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# Functional Biochar and Its Balanced Design

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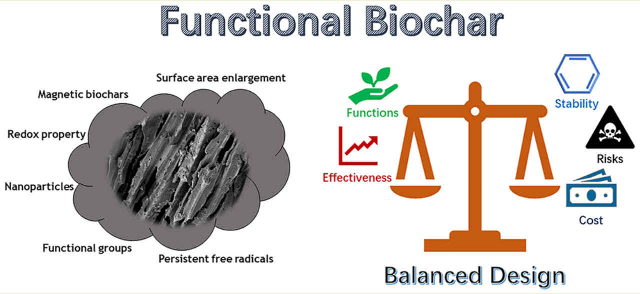
ABSTRACT: Biochar has attracted increasing research attention. Various modification methods have been proposed to enhance a certain biochar function. However, these modifications may also result in an unstable structure, additional energy consumption, secondary pollution, and/or extra cost. Balanced consideration of different aspects will ensure the sustainable development of biochar technology. This review first summarizes the most commonly used methods for biochar modification. These methods are categorized according to the purposes of modification, such as surface area enlargement, persistent free radical manipulation, magnetism introduction, and redox potential enhancement. More importantly, a systematic analysis and discussion are provided regarding the balanced consideration of biochar designs, such as the balance between effectiveness and stability, functions and risks, as well as effectiveness and cost. Then, perspectives regarding biochar modification are presented. This review calls for attention that biochar modifications should not be evaluated for their functions only. A balanced design of biochars will ensure both the practicability and the effectiveness of this technology.



KEYWORDS: *Soil remediation, Regeneration, Stability, Risk, Effectiveness*

## 1. INTRODUCTION

Biochar, a type of aromatic carbon-enriched solid material, can be produced through pyrolysis with limited oxygen. Many types of organic materials, including agricultural biomass and municipal solid wastes, can be used as feedstock to prepare biochar. Considering the ubiquitous presence of feedstock and the low cost of biochar production, the application of biochar has attracted a great deal of research attention. High carbon content and cation exchange capacity, large specific surface area (SA), and stable chemical structure of biochar enable their wide application in many environmental fields, including soil remediation, wastewater treatment, and carbon sequestration.[1] Although biochar has tremendous application potential, the pristine biochar can be modified to optimize its practical application. For example, biochar can be modified with magnetic particles to benefit its separation from the solution and promote its environmental application.

Researchers have developed and used many modification methods to optimize the physical and chemical properties of biochar in order to meet different environmental application requirements, including acid or alkali treatment, oxidization, and metal modification. However, these modifications could change various properties of biochars, which may also include some shortcomings and limit their sustainable application. Therefore, modification strategies need to be carefully evaluated and compared to balance different issues and functions. For example, biochar could be purposefully modified by nanoparticle (NP) decoration or addition of functional groups to introduce more reaction sites; however, these modifications may also reduce the surface area and accessibility of active sites because of the pore blocking after modification. Thus, the reactivity of the modified biochar (MBC) will not be necessarily enhanced if the modification efficiency is not high enough. Another example is that environmental risk could also be increased along with the enhanced functional properties. Biochars with increased reactivity may pose unexpected toxic impacts to the organisms in a setting where these biochars are applied.[2] In addition, various modification methods were proposed, with some being very expensive. The application value of the MBCs should be evaluated based on both their cost and effectiveness.

Though many review articles have summarized the modification techniques and their corresponding applications, investigators seldom analyzed the balance between biochar functions and their costs, including both financial and environmental costs. This work provides a critical review through a systematic evaluation of MBCs and their modification methods. Considering the multiple application potentials of biochars, this review mostly focuses on biochar

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Table 1. Surface Area Enlargement Performance of the Modification Methods Mentioned in This Review

| | Modification | Pyrolysis temperature (°C) | SA before modification | SA after modification | Enhancement rate | ref |
|---|---|---|---|---|---|---|
| Before pyrolysis | Clay impregnation | 450 | 2.3 | 26.2 | 11.4 | 4 |
| | Acid modification ($H_3PO_4$) | 650 | 51 | 802 | 15.7 | 5 |
| | Acid modification ($H_3PO_4$) | 441 | 12 | 102 | 8.5 | 6 |
| | Acid modification ($H_2SO_4$) | 800 | 76 | 140 | 1.8 | 7 |
| | Acid modification ($H_2SO_4$) | 500 | 34 | 47 | 1.4 | 8 |
| | Alkali treatment (KOH) | 450 | 589 | 2183 | 3.7 | 9 |
| During pyrolysis | $CO_2$ activation | 800 | 486 | 1365 | 2.8 | 10 |
| After pyrolysis | HCl washing | 600 | 58.7 | 88.4 | 1.5 | 11 |

applications in pollutant removal. We first summarize the modification techniques and then address issues that researchers should consider when designing functional biochars. We emphasize that biochar is considered a cost-effective and environmentally friendly material. The biochar modifications should maintain these advantages even with their enhanced reactivity.

## 2. FUNCTIONALIZED BIOCHARS AND THEIR MODIFICATION TECHNIQUES

Biochar could be modified by various methods to respond to different application purposes. A brief summary here is to facilitate the following discussion on the balanced design of biochars. For the technical details, it is suggested that readers refer to other reviews specifically focusing on biochar functionalization.[3]

### 2.1. Surface Area Enlarged Biochars

Generally, the surface area of biochar can be increased by various treatments before, during, and after pyrolysis (Table 1). The enlarged surface area of biochar can promote its adsorption performance and consequently the application in the adsorption-related area, such as soil remediation/amelioration and wastewater treatment. In addition, the increased surface area could provide more effective sites for surface coating or complexation, typically when biochars are used as the carrier to increase the stability and thus the reactivity of catalysts.

The surface area of biochar can be enlarged with the mixture of minerals such as montmorillonite and bentonite, followed by pyrolysis.[1] The increased surface area is partially due to the large surface area of the minerals. Also, the minerals could catalyze the pyrolysis, which increases the surface area and pore volume of the biochar. However, when the pyrolysis temperature increases to 500 °C, the enhanced recondensation of volatile organic compounds on the biochar surface may block the pores of the biochar and lead to a surface area decrease.[4] Moreover, the apparent surface area of the biochar may be higher after being mixed with nanomaterials, such as carbon nanotubes and graphene.[12]

An increase of surface area and micropore volume was observed by impregnating biochar with acid. For example, $H_2SO_4$ treated bone biochar increased the surface area by 83% compared to the control,[7] mainly due to the removal of the inorganic compositions, such as $CaCO_3$ and hydroxyapatite in the bone char. Besides the removal of inorganic compositions, P−O−P bond formation in biochar after $H_3PO_4$ treatment can decrease the energy required for biomass decomposition and promote swelling and amplification of the amorphous biochar structure, increasing the surface area and micropore volume of biochar.[5,6]

In addition, the surface area of biochar could be enlarged by alkali treatment of the feedstock before pyrolysis. The preloaded KOH and NaOH could react with the surface carbon structure during pyrolysis, which consequently opens the blocked pores and enlarges the diameter of small pores.[13] For example, KOH activation followed by pyrolysis increased the surface area and Cd adsorption capacity of biochar.[14]

During pyrolysis, the increase of the pyrolysis temperature could lead to the development of microporous structures and an increase of the surface area. It was reported that new micropores were produced and mesopores were broadened when the pyrolysis temperature increased to greater than 500 °C;[15] however, a further increase in temperature may also lead to a decrease of the total pore volume and surface area due to the collapse of the porous structures.[16] In addition, the biochar surface area may be increased by steam treatment during pyrolysis, which promotes partial devolatilization and crystalline carbon formation in the biochar[17] or removes the trapped products of incomplete combustion.[18] Biochar surface area could also be increased by $CO_2$ purging during pyrolysis because of the formation of more micropores with $CO_2$ activation.[10,19] The reason is that $CO_2$ could react with the surface carbon structure, accompanied by CO release and pore formation.

Alternatively, biochar surface area may be enhanced through HCl treatment after pyrolysis because of the removal of the inorganic fraction and solvable organic carbon associated with these inorganic fractions.[11,20] Alkaline treatment has similar modification impacts by removing organic matter from the pores of biochar.[20] These acid or alkaline modifications are generally followed by pH neutralization to ensure the following applications. It is noted that both acid and alkaline treatments could release various chemicals. Therefore, the potential environmental risks of the released chemicals and particle recovery of these treatments should be carefully evaluated.

Although the surface area can be enlarged through these treatments, these additionally exposed surface areas may not have any selectivity to some specific pollutants. Considering the ubiquity of different contaminants in the environment or wastewater treatment systems, enhancing the selectivity of the biochar surface area is also a challenging research area. Moreover, special attention should be paid to the pore distribution altered by modifications, which could influence the accessibility of the surface area to the contaminants. For example, $H_3PO_4$ treatment (impregnation ratio of 0.72) increased the surface area of sawdust biochar from 51 to 802 $m^2/g$, with the major pore distribution changed from mesopores to micropores.[5] However, $H_3PO_4$ treatment with the higher impregnation ratio (1.96) reduced both the micropores and mesopores of the biochar.[7] $H_2SO_4$ treatment

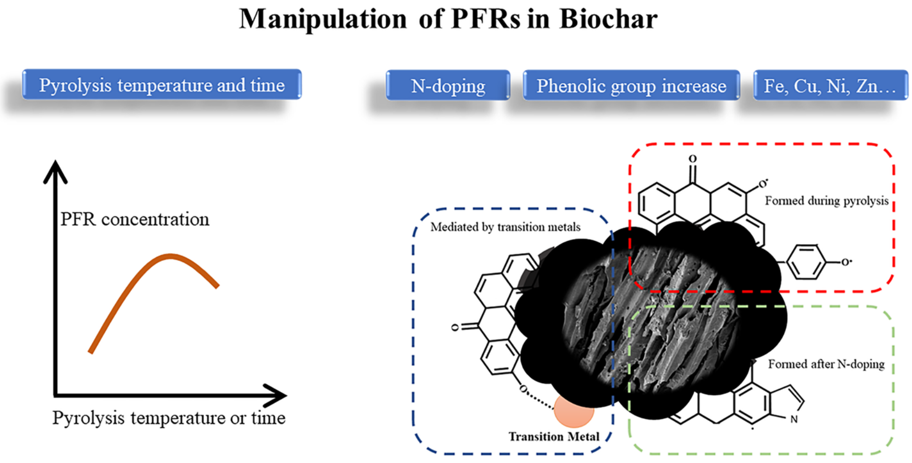

**Figure 1.** Different PFR manipulation methods that have been summarized in this Review.

with the same impregnation ratio (1.96) created more micropores and destroyed the mesopores.

### 2.2. Persistent Free Radical Manipulated Biochars

Recent studies have confirmed the presence of strong and stable electron paramagnetic resonance signals in biochars, categorized as persistent free radicals (PFRs). Compared with other free radicals, PFRs can last for up to several months in ambient air. Organic contaminants can be degraded by free radicals such as hydroxyl radicals or sulfate radicals activated by PFRs[21] or even by direct contact with PFRs,[22] which shows great potential in environmental remediation. However, because of their reactivity, biochars may also pose risks to the environment or even to human health. Therefore, manipulating the PFRs of biochar is critical to both remediation application and risk control.

Pyrolysis temperature and duration time are critical factors to influence the intensity and type of PFRs. The oxygen-centered radicals were predominant at low pyrolysis temperature but were gradually converted to carbon-centered PFRs with increasing pyrolysis temperature and time.[2] However, PFR intensity was not always increased with pyrolysis temperature. For example, the PFR intensity of pinewood biochar decreased when the pyrolysis temperature increased from 500 to 700 °C (Figure 1).[22]

Although the formation mechanism of PFRs during pyrolysis is still not thoroughly illustrated, the concentration, type, and lifetime of PFRs in biochar can be manipulated by loading metals or metal oxides, N-doping, and incorporation of functional groups. For example, the PFR intensity in N-doped biochar is predominantly derived from the pyrrolic-N rather than other heterocyclic-N.[23] PFRs of biochar can also be enhanced by increasing phenolic compounds, including hydroquinone, catechol, and phenol.[24]

Metal loading such as $Fe^{3+}$, $Cu^{2+}$, $Ni^{2+}$, and $Zn^{2+}$ can promote PFR formation in biochar.[24] These metal ions can accept electrons from phenolic compounds, leading to the formation of PFRs (Figure 1). The types and nature of PFRs as affected by the transition metals were also extensively studied. The decreased $g$-factors of PFRs with metal ions suggested that the types of PFRs transformed from carbon-centered to oxygen-centered radicals.[24] For example, phenoxyl-type radicals with $g$-values of 2.0024−2.0040 and semiquinone-type radicals with $g$-values of 2.0050−2.0065 were formed with $Fe_2O_3$ addition, while phenoxyl-type radicals with $g$-values of 2.0029−2.0044 and semiquinone-type radicals with $g$-values of 2.0050−2.0081 were formed with NiO addition.[25]

The types and locations of PFRs in biochars are diverse, and thus, they may have different accessibility and reactivity. A very important aspect of PFRs in biochars is their persistence, which is only reported in several limited studies. For transition-metal-mediated PFRs, their lifetimes are determined by the associated metals, possibly correlated with their reduction potentials.[25] For PFRs generated in the organic matrix, the aromatic structure of biochar may be beneficial in increasing the PFR half-life by stabilizing the resonance of the unpaired electrons.[26] A more complicated situation is that PFR lifetimes could be altered by environmental factors, including oxygen content, humidity, and organic matter. For example, during PFR formation, $Fe^{3+}$ was reduced to $Fe^{2+}$, which is highly solvable. If water molecules are involved in the system, the dissolution of $Fe^{2+}$ may result in a quick dissipation of PFR signals. Thus, the stability of the manipulated PFRs in biochar needs to be extensively assessed especially under their application situations.

### 2.3. Magnetic Biochars

Biochar has shown its potential to be an effective adsorbent for pollutant removal. However, it is difficult to separate the powdered biochar from an aqueous solution. To facilitate the separation of biochar and promote its practical application, magnetic biochar could be produced by incorporation with magnetic elements or oxides.

Magnetic biochar is mainly produced by three methods, namely, impregnation + pyrolysis, pyrolysis + precipitation, and hydrothermal method (Table 2). Preloading of a transition

**Table 2. Feedstock and Preparation Method of Magnetic Biochar**

| Feedstock | Method | ref |
|---|---|---|
| Biomass, Fe(Mn) salt/oxide | Impregnation + pyrolysis | 29 |
| | Pyrolysis + precipitation | 30 |
| | Hydrothermal method | 31 |
| | Ball-milling | 32 |
| | Electrodeposition + pyrolysis | 33 |
| Fe-containing residue/sludge | Impregnation + pyrolysis | 34 |
| | Pyrolysis + precipitation | 35 |
| | Hydrothermal method | 36 |
| Biomass, Fe(Mn) salt/oxide, chitosan | Cross-linking | 37 |

metal followed by subsequent pyrolysis is a generally adopted method for magnetic biochar production.[27] Specifically, the biomass is first impregnated in the solution with transition metals; the particles are then collected, dried, and pyrolyzed under an oxygen-limited atmosphere. Magnetic biochar can also be synthesized by pyrolyzing a mixture of hematite mineral and biomass to incorporate $\gamma$-$Fe_2O_3$ on the biochar surface.[28] The pyrolysis + precipitation method was also used to produce magnetic biochar. Briefly, biochar is dispersed in a solution containing transition metals, followed by the addition of sodium hydroxide, ammonium hydroxide, or reducing agents (sodium borohydride or potassium borohydride) after stirring and centrifugation. The supernatant is removed, and magnetic biochar is obtained after washing and drying the residue. Lastly, in the hydrothermal method, the biomass and transition metal solution are reacted in a reaction kettle at a lower temperature than that used for pyrolysis. The biomass and Fe/Mn salts or oxides were the primary feedstock for magnetic biochar production. Some iron-containing residues could also be used as feedstock.

Besides the above common methods, investigators also tried other techniques to produce magnetic biochar. For example, magnetic corn straw biochar was fabricated under an electric field to embed $Fe_3O_4$ NPs.[33] Ball-milling[38] and cross-linking[37] of mixtures of biochar and iron oxides were also developed to produce magnetic biochar.

Generally, magnetic biochars are used for adsorbing various pollutants,[39] catalyzing the degradation of organic contaminants while using persulfate or hydrogen peroxide as activating agent,[40] and mediating methane generation or organic pollutant removal in an anaerobic digestion reactor.[41] The benefit of magnetic biochars is the easy separation, facilitating the following pollutant treatments and biochar regeneration. At present, different techniques, including with hydrochloric acid, sodium hydroxide, chelating agents, and organic solvents, are used for magnetic biochar regeneration.[39] This regeneration needs to be evaluated for both the reactivity and magnetism of magnetic biochar. For example, the magnetic compositions may be dissolved or dissociated from biochar via acid/basic treatment or physical disturbance. The organic structures of biochar could be altered after the release of dissolved organic matter during biochar application, which could also result in the loss of magnetic compositions. The regeneration methods need to be strong enough to remove the adsorbed pollutants but weak enough to retain the biochar-magnetism complexes. Therefore, the selection of regeneration methods is highly dependent on our understanding of the interactions between biochar and magnetic compositions, which demands further study.

### 2.4. Biochars Enhanced with Redox Property

Redox reactions play a critical role in natural and engineered systems. For example, toxic heavy metals, such as arsenic (As) and chromium (Cr) in soil and sediment, can be reduced or oxidized through redox reactions, which consequently alters their fate and toxicity.[42] The reduction of nitrate to nitrous oxide leads to nitrogen loss in soil.[43] The redox reactions mediated by biochars can also accelerate the degradation and biodegradation of organic contaminants. The reason is that biochars may act as electron donors and acceptors and support chemical or microbial reduction and oxidation of contaminants. For example, electrons can be transferred to or retrieved from biochar by *Geobacter metallireducens* GS-15 during the oxidation of acetate and reduction of nitrate, respectively.[44] The larger electron exchange capacity of biochar derived from pine wood was associated with the higher degradation of *p*-nitrophenol.[45] In addition, the electron shuttle ability of biochar could mediate the electron transfer involved in the environment-related redox reactions. For example, it was reported that the microbial reduction of Cr(VI) was accelerated by biochar due to its electron shuttling ability.[46] In addition, biochar could mediate the chemical reduction of Cr(VI) as an electron shuttle.[47,48]

The redox activity of biochar mainly derives from certain surface functional groups and redox-active metals. A variety of modification strategies can be applied to adjust the redox activity of biochar. Phenolic and quinoid moieties have been recognized as the main functional groups responsible for biochar electron donating and accepting abilities.[49] At pyrolysis temperatures below 600 °C, a linear correlation was observed between electron the donating capacities and phenol contents of biochars.[50] Thus, to enhance the redox activity of biochar, the quantities of these surface functional groups should be selectively increased. $KMnO_4$ treatment and the modified Hummer's method are effective modification methods to increase the electron exchange capacities of biochar.[49] Oxidants such as $H_2O_2$ can also introduce redox-active functional groups on the biochar surface.[51] At pyrolysis temperatures above 600 °C, electron donating capacities of biochar were dominated by the conjugated $\pi$-electron system associated with the aromatic structure.[50]

Besides the specific surface functional groups and aromatic structure, redox-active metals such as manganese and iron oxides in biochar can also increase the redox potential as electron acceptors.[52]

Because the redox potentials of biochars may be related to different structures or locations of redox active sites, the effectiveness of their reaction with contaminants or organisms could be extremely different. To date, investigators have rarely evaluated the overall effectiveness of the redox potential in biochar application, and a quantitative parameter to describe this effectiveness is missing. Several studies have confirmed that the electron-donating and -accepting abilities of biochars are rechargeable.[53] Currently, the redox activities of biochar are quantified through electrochemical or chemical methods. For example, the electron donating or accepting capacity of biochar could be measured in a three-electrode system with electron mediators in the solution.[53] Cyclic voltammetry could measure the redox activity of biochar functional groups by calculating the charging and discharging rate constant.[54] Alternatively, a chemical method was also developed to measure the electron storage capacity through chemical oxidation and reduction reactions.[55] Although the above methods could estimate the redox activity of biochar, how to properly develop a pollution treatment process to use the rechargeable properties fully is still unknown.

### 2.5. Biochars Enriched with Functional Groups

Pristine biochar contains a certain amount of surface functional groups like C−O, C═O, and −OH.[56] Many studies have indicated that these functional groups on the biochar surface are responsible for contaminant removal, such as heavy metals and organic ionic compounds.[57] Therefore, a great deal of research attempted to manipulate the type and amount of surface functional groups to further enhance the pollutant removal performance.[1,58] Treatments before or after pyrolysis are used to introduce specific functional groups through surface oxidation, surface amination, P−O−P insertion, and surface sulfonation.

Surface oxidation is generally accomplished through chemical oxidation using $H_2O_2$, $KMnO_4$, $HNO_3$, or a $HNO_3/H_2SO_4$ mixture.[59] $H_2O_2$ oxidation is commonly used after pyrolysis. The increased carboxylic groups on the biochar surface could increase the cation exchange capacity and decrease the pH of MBC.[60] A previous study showed that the adsorption capacity of $Pb^{2+}$ increased from 76.4 to 169.6 mg/g after $H_2O_2$ modification of a yak manure biochar.[61] Their FTIR results showed that C═C on the biochar surface was oxidized to C═O by $H_2O_2$, which is responsible for $Pb^{2+}$ removal. Carboxylic functional groups can also be introduced on the biochar surface through citric acid and oxalic acid modification.[62,63] These organic acids are rich in carboxyl groups and thus could react with the hydroxyl groups on the biochar surface through esterification.[62] Biochar derived from sawdust showed a high adsorption capacity to methylene blue (178.6 mg/g) after being modified with citric acid.[64] However, $H_2O_2$ modification led to an overall decrease of methylene blue removal from solution.[60] This phenomenon was attributed to the weakened $\pi-\pi$ dispersive forces due to the introduction of the oxygen functionality on the aromatic structure. Therefore, the introduction of oxygen-containing functional groups may not always be effective in increasing biochar sorption properties. The modification effectiveness is highly dependent on the type of biochars and the target pollutants.

Amination of the biochar surface is generally initiated by $HNO_3$ oxidation, with both oxygen and nitrate functional groups introduced on the biochar surface.[65] The nitrate group can be further reduced by the amination process.[66] This $-NH_2$ enriched MBC showed great selective adsorption to Cu(II) even at pH 3, which is due to the low electron densities of Cu(II), which could complex strongly with the amino groups on the biochar surface. The $-NH_2$ groups can also be introduced through one-step heating of $FeCl_3$ laden agar under a $NH_3$ environment.[67] The −OH group in agar power could react with $NH_3$ to produce amino groups. In acid conditions, protonation of these $-NH_2$ groups leads to an increase in $-NH^{3+}$, which contributes to the electrostatic interaction with $HCrO^{4-}$. In addition, the content and chemical species of the doped-N can be tailored by controlling the annealing temperature and time.[68] For example, N species were mainly pyridine-N, pyrrolic-N, and oxidized-N at pyrolysis temperatures of 600−700 °C and were graphitic-N at pyrolysis temperatures higher than 800 °C. Graphitic-N could dramatically increase cation−$\pi$ interactions and promote electron transfer inside the biochar matrix,[69,70] which is beneficial for heavy metal or organic contaminant removal. It is worth noting that N-doped biochar could also be produced from high N content biochar (e.g., protein), but toxic HCN gas would be released during pyrolysis.[71] This toxic gas can definitely pose serious environmental risks.

$H_3PO_4$ treatment of biomass could introduce a P−O−P bond in the carbon structure, which may lead to carbon dilation, amplification of the amorphous form, and lattice defects of the C structure, which are responsible for micropore formation. Research results showed that the specific surface area and total pore volume of $H_3PO_4$ treated MBC were both increased over 10 times.[72] Moreover, the cross-linking of P−O−P and C bonds could enhance the C retention in the organic structure, which greatly increased the yield of MBC.

Sulfonic acid groups can be introduced through concentrated sulfuric acid (~98%), fuming sulfuric acid, or gaseous $SO_3$.[73] Previous studies showed that sulfonated biochars can effectively catalyze transesterification of vegetable oils and esterification of free fatty acids and the catalytic reactivity increased with the density of sulfonic functional groups.[74] Thus, sulfonated biochars show promising potential to be used as cheap and robust heterogeneous acid catalysts in the production of biodiesel.

The aim of introducing functional groups onto biochars is to expand MBC applications and enhance the effectiveness of pollutant removal. However, because chemical modifications were involved, other properties of biochar could also be altered, such as surface area, surface charge, redox potential, PFR, and even particle size. These changes may not always be beneficial for pollutant removal. For example, the introduced oxygen-containing functional groups may increase the wettability of the biochars and the formed water molecule clusters may block the pores, which greatly decreases the effective surface area and sorption. Thus, biochar property changes need to be thoroughly evaluated for pollutant removal. In addition, studies seldom determined the stability of the introduced functional groups. It is still unknown how long the MBC could be effective as designed.

## 2.6. NP Decorated Biochars

NPs could be decorated on biochars through coating or in situ NP formation.[75] The resulted composites displayed great improvement in contaminant removal due to either the catalytic properties of the coated NPs or the increased surface sites provided by the NPs.[76] The coated NPs include metal oxides (such as MgO, $\gamma$-$Fe_2O_3$, $CaCO_3$, and $MnO_2$), carbonaceous NPs (such as graphene oxide, carbon nanotubes, and fullerene), elemental metal (such as zerovalent iron), as well as metal sulfide (e.g., FeS).[77]

The porous structure of biochars makes NPs be well dispersed on the biochar surface, which greatly enhances the effective surface area. Yan et al. showed that the zerovalent iron NPs (nZVIs) can activate persulfate to degrade trichloroethylene (TCE) up to 62.3%.[78] Biochar (BC) can also activate persulfate and lead to 25.3% TCE degradation. When nZVI/BC composites were used, TCE degradation reached up to 99.4%. nZVI/BC composites showed an obviously higher degradation ratio than the sum of two individual particles. The relatively high reactivity of nZVI/BC was attributed to the well dispersed and distributed nZVI particles across the BC surface. For the same reason, NP-biochar complexes showed effective adsorption to phosphate, nitrate,[79] heavy metals,[80] organic contaminants,[81] and inorganic nutrients.[82]

Besides the dispersion of NPs by biochars, the redox properties and electrical conductivity of biochar can promote the reactive or catalytic properties of the introduced NPs. For example, biochars loaded with nZVI exhibited high Cr(VI) removal (96.2 mg/g) in a wide pH range.[80] Both the coated nZVI and the surface functional groups of biochars could reduce Cr(VI) to Cr(III), which would drastically facilitate Cr(VI) removal. Lu et al. demonstrated that a $TiO_2$-biochar composite exhibited higher catalytic activity than that of pure $TiO_2$.[83] This improved catalytic property was due to the synergistic effect of biochar and $TiO_2$. The biochar acted as a channel to transform photoelectrons to prevent the recombination of hole−electron pairs and promote charge separation. Another study also showed that the immobilization of CuO and $Cu_2O$ using biochars could decrease the band gap of photocatalysts by trapping electrons in the conduction band.[84]

Considering that most chemicals tend to concentrate at the interface by adsorption, the possibility of contact between contaminants and NPs is clearly enhanced on the biochar surface, which facilitates the subsequent reactions between the contaminant and the decorated NPs.[1] The reactions at the interface may be further enhanced by adjusting the point of zero charge. The positively charged NPs may increase the adsorption of negatively charged ions (such as phosphate and nitrate) or organic chemicals (such as pharmaceuticals) on the negatively charged biochars. The subsequent separation or redox reactions may ensure good removal of these adsorbed contaminants.[82]

Although NP decorated biochars have shown great potential in pollution removal and control, two concerns need to be carefully evaluated. (1) The particle−particle associations lead to a general concern about their stability. The surface-decorated NPs may be partly dissolved or dissociated during their application. Thus, a parameter to assess the stability of NP decorated biochars is very helpful. Investigators may need to develop a well-described wearing or aging process to obtain this parameter. (2) Both NPs and biochars have sorption or catalytic activities. This modification is meaningful only when NPs and biochars have a synergistic effect. Thus, the function of NP decorated biochars should be examined after comparing the summed functions of NPs and biochars.

Although the functionalized biochars were classified into six types in this review, some modification technologies may change different properties simultaneously. For example, acid treatment of biochar could increase the surface area and create new functional groups on the biochar surface, and the combined effect of the surface area and functional groups improved the metal adsorption on the biochar.[5] Moreover, the modification of iron oxide can improve the magnetic property and redox activity of the functionalized biochars, both of which are beneficial for biochar application in wastewater treatment. However, NP decoration may block some pores in the biochar and decrease the active surface area. In addition, both PFRs and functional groups may be altered during modification. Therefore, biochar property changes should be thoroughly evaluated for a specific modification method to increase the positive effect and decrease the adverse effect.

## 3. A BALANCED APPROACH TO DESIGNING BIOCHAR

### 3.1. Balance between Effectiveness and Stability

Since biochar is more stable than its feedstock, it has great potential in carbon sequestration. However, recent studies have shown that the structure and properties of biochars can be changed after they enter the environment. The aging process of biochars is always associated with mechanical fragmentation, surface oxidation, organic matter release, and mineral dissolution.[85] Although many studies showed the successful modification of biochars, very few mentioned how long the effectiveness of MBCs in removing pollutants can be sustained after their application. For MBCs, two aspects should be evaluated regarding their stability.

(1) The persistence of their functions, or more specifically, the effectiveness in pollutant removal needs to be carefully evaluated. MBCs are known for their great adsorption affinity to various contaminants from aqueous solutions. Liu et al. indicated that carbon nanotubes (CNTs) or graphene oxide (GO) modified biochars had a higher heat resistance compared to the pristine biochars based on their thermogravimetric analysis profiles, which is attributed to the stable structure of CNTs or GO.[86] Meanwhile, the excellent sorption ability of these carbon NPs on MBCs made the MBCs effective in removing heavy metals. However, the stability of the coated NPs on biochar was not specified in this work, which made it difficult to judge whether the removal efficiency of this biochar is effective over time. A similar problem could be noted in other studies.[87] Therefore, a detailed and effectiveness-oriented stability assessment of MBCs is urgently needed.

(2) The stability of the carbon structure is affected by modification. First, part of the carbon structure may be destroyed during the modification, and thus, the yield of the MBC should be carefully evaluated. Considering the carbon loss and the energy consumed, the MBC may not be carbon negative any longer. Second, modification may introduce some structures or functional groups that could be easily oxidized when compared to the pristine biochars (Figure 2). Specifically, when some compositions with active catalytic properties were introduced to form the MBC, the carbon structure may be quickly degraded along with the contaminants. Third, the stability of the biochar structure may determine the carbon sequestration ability of the biochar, which should also be evaluated after the modification. For example, the addition of minerals, including kaolin, $Ca(H_2PO_4)_2$, and vermiculite, could enhance the stability of the biochar.[88,89] Moreover, $H_2SO_4$ modification improved the biochar stability in terms of both chemical oxidation and thermal oxidation.[90] The enhanced stability of the biochar might be due to the enhanced aromaticity. On the other hand, $CO_2$ activation and magnesium impregnation could decrease the stability of the biochar because of the formation of surface oxygen functional groups.[90,91] Long-term analysis is needed to determine if the modified biochar meets the aim of carbon neutralization.

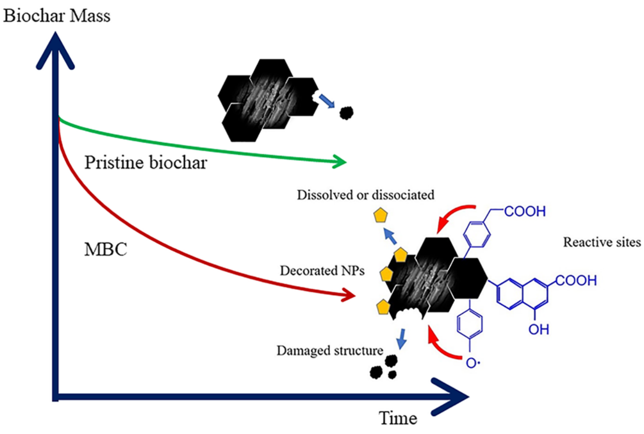

**Figure 2.** Biochar carbon structure stability as affected by modification. Biochar structures can be less stable after modification.

### 3.2. Balance between Desired Functions and Risks

The major purpose of biochar modification we discussed in this Review is to improve the pollution removal performance, but the risk related to the whole life cycle of modification has not been properly addressed (Figure 3). It is essential to develop sustainable and green biochar modification methods

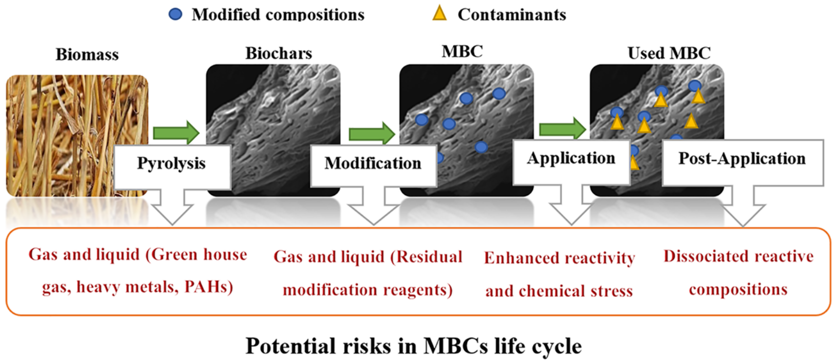

**Figure 3.** Diagram of potential risks from MBCs. The risks of MBCs should be evaluated in their different manufacturing and application stages.

to minimize the environmental risks and maximize social and economic benefits.[77] During the manipulation of biochar functions, their risks should be carefully evaluated in the following aspects:

(1) The reactivity of biochars may pose chemical stress to organisms. These chemical stresses (such as their redox-related reactivity) may be enhanced after modification. PFRs in biochars not only can produce reactive oxygen species but also have strong oxidation activity themselves. They are typically formed in the pristine biochar matrix, and they could be enhanced after modification. For example, PFRs in biochar were changed from carbon-centered radicals to carbon-centered PFRs with an adjacent oxygen atom after modification by $Fe_3O_4$ particles. These MBCs demonstrated an increased reduction activity and showed a higher Cr(VI) reduction potential.[92] A small amount of added metal (around 0.1 mM) could significantly increase the PFR concentration in MBC, which could in turn enhance the activation of reactive oxygen species for the degradation of contaminants.[93]

(2) The chemicals released from MBCs, such as NPs, heavy metals, and even organic compounds, may pose some unexpected risks. A great deal of studies confirmed that the NPs or metal oxides/hydroxides were successfully loaded on biochar, but most of them did not clearly demonstrate what chemical bonds were formed between the introduced NPs and biochars, nor did they show if metal ions could be dissolved into the environment. Because of this missing information, we are not able to clearly evaluate if the complex chemical compositions could be released to pose risks to the environment.

(3) The chemicals involved in BC production may have some toxic impacts. For example, sodium borohydride ($NaBH_4$) is a toxic compound, which was often used to form nZVI. After nZVI is generated on biochars and the synthetic composites are used to treat contaminated water and soil, the leftover manufacturing waste might become another environmental concern. The concentrated acid, base, and unattached NPs left on the MBC surface after modification might also pose environmental risks. Without proper treatment, these chemicals could directly change the local pH and redox potential and pose ecotoxicity where they are applied. In addition, some gases, such as CO, $CH_4$, $NO_2$, $SO_2$, and volatile organic compounds, could be released during biochar production and may threaten human health without appropriate treatment. Thus, gaseous products should be carefully treated through either adsorptive removal or utilization as energy sources.

The "green" fabrication method was encouraged to reduce the risk during biochar production. The nontoxic agents should be given more consideration to substitute some toxic agents such as methanol and $NaBH_4$ for modification. For example, the extracts from banana peels could replace $NaBH_4$ for nZVI loading on the biochar surface.[94] Furthermore, modification methods without toxic agents such as mineral modification and ball milling should be given more attention.[95,96]

## 3.3. Balance between Effectiveness and Cost

From an economic point of view, biochar manufacturers need to carefully compare biochar modification techniques to balance their effectiveness and cost. Studies have summarized that the cost of biochar production is in the range of \$0.67/kg to \$17.80/kg (Table 3). This huge variation results from the expenses of the feedstocks and production conditions (mostly determined by the techniques related to the oven, such as control accuracy of the atmosphere and temperature). The increase of pyrolysis temperature could increase the biochar production cost.[97] The cost of biochars derived from crop residues and woody waste increased from \$1.00/kg to \$1.30/kg with the pyrolysis temperature increasing from 400 to 700 °C. The cost of sludge derived biochar increased from \$0.70/kg to \$ 1.00/kg with the same pyrolysis temperature increment (Table 3).[98] A similar cost variation could be noted for the commercial activated carbon (AC), which is in the range of \$1.40/kg to \$22.0/kg.[99] Investigators generally believe that, even after modification, the biochar price is still much lower than that of AC, with a comparable adsorption capacity for organic contaminants. The removal of contaminants was generally much higher than that of other cheaper adsorbents such as red mud and zeolite.[100,101] It should be noted that different investigators referred to various biochars and ACs with dramatically different prices, because of their different sources. We may not be able to develop an exact reference for the comparison, and thus, we focused on the results of the price comparison in each article. The exact prices listed here are not of any commercial preferences.

Amination is one of the chemical modification methods to enhance biochar sorption to negatively charged chemicals. Aminated MBC showed a sorption capacity of 1.14 mg/g to dimethyl sulfide (DMS), which is almost 4 times higher than that of AC, a commonly used method to remove DMS. However, the price of aminated MBC is \$2.60/kg, which is only 1/8 of that of commercial AC (\$21.00/kg in that work).[102] Importantly, the DMS removal efficiency was reduced by only 23.4% even after 10 cycles. The much lower

**Table 3. Comparison of Production Costs for Biochar, Modified Biochar, and AC**

| Material type | Temperature (°C) | Location | Price ($/kg) | ref |
|---|---|---|---|---|
| *Oiltea camellia* shell biochar | 500 | USA | 0.67 | 103 |
| Water oak wood biochar | 400 | USA | 0.77 | 106 |
| Coconut shell biochar | | USA | 0.80 | 99 |
| Chicken manure biochar | 450 | Korea | 1.30 | 102 |
| Switchgrass biochar | 800 | USA | 5.49 | 106 |
| Tree branch biochar | | Kansas, USA | 11.0 | 99 |
| Virgin wood feedstock biochar | | Massachusetts, USA | 17.8 | 99 |
| Sludge derived biochar | 400 | USA | 0.7 | 98 |
| Sludge derived biochar | 550 | USA | 0.9 | 98 |
| Sludge derived biochar | 700 | USA | 1.0 | 98 |
| Sludge derived biochar | | USA | 0.56 | 107 |
| HCl MBC | 550 | Australia | 0.69 | 108 |
| Si-modified biochar | 500 | China | 1.44 | 103 |
| Amine-MBC | 450 | Korea | 2.60 | 102 |
| $Fe_3O_4$−$MnO_2$ MBC | 350 | Thailand | 10.0 | 104 |
| Commercial oxidized with $HNO_3$ AC | | | 1.40 | 99 |
| Coconut shell AC | | China | 1.50−3.00 | 99 |
| Granular AC | | | 6.40 | 99 |
| Chitosan AC | | Thailand | 15.4 | 109 |
| Commercial AC | | | 21.0 | 110 |
| Filtrasorb-400 AC | | Thailand | 20.0−22.0 | 109 |

cost and higher effectiveness indicated that aminated MBC can be utilized as an effective alternative adsorbent for DMS removal when compared with AC.

However, the choice among modification methods is not always straightforward. For example, the adsorption capacity of Cd by silicate-modified biochar (211 mg/g) was more than 3 times higher than that of raw biochar (62.2 mg/g). At the same time, the producing cost of silicate-modified biochar was twice that of raw biochar.[103] It will be helpful to establish a framework to evaluate the efficiency of biochar modification considering both modification cost and function enhancement.

Similarly, biochar modification by a metal or metal oxide will always dramatically increase the biochar production cost. The benefit of metal or metal oxide modification includes magnetic separation, high adsorption affinity, and environmental friendliness. For example, the surface area increased about 14 times after $Fe_3O_4$ or $MnO_2$ coating onto biochar. The adsorption capacities of this magnetic biochar were 19.9 mg/g for $Cr^{3+}$ and 49.6 mg/g for $Pb^{2+}$, in comparison to 9.80 mg/g for $Cr^{3+}$ and 7.00 mg/g for $Pb^{2+}$ by commercial AC.[99,104,105] The production cost of $Fe_3O_4$−$MnO_2$ MBC was about $10.00/kg, which is much higher than that of the pristine biochar and even higher than that of some of the commercial ACs. It is important to note that one benefit of this modification is to introduce magnetism in biochars to facilitate separation and recovery, which is not applicable for pristine biochars and ACs. How to systematically include the recovery efficiency, the retaining of sorption capacities, and magnetism in the cost evaluation of the MBCs is still unknown.

For biochar production, modification, and application, the costs are mostly from feedstocks, electricity (pretreatment and pyrolysis stage), modifying agents, storage, and transport. Thus, the overall cost should be carefully evaluated. In general, functional biochars require more energy and resources compared with pristine biochars. As presented in Figure 4, although a fraction of biochar particles may be lost during modification (appeared as the decreased yield referring to the feedstock), both cost and effectiveness increased with modification. The effectiveness may reach a plateau with modification, but the cost should always increase and yield will decrease with the modification. It is thus very important to evaluate the optimized point of the modification. Current studies gave special attention to the unique properties of MBCs, with limited attention to the cost of biochar modification and application. To balance the effectiveness and production costs, the selection of appropriate low-cost modification methods, development of new technologies, and improvement of the removal efficiency of target contaminants are the new directions for functional biochar producers in the future. In addition, increasing the biochar duration and recycling times may be an effective method to decrease biochar cost. Some mineral waste could also be used as the additive agent of biochar to decrease the production cost and realize resource recovery. For example, some iron-containing sludges were used to synthesize magnetic biochar.[111]

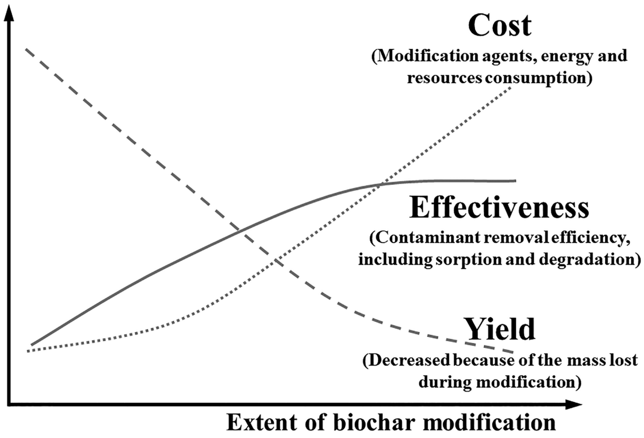

**Figure 4.** Balanced consideration of biochar modification. Yield decreases while cost and effectiveness increase with biochar modification. It is suggested that investigators design and produce biochars with low cost, high yield, and effectiveness.

## 4. PERSPECTIVES IN DESIGNING FUNCTIONAL BIOCHAR

Detailed investigations on the relationships between biochar structure and reaction mechanisms are essential for developing effective modification techniques, especially the reactivity of carbon structures as affected by the implanted modification materials. Many researchers have confirmed the potential of applying biochar in polluted soil or in wastewater treatment, but most of them focused on laboratory or small-scale in situ experiments in a short-term period. Studies on the applications of functional biochar on a large scale are still in their infancy. Because mass engineering and production of biochars are approaching quickly, more attention should be given to the following aspects.

The first issue is the potential environmental risks of MBCs or the risks in relation to the modification processes. The secondary pollution of biochar modification is not clearly addressed, especially the agents involved in the modification, such as metal oxides, oxidants, acids, and bases, which are often used as modifying agents. In addition, the increased reactivity of MBCs may increase their risk concerns. A careful evaluation of the risks of MBCs is a fundamental requirement before their wide and environmentally friendly application.

The second is the cost control of biochar modification. Although numerous techniques have been investigated for biochar modification, the cost was seldom evaluated. Considering that most biochars are produced using organic waste, it is not recommended to use expensive materials to modify biochars. It is suggested that one carefully compare the production cost of biochars and their modification products. Some investigators suggested the use of industrial solid wastes, such as fly ash, red mud, and coal gangue, for biochar modification, which could be a great approach to recycle solid waste. Thermal reaction kinetics of biomass in the presence of these solid wastes should be systematically evaluated for a better understanding of biochar yield and function. In addition, if biochars could be recovered and regenerated, as discussed later, the cost will also be significantly decreased.

The third point is the removal mechanisms of contaminants by the functionalized biochars. Many previous studies indicated that the adsorption mechanisms of heavy metals by MBCs were electrostatic attraction, precipitation, and complexation and the adsorption mechanisms for organic contaminants were hydrophobic effects, $\pi-\pi$ interactions, and hydrogen bonding. Further studies are suggested to identify the quantified contribution of individual mechanisms, and then targeted modifications can be designed and implemented. Also, biochar redox properties have been suggested to play an important role in contaminant removal or detoxification. Extended research is required to distinguish the sorption and redox reactions. It is still unclear which biochar properties control their redox properties and how the modification alters their redox properties.

The recycling/regeneration of the functionalized biochars is the fourth issue that requires further study. The most widely discussed recycling technique is the synthesis of magnetic biochar, which is prepared by the chemical coprecipitation of $Fe^{3+}/Fe^{2+}$ or inclusion of nanosize magnetic particles. Separation and recovery of magnetic biochars are generally practicable in the aqueous phase. However, in wastewater, when magnetic biochars are covered by a large amount of organic matter or even microorganisms, the recovery through magnetic force should be specifically evaluated. Another point is the stability of the loaded magnetic components on biochars. Biochar aging, turbulence, pH change, and microbial activity may all result in the release of the loaded magnetic components.

In addition to the above four points, the persistence of biochar functions should also be determined before application. The surface structure/properties and adsorption properties of the functionalized biochar will gradually change when applied in water and soil environments, which is also known for the aging process. It is necessary to explore the long-term effects of MBC in the removal of contaminants in water and soil. Chemical and biological processes may also result in biochar aging, some of which may be beneficial to biochar function while others may not be. The implanted modification materials, such as metal or metal oxides, may accelerate the aging processes. On the other hand, the aging process may destroy the composited structure. Studies are still very limited on the persistence of MBC functions, especially when they are applied in the environment.

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### Notes

The authors declare no competing financial interest.

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