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Efficiency of engineered/modified biochars-based adsorbents for removal of pollutants from aquatic environment: A critical review

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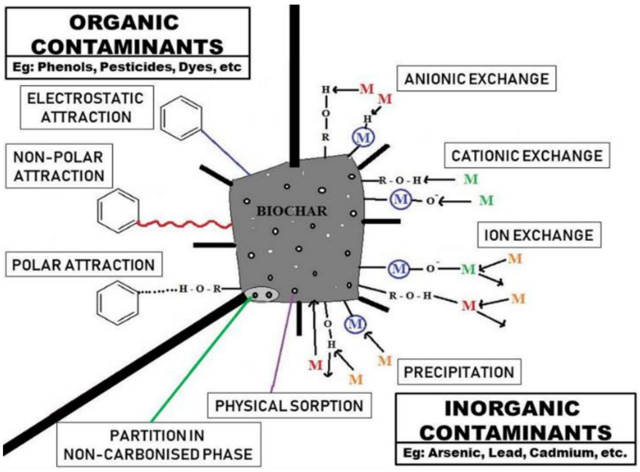
Graphical abstract



Abstract

Biochar shows substantial potential to contribute as a globally applicable adsorbent to decontaminate the water system due to the ample availability of feedstocks and valuable physio-chemical surface properties. This review aims to highlight the modification technologies of biochar, the alteration of characteristics after modification, and the eliminating of organic, inorganic, antibiotics and other pollutants from water systems by modified biochar. Alkali-acid modified and metal-loaded biochar possesses the superior surface functionality; these modifications are greatly favorable for improving the removal of different pollutants from water systems. Acidic- alkaline and metal treatment provides more diverse functional groups on biochar surfaces e.g. produces ample oxygenated functional groups, improve the surface attributes, generates high ratios of surface aromaticity and N/C, these changes provide the more adsorption sites and increase the removal of pollutants. This review also demonstrates the existing problems and future research direction related to modified biochars by acidic and alkaline agents as well as metal loaded composite in the remediation of the pollutants.

Keywords: Functional groups, biochar, removal, modification, pollutants, water system

1. Introduction

Pollutants may cause serious environmental problems and threaten public health due to their toxic and non-biodegradable nature (Ding *et al*. 2016). They are mainly discharged from human activities such as metal plating, mining, and paper industries. Heavy metals, antibiotics, and other pollutants can pose a severe risk to human health, even with micro-concentration (Qu *et al*. 2022). Therefore, some cost-effective methods are needed to be developed to remove heavy metal compounds from wastewater. Most traditional water treatment technologies have disadvantages of either low efficiency or overspending (Thangavelu *et al*. 2022). Over the last few decades, various removal strategies such as oxidation, precipitation/co-precipitation, coagulation, ion exchange, reverse osmosis, membrane separation techniques, and adsorption have served to remove or minimize pollutant concentrations below the World Health Organization (WHO) standards (Rahman *et al*. 2021). Among these options, adsorption is considered one of the most efficient techniques for the removal of pollutants from

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contaminated water as this technique is simple, cost-effective, and produces less waste (Liu *et al.* 2021). Various adsorbents such as clay, modified clay, and clay-supported nano zero-valent iron (nZVI), alumina, activated carbon, graphene, and biochar (BC) have been used to remove pollutants from contaminated waters (Imran *et al.* 2021). In contrast to activated carbon, BC has emerged as an affordable remediation substrate for removing environmental pollutants in natural and wastewater (Liang *et al.* 2021). However, the adsorption efficiency of pristine biochars can be improved by modification with different agents. To improve the adsorption ability of biochar, various modification methods (physical and chemical activation) have been applied (Acid and alkali treatment and iron loading on the biochar surfaces) (Rahman *et al.* 2021). Most of the modification methods could effectively change the surface physico-chemical characteristics of biochar, such as increase in surface area and functional groups change porous structures, O/C and H/C ratios (Murtaza *et al.*, 2022a).

The main purpose of these modifications are to (i) increase the surface area of the biochar, (ii) modify or improve the surface properties of the biochar, or (iii) use the surface as a platform to embed another material (or organism) with beneficial surface properties. The tools, which are available to modify biochar, increase the breadth of chemical pollutants, which can be removed from water using biochar. This review will provide an introduction of various modification approaches (alkali, acid, and metal oxide modification of biochar), explain how the modifications alter the surface properties of biochar, and demonstrate how these modifications enhance the remediation of pollutants from aqueous solutions.

2. Common pollutants in water

The remediation and prevention of water pollution is one of the mostinclusive challenges facing in 21st century (Dudgeon *et al.* 2006; Murtaza *et al.* 2023a). Anthropogenic interruption of bio-geochemical cycling of elements has altered the chemical form, and increased the several elements concentration in the surface and ground waters. Cost-effective, sustainable, and efficient remediation approaches for these pollutants are urgently needed.

Toxic pollutants, such as heavy metals, antibiotics, and PAHs are often discharges from the pharmaceutical industry, sewage treatment, electronics and alloys smelting and mining, dyes and pigments and manufacturing of batteries (Qasem *et al.* 2021; Thangavelu *et al.* 2022). These contaminants can have long-term toxicity when they bioaccumulate through food chains and have ecotoxicological effects on water ecology when present in high concentrations. The majority of contaminants are mostly found in the environment as divalent cations. Compared to mercury, copper, and lead, some heavy metals, like zinc and cadmium, have larger radii, which results in a lower charge-to-radius ratio and ionic potential. Because of this, compared to cadmium and zinc, mercury, copper, and lead are less mobile because they more easily form connections with functional groups on surfaces. Increased concentrations of nutrients, such as NO_3^-, PO_4^{3-}, and NH_4^+, are seen in surface and subsurface waters, primarily as a result of inefficient use of sewage effluent and agricultural fertilizers (Martinez-Dalmau *et al.* 2021). Because freshwater discharges into seas have an elevated nutrient status, they can lead to hazardous algal blooms and low dissolved oxygen concentrations, which can result in hypoxic "dead zones" and other ecological damage in estuaries and coastal zones (Priya *et al.* 2022). Compared to the metal cations previously examined, NH_4^+ has a substantially smaller charge-to-radius ratio even though it is positively charged and attracts negatively charged surfaces. Since NH_4^+ acts similarly to alkali metal cations (such as Na^+ and K^+), it is less likely than divalent metal cations to establish stable connections with surfaces. In contrast to NH_4^+, PO_4^{3-} and NO_3^- are oxyanions that behave differently from one another. Although both are negatively charged and drawn to positively charged surfaces, $NO_3^-$is far more mobile than PO_4^{3-}, which attaches itself to water-soluble colloids with ease (Biswal *et al.* 2022). Redox-sensitive elements As and Cr show distinct variations in mobility and toxicity when redox circumstances change. Trivalent arsenite, As (III), or pentavalent arsenates, As (V), are the two forms of inorganic As that are present in the environment. While arsenite (AsO_3^{3-}), which is more poisonous to humans and more mobile, occurs in anaerobic circumstances, such as groundwater, arsenates (AsO_4^{3-}) are found in aerobic environments (Qu *et al.* 2022). Utilizing organic materials Human populations have been widely poisoned as a result of using contaminated groundwater for irrigation of rice crops and drinking water, particularly in Bangladesh. There are two forms of Cr: hexavalent Cr (VI) and trivalent Cr (III) (Sharma *et al.* 2022). Chromium most notoriously contaminates surface waters due to discharge of tannery effluent. To decrease the concentrations of these pollutants of concern in water systems it is necessary to treat point source discharges of industrial, domestic, agricultural wastewater before disposal into water environment. Current waste-water treatment strategies to eliminate pollutants are energy intensive and costly. These limitations of recently available technologies provide a demand for a selective, cost-effective, efficient, adsorbent material. Biochar modification could provide the low cost, versatile, and sustainable solution to removal of various pollutants from water.

3. How the modified-biochar traits influence the removal of pollutants from aqueous medium

There are various mechanisms responsible for high removal capacity of biochar for the specific contaminants. Biochars have a higher –surface area due to a vast distribution of meso or micro-pores. The higher surface area, greater amount of micropores of biochar and the more surface sites upon which contaminants can adsorb. Many authors have described a relationship between biochar surface area and pollutant removal capacities (Kim *et al.* 2013; Xia *et al.* 2022). Niu *et al.* (2013) demonstrated that surface functionality also influence the biochar sorption capacities. Removal of the pollutants thru biochar is a result of surface precipitation, electrostatic attraction, and ionic exchange (Beesley *et al*. 2015; Dong *et al*. 2023).

3.1. Precipitation

Precipitation of pollutants (mainly metal cations) with insoluble salts occurs on surface of adsorbents (biochar and biochar based composite) with high mineral ash content e.g. precipitation of the lead has been exposed on surface of phosphate en-rich biochars produced from animal manures (Cao *et al*. 2009; Qu *et al*. 2022). The pH of the solution may be raised by treated biochar, causing the metal oxides—which are primarily poorly soluble—to precipitate.

3.2. Electrostatic attraction

It is called physical sorption, occurs between positively charged ions in the water and delocalised cloud of electrons linked with aromatic groups on surface of modified-biochars, creating cation-π interactions with the C=C aromatic bonds (Harvey *et al*. 2011; Sharma *et al*. 2022). Physical sorption does not need stoichiometric release of protons or cations from biochar but chemical sorption require this mechanism.

3.3. Chemical sorption

Chemical sorption mechanism occurs due to ion-exchange with ample functional groups on the biochar surface, including phenolic, hydroxylic and carboxylic groups (Biswal *et al*. 2022; Murtaza *et al*. 2023b; Lee *et al*. 2010). These functional groups give cation exchange capacity to biochar depending on pyrolysis temperature with a peak of cation exchange capacity at around 350-400°C, possibly due to loss of oxygenated functional groups above this temperature (Gao *et al*. 2023; Gomez-Eyles *et al*. 2013). Since chemical sorption is stoichiometric, sorption efficacy is pH dependent and hence dictated by the pH of medium.

Functionality and surface area can be changed through the modification of biochar to increase sorption capacities for contaminants. Modifications often have the objective of enhancing the anion sorption capacity while activation usually increases the metal cation sorption capacity of biochars. However, variations in the pyrolysis temperature can lead to significant variations in the surface area and functioning of biochars.

3.4. Complexation

The arranging of multi-atom creation through the interaction of particular metal ligands to produce complex is included in this method of metal complexation. Because the low-temperature-produced biochar contains oxygen in its structure, it can bind with heavy metals. Examples of these functional groups are carboxyl, lactonic, and phenolic. This oxygen presence may cause the biochar's surface to oxidize more, which would improve the metal complexation (Qiu *et al*. 2022). When compared to biochar made from animal sources like dairy manure and poultry litter, it has been demonstrated that biochar made from vegetal biomass has a high efficiency in binding potentially metals like Cu, Cd, Ni, and Pb to form metal complexes with carboxylic and phenolic functional groups (Chen *et al*. 2022; Murtaza *et al*. 2021a). They reached the conclusion that biochar produced from plants has excellent ion exchange and surface complexation capacities. However, more research is needed in order to determine the biochar metal complexes' formation using sophisticated spectroscopic techniques such as X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (Lu *et al*. 2022).

3.5. Partitioning

The adsorbate material diffuses into the pores of the biochar's non-carbonized section during this phase. This part interacts with the organic adsorbate with ease, causing it to sorb. However, the properties of the carbonized crystalline and graphene fractions of the biochar as well as the non-carbonized biochar (crystalline or amorphous carbon) determine the adsorption of organic pollutant molecules. Iqbal *et al*. (2022) reported that using organic carbon (OC) fractions of biochar, biochar made from swine and dairy dung at pyrolysis temperatures of 200 and 350°C exhibits significant sorbate partitioning of atrazine contaminant. Similar results were found by Ambika *et al*. (2022) showing that organic fractions of biochar prepared from wood and grass can enhance the adsorption of norflurazon and fluridone by partitioning. In general, the partitioning mechanism is more visible and highly efficient when the biochar has high volatile matter content and at high concentration of organic contaminants (Xia *et al*. 2022).

3.6. Pore filling

During this procedure, organic pollutants are present at the surface of biochar that has both micropores (less than 2 nm) and mesopores (between 2 and 50 nm). The polarity of the organic contamination and the kind and composition of the biochar determine the pore filing mechanism. Gupta *et al*. (2022) reported that biochar prepared from gamma grass, oak and loblolly for the sorption of catechol using micropore filling mechanism is more dominant than other adsorption mechanisms. In general, to have high efficiency of this pore filling process, the biochar must contain a small amount of volatile matter and occur at low concentration of organic contaminants.

3.7. Electron donor and acceptor interaction

The adsorption of aromatic chemicals on biochar with a structure resembling graphene is primarily facilitated by the electron donor and acceptor interaction mechanism. During the biochar preparation process, a temperature greater than 1100 °C must be reached in order to achieve complete graphitization (Dong *et al*. 2023). However, the temperature at which the biochar is pyrolyzed determines the electron density that it will produce: if the temperature is below 500°C, the biochar's π aromatic system functions as an electron acceptor, and if the temperature is above 500 °C, the biochar will act as a donor (Sinha *et al*. 2022). In their attempt to adsorb sulfamethoxazole, Gao *et al*. (2023) used reed-derived biochar that had been enriched with π-electron graphene on its surface. The graphene surface of the biochar and the aniline-protonated rings of sulfamethoxazole showed a strong sorption. Besides they claimed that the π-electron donor/acceptor interaction between the electron-withdrawing substituent of chlorine and aromatic carbon on the surface of biochar enhances the adsorption of atrazine compound.

4. Methods of modifying Biochar and effects of modification on the properties of biochar

Innovative methodologies for modifying biochar have been developed to enhance the adsorption of the pollutants from water (Dong *et al*. 2023). Modifications methods are performed either pre-or post- pyrolysis of the biochar (or both). The more prevalent changes, known as post-pyrolysis ones, involve treating biochar after it has already been generated. After pyrolysis, alkali, acidic and metal oxide modification is typically carried out (Sinha *et al*. 2022). The process of producing biochar-based composites, which is the most extensively studied method for making sorbents to treat contaminated water, involves incorporating various elements into the biochar structure either before or after pyrolysis (Lu *et al*. 2022). The primary aim of all these modification methods is to enhance the efficacy by which the biochar removes pollutants from water, generally by changing its physical or chemical properties, such as surface area, or surface functionality (Gupta *et al*. 2022). There are many classes of novel modification strategies, with only the key ones reviewed in this work. It is noteworthy that the applicability of modification methods (e.g. acid, alkaline and metal oxide modification) has been expanded (i.e., from contaminant adsorption in wastewater). Therefore, there is a need for efficient, novel materials and techniques to eliminate inorganic and organic contaminants from nature, including dyes, heavy metal, pesticides and antibiotics. Applying biochar to improve the quality of water by removing pollutants has been regarded as feasible strategies that are cost-effective.

4.1. Acid modification

The aims of acid modification are to clear the pores of biochar and introduce acid binding sites (carbonylic, lactonic, and phenolic functional groups) for pollutant adsorption (Wang *et al*. 2019). A number of studies have discussed the effects of acid modification on functional groups, pore volumes, and - specific surface area. After modification with sulphuric acid, citric acid, oxalic acid, hydrochloric acid, and phosphoric acid, the resultant biochar typically possessed much surface area; higher pore volume, hydrophobic or more acidic groups for contaminant adsorption, and higher carbon retention (Ma *et al*. 2016). Modification by acids improved the characteristics of biochars (Table 1). It is hypothesized that acid modification decreased biochar pH by introducing acid groups onto biochar surface, making the alkaline substances more labile and soluble. Acid modified increased the specific surface area, volume of micropores, and total pore volume after treatment of pine tree sawdust with diluted H_3PO_4 (Zhao *et al*. 2017). Hadjittofi *et al*. (2014) modified a biochar derived from cactus fibres with nitric acid to increase the abundance of carboxylic groups on the surface since these groups act as strong Cu^{2+} binding sites.

4.2. Alkali modification

The major aims of alkaline modification are to increase specific surface area as well as the number of oxygen-containing functional groups (e.g., hydroxyl, carboxyl, carbonyl, ether) of pristine biochar, thus promoting the adsorption of a variety of pollutants (Wang *et al*. 2019). The most widely used alkaline agents are potassium hydroxide and sodium hydroxide (Ma *et al*. 2016). After alkaline modification, blocked pores are cleaned, resulting in greater porosity. Alkaline modification is a relatively simple modification method, since it only involves the mixing and washing processes under mild conditions. It is thus a promising and applicable modification method in environmental applications such as removal of pollutants from wastewater (Jin *et al*. 2014). Treatment of biochars with alkali increases adsorption by increasing porosity and surface area and by creating of a greater number of oxygenated functional groups on the surface of the biochar. These oxygenated functional groups play vital role in the removal of pollutants from water system. The increase in surface area resulting from modification of biochar with potassium hydroxide also increases the adsorption of oxyanions from solution (Petrovic *et al*. 2016). After alkali modification biochar properties significantly changed (Table 2).

4.3. Metal oxides

Ensuring a uniform distribution of the metal across the biochar surface is the aim of this method for producing composites based on metal oxide biochar. In essence, the biochar serves as a porous carbon scaffold that allows metal oxides to precipitate and increase in surface area (Wang *et al*. 2019). Generally, biochars or their feedstocks are impregnated with metal oxides by soaking them in solutions of metal nitrate or chloride salt solutions (Figure 1). The most frequently used impregnation agents in the literature are FeS, $FeCl_3$, $MgCl_2$ and Fe $(NO_3)_3$. After treatment of biochars with metal salt solutions, biochar is heated under atmospheric conditions (i.e. not low-oxygen conditions) at temperatures 50-300 °C to allow nitrates or chlorides to be driven off as Cl_2 and NO_2 gases and convert the metal ions to metal oxides. Agrafioti *et al*.(2014) presented that the treating municipal waste biomass and rice husk biochars in $FeCl_{3,}$ iron powder and CaO, prior to created $Fe^{3+,}$ Ca, and Fe^{+} modified biochars. These modifications altered the physiochemical traits of biochars and enhanced the ability of biochars to eliminate the pollutants from water. Most metal oxide modifications result in a reduction in the surface area of the biochar due to clogging of pores with metal oxide precipitates (Zhou *et al*. 2017). After the treatment of biochar by metal salts and oxides, biochar's properties enormously altered (Table 3).

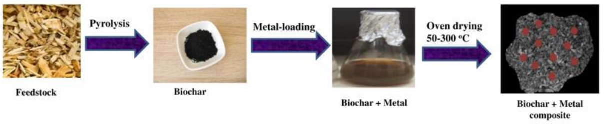

Figure 1. Diagram outlining the procedures used to modify biochars with metal salts to create metal oxide biochar-based composites

Table 1. Physiochemical changes of biochar after the acid modification

Biochar	**Prepared temperature**	**Modifier agent**	**Alterations in biochars properties after modification**	**Reference**
Tea waste biochar	300^{o}C, 500^{o}C and 700^{o}C	HNO_3	• Significantly higher cation exchange capacity were observed in modified biochar • The acid treated biochars had low PZC values and showed a decrease in the ash content as a result of the demineralization and the introduction of acidic functionalities • Carboxylic functional groups increased aromatic pyridonic-N and pyridinic-N increased which further suggests that the aromaticity of modified biochar	Peiris *et al*. 2019
Tea waste biochar	300^{o}C, 500^{o}C and 700^{o}C	H_2SO_4	• C contents increased and O contents decreased as compared to un-modified biochar, molar H/C and molar O/C ratios significantly changed • After modification alkaline biochar changed in acidic pH • Specific surface area expressively increased	Peiris *et al*. 2019
Poultry manure	300^{o}C	H_3PO_4	• Increases in surface area and functional groups after acid modification of biochar • EC increased and pH decreased • Elemental composition altered	Sahin *et al*. 2017
Rice straw and swine manure	700^{o}C	H_3PO_4	• Surface area enhanced • enhanced the content of C, N and S, but reduced the content of O • no significant improvement on functional groups	Chen *et al*. 2018
Wheat straw and cow manure	450^{o}C	HNO_3	• Both the bulk and surface C contents of the biochars consistently decreased after HNO_3 treatment, suggesting that part of the biochar C was oxidized by HNO_3 • Bulk and surface O contents of the treated biochars were higher than those of the un-modified biochars • formation of oxygenated functional groups, mainly C=O and COO- groups • HNO_3 treatment also leads to the increase in bulk and surface polarity	Jin *et al*. 2018
coconut shell	800^{o}C	HCL	• channel structure was clearly visible • effectively remove or dissolve impurities of biochar • significantly increase its surface area and porous volume • introduce the acidic functional groups (such as-COO and-OH)	Liu *et al*. 2018
Peanut shell	500^{o}C	H_2SO_4	• pH of the zero point of PBC (pH_{PZC}) was reduced by removing the ash from the biochar surface • biochar samples had highly microporous structures, and the surface area and pore volume of the micropores after modification • massive oxygen-containing functional groups	Wang *et al*. 2019
Corn stover	600^{o}C	HCL	• The pH of unaged AC and biochar was highly alkaline (9.61 and 9.91 respectively) and was reduced following chemical modification in most cases and by up to 3 units • most pronounced change in absolute cation exchange capacity values was observed • specific surface area significantly enhanced	Hale *et al*. 2011
Rice straw	350^{o}C 500^{o}C 700^{o}C	HNO_3/H_2SO_4 mixture	• Some floccules were formed on the surface of biochars after HNO_3/H_2SO_4 treatment • O/C ratios were increasing and the nitrate and nitro surface groups were formed after HNO_3/H_2SO_4 modification • Formation of carbonyl and carboxylic functional groups on the surface of aged biochar was also observed	Qian *et al*. 2015

Table 2. Physiochemical changes of biochar after the alkali modification

Biochar	Prepared temperature	Modifier agent	Alterations in biochars properties after modification	Reference
Corn stover	300°C	NaOH	• The largest enhancement of basic groups occurred for the BCs treated with increasing concentration of NaOH (by 21–154%) • pH of modified biochar was significantly elevated after treating with NaOH concentration. • Treatment with NaOH caused increase of volume of pores from 5 to 40 nm (by 109–239%) and surface area (by 21–82%)	Boguta *et al*. 2019
Peanut shell	°C	KOH	• Increased the specific surface area of biochar, resulting in the increase of adsorption sites • Specific surface area remarkably increased	An *et al*. 2018
Tea residue	300°C	NaOH	• Improved reportedly the mesoporous structure • Increased the quantity of oxygen-containing surface functional groups, thus improving the surface alkalinity of biochar • Improve the adsorption	Mu and Ma, 2021
Bamboo waste	°C, 600°C	KOH	• highly developed microporous structure with an ultrahigh specific surface area (increase to 700–3000 m^2/g)	Chen *et al*. 2020
Rice straw	500°C	KOH	• Micro-porous structure, higher specific surface area, higher cation exchange capacity • New surface functional groups that appeared on modified biochar surfacepresence of high soluble K ions on biochar surface • presence of high soluble K ions on biochar surface	Bashir *et al*. 2020
Spent coffee	500°C	NaOH	• significantly changed the structure of modified biochar • More pores were created on surface • NaOH treatment expressively changed the pore structure • enhanced specific surface area and developed heterogeneous pores • Abundant oxygen polar functional groups observed	Nguyen *et al*. 2021
Corn stalk	°C	KOH	• Surface area of alkali-modified biochar was found to enhance 14-fold • Surface functional groups were mainly basic • Reduced the number of acidic groups • specific surface area of modified biochar 22.6887 m^2g^{-1} observed higher than pristine biochar • total pore volume in KOH-treated biochar was 10-fold greater than fresh biochar	Wang *et al*. 2019
Dairy manure	300°C	NaOH	• Nitrogen and ash contents, element percentage and pH enhanced after modification • oxygen containing functional groups improved • effectively increased lead removal from wastewater	Zhou *et al*. 2014

Walnut shell	550°C	KOH	• More conducive to the formation of pores • Highest specific surface area after modification • Large number of oxygen-containing functional groups observed • Crystallinity increased • Dissolved the amorphous structure • Large number of large pores were generated on the surface	Liu *et al*. 2020
Peanut shells	600°C	Na- humate	• Biochars yielded higher surface areas after modification • Extend in mesopore region • Mesopore volumes significantly higher	Dou and Jiang, 2019
Bamboo hardwoods	400°C	NaOH	• more roughness, with a more granular massive structure than that observed on the modified biochar	Wu *et al*. 2019
Corn straw	500°C	KOH	• Surface area is greater than pristine biochar after KOH-treatment • H/C ratio significantly dropped • Increased the O-containing groups • Structures of KOH-treated biochar were not homogeneous, and irregular pores with different shapes and sizes were observed	Tan *et al*. 2016
Dairy manure	300°C	NaOH	• NaOH modification increased the specific surface area • Enhanced the ion-exchange capacity • Increased the oxygen-containing functional groups	Chen *et al*. 2019
Poplar wood	300°C, 500°C 700°C	KOH	• contents of biochars were increased • Increased H contents • Low ash content • Removed more non-fixed carbon • Surface oxygen functional groups of biochars substantially increased by KOH-treatment	Huang *et al*. 2017
Apple tree branches	500°C	KOH	• Enhanced the O/C, H/C and (O+N)/C values • Increasing the hydrophilicity • Porous structure, specific surface area micropore volume	Duan *et al*. 2021
Rice hull	400°C, 500°C	NaOH	• Reduce the surface area • Average pore size and total pore volume • Relatively large pores are developed	Seo *et al*. 2020

Table 3. Physiochemical changes of biochar after the metal loading treatment

Biochar	Prepared temperature	Modifier agent	Alterations in biochars properties after modification	Reference

Rice husk	300°C	MnO_2	• Noticed large number of reactive hydroxyl groups on the surface • substantially more carboxyl functional groups • H and C element dramatically reduced after the modification • contents enhanced from 5.16% to 17% • specific surface area found greater than un-modified biochar • Average pore diameter enhanced (3.8 nm) • Formation of various porous structures • Micro-spherical structures greatly enlarged	Zhou *et al*. 2017
Corncob	500°C	$Fe(NO_3)_3$	• showed acidic pH and also enhancing of capacity to exchange anionic forms after modification • Significant decrease in surface area • Destroying some carbon walls of internal structures • Iron situated mainly in pores structures of biochar	Frišták *et al*. 2016
Oak wood	400°C	Fe^{3+}	• specific surface area increased from 2.04 to 6.1 m^2/g after Fe^{3+} treatment • Found high iron contents in modified biochar • loss micro-porosity • Abstraction of a larger amount of organic matter from treated biochar	Mohan *et al*. 2014
Sewage sludge	700°C	$FeCl_3$	• Showed acidic characteristics after treatment • Fe content was increased 176.2 to 228.2 mg/g • specific surface area of modified biochar increased to 6.6 to 24.02 m^2/g • Formation of amorphous Fe- hydroxides /oxide on modified biochar surface • Observed higher amounts of C, O, N, and Fe in modified biochar	Rahman *et al*. 2022
Pinewood	450°C	Fe_2O_3	• Fe contents of modified biochar was 118 times greater than that of pristine biochar • higher ash content observed • amounts of volatile elements such as N, H, and C and non-volatile elements such as P, K and Ca in treated biochar were lower • Slightly surface area decreased • Showed numerous small aggregates stabilized on the modified biochar surfaces	Wang *et al*. 2015
Peanut hull	450°C	Fe_2O_3	• Development of porous structure • Total Fe contents enhanced • Surface area reduced	Han *et al*. 2016
Hyacinth	250°C	Fe^{3+}	• pH values reduced • Higher amount of carboxylic functional groups observed • Low anion exchange capacity • Reduce specific surface area substantially • Forming inner-sphere	Zhang *et al*. 2016
Grape husk	600°C	$FeSO_4 \cdot 7H_2O$	• specific surface area reduced after modification • Well-developed structure • Smaller range of pH values was noticed • PZC decreased after modification • cation exchange capacity increased significantly	Trakal *et al*. 2016

5. Effects of modified biochar on the removal pollutants

Modification to create biochar-based composites uses the biochar as a scaffold to embed new materials to form surfaces with novel surface attributes upon which inorganic and organic contaminants can sorb. Sorption of the inorganic/organic contaminants through modified biochar results from surface precipitation, electrostatic attraction, and stoichiometric ionic exchange. In this section, we demonstrate how the modified biochar composite increases the elimination of inorganic/organic pollutants from wastewater. Figure 2 illustrates the modified/unmodified biochar possible adsorption mechanisms for inorganic and organic pollutants (adapted from Murtaza *et al*. 2022).

6. Influence of Acid modified biochar on the removal of pollutants

Artificially accelerated simulated modification can enhance the cation exchange capacity and oxygen content of biochar surface but pollutant type and type of biochar have various effects on removal capacity of the biochar before and after modification. After nitric acid treatment, biochar derived from cotton seed was noticed to be rich in carboxylic groups and presented significantly greater Zn, Cu, and Pb removal capacity than the pristine biochars, it might be presence of abundant oxygen enrich functional groups on the surface of modified biochar (Uchimiya et al. 2012). Xu et al. (2013) demonstrated that the removal capacity of acidic modified animal manure biochar for Cd, Zn, Cu, and Pb were higher than unmodified biochar. The reason of this higher removal ability because the precipitation with mineral components e.g. PO43-, CO32- contained in modified biochar was proposed to be responsible for elevated removal efficacy of these pollutants. Jin et al. (2018) found in a study, the maximum removal capacity of nitric acid modified wheat straw biochar for uranium was 40 times greater as compared to unmodified biochar. The higher uranium removal capacity of HNO3-tearted adsorbent was attributed to higher negative surface charges and increased COO- surface groups. This result shows that HNO3-treated wheat straw biochar are promising adsorbent for the clean-up and improvement of uranium and pollution control. Wang et al. (2019) demonstrated that H2SO4 modified Alternanthera philoxeroides biochar were significantly changes in removal capacity for lead (286.07 mg/g-1) than fresh biochar (134.55 mg/g-1), it might be remarkably alterations in surface morphology and increased the COO- functional groups on the biochar surface after H2SO4 treatment. Shakoor et al. (2018) found in a study, citric acid modified biochar of water melon rind showed highest Arsenic (III) and Arsenic (V) removal percentage 98 and 98% respectively. It may be due to hydroxyl, carboxylic and xanthate functional groups appear during acid modification mechanism on the surface of treated biochar. Liu et al. (2019) demonstrated that the phosphoric acid modified corn stalk biochar showed maximum removal capacity 406.43 mg/g-1 for methylene blue. Phosphoric acid modification significantly increased the removal methylene blue onto modified biochar, particularly more than unmodified biochars. Modification raised the oxygenated functional groups of cornstalk biochar; it might be the main reason enhanced the removal capacity. Mechanism of adsorption between biochar and methylene blue involved hydrogen bonding π-π interaction, physical interaction, and electrostatic interaction. H2SO4-treated walnut shell biochar exposed higher adsorption capacity for methylene blue because e large amount of oxygen-enrich functional groups on surface provided more adsorption sites for methylene blue removal, which was useful to removal reactions. After modification, specific surface area of modified biochar enhanced, larger pore size, and mesoporous distribution provided the higher removal of methylene blue (Liu et al. 2020). Choudhary and Philip (2022) investigated removal capacity of H2SO4-treated palm branches biochar produced at 250oC. Results showed that, with maximum removal capacities as 35.4 mg/g triclosan, 38.8 mg/g ibuprofen, 51.7 mg/g methyl paraben, and 62.2 mg/g carbamazepine, these removal capacities was higher than un-treated biochar. Removal process was found to be channel diffusion, van der Waals force, n-π and π-π interactions, and hydrogen bonding. Zeng et al. (2022) described that the removal capacity of H3PO4-modified biochar for sulfadiazine was remarkably increased 9.66 mg/g to 139.2 mg/g. The heightening in the removal of sulfadiazine was due to confinement influence of hydrophobic cavities from micro-porous structure and π-π electron-donor-acceptor interaction. Chen et al. (2019) presented that, the H3PO4-modified biochar of chicken feather eliminate the cadmium and lead notably it was higher removal capacity than the unmodified adsorbent, it might be due to phosphate precipitation, electrostatic interaction, and O-H bonds were mainly removal mechanism. The enhanced N-enrich heterocycles H3PO4-modified biochar accounted for the improved lead and cadmium removal. Chen et al. (2021) found in a study, the H2SO4-modified biochar of corn stalk showed the removal capacity for ammonium was expressively increased, maximum adsorption of modified biochar 1.6 times greater than unmodified biochar, this enhancement due to the presence large amount of acidic O2-comprising functional groups on the surface of adsorbent after modification. The biochar treatment with acids leads to more acidic functional groups on the surface, e.g. increasing oxygen content results in enhanced H/C and O/C molar ratios with acid modification. Acid modification increases micropores into macro or meso pores, breaks pores wall, and achieved acidic-treated biochar holds more acidic functional groups for instance, ketonic, hydroxyl and carboxylic. The resulting enhance in polarity of treated biochar can lead to chemisorption of contaminants from polluted water. Adsorption capacity of acid-modified biochar in the elimination of pollutants in contaminated water (Heavy metals and organic contaminants) displays in Table 4.

Table 4. Adsorption capacity of modified biochar in the elimination of pollutants in contaminated water (Heavy metals and organic contaminants)

Biochar	Modify agent	Pyrolysis temperature°C	Pyrolysis time	Pollutant	Enhancement in adsorption	Involved mechanism	Reference
Rice husk	Fe	300	1h	Cr^{6+}	Elimination percentage of Cr^{6+} was marginally enhanced after use the engineered composite	Electrostatic interaction, repel negatively charged Cr^{6+}	Agrafitoti *et al*. 2014
Rice husk	Ca^{2+}	300	1h	As^{5+}	Removal efficiency of As^{5+} enhanced from 70 % than pristine biochar.	Owing to alkaline solution of calcium oxide eliminate As^{5+} by precipitation.	Agrafitoti *et al*. 2014
Solid waste	Ca^{2+}	300	1h	Cr^{6+}	Removal percentage of Cr^{6+} significantly enhanced with modified biochar	Repulsion negatively charged Cr^{6+} and Higher pH of engineered biochar deprotonate their functional groups	Agrafitoti *et al*. 2014
Solid waste	Fe	300	1h	As^{5+}	Removal capacity of As^{5+} expressively with using Fe-modified biochar	As^{5+} eliminate via co-precipitation	Agrafitoti *et al*. 2014
Pine wood	Hematite	600	1h	As^{5+}	Theseϒ-Fe_2O_3 particles serve as sorption sites for As^{5+} and enhance removal efficiency of As^{5+}	The electrostatic interactions observed leading mechanism in adsorption. Modified biochar has showed magnetic characteristics owing to conversion of hematite intoϒ-Fe_2O_3 particles with magnetic traits.	Wang *et al*. 2015
Bamboo	ZnV Iron	600	1h	Methylene blue	By modified biochar achieved the maximum methylene blue removal capacity	-	Zhou *et al*. 2014
Bamboo	Montmorillonite	400	1h	Phosphate	Removal efficiency for P is 8 times greater than pristine biochar	Phosphate adsorption was accelerated by electrostatic attraction	Chen *et al*. 2017
Bamboo	ZnV Iron	600	1h	Pb^{2+}	About 90% of Pb^{2+} was eliminated	Electrostatic attraction among ZnV Iron particles and anions on engineered biochar surface	Zhou *et al*. 2014
Bamboo	Montmorillonite	400	1h	Ammonium	Observed higher adsorption capacity	Mechanism occurred by Surface adsorption onto modified biochar	Chen *et al*. 2017
Bamboo	ZnV Iron	600	1h	Phosphate	Removal enhanced from 55%	Co-precipitation	Zhou *et al*. 2014
Sorghum bagasse	Bentonite	400	4h	Zn^{2+}	Removal efficiency of modified adsorbent was lower for Zn^{2+} than pristine biochar and bentonite	The anionic functional groups on the BC that partially bind with the cationic compounds in bentonite and block pores.	Fosso-Kankeu *et al*. 2015
Bamboo	ZnV Iron	600	1h	As^{5+}	Adsorption capacity of As^{5+} by ZnV Iron modified biochar	Electrostatic attraction	Zhou *et al*. 2014

					enhanced from 70%		
Hickory chip and Bamboo bagasse	Montmorillonite	600	1h	Methylene blue	Removal capacity of methylene blue with both engineered biochars has been increased than unmodified biochars	The higher ion exchange capability of montmorillonite clay enhanced the adsorption rate of modified biochar.	Yao *et al*. 2014
Sorghum bagasse	Bentonite	400	4h	Cr^{6+}	Removal rate of Cr^{6+} by bentonite-modified biochar is greater than pristine biochar and bentonite	Surface adsorption onto modified biochar	Fosso-Kankeu *et al*. 2015
Bamboo	ZnV Iron	600	1h	Cr^{6+}	The elimination of Cr^{6+} enhanced with addition of ZnV Iron-modified biochar	Electrostatic attraction among ZnV Iron particles and anions on engineered biochar surface	Zhou *et al*. 2014
Hickory chip and Bamboo bagasse	Kaolinite	600	1h	Methylene blue	Removal capacity of methylene blue by modified biochars slightly enhanced than raw biochar	-	Yao *et al*. 2014
Sorghum bagasse	Bentonite	400	4h	Malachite green	Adsorption capacity of malachite green was greater comparted to raw biochar	negative charge of modified biochar is enhanced the attraction of cationic dyes through electrostatic interactions	Fosso-Kankeu *et al*. 2016
Gum wood	Carbon nanotube and graphene oxide	600	1h	Cd^{2+}, Pb^{2+}	Removal capacities for Cd^{2+}, Pb^{2+} were greater compared to raw biochar. graphene oxide modified biochar exhibited greater removal of Cd^{2} and Pb^{2+} than carbon nanotube modified adsorbent	Co-precipitation	Liu *et al*. 2016
Bamboo	Chitosan	600	1h	Pb^{2+}	Elimination of Pb^{2+} higher from 35% compared to un-modified biochar.	Amine functional groups of chitosan have resilient association to cationic metal ions in aqueous	Zhou *et al*. 2014
Wheat straw	Graphene	600	1h	Mercury, phenanthrene	Removal capacity of mercury and phenanthrene improved with the enhance in graphene amount	Engineered biochar surface showed more O-enrich functional groups which enhanced the removal of mercury and phenanthrene.	Tang *et al*. 2015
Bamboo	Chitosan	600	1h	Cr^{6+}	Removal of Cr^{6+} increased from 27% than pristine biochar	Co-precipitation	Zhou *et al*. 2014
Pine wood	MgO	600	1h	Nitrate and phosphate	Removal rate of nitrate was 5%, and Removal rate of phosphate was 0.5%	Electrostatic repulsion	Zhang *et al*. 2012
Bamboo	Chitosan	600	1h	Methylene blue	Adsorption efficiency was high	Surface of chitosan modified and	Zhou *et al*. 2014

						pristine biochar negatively charged.	
Peanut shell	MgO	600	1h	Nitrate and phosphate	Adsorption efficiency was high for both pollutants	Complexation mechanism	Zhang *et al*. 2012
Sugar beet	MgO	600	1h	Nitrate and phosphate	Adsorption rate of phosphate was 66% and nitrate adsorption rate was 11%	MgO has strong attraction for P in aqueous owing to its high affinity for anions via mono nuclear -, bi nuclear, and tri nuclear complexation.	Zhang *et al*. 2012
Corncob	$Fe(NO_3)_3$	500 and 700	2 and 3h	As	Engineered biochar show about 20 times enhance of removal for As than pristine biochar	Co-precipitation	Fristak *et al*. 2017
Bamboo	Chitosan	600	1h	As^{5+}	Did not eliminate anionic As^{5+} from solution	-	Zhou *et al*. 2014
Corncob	Mn	500 and 700	1h	Pb^{2+}	Biochar soaked with 3% Mn showed the Maximum Pb^{2+} removal percentage (99%).	Large amount of hydroxyl group accelerated the Pb^{2+}removal	Wang *et al*. 2015
Switch-grass	Magnetic-composite	425	2h	Metribuzin (herbicide)	Adsorption capacity was 39.6 mgg^{-1}, was greater than fresh biochar	Hydrogen-bonding and electrostatic interaction	Essandoh *et al*. 2017
Rice husk	Fe(III)	300	1h	Cr^{6+}	Removal percentage of Cr^{6+} by Fe (III)-modified biochar enhanced with the reduction of Fe (III) quantity in modified material.	Strongly acidic conditions cause an influence on solubility of Fe (III) and which is negatively affected Cr^{6+}adsorption on biochar.	Agrafitoti *et al*. 2014
Rice husk	Fe(III)	300	1h	As^{5+}	Removal rate of As^{5+} thru Fe (III)-modified enhanced from about 47% than pristine biochar	Greatly acidic nature of solution stimulates electrostatic interactions between negatively charged As^{5+} species and positively charged biochar surface	Agrafitoti *et al*. 2014
Bio solid	Fe	500	4h	As(V)	Removal capacity archived 67.2 mg/g was higher than pristine biochar	Owing to strong affinity of arsenate active sites, and endothermic mechanism	Rahman *et al*. 2022
Bio solid	Zr-Fe	300	30 min	As(V)	Zr-Fe modified biochar achieved 62 mg/g, it was more higher than raw biochar	adsorption process was endothermic and spontaneous, formation of the inner-sphere, and electrostatic attraction	Rahman *et al*. 2020
Coffee husk, and corncob	ZnO	600	2h	As(V), Pb^{2+}	Removal capacity of As (V) 25.9 mg/g and Pb^{2+} 25.8 mg /g respectively	improved the microstructure of modified biochars increase the active sites, electrostatic attraction	Cruz *et al*. 2020
Rice straw	$FeCl_3$	450	1h	As(V)	As compared to pristine	Resilient electrostatic attraction	Nham *et al*. 2019

					biochar, Fe-loaded biochar exhibited much higher capacity to eliminate As (V) from waste-water	between surface functional groups and anions species in solution that could boost adsorption mechanism.	
Rape straw	Ferrihydrite	400	2h	Cd (II)	Higher adsorption capacity observed 18.18 mg g^{-1} as compared to pristine biochar was 5 times higher	Complexation, ion exchange and electrostatic interaction	Tian *et al*. 2022
Date palm leaves	$Fe(NO_3)_3$	300, 500 and 800	4h	As	Fe $(NO_3)_3$-treated composite achieved great removal capacity up to 97%	Enhancing sorption sites because of higher changes in biochar characteristics	Kirmizakis *et al*. 2022
Bamboo	CO-Fe	500	2h	Cr^{6+}	Maximum adsorption (51.7 mg/g) capacity observed, it was 5 times higher than un-treated biochar	CO-Fe-binary oxide was uniformly generated, and higher surface area after loading Co-Fe on biochar, strong electrostatic attraction	Wang *et al*. 2013
Poplar	$FeCl_3$	300 and 600	2h	As^{3+} and As^{5+}	increased the adsorption from 86.8 - 99.9% for As^{5+} and 73.8 - 99.9% for As^{3+}	Spatial distribution and species of Arsenic, introduction of calcite on the composite surface	Xu *et al*. 2020
Populus wood	$FeSO_4$	300 and 600	2h	Hg^{2+} and Cr^{6+}	Fe-treatment boosted the removal capacity fromHg^{2+} (62.5%) and Cr^{6+} (97.0%)	Redox reaction accelerated to the elimination process	Feng *et al*. 2019
Wheat straw	$Fe(NO_3)_3$	650	3h	Se(VI)	Modification greatly improved biochar's capacity for Se(VI) removal, adsorption capacity was noticed (14.3 mgg^{-1})	Creation of Se complexes with the Fe compounds existing on the surface of biochar	Godlewska *et al*. 2020
Macroalgal biomass	$FeCl_3$	300, 450 and 750	1h	Molybdenum, arsenic and selenium	Fe-modified biochar showed higher sorption capacity for molybdenum (64-78%), arsenic (62-60%) and selenium (14-38%) was higher than raw biochar	High affinity for oxyanions, and electrostatic interaction	Johansson *et al*. 2016
Food waste	$Fe(NO_3)_3$	300, 450 and 600	4h	Se(VI)	Attain the maximum selenium removal applying modified biochar	Endothermic adsorption mechanism	Hong *et al*. 2020
peanut shell	$Fe_2H_2O_4$	600	1h	Cu^{2+}, Cd^{2+}	Excellent performance for adsorption of Cu^{2+} and Cd^{2+} for 34.1 mg $g^{-1}$and 29.9 mgg^{-1} respectively	Complexation and surface adsorption	Li *et al*. 2020
Rice husk	S	550	2h	Hg^{2+}	Removal capacity noticed 73%, was higher than other used	Surface deposition and pore filling	Connor *et al*. 2018

					unmodified biochars		
Peanut shell	Hydrated-MnO	400	1h	Pb^{2+}	Showed higher sorption capacity compared to raw biochar	Complexation, ion exchange and electrostatic interaction	Wan *et al*. 2018
Cotton-wood	layered double hydroxides	180	2h	PO_4^{3+}	Achieved the adsorption (386mgg^{-1}), was greater than used other unmodified biochars.	Surface adsorption	Zhang *et al* 2014
Tomato-leaves	Mg-loaded	600	2h	PO_4^{3+}	Adsorption capacity was 100 mgg^{-1} higher than unmodified biochar	Surface deposition and precipitation	Yao *et al*. 2013
Cotton-wood	$AlCl_3$	600	2h	PO_4^{3+}	Adsorption capacity archived 835 mgg^{-1}	Surface adsorption	Zhang and Gao, 2013
Wood waste	MgO	600	2h	PO_4^{3+}	Adsorption capacity archived 116.4 mgg^{-1}	Surface adsorption and precipitation	Xu *et al*. 2018
Bamboo	Mg/Al	600	2h	PO_4^{3+}	Adsorption capacity archived 13.11 mgg^{-1}	Surface adsorption and anion exchange	Wan *et al*. 2017
Hickory-wood	Aluminum salt	600	2h	Phosphorus	Sorption capacity achieved 8.346 mgg^{-1}	Electrostatic attraction	Zheng *et al*. 2019
Peanut shells	$MgCl_2$	600	2h	NO_3^-	Sorption capacity achieved 94 mgg^{-1}	Surface adsorption	Zhang *et al*. 2012
Wheat straw	Mg/Fe	600	2h	NO_3^-	Adsorption capacity archived 24.8 mgg^{-1}	Anion exchange and surface adsorption	Xu *et al*. 2016
Wood waste	MgO-treated	600	2h	NH_4^+	Adsorption capacity archived 47.5 mgg^{-1}	Surface precipitation	Xu *et al*. 2018

7. Influence of Alkaline-modified biochar on the removal of pollutants

Various authors have focused on alkaline-modified biochar and noted the modification could increase the removal capacity of biochar to pollutants. An *et al*. (2018) conducted a study; the biochar obtained from peanut shell was treated by KOH. Modified biochar showed higher adsorption capacity for nickel reached 88 mg/g^{-1}, it's due to larger number of amine groups found on the surface of KOH-treated adsorbent could form NH_2-Ni with Ni(II) thru complexation and increased the specific surface area after modification, resulting in enhance of adsorption sites. Mu and Ma (2021) carried an experiment, prepared NaOH-treated tea biochar for the removal of orange-II and methylene blue. The maximum removal capacities of modified biochar of orange-II 250 mg/L and 105.27 for methylene blue were noticed, these removal capacities higher than pristine biochar, it might be abundant mesoporous structure appeared after modification and electrostatic attraction made a pronounced contribution to removal of orange-II onto modified biochar. Nguyen *et al*. (2021) demonstrated that the removal performance of NaOH-modified biochar of coffee for tetracycline, the removal capacity of modified biochar revealed 3 times than that un-modified biochar. It might be due to the meso-porous structure and large specific surface area (116.591 m^2 g^{-1}) than un-modified biochar (3.644 m^2 g^{-1}). Removal capacity of enrofloxacin on the KOH-modified corn stalk biochar enhanced by 54.08%, it might be biochar specific surface area, total pore volume increased and blocked impurities in pores of adsorbent were removed after KOH-treatment. The oxygen-enrich functional groups and surface structure of modified adsorbent affected its removal to organic matter (Wang *et al*. 2019). The removal of lead observed significantly greater by dairy manure biochar modified with NaOH, it was higher than unmodified biochar. It due to oxygen-content comprising functional groups, elemental percentage, nitrogen content and ash was remarkably enhanced after NaOH-treatment, this improvement in physiochemical properties played important role in higher removal of lead (Yuan *et al*. 2015. After KOH-modification, the removal rate of methylene blue enhanced expressively, it was increased 30 % more than un-modified biochar, KOH modification efficaciously made holes in walnut shells. After modification treatment, -OH enhanced, showing that after KOH-treatment, the oxygen-enrich functional groups on adsorbent surface enhanced, these changes accelerated the removal capacity (Liu *et al*. 2020). Sodium humate treatment increased the removal rate of methylene blue onto biochars (from 8.62 to 11.03 mg/g and 10.79 to 16.21 mg/g) for white clover residues and peanut shells respectively. Outcomes suggest that removal mechanism of methylene blue onto sodium humate treated adsorbents is controlled by film diffusion and intra-particle diffusion. Possibility of sodium humate to alter the surfaces of adsorbent and improved its removal ability with pollutants (Dou and Jiang, 2019). Huang *et al*. (2017) used KOH-modified adsorbents to eliminate tetracycline. Results exhibited that KOH treatment could decrease or increase tetracycline removal onto adsorbents depending on various pyrolysis temperatures. Maximum removal capacities of tetracycline in treated adsorbent from a low pyrolysis of 300°C increased up to 21 mg/g^{-1} relative to 5 mg/g^{-1} in un-treated adsorbent of 300°C (final TC concentrations were 9 and 26 mg/L^{-1}, respectively). Contrastingly, decreased from 8 and 12 mg/L^{-1} to 5 and 8 mg/L^{-1} in adsorbents from higher pyrolysis of 500°C and 700°C with and without treatment, respectively, even with an enhance in specific surface area. Seo *et al*. (2020) demonstrated that they loaded four alkalis (potassium carbonate, sodium hydroxide, sodium carbonate and potassium hydroxide) to rice biochar and studied the removal properties for hydrogen sulfide. Hydrogen sulfide removal rate of alkaline soaked biochars far better that of coconut shell activated carbon (8 mg/g) and pristine biochar (3 mg/g). NaOH had a higher degree of adhesion onto rice adsorbent and greater hydrogen sulfide removal ability than other three alkaline modified adsorbents. Liu *et al*. (2016) demonstrated that they modified the cotton stalks, corncobs and peanut shells with NaOH for the removal of ammonium. Treated adsorbents exhibited strong removal ability to NH_4^+ in water with fast adsorption kinetics and enormously higher removal capacities. The Langmuir maximal removal capacities of the treated adsorbents were all greater than 250 mg/g, which is similar to that of several other greater efficacy biochars. However, alkaline modifications develop biochars with a greater ratio of surface aromaticity, larger specific surface area. The enhance N/C ratio indicates that more groups comprising nitrogen to which the basic traits of biochar are ascribed are present on treated adsorbent surface. This increases the removal of negatively charged ions and organic contaminants form polluted water. Adsorption capacity of alkaline-modified biochar in the elimination of pollutants in contaminated water (Heavy metals and organic contaminants) displays in table 4.

8. Influence of metal oxides or salts-modified biochar on the removal of pollutants

Scientists have made efforts to develop metal loaded biochars to ensure an effective and better removal of pollutants from polluted water. This technique is employed by various researchers to make high quality biochar for pollutants removal. Fe-modified biochar of corncob obtained at 500°C showed removal capacity for arsenic higher 20 times than pristine biochar. Nitrogen contents in Fe-treated adsorbent exhibited greater values signifying the retention or sorption of nitrates during the modification played important role in removal process (Fristak *et al*. 2016). Jack *et al*. (2019) found that maximum removal amount of 23.9 mg/g was attained of phosphorus by Fe-loaded biochar; it was comprehensively higher than un-modified biochar. Further properties of Fe-treated adsorbents showed adsorption predominantly thru P-OH bonding on adsorbent surface. Agrafioti *et al*. (2014) examined the Fe and Ca modified biochars of rice husk in order to use for elimination of hexavalent and arsenic as (V) from aqueous medium. The modified adsorbents showed great as (V) elimination rate (95%), except for case of rice husk loaded with ferric oxide, whose elimination capability touched only about 55%. All treated adsorbents displayed far outperformed as (V) elimination capacity than non-modified adsorbents. Conversely, the chromium hexavalent removal capacity was not as higher like as (V). The highest chromium hexavalent removal was noticed in case of rice husk adsorbent modified with 2.3% Fe^{3+} whereas the most of the impregnation agents scrutinised did not achieve to increase the biochar's chromium hexavalent removal ability. These findings proposed that the mechanisms of chromium hexavalent and as (V) removal were possibly electrostatic interactions and metal precipitation between the adsorbate and modified biochars. Adsorption capacity of metal-oxide modified biochar in the elimination of pollutants in contaminated water (Heavy metals and organic contaminants) displays in table 4. (Komnitsas and Zaharaki, 2016; Murtaza *et al*. 2021b) found FeCl$_3$-modifed biochars showed enhanced phenol removal efficiency compared to un-modified and commercially available activated carbon. Higher specific surface area and Porosity considered the main criterions that affect adsorbent characteristics after treatment, these changes played vital role in adsorption of phenol from solutions. Mohan et al. (2014) conducted an experiment for examined the removal efficiency of Fe^{2+}-modified biochars of oak bark and oak wood for lead and cadmium. These treated biochars removed cadmium and lead better than non-modified biochars, adsorbing more metal ions than probable based on their SBET values. It might be the organic functional group was established on the surface of bath adsorbents, specific surface area enhanced changes in porosity after treatment leading enhanced the removal of cadmium and lead. Trakal et al. (2016) discussed the lead and cadmium removal efficiency of FeSO$_4$-modifed biochars. Treatment with FeSO4 removal rate was also expressively enhanced, specifically for cadmium removal on plum stone and nut shield biochars (16 and 10 times enhance, respectively). The findings showed that cation exchange was strengthened after modification, which partial the desorbed quantity of cadmium and lead. Contrastingly, the modification of grape stalk adsorbent reduced lead sorption in comparison with that of un-modified biochar. Ferric treatment is, therefore, more effectual for biochars with well- originated structure and for other mobile metals, e.g. cadmium. Cui et al. (2021) investigated the Fe$_2$O$_3$-modifed biochar of bush and peanut shell for the removal of 2, 4, 6-trichlorophenol. Biochar modification enhanced the removal rate of 2,4,6-trichlorophenol, the 2,4,6-trichlorophenol adsorption rate of treated-peanut shell and modified-bush biochar was enhanced by 7.4–38%, and 1.0–11% respectively. These results due to increased pore volume and specific surface area, as well as oxygen and carbon containing functional groups (such as C=O, -COOH, O-C=O) on its surface, which were also linked with the removal behaviour of 2,4,6-Trichlorophenol (2, 4, 6-TCP). Fe2O3 – treated pinewood biochar not only had powerful magnetic trait but also exhibited much higher removal ability for arsenic, likely because ϒ- hematite particles on adsorbent surface assisted as removal sites by electrostatic interactions (Wang et al. 2015). Modification with metal oxides can enhance the cation exchange capacity and change the amount of functional groups of the biochar surface, but the type of pollutant and type of biochar have different effects on the removal capacity of biochar after modification.

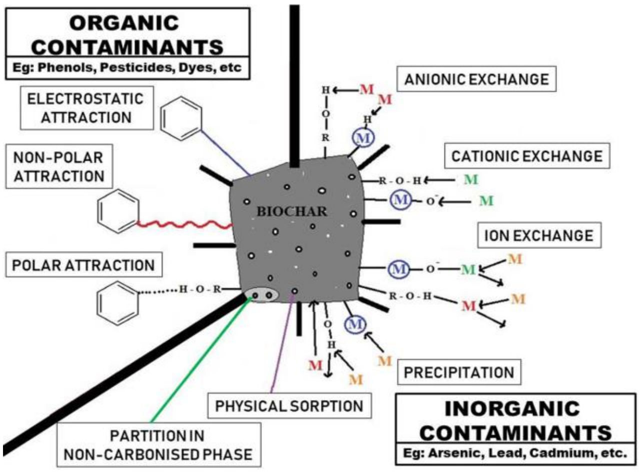

Figure 2. Modified/unmodified biochar possible adsorption mechanisms for inorganic and organic pollutants (adapted from Kumar and Bhattacharya, 2021)

8.1. Factors influencing adsorption

The surface area of the biochar, the type and starting concentrations of the adsorbate, the pH and temperature of the solution, the presence of any interfering compounds and the amount of adsorbent all affect the adsorption rate. In general, adsorption is correlated with the surface area available for adsorption; however, the magnitude varies (Premarathna *et al*. 2019). Because of the improved mass transferring processes, materials with greater pores and surface area typically increase adsorption; however, this also depends on a number of other aspects, including the adsorbate's size, speciation, and chemical makeup. In the case of a composite preparation, overcoating a material may cause pore obstruction, which lowers the pore volume and, thus, the adsorption capacity (Shukla *et al*. 2021).The adsorbent's physicochemical makeup has a significant effect on both the adsorption rate and capacity. Because of their increased surface area, fine powder adsorbents have a higher adsorption capacity than those made of big particles (Amusat *et al*. 2021). Because surface functional groups encourage chemical interactions, it is possible to increase the adsorption capacity by increasing the concentration of the right functional groups; however, depending on the functional group's composition, this may have a detrimental effect. An essential process in the removal of heavy metals is the adsorbent's ion-exchange capacity, which may be improved by the presence of cations or anions on its surface (Sutar *et al*. 2022). The molecular size of the adsorbate influences the adsorption rate and capacity since adsorption takes place inside the adsorbent's pores. If intra-particle mobility governs the rate, the adsorption rate will rise as the molecular weight of the adsorbate molecules decreases (Fang *et al*. 2020). Furthermore, pH directly affects the adsorbate's ionization or speciation as well as the chemical form of the contaminant and surface charge, all of which have a significant impact on the adsorption process. A material's incorporation during the composite's creation may have an impact on pHpzc (Ambika *et al*. 2022). Because adsorption reactions are exothermic; their temperature dependence means that they usually increase as temperature rises. Furthermore, the presence of organic or inorganic molecules that interfere might have a favorable or negative effect on adsorption. In addition, depending on the characteristics of the adsorbate, the presence of natural organic matter may have a favorable or negative effect on adsorption. According to a study, cadmium ions (Cd^{2+}) neutralize the surface of BC, which affects SMX adsorption (Biswal *et al*. 2022; Murtaza *et al*. 2022b). Competitive adsorption between several chemicals often takes place at the solid–water interface, where it might affect the adsorbent's affinity and sorption properties for each pollutant. The adsorption of carbaryl (CBL) on the original BC (made at 600 and 700 °C) is strongly inhibited by the presence of oxytetracycline (OTC), suggesting a competitive impact between OTC and CBL adsorption (Premarathna *et al*. 2019).

9. Conclusion and future direction

The development of approaches to modify biochars to improve their various contaminants sorption capacity or to magnify the breadth contaminants that they can be eliminated from water system is in its infancy. Acidic and alkaline treatment of biochar can enhance the specific surface area and enhance the abundance of oxygen and carbon-enrich functional groups to increase adsorption. Loading the metal oxide or salts on biochar surface can modify the attributes of the surface by generating metal-based biochar, facilitating the removal of various pollutants from aqueous medium. Researches into metal-loaded adsorbents have been developed by embedding various metal oxides to enhance the removal capacity. The removal performance and physiochemical traits of biochars are affected by metal-loading, acidic and alkaline treatment. Applying modified biochar to polluted water has been substantiated to be effective tool to amend the water systems. The removal mechanisms of the pollutants include pore-filling H-bonding, cation/p/π–π interactions, hydrophobic interactions, electrostatic and interactions. Based on this review literature, aspects outlined below require more study before prior to attaining the operational application of the modified biochar to amend the contaminated water and minimize the knowledge gap in this field:

- To accomplish large-scale water remediation applications, it is essential to conduct in depth examination on the biochar modification, associated toxicity, desorption of adsorbed contaminants in fluctuating environmental conditions.
- And the removal efficiency of aged biochar by artificial methods such as dry-wet method and freeze thaw cycles should be studied as well as desorption of pollutants should be investigated. Because due to these aging methods biochar significantly changes in physiochemical properties it could be cost effective and cheap adsorbents for the pollutants removal from water system.
- Compared to unmodified biochars, modified biochars showed higher removal effect for the pollutants in water system. Though, extensive research is needed to verify the superiority and efficacy of modified-biochars in eliminating pollutants from water system. The momentous binding of pollutants onto biochar decreases desorption of the adsorbed materials. Consequently, it has an effect on the re-usability of used biochar. Biochar functionalization is required to reduce the binding energy of adsorbed contaminants on biochar, hence raising the de-sorbability and recyclability of used adsorbent, specifically for removing contaminants in unclean water, where it is highly desirable to reuse consumed biochar.
- The review confronts an inclusive understanding of the biochar modification with acid, alkaline, metal oxides and their potential applications in removing pollutants from water. We expect that extended studies concentrated on mitigating the existing constraints would enable more people to adopt modified biochars to protect the environment sustainably.

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