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Review Article

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## Functionalized Biochars for Enhanced Removal of Heavy Metals from Aqueous Solutions: Mechanism and Future Industrial Prospects

Felix S. Nworie <sup>1\*</sup>, Nkoli Mgbemena <sup>2</sup>, A. C. Ike-Amadi <sup>3</sup>, Jane Ebunoha <sup>1</sup>

<sup>1</sup> Department of Industrial Chemistry, Ebonyi State University, Abakaliki, Ebonyi State, Nigeria.

<sup>2</sup> Department of Industrial Chemistry, Madonna University, Elele, Nigeria.

<sup>3</sup> Department of Chemistry, Abia State Polytechnic, Abia State, Nigeria.

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### Abstract

Development of efficient modified bioinspired material for the sorption of heavy metals is currently on the fore front of environmental heavy metals remediation research. Functionalized biochar for heavy metals removal is highly advantageous because of striking properties such as regenerability, simplicity, low-cost, high efficiency, and mechanical stability, chemical inertness to many organic solvent, surface polarity, functionality, chelation property and decreased hydrophobicity absent in naked biochar. This review surveyed the sources of heavy metals, the bioavailability and effects on man and biota, and previous work on the method of preparation of the biochar, its modification, and its characterization. The paper also presented critical analysis on the preparation of biochar, modification methods, surface chemistry, mechanisms of interaction, extraneous variables, and characterization methods. A comparative treatment of the preparation conditions, characterization methods, and surface functionalities was presented. The perceived disadvantages were listed, and the future prospects of the new research area for industrial scale applications were thoroughly presented.

**Keywords:** Biochar; Heavy Metals; Functionalization; Adsorption Studies; Mechanism; Characterization.

### 1. Introduction

Recently, much research has been conducted, and much more is ongoing, on the environmental and health hazards associated with heavy metal contamination [1–3]. The toxicity, non-biodegradability, teratogenicity, bio-accumulative potentials, and carcinogenicity of heavy metals in water and other sources proximate to humans and biota have received considerable attention in recent years. The heavy metals are discharged into water bodies, soils, and air from industrial and commercial sources and products such as cosmetics, textiles, mining, and metal works; electroplating; metal fabrication; glass and ceramics; nuclear power plants; polyvinyl chloride materials; paints and coloring materials; batteries or cells; lasers; television screens; phosphate fertilizers; recasting; and recycling of heavy metals-containing materials [3, 4]. Heavy metals are present in environmental matrices and bioaccumulate in the food chain. This raises serious concerns about the removal of contaminants from water, soil, and other environmental matrices through the use of a dependable technology-driven technique. This is important to protect our biota, humans, and the environment (food chains) [3].

\* Corresponding author: [nworie.sunday@ebsu.edu.ng](mailto:nworie.sunday@ebsu.edu.ng)

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Heavy metals (Zn, Pb, Hg, Cd, As, and Cu etc.) carcinogenesis from ages has remained a debilitating problem in the health and environmental sectors. This is because heavy metals have no established physiological role, constitute serious environmental and human health risks, and are highly deleterious at high doses, implicating or inducing kidney, liver, pulmonary, and bone damage, as well as other general debilitating health conditions [5, 6]. The natural occurrence of heavy metals is known to mostly be in combination with one another as ores and other alluvial deposits. The anthropogenic sources of heavy metals include their presence in industrial products, where they are used in combination with other elements in synthesis. Typically, heavy metals are present in polyvinyl chloride (PVC) materials and in nuclear power stations as stabilizers and neutron absorbers, respectively. They are also present in other industrial products such as pigments in coloring materials, nickel-cadmium cells, lasers, cosmetics, television screens, phosphate fertilizers, recasting, and recycling of heavy metals-containing materials. Bio-accumulation of heavy metals by fibrous plants and its consumption is an established dietary heavy metals ingestion pathway. Some heavy metals, such as cadmium, have been implicated as being present in some fibrous plants consumed by humans [7]. The toxicity of heavy metals includes alteration in DNA, inducement of oxidative stress through liberation of reactive oxygen species, alteration of synthesis of heme, apoptosis due to mitochondrial malfunctioning, impairment of the physiological functions of Na or Mg due to competitive interaction in the protein structure, and complexation interaction between heavy metals and sulfhydryl species [8].

Different researchers have used different technologies to remove heavy metals from media, such as the electrochemical method, ion exchange, chemical precipitation, reverse osmosis, electroplating and membrane separation, cloud point separation, solvent extraction, and adsorption [9–13]. The different treatment technologies are faced with one limitation or the other except adsorption. The limitations include time wastage during operation, the matrix effect, outrageous costs, low sensitivity, emulsion formation, a low concentration to volume ratio, and the generation of secondary waste [14–16]. Adsorption, among the various technologies, remains the most preferred because the method employs low cost, simple, regenerable, recoverable, recyclable, mechanically stable, readily available in needed quantities, and chemically inert functional materials whose surface activity can be manipulated or fine-tuned through modification, doping, or impregnation [10, 17]. Similarly, the adsorption procedure is fast, convenient, efficient, and effective without generating environmentally unfriendly secondary pollutants [11, 19].

The commonest biomaterial for this purpose is biochar, a carbon-rich sorbent derived from the pyrolysis or carbonization of lignocellulosic or organic materials. Biochar is derived from precursors such as fruit peels, wood, grasses, and animal dung. The biosorbent, which is usually porous and fine-grained, can be activated and modified using dopants with hydroxyl, carboxyl, amine, and phenolic functionalities to increase the adsorption capacity [10, 17]. Several studies have proven that biochar and functionalized nanocomposite can sorb environmental pollutants such as dyes, heavy metals, and myriads of organic toxicants such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and phthalates [18–20]. Functionalized nanocomposite biochar is favoured over naked biochar and industrial biosorbents such as activated carbon primarily because immobilization increases the interaction between heavy metals such as cadmium and the composites. This is due to increased surface complexation, ion exchange, and precipitation resulting from increased surface polarity, functionality, chelation property, and decreased hydrophobicity. Thus, the stability, regenerability, increased surface area, and porosity of functionalized nanocomposites place them at an advantageous point when compared with other sorbents [21–23].

Surface modification of biochar can be achieved using different approaches involving chemical and physical processes such as functionalization, impregnation, and chemical grafting [12, 13]. Current area of research is on the use of immobilized biochar for the removal of heavy metals and other toxicants from aqueous media which compares favourably with industrial sorbents implicated to be of high cost and not readily available.

The review is primarily concerned with identifying the occurrence (natural and anthropogenic) and bioavailability of heavy metals, probing into the effects of heavy metals on man and biota, assessing the traditional methods of removal and drawbacks, identifying the various biochars and synthetic technologies, and assessing the different functionalization procedures for the generation of nanocomposites. The review discussed the advantages of functionalized biochar over naked biochar and physicochemical methods of characterizing them such as Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). The mechanism of adsorption invoking surface chemistry in relation to the pH of adsorption will be reviewed. Other extraneous variables such as time of contact, temperature, and initial metal ion concentration will be examined with a focus on the adsorption equilibrium and kinetic studies. Reusability of the functional materials and comparison of data from several researchers with a focus on future prospects will be critically reviewed.

A literature survey was conducted using different search terms such as impregnation, immobilization, doping, functionalization, and modification of biochar for adsorption or removal of heavy metals from solutions using different search engines. Different works on the use of modified biochar for the removal of heavy metals have been assessed, including a highly promising study by Zhou and coworkers on bamboo biochar modified with chitosan [24]. Many works were seen online on the removal of heavy metals using impregnated, modified, grafted, immobilized, doped, or functionalized biochar. A critical comparison of the adsorption capacity, mechanism of adsorption, and other preparation and surface-related characteristics of the functionalized biochar was presented.

## 2. From Biomass to Biochar: The Different Synthetic Methods

The overall characteristics of biochar are a function of the source of the biochar, the carbonization or pyrolysis treatment, and extraneous pyrolytic factors such as heating rate, residence time, temperature of pyrolysis, and reactor type. The production of biochar through thermochemical processes can be achieved through conventional gasification, fast or slow pyrolysis, flash carbonization, and microwave-assisted pyrolysis [25–28]. The removal of pollutants from matrices using biochar hinges on the varied excellent and complex chemical and physical functionalities. Data from SEM-EDX, elemental composition evaluation techniques, and classical characterization methods such as proximate analysis have shown that the elemental composition of biochar is dependent on the carbonization temperature [17]. Low temperature carbonization between 300–400 °C contains more of C-H and C=C functionalities with several organic properties such as high ion exchange, decreased aromatic characters, and structural relationships to cellulose and aliphatic groups [29]. Similarly, there is an observed decrease in H and O content, increased aromaticity, decreased cation exchange capacity, and well-structured C layers in high temperature carbonization (600–700 °C) as a consequence of deoxygenation and dehydration of the biomass [29].

The biomass from which the biochar is derived is a factor for much consideration as it determines, during pyrolysis, the quantity of biochar, bio-oil, and gas generated from the ratio of cellulosic, lignin, and hemi-cellulosic content. Biomass is a feedstock living or dead which serves as energy source, readily accessible in the environment, contains sulphur at negligible ratio, can be renewed, carbon-neutral and its utilization can lead to decrease in global warming, pollution reduction and generation of clean energy being a sustainable alternative to fossil fuels [29, 30]. Research studies have indicated that carbonization at temperatures within 500 °C using biomass high in lignin can probably generate high yields [30]. Biomass is classified based on origin into municipal solid waste (MSW), residues, and virgin resources. The MSW are waste biomass from municipalities (residential and non-residential) such as plantain, banana and paper. Biomass residues include forest and other agricultural based residues such as wood, crop, and livestock residues such as animal droppings and animal dung. Virgin residues include forest and agricultural resources such as cereal crops and leaves. The use of these feedstocks in the pyrolytic generation of biochar has been extensively studied with different authors utilizing biomasses such as animal dung, plantain peel, banana peel, wood residues, tea waste, sewage sludge, rice husk, rice straw, wheat straw, aerobically composted manure, sawdust, macroalgae, microalgae, chicken feather, pristine, kiwi branch, reed, and pine [31–36].

### 2.1. Conventional Pyrolysis

Conventional pyrolysis involves the use of traditional heating system such as radiation, conduction and convection to externally effect transfer of heat to the feedstock with variation in some extraneous variables such as vapour residence time, moisture content of biomass, heating rate and pressure. The properties of biochar are significantly affected by the temperature and pressure of the operating system, as well as the moisture content of the biomass. Generally, as peak temperature increases, the biochar fixed content also increases [30]. Studies with biomass of sugar cane bagasse, eucalyptus wood, and radiate pine at different pyrolytic pressures have shown an inverse relation between pressure and the total surface area of the biochar [37]. Similarly, an increase in the moisture content of biochar leads to an increase in the yield of biochar at high pressure [30]. Some authors have reported a decrease in BET surface area from 161.7 m<sup>2</sup>/g to 0.137 m<sup>2</sup>/g as pressure increased from 0.1 MPa to 2.6 MPa and opined that at high pressure the biochar pores are filled up, causing the decrease in total surface area [37]. The disadvantage of the conventional pyrolysis process is that its efficiency is dependent on the externally supplied conventional current and the thermal conductivity of the feedstock. The technique, in comparison to other biochar preparation methods, is slow and inefficient [38, 39].

### 2.2. Microwave Assisted Pyrolysis

Microwave-assisted pyrolysis is one of the most efficient, effective, and promising methods of biomass conversion to biochar and, by extension, other thermochemical processes. The process is achieved in a short period of time with high efficiency and reduces residence time and energy use [40–42]. Dielectric heating is used to achieve energy conversion processes involving electromagnetic to thermal energy [41]. In microwave pyrolysis, temperature concentration is at the centre of the feedstock than what takes place in conventional pyrolysis where the highest temperature is at the surrounding and surface of the biomass [41]. Consequently, the heat is spread throughout the entire feedstock volume instead of coming from an external source as observed in conventional pyrolysis [40]. By and large, the pyrolytic process used by a particular researcher depends mainly on the availability of equipment and a source of energy or heat. Furthermore, the nature of the biomass and the treatment conditions applied to the biomass are important considerations.

### 2.3. Why the Modification of Biochar?

Surface modification is primarily undertaken to increase the stability, regenerability, surface area and porosity and entire structural change of sorbents. It is mainly achieved through textural characteristics modification, addition of homo

or hetero atoms and generation of new functional groups through introduction of functional moieties [42]. The surface functionalities, porosity, properties of the sorbate and interaction between the sorbent and sorbate influences to a noticeable extent the adsorption capacity of the biochar [43-46]. Therefore, surface modification exerts noticeable impact on the adsorption capacity of biochar. Majority of the studies on surface modification of biochar basically involve the addition of atoms such as oxygen, hydrogen, Sulphur, phosphorus, nitrogen or other atoms or functional groups such as hydroxyl, carboxyl or amine to effect changes in the surface chemistry of the sorbent [47]. There are various chemical and physical treatment techniques employed to improve the sorbent-sorbate interaction thereby increasing the adsorption capacity. To achieve this, chemicals such as bases/alkalis, acids, oxidizing agents, metal salts, amines, ligands or complexing agents and surfactants are commonly used [46, 47].

### 3. From Naked Biochar to Functionalized Biochar: Modifying the Surface Functionalities of Biochar

Surface modification of biochar can be achieved using different approaches such as functionalization, metal impregnation and chemical grafting [45-47]. Some authors however extended the list of techniques for the synthesis of surface modified biochar to include hydrothermal synthesis or hydrothermal reduction, co-precipitation, covalent binding, co-condensation, ligand exchange, sol-gel synthesis, surface coating and modified Stöber synthesis [43]. Chemical modification of biochar is a one or two step process. In the former process (one -step), there is simultaneous pyrolysis and activation using the reagent of interest whereas the later process (two-step) involves pyrolysis of the biomass followed with the chemical treatment with an activation reagent or activation reagent treatment of biomass before pyrolysis [43]. The chemical modification methods are shown in Figure 1, but some of them will be treated herein.

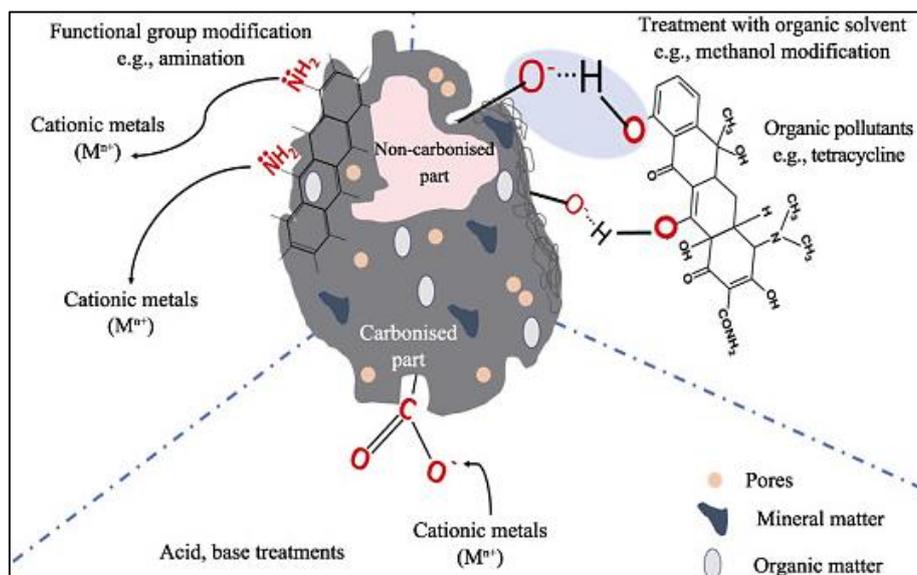


Figure 1. Chemical modification methods

#### 3.1. Chemical Grafting or Covalent Binding

Chemical grafting involves the process by which the surface of the biochar and the species are held by covalent interaction as the chemical species is fixed onto the biochar surface. The process generates composite of low adsorption capacity due to low total surface area; the adsorption is kinetically faster and the composite stable during regeneration [48].

#### 3.2. Impregnation

Impregnation involves a physical process of fixing the chemical species inside the pores of the biochar to modify the pore volume and pore diameter through structural regulation [47, 48]. The impregnation process is a two-step process involving application of the dopant layer for the textural and surface modification and the second step involving thermal activation for functionalization involving functional group or chemical species retention in the inter-particle spaces of the surface is achieved by depositing the dopant on the sorbent [49]

The impregnation method which is facile and produces composite of high adsorption capacity can be achieved either using wet or dry technique [50]. In wet impregnation method, chemical solvent in excess of the volume of the sorbent pores are added and after pore filling, the left-over solvent is discarded or dried thereby controlling the loading of the

chemical component of interest [49]. However, in dry impregnation, the amount of chemical solvent to be added to the sorbent is regulated such that the sorbent pores are filled without room for drying excess solvent [49]. The advantages of impregnation include increase in surface active sites when anionic surfactants are used, formation of metallic oxide films or layers which increases sorbent life time and decreases regeneration temperature when metal salts are used, high stability, large surface area, high porosity and regeneration ability [50].

### 3.3. Functionalization

Functionalization is a process of introducing functional groups or moieties into the surface pores of sorbent to increase the versatility by removing the drawbacks such as low sorption capacity and regenerability. Functionalization of biochar surface primarily alter their bulk characteristics and radically modify their surface properties such as stability, dispensability, mechanical strength, biocompatibility, reactivity, charge density, ion exchange capacity, aromaticity and porosity. Some authors have shown that functionalization of surface for increased adsorption capacity is greatly influenced by surface charge of the functional materials, active sites availability and competition between the metal ions in solution [41-45].

Similarly, some authors have alleged that surface functionalization using magnetic or iron-oxide dopant enhances the stability, adsorption capacity and reduces oxidation of sorbents [46]. Magnetic functionalized materials are acid sensitive and its vulnerability can adversely affect the performance and stability. To avert this, some authors have suggested the use of silica to coat the magnetic composite being that silica is inert to redox processes, stable in acid medium and contains hydroxyl groups which increases the functionality of the biochar [32, 51]. Separate studies of some authors noted that surface modification of nanocomposites not only eliminate aggregation but also positively impacts on the core shell structure suspension medium dispensability of nanocomposites [47, 52]. Some of the modification methods for producing engineered biochar is shown in Figure 2.

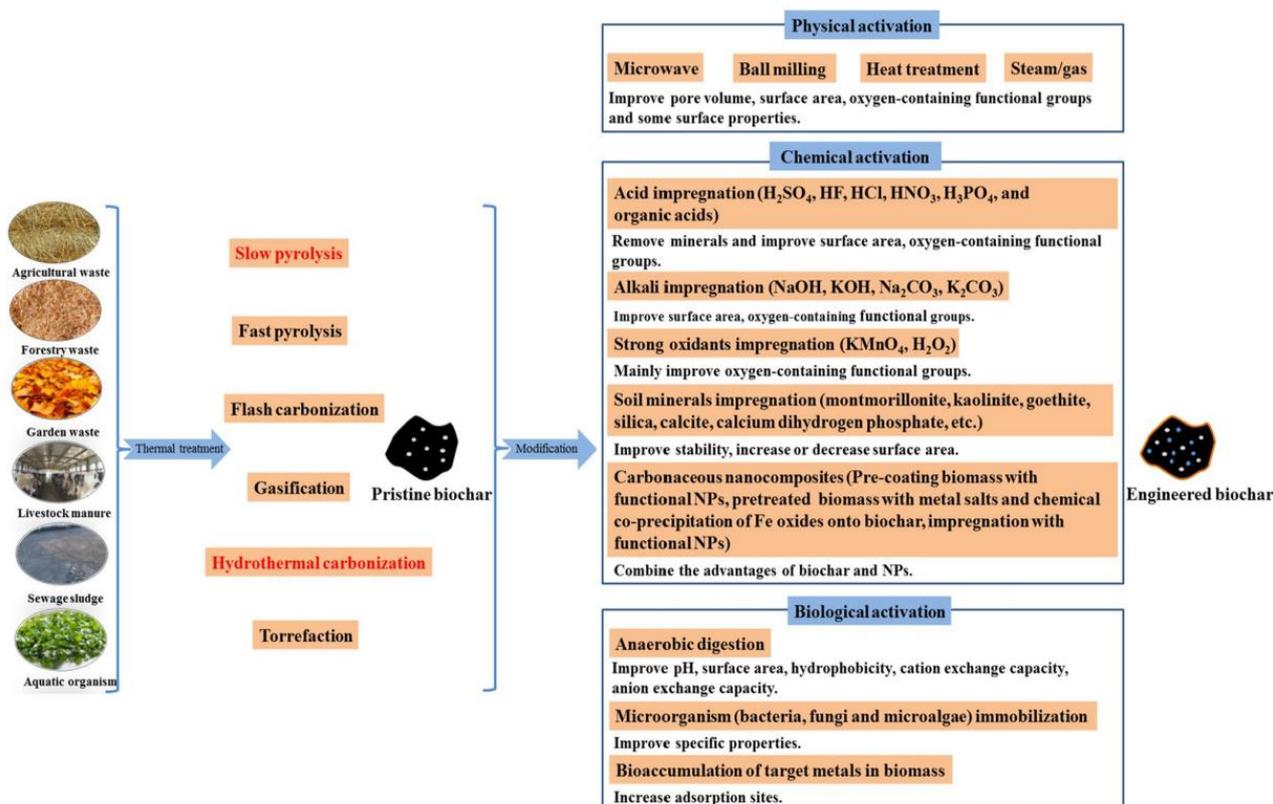


Figure 2. The modification methods for engineered biochar production and their effects on physicochemical properties of biochar (Wu et al. (2020) [53])

### 3.4. Surface Chemistry

The surface of biochar is heterogeneous and made up of atoms whose composition varies depending on the treatment conditions. The edge of adjacent phenolic rings and surface carbon atoms serve as point of linkage for the heteroatoms leading to formation of several compounds [32]. Structurally, biochar is non-polar, tends to be organophilic and acquires some level of polarity when modified using surface active agents [52]. The heterogeneity of the atoms on the biochar surface which germinates from the functional groups determines the efficiency of the adsorption process. The

adsorption mechanism of any given biochar is a function of the surface chemistry heterogeneity which differs markedly for the adsorption of a particular sorbate using different sorbent due to different functionalities [32]. The surface chemistry is mechanistically controlled by some force of interaction such as hydrogen bonding, repulsive and dispersive forces and functional group characteristics which regulates the adsorption capacity as determined by oxygen groups resident in the surface of the functional material [52-56].

The surface functional groups is a main factor for consideration as it affects both physical and chemical properties of adsorption such as acidity, polarity and adsorption capacity and are usually resident at the edge of bio-sorbent structure shown by different chemical bond structures from host atoms [56]. Oxygen containing functional groups (OCFGs) occur in large amount in sorbents and because of its electronegativity impacts on the adsorption of many species especially the polar sorbates [56, 57]. The OCFGs are prone to modification to fine tune the textural and structural properties of sorbent using gas phase oxidation which primarily increases the carboxyl and hydroxyl functional groups concentration whereas aqueous phase oxidation increases the carboxylic acid concentration [32]. Surface functional groups can be determined using both chemical techniques involving polarity, acidity, basicity and surface charge and physical technique which mainly involves bonding energy determination [49]. Pore structure and surface chemical structure shown by aromatic rings distributed in the entire sorbent structure determines the adsorption capacity of biochar [52]. The adsorption capacity of biochar is largely influenced by the differences in arrangement of the electron cloud of carbon atoms which amounts to liberation of unpaired electrons and unsaturation of valency creating a highly reactive surface (which may be basic or acidic) for sorption of species [32]. Surface chemistry of an adsorbent can be modified for specific removal or adsorption of pollutants and is of high importance when specificity is sought with interaction mechanisms mainly controlled by electrostatic attraction and dispersive interaction [49, 58]. Enhancement of adsorption can be achieved by redesigning the surface functionalities of a biomaterial using carboxyl and hydroxyl groups whose interaction exhibit chemisorption processes [49].

### 3.5. Acidic or Basic Group Functionalization

Physicochemical properties of biochar can be altered or fine-tuned through acidic or basic surface modification. Biochar modification with groups that contain carboxylic moieties or other OCFGs such as ethers, phenol, hydrogen peroxide, lactone, quinone, potassium permanganate, ozone, carbonyl, hydroxyls and chromene are mainly responsible for acidity of the surface [57]. The acidic groups controls the chemical nature of the biochar surface and are resident on the outer surface of biochar composite [59]. Therefore, increase in the amount of oxygen leads to increase in cation exchange capacity and low hydrophobicity or treatment with OCFGs leads to increase of O/C and H/C atomic ratios [49]. Acid treatment converts micropores into mesopores or macropores as the acid shatters and expands the pore wall of the biochar [59].

Acid treatment of biochar enhances acidic properties, lowers the mineral present and increases the water resilience nature as the surface is oxidized [59]. The inorganic acids such as  $H_3PO_4$ ,  $H_2SO_4$  and  $HNO_3$  are commonly used to generate OCFGs on the biochar surface [59]. Oxidation processes initiated using gases (such as  $CO_2$ ,  $O_2$  or steam) and oxidants in aqueous solution (such as  $H_2O_2$ ) are the most common activation technique for producing OCFGs [56-59]. Some authors [56] have demonstrated an increase in OCFGs on the surface of peanut hull biochar immobilized with  $H_2O_2$ . The  $H_2O_2$  modified biochar showed high adsorption capacity for divalent Cd, Pb and Ni and compares favourably with commercially available bio-sorbent. The researchers concluded from their batch and column adsorption experiment that the  $H_2O_2$  modified biochar may serve as an effective, efficient, low cost and benign adsorbent for myriads of environmental applications.

Strong acidic functional groups such as carboxylic acid and weak acidic functional groups such as phenol are generated when oxidation is done at low and high temperature respectively. Oxidation using gas phase process improves the carbonyl and hydroxyl content resident on the biochar surface whereas liquid phase oxidation merely magnifies the concentration of phenolic and carboxyl groups [58]. Liquid phase mediated oxidation requires less energy as it proceeds at low temperature and generates greater OCFGs at biochar surfaces [59]. The OCFGs are importantly utilized for heavy metal adsorption from solutions as negatively charged acidic surface interacts with positively charged metal cation to form metal-complexes [58]. Inner sphere complexation of the OCFGs with alkaline-earth metals and chelation with main group elements is a common discovery in adsorption and the mechanism shown in Equations 1-3 which proceeds by cation exchange.



where  $R_1$  represents the surface of the biochar,  $R_2$  the surface of immobilized biochar, M the metal ion (such as cadmium) and R an alkyl or aryl group.

Treatment of biochar with alkaline solution such as amines yields composites of higher aromaticity, lower O/C ratio, higher N/C ratio, larger surface area and decreased hydrophilic properties [57]. Alkaline modification promotes adsorption of negatively charged species and organic contaminants from environmental matrices [29, 57].

The basic modified surface of a biochar is characterized by delocalized  $\pi$ -electrons in the aromatic structures and nitrogen functionalized basic groups that can easily bind proton rich surfaces. The Lewis basicity of alkaline modified biochars is a function of the  $\pi$ -electrons resident in the carbon or graphitic layers [14]. Functionalization with nitrogen enriched species increase the basic character through hydrogen bonding, covalent interaction and dipole –dipole attraction which improve the carbon surface and acidic layers interaction [14].

Alkaline treatment of biochar substantially generates positive charges on the surface and is achieved by treatment with species such as ammonia, hydrogen, amide, imide, amine, pyridine, pyrrole and lactam which are precursors to nitrogen [59]. Basic nitrogen groups are generated at high temperature treatment (400-900 °C) of biochar with nitrogen-rich precursors and this enhances adsorption of negatively charged contaminants as OCFGs are eliminated [58].

#### 4. Modification of Biochar Surface Functional Moieties by Amination and Carboxylation

The functional group resident on the biochar surface can be chemically modified to give composite of interest for remediation of polluted soils removal of pollutants from aqueous solutions. Chemical oxidation of biochar such as carboxylation is a facile, single step and low temperature process of introducing OCFGs [59, 60].

Nitrogen containing functional groups (NCFGs) significantly used for the adsorptive removal of divalent heavy metals such as Cd, Pb, Zn and Cu are functionalized into biochar surface through nitration and reduction processes [61, 62]. Treatment of biochar surface using  $\text{HNO}_3$  dissociates to liberate nitronium ion ( $\text{NO}_2^+$ ) which attacks the phenolic rings generating nitrated specie ( $\text{NO}_2$ ) [61]. The reaction is slow and catalysed by simultaneous addition of  $\text{H}_2\text{SO}_4$  for increased yield of  $\text{NO}_2^+$  and proceeds through electrophilic substitution followed by reduction using sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) [25]. Some authors have employed surface amination to generate NCFGs that imparts basic characters to biochars and strong affinities for metal cations in solution [62-64]. The research of Zhou et al., (2013) [23] using chitosan for amino functionalization of bamboo biochar for the sorption of Pb, Cu and Cd indicated improved adsorption capacity for the metal cations. They deduced that the chitosan functionalized biochar which is eco-friendly, efficient and of low cost can be used in soil amendment and in remediation studies involving waste water contaminated areas. Furthermore, they demonstrated that the high adsorption capacity of the chitosan functionalized sorbent was due to strong chemical bonds between the amine groups of biochar composite and positively charged metal species.

##### 4.1. Modification with Organic Reagents

Inexpensive organic reagent such as methanol can be used to increase OCFGs (specifically carboxylic group) on the surface of biochar through esterification and then reaction between methanol and carbonyl functional groups [25, 34]. Liu et al. [34] indicated methanol functionalized rice husk biochar as a sink for OCFGs such as ester and hydroxyl groups which can effectively capture tetracycline with 45.6% improvement in adsorption capacity owing to  $\pi - \pi$  electron donor- acceptor relationship between adsorbent and adsorbate.

##### 4.2. Modification with Surfactants

Anionic and cationic surfactants have currently gained prominence for the modification of biochar surface for adsorption of pollutants. The mechanism for the sorption is still not fully understood, however hydrophobic interaction between the surfactant and biochar surface have been implicated [65]. Ahn et al. [66] impregnated activated and granular carbon with anionic sodium dodecyl sulphate (SDS) and non-ionic triton-X100 (TX100) for the sorption of cadmium. They observed that adsorption increased with increase in SDS dosage and nitric acid treated activated carbon adsorbs up to 8.7 folds than the untreated counterpart. The study concluded that increased chelation of cadmium to the SDS is responsible for increase adsorption.

In another study, surfactant (Sodium dodecyl sulphate) modified spent coffee grounds was fabricated using hydrothermal process for enhancement of sorption property of cadmium and the composite characterized using FTIR, and SEM-EDS [16, 67]. The modified biochar was a superior composite than the naked form based on the maximum sorption capacity which are 10.67 and 4.82 mg/g respectively. Result indicated the cadmium sorption process involve chemisorption, and spontaneous and endothermic changes. The authors recommended the functionalized biochar as a potential sorbent for remediation of metal-polluted media.

The adsorption of cadmium on steam activated cetyltrimethyl ammonium bromide (CTAB), SDS and (TX100) surfactant functionalized carbon derived from *Moringa Oleifera* was investigated at pH of  $8.0 \pm 0.2$ , temperature of  $30 \pm 0.5$  °C, contact time of 120 min, agitation speed of 160 rpm, initial metal concentration of 30 mg L<sup>-1</sup> and sorbent dosage of 1.0 g L<sup>-1</sup>[65]. The authors observed translation of percentage removal of cadmium from 73.36 to 81.50 and 95.60 % for the untreated, TX100 and CTAB modified activated carbon respectively. The improved porosity and enlarged surface area of the CTAB and TX100 modified activated carbon were noted to be responsible for the increased adsorption from SEM and BET surface characterization.

The removal of cadmium using nitric acid activated sodium dodecyl benzene sulfonate (SDBS) modified carbon of lignite origin was studied by Sun et al. [44]. Inferential statistical analysis based on response surface methodology was applied for appraising the acid concentration, temperature and surfactant concentration. The higher adsorption capacity observed with SDBS modified carbon was attributed to the negative charges (Figure 3), increased functionalities and surface area. The maximum adsorption capacity of the surfactant modified activated carbon was observed to be 44.21 mg/g and was 7 folds greater than the unmodified activated carbon. There is dearth of data on modification of biochar surface with surfactants for the adsorption of heavy metals but the technique based on activated carbon and other biomaterials looks promising and future research on the area is advocated.

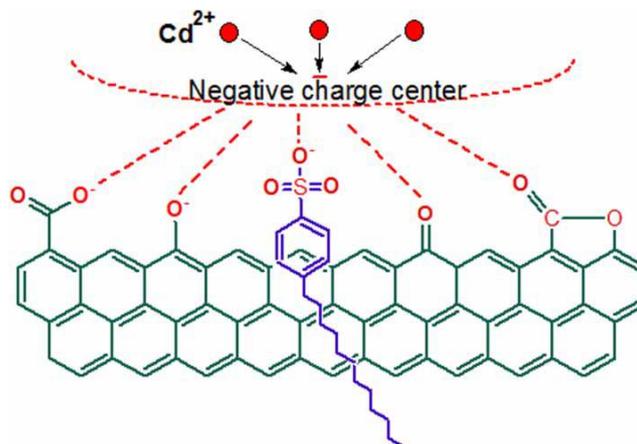


Figure 3. Schematic of proposed negative charge center structure on nitric acid surfactant modified activated carbon oxygenated surface [44]

## 5. Functionalization of Biochar Surface with Ligands or Chelating Agent

Current research on biochars immobilized with ligands or complexing agents for the adsorption of heavy metals through  $\pi$ -electron donor-acceptor properties is trending. Some group of authors [55], prepared composite using hexagonal mesoporous silica modified and 3-aminopropyltriethoxysilane functionalized natural biomass ash from agricultural source and characterized the product physicochemically and morphologically using SEM, TEM-EDS, FTIR, BET and ICP-OES. The authors surveyed the influence of extraneous variables of equilibration time, pH, initial metal ion concentration and temperature and discovered that the functionalized agricultural biomass exhibited high affinity for cadmium with highest adsorption capacity of 23.95 mg/g observed at pH 5, time of contact and concentration of 90 min and 50 mg/L. The study which followed pseudo-second order kinetics and fitted well in Langmuir equilibrium model also indicated spontaneous and endothermic sorption process with recommendation by the researchers that the functionalized biomass is effective, green and can efficiently decontaminate cadmium polluted site.

In another study [10], the researchers employed chemical process for the functionalization of rice husk biochar using cystamine dihydrochloride as chelating reagent and glutaraldehyde as crosslinking agent. The amino group and disulphide bonds enriched biochar was characterized by FTIR, SEM, XPS, BET and TGA to study the mechanism of sorption and understand the surface functionalities. The study discovered that the functionalized biochar granular nanopolymer surface-laden primary amine functionalities and disulfide bonds adsorb cadmium cation through surface complexation and electrostatic attraction. The adsorption capacity of 81.02 mg/g was observed to be ten folds higher than that of the naked biochar with recommendation of the modified biochar to be specifically used for cadmium removal from solutions.

Zhang et al. [68], prepared 3-mercaptopropyltrimethoxysilane grafted biochar derived from agricultural waste through Ionic Imprinted Technique for the removal of heavy metal ions from solutions. The study characterized the composite using FTIR and XPS and evaluation of adsorption factors at maximum indicated pH range of 3.0-8.0, concentration of 2.0 g/L and contact time of 960 min. The study indicated that the sorption process followed Langmuir model and pseudo-second order kinetics with the stoichiometric displacement theory of adsorption and thermodynamics study indicating the process to be spontaneous and endothermic. The selectivity and regenerability of the functionalized biochar places it as a better adsorbent than the naked counterpart.

### 5.1. Magnetic Modification of Biochar

Biochar in the powdered form which show high surface area and porosity with negative charges is limited in the naked form practically because separation from water after sorption is extremely difficult and sorption of negatively charged species such as As (III) and As (V) is very low [69]. To overcome these drawbacks, researchers have devised a better and promising route (pyrolysis and co-precipitation) for producing modified biochar that can effectively and efficiently employed in all areas of adsorption of heavy metals and other pollutants. Some authors reported the use of pyrolysis previously discussed to functionalize biochar for the sorption of heavy metals such as arsenic, copper, lead and chromium with promising result [68-72].

## 5.2. Magnetic Modification of Biochar by Co-Precipitation

This is a facile solution process whereby an agent induces the precipitation of a solute from solution which then attaches to the agent instead of reverting to the solution. The preparation method is advantageous because the characteristic of the magnetic biochar such as dimensions or size can be manipulated or fine-tuned as desired [73]. Some researchers [74-75] worked on magnetic biochar prepared using co-precipitation technique for the removal of both cationic and anionic pollutants from matrices.

Specifically, Yu et al. [17] prepared  $\text{FeCl}_3$  and  $\text{FeSO}_4$  magnetic modified sugarcane bagasse using chemical precipitation technique for the sorption of cadmium and lead cations. The adsorption capacities of 1.2 and 1.1 mmol/g obtained from the study indicated competitive adsorption process with inhibition of cadmium adsorption by lead proportional to the initial cadmium and lead concentration. The study recommended the magnetic biochar for the removal of heavy metals from polluted water. Magnetic biochar nanocomposite prepared by the modification of biochar using zero-valent iron was evaluated for the sorption of Cd (II), Co(II), Zn (II) and Pb(II) at different contact time, pH, initial metal ion concentration, sorbent dosage and temperature [76]. The study discovered the optimum conditions for sorption of the metal ions using the magnetically engineered nanocomposite as 295 K, 360 min, pH 5 and 5 g/dm<sup>3</sup> for the temperature, time of contact, pH of solution and initial metal ion concentration respectively. The study was observed to follow pseudo-second order kinetics and Langmuir isotherms with the thermodynamics result indicating an exothermic and spontaneous process. The fabricated nanocomposite was characterized using FTIR, SEM, XRD, XPS and TGA and regeneration of the metal-impregnated magnetic nanocomposite was effected using 0.1 mol/dm<sup>3</sup>  $\text{HNO}_3$ .

Sol-gel/ pyrolysis technique was used to fabricate  $\text{MnFe}_2\text{O}_4$  corn straw magnetic biochar in the presence of egg white abundant in amino and carboxylic acid functionalities [14]. The prepared magnetic composite was characterized using SEM-EDX, BET, XRD and VSM to identify the composition, structure and morphology. The sorption study was undertaken using the batch process and some extraneous factors such as pH, time, temperature and initial metal ion concentration evaluated. The result of the study indicated the optimum conditions for sorption as 2 h and pH 5 with the sorption well fitted in the pseudo-second order kinetics and Sips (Freundlich-Langmuir) model. The maximum adsorption capacity for the removal of cadmium and lead was 154.94 and 127.83 mg/g respectively. The study noted that complexation involving Cd/Pb-O and ion exchange are mainly prevalent and recommended the use of the magnetic biochar in Cd(II) and Pb(II) removal from contaminated water.

Magnetic biochar was prepared and compared with functionalized multiwall carbon nanotube (FMWCN) for the removal of cadmium from solution [77]. The study evaluated parameters for sorption and discovered the optimum conditions to be agitation speed of 100 rpm, contact time of 90 min, pH of 5 and sorbent dosage of 1.0g and initial metal ion concentration of 10 mg/L. Result of the study as reported indicate d the maximum adsorption capacity of FMWCN and magnetic biochar to be 83.33 and 62.5 mg/L respectively with cadmium removal percentage of 90 and 82 % for FMWCN and magnetic biochar respectively. The study whose data was optimized statistically concluded that FMWCN is a better sorbent than the magnetic biochar for the removal of cadmium. The synthetic route of magnetic biochar and characterization method was proposed as shown in Figure 4 [78].

## 6. Application of Immobilized or Functionalized Biochar for Adsorption of Heavy Metal

Development of efficient modified bioinspired material for the sorption of heavy metals currently took the centre stage of environmental heavy metal remediation with researchers employing different modification strategies, dopants or surface functional groups and characterization methods.

In other to deal with the disturbing nature of cadmium pollution with the aim of finding lasting solution, some group of authors [79] prepared three different alkaline,  $\text{KMnO}_4$  and  $\text{FeCl}_3$  modified biochar for arresting cadmium pollution misnomer. The fabricated composites were physicochemically characterized using SEM, FTIR and Boehm titration and result shows inner sphere complexation mainly observed with the OCFGs from  $\text{KMnO}_4$  modified biochar. The  $\text{KMnO}_4$  functionalized composite indicated greatest micropores with adsorption capacity of 81.10 mg/g with adsorption process obeying pseudo-second order kinetics and Langmuir models. Recommendation on the use of  $\text{KMnO}_4$  modified biochar for cadmium removal from solution was made.

Sodium hydroxide-acetone modified almond shells biochar was produced for the simultaneous adsorption of Cu(II) and Cd(II) ions from aqueous solution and the sorbent characterized using FTIR and SEM [9, 80]. The adsorption process optimized at pH 6 and 5 for Cu(II) and Cd(II) ions respectively and temperature of 298 K had maximum adsorption capacity of 46.73 and 35.84 mg/g for Cu(II) and Cd(II) ions respectively. Result of the study indicated the sorption process obeyed pseudo-second order kinetic model and the data fits well into Freundlich, Langmuir and Dubinin-Radushkevich isotherm models implication combination of monolayer and multilayer adsorption process.

Functionalization using N-doping technique was performed by annealing of crop straws in  $\text{NH}_3$  to increase the sorption capacity of Cu(II) and Cd(II) ions through increment of surface N amount of the composite [35, 81]. The N amount in the functionalized biochar surface was twenty times greater than the non-modified crop straw with maximum adsorption capacity for the Cu(II) and Cd(II) ions as 1.63 and 1.76 mmol/g respectively, an amount four times more than the value for the non -modified biochar. The authors noted non -interference of acidic situations on the performance

of the composite and based on the characteristic method employing XPS and FTIR implicated the mechanism of sorption to be surface complexation interaction between graphitic-N and biochar hydroxyl functionalities and cation  $\pi$ -bonding. Similarly, the use of metal salts of Mg, Fe, Mn and Al to improve the sorption capacity of industrial tea waste biochar was investigated for the simultaneous removal of Cd(II) and  $\text{PO}_4^{3-}$  from aqueous solution [33]. Characterizing the immobilized biochar surface revealed oxides or hydroxides of the metal with the Mg salt functionalized biochar with the highest sorption capacity for both Cd(II) and  $\text{PO}_4^{3-}$ .

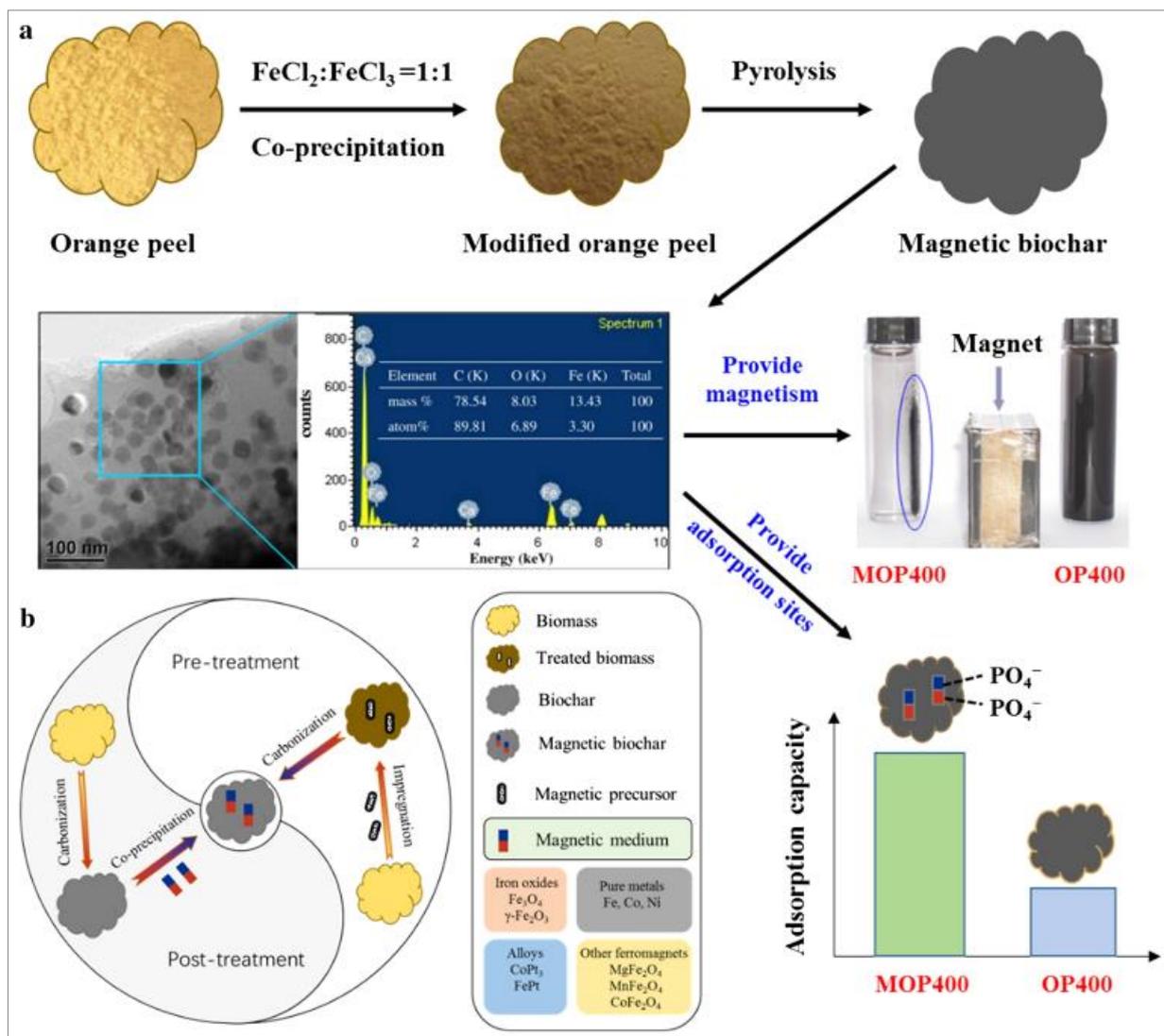


Figure 4. (a) The schematic diagram of synthesizing magnetic biochar by Chen et al. (2011) [69] and its characterization by TEM and EDS analysis, photo of magnetic separation, and adsorption capacity; (b) general approach of synthesizing magnetic biochar with different magnetic medium via two approaches.

The sodium alginate beads (SABs) surface modification of marine algae (*Ulva fasciata*) for efficient removal of cadmium was championed by some authors [82, 83]. The research employed both Plackett-Burman and face centered central composite design to evaluate the most extraneous variables responsible for cadmium sorption and characterized the feedstock using SEM, FTIR and EDS. The optimized conditions of cadmium removal were 200 mg/L as initial metal ion concentration, pH of 5, temperature of 25°C, equilibration time of 60 min, 4 g of biomass and removal efficiency of 99.96 % for the naked biochar. Comparatively, upon immobilization of the feedstock with SABs, with variation only in time of contact from 60 min to 4 h, the removal efficiency translated to 99.98 %. The use of the biomass which is eco-friendly, cost effective, reliable and efficient for the removal of cadmium from solution was advanced.

Bamboo-derived biochar modified using  $\text{HNO}_3$  and surface activated using  $\text{ZnCl}_2$  was fabricated by some authors for the removal of cadmium from wastewater applying simulation method [84]. The adsorption process followed pseudo-second order kinetics and Freundlich models with maximum adsorption capacity obtained as 16.62 mg/g and removal efficiency of 95.53 %. Regeneration experiment on the loaded composite was performed and observation indicated four cycle extraction as effective for desorption of loaded cadmium. The low-cost biochar was recommended as a sorbent for cadmium.

In 2018, a polyacrylamide-based hydrogel biochar for cadmium sorption was advertised [85]. In the work, several ratios of biochar (1, 3 and 5 %) were used for the synthesis of polyacrylamide hydrogel -biochar composites (PAHBC) and data simulated into adsorption isotherms. Observed result indicated gradual increase in the highest adsorption capacity (30.63, 59.21 and 63.58 mg/g respectively for 1, 3 and 5% biomass weight) as weight of biochar increased. Formation of biochar scattered particles and ionic attraction fields resident on the surface of the biochar due to functional groups emanating from the dopant were said to be responsible for increased cadmium sorption and projection was made that 3 % biochar is ideal for modification. It was suggested that cadmium adsorption can be effectively and efficiently carried out using PAHBC.

Some groups of authors have also employed Mg-Fe layered double hydroxide -kiwi branch biochar for the removal of cadmium from solution [86]. The synthetic route involving liquid-phase deposition produced the composite at ratio of Mg: Fe of 3:1. The adsorption process was optimized using effects of pH, interfering ions, time of contact, ion strength and initial metal ion concentration. Result indicated maximum adsorption capacity of 25.6 mg/g and composite recommended for remediation of contaminated water and soil.

Manganese oxide nanoparticles loaded water hyacinth biochar was synthesized through redox precipitation for the removal of Cd(II), Cu(II), Zn(II) and Pb(II) [87]. Investigation into the nature of the nanocomposite revealed MnO<sub>2</sub> nanosheets which increased the sorption capacity of the nanocomposite due to increased pore volume and specific surface area. Column extraction and desorption studies revealed sorption increased with increase in MnO<sub>2</sub> amount up to 26.6 %. The study recommended the use of the nanocomposite for the removal of heavy metals from electroplating and spiked waste water. In a related study, nitrogen functionality was grafted into *Desmostachya Bipinnata* through novel treatment with hydrazine monohydrate for the adsorption of Cd(II), Cu(II) and Zn(II) [88]. Different amination options were used to arrive at the functionalized materials. Result indicated that the sorption process followed pseudo-second order model with maximum adsorption capacity of 76.80, 72.10 and 58.16 mg/g for Cd(II), Cu(II) and Zn(II) respectively. In current time, several heavy metals have been sorbed using modified biochar with a projection of devising a workable system for simultaneous removal of heavy metals from aqueous solution. This research is currently at the forefront of research and development for industrial applications with the intention of applying chemometric techniques for optimum performance.

### 6.1. Characterization of Biochar Surface

Characterization of the surface of biochar entails the understanding of the nature and functionalities always achieved through Boehm titration, elemental analysis (EDX), FTIR, SEM, XRD and other physicochemical techniques.

**Boehm titration:** This is an acid/base titration primarily used to quantify and differentiate the basic and acidic functional groups present in the adsorbent surface [89]. The principal stems from the proposition that carboxylic group can be neutralized by NaHCO<sub>3</sub>, carboxylic and lactone moieties can be neutralized by Na<sub>2</sub>CO<sub>3</sub> and carboxylic, lactone and phenolic moieties neutralized using NaOH. Amount of basic functional groups can be evaluated upon reaction with HCl of carbon surface groups and the amount of either base or acid consumed during neutralization quantified using HCl or NaOH back titration respectively. Unfortunately, this method can only be applied to large samples and approximately half the overall oxygen in biochar sample can be measured without extensive evaluation of basic surface functionalities.

**Fourier Transform Infrared Spectroscopy (FTIR):** FTIR is used for evaluating the changes that occur during biochar formation and modification processes and the chemical functional groups on both the original and functionalized composite. Surface functionalities such as -OH, C=C, C=O, C-O-C and -COOMe stretching vibrations at 3600-3100, 1740-1600, 1097 and 1400-1500 cm<sup>-1</sup> respectively and others are always identified before and after changes such as modification which helps in determining bonds that are formed or decomposed in the biochar transformation process [4, 87]. FTIR is a modification of IR which was formerly in use but limited because of ambiguity and difficulty in spectra interpretation.

**Scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX):** The surface morphology and macro porosity of biochar can be correctly and unambiguously determined using SEM [35, 81]. The micrograph generated from SEM analysis can be reliably used to identify the biochar surface as into rough, smooth or corrugated and others. The advantage of SEM is that images are formed using electron rather than light thereby ensuring higher amount of sample to be brought to focus with image of significantly high resolution. Recently SEM coupled with energy dispersive x-ray (EDX) spectroscopy (SEM-EDX) (Figure 5) which enhances dual role of high magnification of the surface and determination of the elemental composition of the biochar. The EDX gives the amount of each element in the biochar before and after modification. From such result, important biochar properties such as aromaticity, cation exchange capacity and hydrophobicity can be evaluated [76].

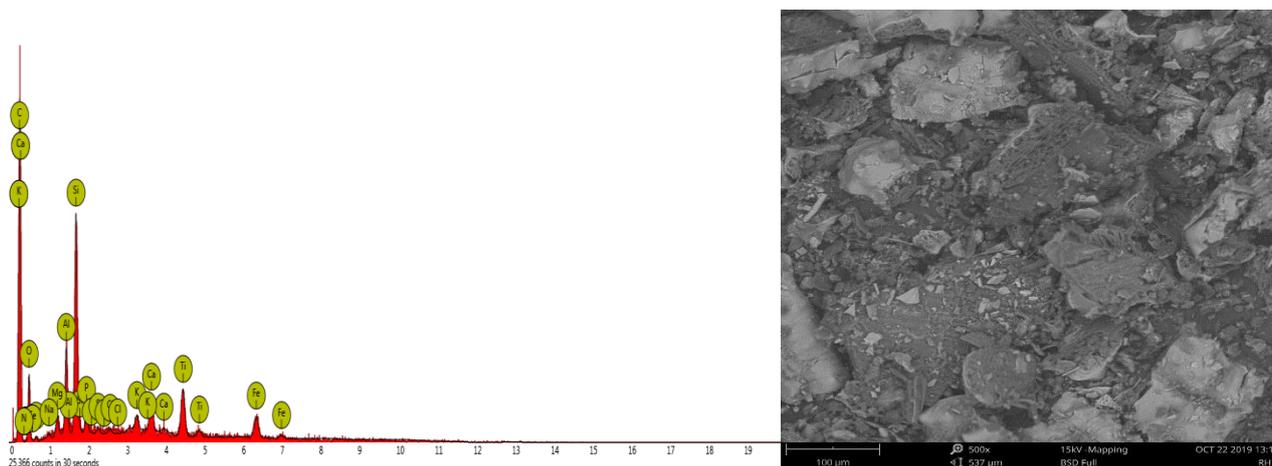


Figure 5. SEM-EDX showing elemental composition and structure of biochar [36]

**Brunauer, Emmett, Teller (BET):** This method helps to determine the specific surface area and pore size of biochar. In any BET measurement, the effective area where capturing of particulates can take place under controlled experimental conditions for mesoporous, macroporous and nonporous solid is the probe accessible region. The BET isotherm plot which indicates the nitrogen adsorption/desorption isotherms of the biochar gives a picture of the adsorption capacity of the biochar which is dependent on pore size and specific surface area. Several studies have shown that the degree of removal of heavy metal particulates or contaminants from aqueous solution is directly proportional to the pore size and specific surface area [81-91].

**Temperature Programmed Desorption (TPD):** The relative thermal stability of biochar samples can be a tool for surface functional group determination. This can be achieved by evaluation of the concentration of functional groups that depicts the thermal stability using TPD technique [91]. The OCFGs are mainly analyzed using this technique and decomposition of various functional moieties such as carboxyl and lactone gives  $\text{CO}_2$  and that of carbonyl, quinone, phenol and ether generates CO. The principle basically lies on low temperature and high decomposition of OCFGs to liberate  $\text{CO}_2$  and CO and  $\text{H}_2\text{O}$  and  $\text{H}_2$  respectively. Recent studies on the use of TPD techniques concentrates on modifying deconvolution methods of the spectra which previously suffered drawback of overlap.

**X-Ray Photoelectron Spectroscopy (XPS):** Elemental quantitation and identification of chemical states of the biochar surface elements can be correctly and unambiguously executed using a non-destructive analytical technique regarded as XPS [13, 83]. The technique modulates core changes in the biochar surface during functionalization process involving acid or basic activation and oxidation. Four separate binding energies showing succinctly four functionalities are identifiable in XPS spectra and include C-C, C-H, C-O, C=O and O-C=O but however suffers drawback of inability to distinguish functionalities with close binding energies such as C-O-C and C-OH and C-C and C-H [76]. The technique widely used in modification involving nitrogen functionalities is extremely limited been unable to detect hydrogen atom. A close look at Table i will show some authors who have used the method for biochar characterization.

**X-Ray Diffraction (XRD):** Biochar surfaces can be characterized for structural nature (crystalline and amorphous) using XRD and size of crystalline sample evaluated applying Scherrer equation into micro, macro and mesoporous materials. The XRD peaks indicate the presence of characteristic compounds based on the peak resolution. Some authors [76] have used XRD to characterize iron-modified biochar for heavy metal adsorption with discoveries that calcite and dolomite are present in the functionalized biomaterial.

## 7. Mechanism of Heavy Metals Adsorption unto Modified Biochar

The adsorption of heavy metals from polluted sites have been widely studied and the mechanism guiding the metal-chelation process basically divided into two; chemisorption and physisorption [71]. The chemisorption process include familiar processes of complexation or chelation and ion exchange whereas physisorption involves precipitation or bioaccumulation. Some authors have reported wider interactive mechanism between heavy metals and biosorbent such as physical adsorption or surface adsorption which includes hydrogen bonding, electrostatic attraction, Van Der Waals forces, ion exchange, chelation, precipitation, hydrophobic interactions, covalent interaction and oxidation or reduction process [57, 87].

Varieties of proposition exists but five different mechanistic processes govern the adsorption of metal ions from aqueous solution and includes complexation, cation exchange, electrostatic interactions, chemical reduction and precipitation. Spectra shift of the hydroxyl group, always indicate complexation interaction and co-precipitation which leads to the formation of metal hydroxide, metal oxide and metal ammine carbon dots linkages. Complexation will cause

significant interaction between the functional group in the nanocomposite and the metal ion as shown in Equations 4 to 9. Consequently, variation of FTIR wavelength of O-H is a confirmation that  $M^{2+}$  is bonded to free hydroxyl group through inner-sphere complexation common among other divalent cations. Similarly, complexation of  $M^{2+}$  through N atom of the imine could be a possibility and illustrated in Equation 7 due to wavelength shifts. Co-precipitation could also be possible due to the interaction between  $M^{2+}$  and  $PO_3^{4-}$  or other anionic species clearly shown by the wavelength variation. Spectra shift of the C=O group indicates cation exchange and can be a plausible mechanism for the removal of  $M^{2+}$  from aqueous solution. Some authors [89, 90] have implicated cation exchange, inner sphere complexation, co-precipitation, electrostatic interaction and hydrophobic  $\pi - \pi$  interaction as the mechanism for sorption of heavy metals using modified biochar.



### 7.1. Extraneous Sorption Factors

Some factors have been widely varied by authors in the removal of heavy metals from polluted sites. These factors include temperature, pH, time of contact, initial metal ion concentration, and sorbent dosage. Critical examination of the factors indicates that most authors chose a pH of between 5 and 8 and ambient temperature (room temperature). Other factors, such as time of contact, sorbent dosage, and initial metal ion concentration, were widely different. Careful manipulation of the extraneous factors influences the adsorption capacity and mechanism for sorption. Some authors strongly believe that sorption at high pH is mechanistically governed by the chemisorption process [16–18]. Adsorption may decrease at pH values of 2-4 (low) due to increased electrostatic attraction between the metal ions and the biochar surface. Possibility of formation of  $M(OH)^+$  due to lowered electrostatic repulsion between  $M^{2+}$  and the nanocomposite surface functional group exists increasing the adsorption capacity at the pH 5 as widely reported. Decreased adsorption at higher pH values, such as 9, leading to a regression in adsorption capacity, could be due to the precipitation of  $M^{2+}$  ions in the form of  $M(OH)_2$  [14]. High adsorption at very high pH, say 10 or 11, could probably be because of the electrostatic attraction between the positively charged metal ions and the negatively charged nanocomposite surface functional groups and the consequent formation of stable metal hydroxo species. At low pH, deprotonating of the carboxylate group, ligand degradation, demetallation and competitive complexation between the  $H^+$  and modified biochar surface could be the driving force [15, 90].

An increase in contact time causes an increase in adsorption until equilibrium is reached, and then a decrease in sorption. Similarly, as the concentration of  $M^{2+}$  ions increased, exposed sites of the nanocomposite will be gradually filled due to surface electrostatic interaction, cation exchange, intermolecular hydrogen bonding, precipitation or surface complexation and upon saturation there will be absence of more exposed surface and regress or steady state adsorption [11]. Profiling the equilibrium adsorption models of modified biochar and its use in cadmium adsorption indicates the interplay of monolayer and multilayer adsorption processes. Some authors have argued that the versatility of the functionalized sorbent is responsible for this feature [11]. Adsorption studies involving temperature variation have shown that the sorption of heavy metals using modified biochar is spontaneous and endothermic based on the values of the thermodynamic parameters [80].

### 7.2. Regeneration of Used Functionalized Biochar

Used modified biochar may become an environmental hazard if not properly handled or disposed. There is a need for an effective, efficient, and economical method for the desorption of used modified biochar using different concentrations of  $HNO_3$ ,  $KNO_3$ ,  $HCl$ ,  $NaCl$ ,  $NaOH$ ,  $EDTA$ , and  $NaNO_3$  at several desorption cycles. Some authors have successfully used acid solutions at different concentrations to supply ions that can exchange or displace the heavy metal ions on the modified sorbent [92]. Generally, desorption is believed to proceed faster with acid solutions as adsorption is hindered in high acid conditions due to competitive complexation and degradation of adsorption bonds or sites [93–95]. Regeneration of used functionalized biochar increases reusability, reduces cost, and enhances eco-friendliness, thereby aligning with the objectives of the sustainable development goals.

## 8. Conclusion and Future Prospects

This review critically examined the nature, effects, and bioavailability of heavy metals; the sorption of heavy metals using modified biochar; different preparation methods of the biochar; different functionalization methods or attachment of surface functionalities; different physicochemical methods of identification; the mechanism of heavy metal removal; and extraneous factors that influence the sorption. Acid functionalization produces surfaces with highly oxygenated groups, while base modification yields surfaces of high aromaticity. Magnetic, ligand, and surfactant-modified surfaces were appraised in the review. A critical comparison of the modified biochar with its non-modified counterpart shows that the former exhibits higher adsorption capacity, reusability, and functionalities. The complexity of heavy metal removal and the existence of competitive ions in matrices call for the redesign of biosorbents, which are currently trending in the area of environmental science and engineering. This is done to generate material that is not only eco-friendly but also has multiple characteristics such as simplicity, high textural characteristics, reusability, ease of application, and a higher surface area. Close look on the achievement of the functionalized biochar entails development of hybrid bioinspired nanocomposite for capturing CO<sub>2</sub> from the environment to reduce global warming. Similarly, some adsorption processes, especially those involving surfactant-modified surfaces, are mechanistically yet to be understood, and further research is needed to simplify this. Of serious concern is the use of some of the dopants based on the cost of modification and the environmental concerns of the used chemicals. Therefore, both the sorbent and the chemicals need to be regenerated in the adsorption process to keep the environment clean. Thus, a novel, benign, facile, and eco-friendly modification approach is required, and plasma treatment involving needed surface charge generation for pollutant decontamination is advocated. As the use of various dopants for modification of biochar for removal of heavy metals intensifies, the author proposes that facile, efficient, benign, and effective methods for sorption are explored with improved adsorption and regeneration capacity.

## 9. Declarations

### 9.1. Author Contributions

Conceptualization, N.F. and E.J.; software, M.N.; validation, I.-A.C. and E.J.; formal analysis, N.F.; investigation, E.J.; resources, N.F.; data curation, N.F.; writing—original draft preparation, M.N. writing—review and editing, N.F.; visualization, E.J.; supervision, N.F.; project administration, N.F.; funding acquisition, N.F. All authors have read and agreed to the published version of the manuscript.

### 9.2. Data Availability Statement

Data sharing is not applicable to this article.

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### 9.5. Institutional Review Board Statement

Not applicable.

### 9.6. Informed Consent Statement

Not applicable.

### 9.7. Declaration of Competing Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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