2AsO_4^{-1}$ and $HAsO_4^{2-}$, which were strongly attracted to the positively charged surface. From the change in the FTIR peaks of the O containing groups, it was suggested that the change in the O containing groups were due to the formation of Mg−O and Mg−OH groups on the adsorbent surface. Further, the adsorption capacity of the adsorbent was improved by the formation of similar complexes to the heavy metals on the surface of the adsorbent. Fe_2O_3 modified rice/wheat husk was used as a biochar hybrid surface and arsenic (As) contaminant was removed from groundwater by forming monodentate ($Fe-OAs(OH)_2$) and bidentate ($(Fe-O)_2AsOH$) complexes on the Fe−OH surface of the biochar. A maximum adsorption capacity of 111 μg/g was observed and excellent adsorption was found in the pH range of 3-10. Further, the biochar hybrid showed a slight reduction in its capacity for the removal of As(III) in the process of regeneration in four successive rounds [28-30]. Compared to unmodified biochar, which had maximum adsorption capacities of 63.29, 27.05, and 15.23 mg/g, respectively, the increased number of adsorption sites for Pb(II), Cu(II), and Cr(VI) given by Zn nanocomposites were 135.8, 91.2, and 24.5 mg/g, respectively. Very unstable nanoparticles form from an aqueous solution of efficient, cheap and environmentally friendly reducing agent iron(II) sulphide. The researchers found that the surface of biochar was coated with nanoparticles of iron sulphide (FeS) stabilized with carboxymethyl cellulose (CMC), which enhanced the efficiency of the removal of Cr(VI). The researchers documented the formation of Cr(III)−Fe(III) complexes through ion exchange, and they documented the sorption of Cr(VI) via surface pores and functional groups containing oxygen.

Students should be Exposed to the Effects of BNHS on Living Things

Over the last ten years, biochar (BC) made from biomass thermochemically treated with oxygen has found usage in a variety of applications, including enhancing soil and plant health, cleaning up polluted water and soil, decreasing the need for fertiliser and greenhouse gas emissions, and serving as an industrial catalyst and soil supplement. However, two potential threats have been barely studied: unwanted effects of BC on ecosystems and human health. There are two main areas that require further research: (1) the increased use of harmful chemicals in the production of biochar adsorption materials, and (2) the release of pollutions from biochar-based adsorbents. Dioxins, (PAHs) and furans are among the many harmful substances formed in incomplete/partial pyrolysis or oxidized pyrolysis. Research has demonstrated, however, that organic molecules produced during pyrolysis can be partially burnt by moisture in totally dry biomass, which may lead to a decrease in PAH release. Corrosive contaminants include materials used during manufacturing or the alkali/acids needed for the activation of the adsorbent and are the cause of environmental degradation [31, 32]. Other features of BCs are phytotoxicity and cytotoxicity. It is impossible to prevent the release of nano components into the environment during BNH manufacturing and application, therefore there is possible risk of nanotoxicity even though the toxicity of the BNHs is likely to be minimized when compared to the toxicity of nanoparticles. A fundamental part of the use of BNHs – one of the crucial aspects of safer, more environmental and green chemistry – has now been explored and considered in connection with the synthesis of nanoparticles. Toxic and expensive chemicals are used in the production of chemicals, but green synthesis using various crops and their waste promises a better environment. To keep things risk-free, BNHs need to be stable enough to not give nanotoxicity. Therefore, long-term studies of the physicochemical interactions between BNHs and their natural habitats are required. As BC expands and its nanohybrid research grows, plans need to be developed to address the potential adverse impacts of BC. More detailed research is required in understanding the potential hazards of BNHs to the human and environmental systems before safer BNHs can be developed [33, 34]. So far, there is no in-depth study that compares the different methods of biochar risk mitigation due to its low density and porosity, which can disperse in the atmosphere and pose a potential hazard. It is essential to assess BNHs production and management practices critically in a manner that allows for the safety of humans and the environment to be guaranteed.

Soils Contaminated: Treated with Biochar

Soil heavy metal (HM) pollution is a severe environmental issue that is attributed to various human activities such as mining, smelting, transportation, industrial emissions, pesticide and fertilizer applications. The last fifty years witnessed the accumulation of the large HM pollutants in the worldwide environments due to anthropogenic contributions that exceed 30 million tonnes of Cr and 80 million tonnes of Pb. The problem of soil poisoning occurs in the entire world, but is particularly prominent in industrialized countries. Today, more than half a million polluted industrial sites in the EU need to be cleaned up—and approximately 600,000 ha of farmland in the US has become unsuitable for use due to HM accumulations. In developing countries, the situation with respect to pollution is not good. HMs such as Cd, Pb and As deposit in soil can cause multiple hazards to ecosystems and human health. These long-term pollutants affect the microbes and enzymes in the soil, leading to reduced soil fertility and yields that will hamper nutrient cycling and decomposition of organics. When the HM ions travel to another medium like groundwater or airborne particle, they can amplify the environmental risks they present, which is called "cross-media pollution [33-35]. Leaded glass and cadmium are known to cause neurodevelopmental disorders, kidney failure, and cardiovascular disease in humans when inhaled, or come into contact with the skin or through ingestion of contaminated plants. Their carcinogenic potential, particularly for Cr and As, aggravates this effect on public health in the long run. These risks are accentuated further up the food chain, as bioaccumulated in crops and biomagnified in cattle, increasing human consumption. So, the problem of remediation of contaminated soil with HM has been turned into an urgent environmental issue. When it comes to soil remediation, there are now three primary approaches: physical, chemical and biological. There are many complaints about physical remediation, including time, budget, and effectiveness. Phytoremediation uses hyperaccumulator plants to remove soil without destroying the agricultural value of the soil in an economical and non-invasive manner. It is not widely used because it is inefficient in systems that have numerous contaminants, low root-depth coverage, and a slow extraction rate of metals. Metal resistance is a characteristic of microbes used in microbial remediation, which can be used to transform or immobilize pollutants, but requires careful regulation of pH, organic matter and temperature. However, the use of phytoremediation may result in secondary contamination via the disposal of plant biomass and bioaugmentation is a time consuming and costly solution for the issue of low microbial viability under high metal stress. There are two types of chemical methods, chemical passivation and chemical leaching. Chemical leaching with acids or chelators can be problematic with respect to secondary contamination from leaching reagent residues [36, 37]. The chemical passivation, however, gives immediate effect with a minimum of effort through stabilization of metals with inexpensive additives (for example charcoal or phosphates). The fact that biochar can be readily prepared, is abundantly available and has an excellent adsorption capacity makes it an interesting choice for use as a passivation material on a large scale.

The Biochar Method for HM Removal

Physical adsorption, co-precipitation, and redox reactions are some of the many mechanisms involved in the process of employing biochar to remediate soil that has been contaminated with HM. How well biochar immobilizes HM ions is dependent on the complementary effects of these processes. The next sections will discuss some of these immobilisation mechanisms in more detail, along with the mechanism of action for their removal of HM.

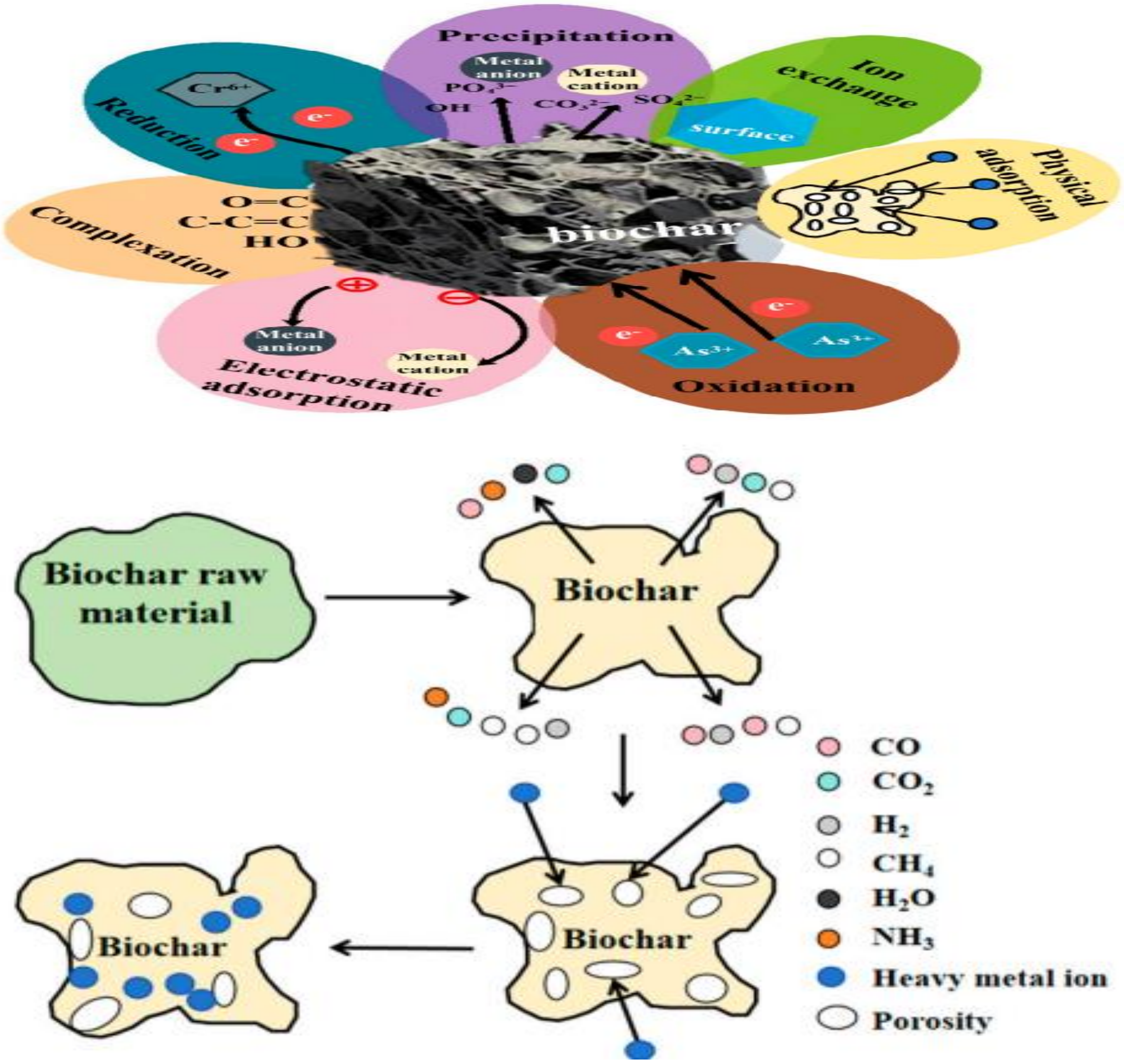

Figure 5. Mechanism of HM adsorption by biochar materials.

Physical Adsorption (PA)

Physical adsorption is the basis for soil treatment in the case of HM contamination. The main reason for this is the extremely large surface area to volume ratio (SSA) and porous structure of Biochar that enables the adsorption of HM ions through Van der Waals forces. Instead of forming bonds, as in chemical adsorption, HMs are retained through weak intermolecular interactions in physical adsorption. The pore structure of biochar has a large number of adsorption sites, which can trap and immobilise soil HM ions. Besides, its high SSA makes the adsorption efficiency much enhanced as more contact with the pollutants. The physical adsorption, which is primarily governed by the micropore filling and van der Waals interactions, generally remains constant under slightly acidic to slightly alkaline environment. Unlike electrostatic adsorption it is not affected by the variation of surface charge. In highly acidic soils (pH<5) an increase in hydration shells and a competition with protons can hinder metal ion migration into the micropores and thus decrease the adsorption effectiveness. Therefore, physical adsorption is not affected by the pH of soil and only works under specific chemical soil conditions. Biochar is intrinsically limited in its physical adsorption of HMs due to its poorly formed pore structure with low surface reactivity [38-40]. However, biochar with extremely low specific surface area (SSA) of only 3.9-10.7 m2 ·g −1 and less than optimum Pb2+ adsorption rates (less than 20%) is produced from bagasse if the pyrolysis temperature is kept low (200-300 ◦C). Due to these drawbacks, chemical changes of the biochar are needed to enhance its structural and adsorptive properties. To create hierarchical pore topologies, metal-based alterations, especially those involving the incorporation of oxide nanoparticles, have been successful. The MgO-functionalized biochar had higher SSA (380-fold) and Pb2+ removal efficiency (from 0.07 to 26.56 m2 ·g −1 and from 23% to 74%, respectively) compared to virgin biochar. This enhanced mechanism is a result of the combination of two effects: (1) the enhanced pore network, which will allow the intraparticle diffusion of metal ions and (2) the presence of extra binding sites as a result of surface complexation by MgO nanoclusters. The biochar surface properties can be significantly altered by different modification processes such as impregnation with SC(NH2)2, H2O2 oxidation, KOH activation, and others [41-43]. Immobilisation efficiency of HM by biochar is governed by non-linear surface changes-immobilisation efficiency relationship, and there are several synergistic mechanisms that control HM immobilisation. The alteration of biochar has been shown to result in a reduction of the SSA, and the complexation from the thiol groups (R-SH) with the Cd2+ has been shown to increase HM immobilisation. But, it does not always correspond that adjusting something to improve the SSA also increases the efficiency of immobilisation [44, 45]. One instance is when biochar was treated with acid, which diminished its aromaticity, broke its π-conjugated aromatic structure, and diminished cation-π interactions. This made the formation of stable complexes with Zn2+ more difficult.

Adsorption by Electrostatics

When biochar has a small surface area and pore volume, physical adsorption isn't very effective. Electrostatic adsorption becomes extremely important when biochar surfaces are charged in order to make up for this constraint. Surface functional groups of biochars like phenolic hydroxyl groups (Ar-OH) and -COOH will be degraded at specific pH range, resulting in a net negative charge. This charge results in the electrostatically binding of soil HM ions to the charcoal surface, thereby enhancing their immobilization. The effectiveness of electrostatic adsorption depends on the type of functional group, the surface charge density of biochar, the ionic strength and soil pH. At higher pH value, dissociations of -COOH and Ar-OH are increased, resulting in more negative charge on the biochar surface and more electrostatic interaction with the HM cations. Biochar is even more effective as an immobilizer in contaminated soils if it has a high CEC value to more positively charged metal ions.

By modifying its surface charge, biochar is able to immobilize HMs electrostatically through ion exchange mechanisms that are pH dependent. In acidic soils (pH < 5.5). The soil pH increased after being displaced by ions, which resulted in the adsorption capacity of Cd2+ by the biochar being 3.22 times greater than that of the pure biochar. Fan et al. further validated the pH-regulated charge reversal mechanism with the use of nZVI/BC composites (pHpzc = 8). When applied to soils with a pH of 7.9, the electrostatic attraction of the HAsO4 2− species was able to immobilise more than 90% of the As on the surface of biochar, preserving negative charges (pH < pHpzc). The multi-mechanistic cooperation in biochar-based degradation can be seen in this two-fold action, exchanging alkaline ions by cationic metals (e.g., Cd2+) and adsorbing oxyanions (e.g., As5+) depending on pH. In all species, the electrostatic mechanism which depends on pH regulates the immobilisation of HM. Building on the idea of pH regulated electrostatic adsorption presented for Cd2+ and As5+ previously. They studied the speciation of Cr and found that direct adsorption onto protonated biochar surfaces was the major pathway for the removal of Cr6+ under the acidic conditions (pH < 4) studied. The universal trigger for HM sequestration is surface charge modulation since the electrostatic priority matches with the increased adsorption of Cd2+ in the alkaline catalysis [45-47]. In this study, Cr3+ was also observed to be completely dependent on the initial electrostatic capture efficiency, like the multi-stage immobilisation pattern observed in Cr2+ and Cr6+ systems, despite the occurrence of subsequent Cr6+ reduction and precipitation.

Biochar in Conjunction with Plants

The presence of numerous contaminants and high HM concentrations are two of the main obstacles to remediating soil polluted with HM. It is often necessary to combine numerous ways to remediation because a single technology is not enough to provide successful therapy. Phytoremediation has been widely applied in soil remediation due to its cost effective and low environmental impacts. The combination of ryegrass, castor seedlings and Angelica seeds has been proven to significantly enhance soil HM stabilization when combined with biochar. Biochar is not only able to enhance soil properties for plant growth, but also directly immobilizes the HMs, increasing the plant's ability to accumulate HMs and contributing significantly to this enhancement. Biochar can also enhance the remediation efficiency by affecting the translocation and dispersion of HMs in plants. The selection of HMST plant species as the first priority is followed by considering their life cycle, their distribution throughout the world, the structure of their root systems, biomass production and their reaction to a range of soil pH. In this context, the plants with different functions: hyperaccumulators (like B. juncea and Sedum alfredii), crops (like maize and ryegrass) used for Phyto-stabilization. Chelation by root exudates (organic acids like citric, oxalic and malic acids) can make heavy metals more mobile. Furthermore, these exudates help the microbial transformation and neutralize the pH in the rhizosphere thereby enhancing the remediation process. This integrated remediation approach is currently being used in a realistic way to remediate soil contamination [48, 49]. The findings revealed that sunflower plants not only exhibited increased rate of growth, but also produced a significant remediation effect on HMs when biochar was applied. Overall, the deposition of all 3 metals, Pb, Cd and As, increased by 15.8-110% in sunflower plants when the biochar was applied. However, biochar and plant-based remediation still offers some challenges: (1) systematic scientific methods to understand the mechanisms of various biochar-plant combinations; and (2) specific technical guidelines for choosing which biochar-plant combinations is best suited to the field, depending on local conditions. Thirdly, it is crucial to prevent HMs absorbed by plants from re-entering the soil environment; farmers should also think about the plants' monetary worth.

Utilizing Microorganisms with Biochar

As with phytoremediation, the ability of microorganisms to withstand HMs must be thoroughly assessed before applying them to a soil contaminated with HM. The primary goal of the joint use of microorganisms and charcoal is to enhance their resistance to and remediation of HMs. Biochar, as a microbial carrier, is essential for such an approach since it creates a more stable environment of the microbial community and increases its ability to adapt to polluted environments. Biochar reduces HMs through bioadsorption, bioaccumulation and biotransformation by providing a favorable environment for the microbial activity. The most common microorganisms used in this process are pseudomonas, bacillus, enterobacter and phosphate-solubilizing bacteria. Algae and fungi grow slowly, require specific growing conditions and specific aquatic conditions to grow and are therefore less frequently used in algae and fungi, respectively, for HM cleanup. Specific groups of fungi are important in synergistic phytoremediation systems, such as arbuscular mycorrhizal fungi (AMF). Finally, AMF can help counteract the effects of biochar because of its ability to improve heavy metal uptake, tolerance, and interactions with the soil, which can increase the efficacy of remediation. Although not extensively studied for biochar-assisted remediation methods, their application in multi-component remediation frameworks may be taken into account when researching the use of biochar. In addition, biochar-assisted restoration may have an impact on the native microbial community, because there may be competition between native and introduced strains. Therefore, in practical use, it is important to reduce the risk of potential ecological disturbances and to effectively manage the combined benefits of biochar and microbial inoculation. The microbial consortiums of particular interest for redox-mediated transformations are not just for microbial inoculation, but can also contain Sulfur-reducing and Iron-reducing bacteria, which can facilitate redox transformations by biochar-microbe systems. Low molecular weight organics (LMO) from biochar or root exudates may enhance the mobility of HM in biochar, but biochar has the potential to increase microbial colonization and activity [50]. The overall remediation outcome is thus a function of the immobilisation versus potential mobilization under site-specific conditions.

Use of biochar to remove HM-Toxicity from soil

Biochar is beneficial for soil remediation for a variety of reasons, such as improving soil quality, reducing emissions, and there is significant carbon sequestration. Biochar can contribute to carbon sequestration in the long-term by being a stable reservoir of carbon that increases soil carbon pools. This plant's long-term carbon sink potential is due to its very stable carbon structure, which is difficult for microbes to break down, remaining in the ground for hundreds of years or more. In addition, biochar use will likely indirectly lower energy consumption associated with fertilizer production due to the decrease in chemical fertilizer use. The other mechanism of greenhouse gas emissions reduction is accomplished by changes in soil microbial activity through changes in the redox potential of the soil caused by biochar, which also has the effect of reducing GHG emissions of CH4 and N2O. The organic carbon in biochar also has the positive effect of helping to retain water and nutrients, particularly N, K and P, in the soil which is beneficial in addition to reducing CO_2. Better crop growth and productivity leads to higher soil carbon storage as well, emphasizing the multifunctional value of biochar in carbon capture and storage and emission reduction.

One multipurpose solution that has emerged to address HM pollution and boost agricultural production is the careful use of biochar. Biochar has a threefold remediation mechanism that it orchestrates. The first is direct immobilisation due to surface sorption and precipitation by pH change. Improvement of structure by means of hydraulic control and aggregation mediated by pores. Thirdly, metal stabilization by biological activation of microbial-plant interactions. It is essential in its process that it can change the pH of the soil. The natural alkalinity of biochar (pH = 8-12) increases the pH of acidic soils when added to them. At this acidic pH, the pH of the solution is lower and carbonate precipitation of the cationic HMs (such as Cd2+ and Pb2+) reduce their mobility and solubility by changing their speciation equilibrium. Besides the pH regulation, biochar has a tremendous influence on the physicochemical functions of soil. This material has functional groups containing oxygen, with a high surface charge density increasing CEC by 20-50%, and surface complexation and ion exchange sites for the immobilisation of HM that remain available for a long time. Biochar simultaneously improves the food retention and reduces the bioavailability of metal ions, while also releasing dissolved ions (K+, Ca2+, Mg2+) that accounts for 20% increase in electrical conductivity. The structural changes in soil are caused by biochar's hierarchical pore network and expansive SSA. Soil porosity can be increased by 59-66% and the production of stable macroaggregates (>250 µm) can be enhanced by these characteristics, which encourage particle aggregation. Conditions for good establishment of plants in polluted soils are good hydraulic conductivity and aeration, minimizing the danger of waterlogging and erosion and maximizing gas exchange in the soil. In this virtuous circle, biochar enhances soil quality and strong plant life provides even greater structural stability to soil. Biochar also has a strong adsorption capability, which can help to enhance soil characteristics by absorbing organic molecules. This makes it possible for good bacteria to grow. Soil microbes improve the organic matter in soil and improve soil structure through decomposition of organics and nutrient cycling. Biochar can be designed with consideration to site-specific factors such as soil pH, pollutant speciation, and co-existing stressors to enhance field usability. Precipitation and pH buffering from minerals may be more effective for immobilizing the contaminants in acidic mine soils from manure and sludge biochars at high temperatures [51]. The lower temperature biochars might, however, possess sufficient adsorption capacity to ensure soil structure and microbial compatibility in neutral soils for agricultural use, while containing low concentrations of HM. It is possible to selectively apply modification techniques (Fe/Mn oxides, thiol groups) as a function of the prevalent metal species and the redox conditions. These factors may be used as guidance in the future for material selection and optimization in a scenario.

Conclusions

Over the past five years, the adsorptive properties of BC based nano-adsorbent (BNHs) which includes its adsorption capacity, surface functions and surface area and active sites have attracted much attention. The advantages of BNHs have been thoroughly investigated and various synthetic methods have been reviewed, as well as the performance of BNHs in enhancing their adsorption properties. The effect of biomass feedstock type, doped metal precursor, and preparation method is remarkable, which can be verified through differences in the surface morphology, and associated mechanisms. Both untreated and modified BC have been successfully used in wastewater and other areas are still in need of research. Prior to creating successful formulations, it is important to determine the stability of BC, nanoparticles, and hybrids of the two. To improve its functional properties, BC needs to be modified by nanometals, metal oxides or metal hydroxides. This modification may be to impact the functional properties of the biochar, which depends on the size of the nano counterpart used to modify the BC, so the adsorption of heavy metal ions may be affected. Although the precise control of the surface characteristics and functionalities of nano-modified BC has not been achieved yet, optimizing the size of nanoparticles can help to minimize nanotoxicity and to demonstrate the effective removal of heavy metals. Numerous studies have been published on the adsorption of selected metal ions and elements from spiked water solutions by BC/BNHs. Although these studies demonstrate the potential for HM removal by BC/BNHs, the practical application of BC/BNHs in wastewater treatment has not yet been realized. The presence of many contaminating metals in wastewaters might cause a decrease in the adsorption of one metal element compared to others. This is because that each metal ion has the same adsorption site in polluted fluids. To evaluate the adsorption potential of the nano-adsorbents, competitive adsorption of various metals needs to be studied. To find out how effective the screened formulations are at remediation, it is necessary to conduct pilot scale research on the use of BC nanohybrids. The aim is to make a direct comparison between the biochar nanohybrids and their bulk counterparts with regard to the biochar's actual quantitative HM adsorption potentials. It is not possible to reanalyse the samples using any of these methods. Unlike traditional approaches, noninvasive powerful 2D, 3D, or even complete multiscale simultaneous/cascade driven separation and detection methods will be employed to reevaluate the adsorbed pollutants and the adsorbent substrate, such as conjugate spectroscopy-microscopy, multiple detection spectroscopy systems including (HSI/S), (EEMFS), and (2D-COS). Hyper-spectral spectroscopy/imaging techniques offer a fast and sensitive on-site measurement of heavy metals in land, tailing pond water, groundwater, rivers, wastewater, soil and plant tissue. However, HSI has now developed beyond the remote sensing to the in-situ or ex-situ spectroscopic imaging analysis of soil samples contaminated with heavy metals. The benefit of this approach is that it could analyze soil and water without destroying them, and with high sensitivity and throughput, which are crucial for deriving accurate conclusions about the concentration and distribution of heavy metal elements. This method allows potential comparison and identification of the 3D dynamics and changes of a chromophore without degradation of the sample to be used in soils and water samples polluted with heavy metals. By tracking the quenching of signals from organic matter components like humic and fulvic acids, short peptides (amino acids-tryptophan, tyrosine containing peptides), and other substances, heavy metal transformation events can be identified. The 2D-COS is an analytical method that can be combined with many types of spectroscopies, including optical UV−vis, fluorescence, X-ray, and NMR, as well as vibrational IR, near-infrared, and Raman spectroscopy, as well as chromatography and microscopy. By generating sophisticated cross correlation analysis, it may be used effectively to determine the relative effect of external perturbations on any analytical signal, making it ideal for heavy metal absorption/transformation studies involving temperature, pH, and interfering ion concentration. These methods are sensitive enough to analyze a wide range of environmental samples and include various synchrotron radiation-based techniques such as (SR-νXRFS), SR-XCT, SR-XRDS and SRNEXAFS, which can be used to identify relative speciation and/or the metal element within the different carbon fractions of the sample. Many studies have documented the harmful effects of heavy metal/metalloid contamination, either in the groundwater, in soil, in dissolved organic matter from the groundwater, in human remains, or in the soil-plant system, using synchrotron-based X-ray techniques. We can make 3D maps of microbial habitats and chemical environments, and 3D maps of complicated environmental samples like soil matrices, using these methods.

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