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Preparation of biochar-based composites and their use in the remediation of environments contaminated with organic pollutants

Fayun Li[1,2,*], Meixia Lin[3,4], Xiaotong Li[1,4], Wei Wang[1,4], Kokyo Oh[5]

[1] School of Ecological Technology and Engineering, Shanghai Institute of Technology, Shanghai 201418, China

[2] Institute of Beautiful China and Ecological Civilization, University Think Tank of Shanghai Municipality, Shanghai 201418, China

[3] School of Resources and Environmental Science, Hunan Agricultural University, Changsha 410128, China

[4] Center for Urban Road Ecological Engineering and Technology of Shanghai Municipality, Shanghai 201418, China

[5] Center for Environmental Science in Saitama, Saitama 347-0115, Japan

* Corresponding author: Fayun Li, lnecology@163.com

Abstract: Biochar offers several advantages, including high carbon content, a large specific surface area, a well-developed pore structure, and excellent adsorption capabilities. It is extensively utilized in improving soil quality, remediating environmental pollution, and contributing to carbon sequestration and emission reduction. However, practical challenges such as the low bulk density of biochar, difficulties in solid-liquid separation, and the need to enhance its long-term effectiveness and stability persist. To address these issues, biochar composites with improved remediation efficiency for polluted environments have been developed by combining biochar with metal materials, photocatalysts, and clay minerals, garnering significant attention. This systematic review examines the preparation methods and applications of biochar-based composite materials in environmental pollution control, analyzes the mechanisms for removing organic pollutants, and discusses future research and development trends for biochar materials, aiming to provide new insights for the creation and practical use of high-efficiency biochar composites.

Keywords: biochar; composites; organic pollution; environmental remediation

Biochar usually refers to the fluffy porous material with high carbon content formed by the pyrolysis of biomass resources under anoxic conditions through a series of processes such as dehydration, pyrolysis and aromatization [1], which is mainly composed of simple carbon, aromatized carbon and graphite carbon [2]. Common biochar preparation materials include sludge biochar, straw biochar, wood biochar and core-shell biochar [3]. Previous studies and applications have shown that biochar has many advantages, such as large specific surface area, developed pore structure, small bulk density, rich surface functional groups, high cation exchange capacity, strong chemical stability and thermal stability [4]. In addition, it has a wide range of sources and low economic cost. It can be used as an adsorbent and catalyst for pollutant control in the environment at the same time. As an adsorbent and carrier material with excellent performance, it is widely used to treat organic dyes, polycyclic aromatic hydrocarbons, antibiotics, pesticides, pesticides and other organic pollutants in the environment [5].

Biochar is used to control environmental pollution, and its treatment effect is closely related to its dosage, organic concentration, pH, temperature, reaction time and other factors. In addition, the carbonization temperature of biochar and the types of biomass materials also greatly affect its adsorption performance [6]. Generally speaking, the higher the carbonization temperature, the larger the specific surface area

and the better the adsorption performance. However, some studies have shown that when the surface functional groups of biochar play a leading role, the biochar prepared under low temperature shows better adsorption performance for the antibiotic sulfamethoxazole because it has more surface functional groups [7]. The adsorption mechanism of biochar for organic pollutants mainly includes hydrophobic interaction, π-π interaction, hydrogen bond, covalent bond and electrostatic interaction [8]. Through confocal laser scanning microscope observation and density functional theory calculation, some scholars found that π-π interaction played a dominant role in the adsorption process of biochar for antibiotics [9].

Although biochar has many advantages in environmental pollution control, it is difficult to meet the requirements of efficient removal of organic pollutants in the environment for single-phase biochar in terms of adsorption capacity and kinetic rate. In addition, the volume density of biochar is small. When it is used to adsorb organic pollutants, it is difficult to achieve solid-liquid separation, and the quantitative and accurate evaluation of its long-term effectiveness and stability still faces some challenges. Therefore, the preparation of composite materials with unique repair properties using biochar as carrier or auxiliary catalyst has attracted more and more attention of scientific researchers [10].

According to the different properties of biochar and its composites, they can be divided into biochar metal composites, biochar photocatalyst composites and biochar clay mineral composites. In this paper, the methods of preparation and characterization of physical and chemical properties of biochar and its composites are systematically summarized, the mechanism of its removal of environmental organic pollutants is analyzed, and the related research progress of its application in the remediation of organic polluted environment is described, in order to provide new ideas for the application of biochar based composites in the field of environmental remediation.

1. Biochar based composite repair materials

1.1. Preparation and performance characterization of biochar matrix composites

Taking biomass resources from a wide range of sources such as agricultural and forestry wastes, agricultural product processing residues, animal feces, activated sludge, etc. As materials, different types of biochar materials are prepared by high-temperature pyrolysis or hydrothermal carbonization. The pyrolysis process mainly involves biomass dehydration, cellulose and hemicellulose decomposition, lignin decomposition, aromatization, cyclization, carbonization and other processes [11]. The surface structure and physicochemical properties of biochar are affected by the material and carbonization temperature of biomass. Carbonization temperature mainly affects the adsorption performance of biochar in terms of its yield, pH, ash content, element composition, surface functional groups and specific surface area [12]. Research shows that the thermal decomposition process of lignin is often accompanied by chemical bond breaking and aromatization reaction. The higher the lignin content in biomass, the greater the aromatic carbon content and c/n ratio in the generated biochar materials. For example, the carbon content of animal biochar is generally

lower than that of plant biochar [13].

Because biochar has the advantages of large specific surface area, developed pore structure, rich surface functional groups and good conductivity, it is used as an auxiliary catalyst or carrier to combine with metal oxides/metal hydroxides, semiconductor Photocatalysts and clay minerals to prepare various types of biochar based composite repair materials through different methods such as immersion pyrolysis, coprecipitation, solvothermal, ball milling, cross-linking and direct mixed pyrolysis [14], then, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM)/transmission electron microscope (TEM), bet (Brunauer, Emmett and teller) The physical and chemical characteristics were analyzed by ultraviolet and visible diffuse reflection spectrum (UV VIS)/photoluminescence spectrum (PL), electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS), as shown in **Figure 1**.
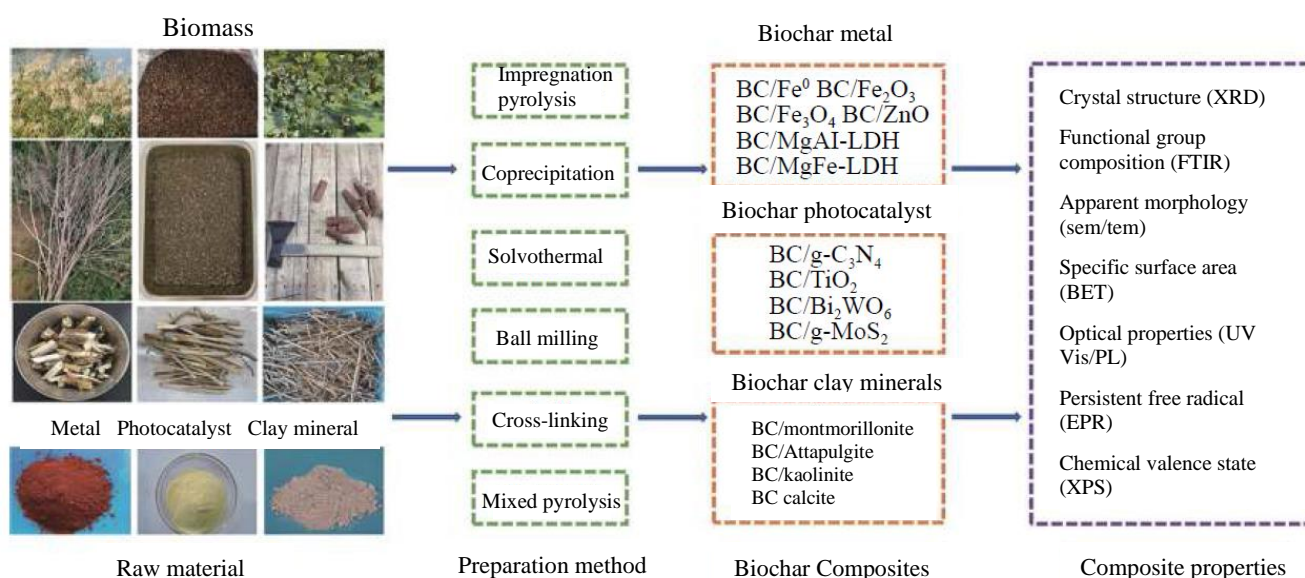

Figure 1. Biochar-based composites preparation and physical and chemical properties characterization.

XRD is mainly used to analyze the crystal structure of biochar based composite repair materials, and FTIR can detect the functional group composition of the materials. Zhu et al. [15] characterized the Magnolia petal biochar (BC), graphite phase carbon nitride (g-C_3N_4) and biochar carbon nitride composites (bc/g-C_3N_4) by XRD and FTIR. The XRD results showed that the bc/g-C_3N_4 composites were θ There are three characteristic diffraction peaks at 13.8°, 27.8° and 21.5°, indicating that the composite has the structural characteristics of BC and g-C_3N_4 at the same time, indicating that BC has been successfully introduced into the skeleton structure of g-C_3N_4. In the FTIR spectra of the composite, the characteristic peaks of BC and g-C_3N_4 functional groups were observed, and no significant changes were observed. The results confirmed that the introduction of BC would not change the chemical composition of g-C_3N_4.

SEM and TEM can effectively observe the apparent morphology and detailed structure of the composites, and analyze the distribution of different substances on the

surface and pore structure of biochar. Bet is an important performance index for evaluating biochar composites. The larger the specific surface area of the composites, the more active sites, and the stronger the adsorption performance. As metal oxides/metal hydroxides, semiconductor Photocatalysts and clay minerals all have certain surface characteristics, the specific surface area of the composite formed by their coupling with biochar is usually larger than that of the original biochar material [16]. However, when the biochar loaded material occupies part of its surface sites or blocks part of its pore structure, the specific surface area of the biochar composite is also smaller than that of a single biochar material [17]. UV Vis and PL are typical characterization methods to analyze the visible light response ability and photogenerated charge separation efficiency of biochar photocatalyst composites, and they are also important indicators to evaluate the catalytic performance of composite photocatalysts. EPR can track and detect the persistent free radicals on the surface of biochar. The persistent free radicals on the surface of biochar can induce the production of reactive oxygen species, thus promoting the transformation and removal of organic pollutants in the environment [18]. XPS is often used to analyze the element composition and chemical valence state of biochar composites.

1.2. Biochar metal composites

Nano zero valent iron, metal oxides, layered double hydroxides as adsorbents and heterogeneous catalysts have attracted much attention in many fields, such as catalysis, energy storage, electrochemistry and environmental remediation. Nanoscale zero valence iron (NZVI) has the advantages of high reaction activity, strong reduction ability and large specific surface area. It can reduce soluble hexavalent uranium (U (VI)) to low solubility and low toxicity tetravalent uranium (U (IV)), reducing its risk of polluting the ecological environment [19]. The size of nano metal oxide varies from 1 to 100 nm. It has significant advantages such as large specific surface area, high diffusion activation energy, strong quantum effect, oxidation-reduction and adsorption capacity. As a low-cost, green and environmental friendly catalytic material, it is widely concerned in the field of environmental remediation [20]. Layered double hydroxides (LDHs) is a two-dimensional nanostructure material composed of bimetallic hydroxide layers. Due to its good layered structure, large specific surface area, porosity and high ion exchange capacity, people show great interest in its application as a high-efficiency adsorbent [21]. However, nano metal materials usually have small particle size and high surface energy, and are prone to agglomeration in practical applications. It was found that in order to avoid agglomeration of nano metal materials and provide them with a well dispersed active site, nano metal catalyst species can be fixed on the porous surface [22]. In this respect, biochar as a low-cost porous support material has broad application prospects in the field of catalysts.

The combination of nano metal materials and biochar to prepare biochar metal composites can not only effectively improve the specific surface area, adsorption performance and solid-liquid separation capacity of biochar, but also greatly improve the catalytic activity and redox capacity of metal nanoparticles, so as to achieve the purpose of collaborative adsorption and degradation of different pollutants. Zhang et al. [23] successfully synthesized A-BC-NZVI composite by aqueous phase reduction

method with longan shell as carbon source in nitrogen atmosphere at 800 ℃. It was found that the maximum Langmuir adsorption capacity of A-BC-NZVI for u (VI) was 331.13 mg/g, which was much higher than that of biochar and other biochar based materials. The degradation of phenol by biochar supported feal layered double hydroxide (feal LDH) synthesized by hydrothermal method showed that feal-LDH@BC0.25 The degradation efficiency of phenol (80 mg/L) was 85.28%, and only a small amount of iron was leached during the degradation process. The prepared material had good reusability. Further soil remediation experiments show that feal-LDH@BC0.25 It can also effectively degrade phenol in soil, but the degradation efficiency is lower than that of aqueous solution [24].

1.3. Biochar photocatalyst composites

Photocatalysis oxidation has the advantages of mild reaction conditions, high treatment efficiency, strong oxidation capacity and green environmental protection. It can solve the problems of environmental pollution and energy conservation at the same time. At present, the commonly used Semiconductor Photocatalysts include WO_3, Fe_2O_3, ZrO_2, $g-MOS_2$, tio_2 and $g-C_3N_4$. Among them, graphite phase carbon nitride ($g-C_3N_4$), as a metal free organic polymer semiconductor material, has good thermal and chemical stability, wide range of pH application and strong oxidation capacity. Since it was found that $g-C_3N_4$ can be used for photolysis of water to produce hydrogen [25], as a new photocatalyst material, it is gradually being used in the fields of CO_2 reduction and degradation of organic pollutants [26,27]. However, $g-C_3N_4$ itself has some defects, such as small specific surface area, low light quantum efficiency and poor response to visible light. Exploring reasonable modification methods to improve its surface properties and further improve its photocatalytic efficiency is favored by many materials science and environmental protection scientists. Biochar has large specific surface area, rich oxygen-containing functional groups and good electrochemical stability. Combining it with $g-C_3N_4$ can effectively make up for the defects of $g-C_3N_4$ itself [28].

Meng et al. [29] prepared $g-C_3N_4$ coupled rice straw biochar composites through π-π interaction and ether bond bridging mechanism. Biochar is used as electron storage, and its addition directly affects the photocatalytic performance of the materials. The appropriate amount of biochar can promote the effective separation of $g-C_3N_4$ photogenerated charges. Excessive biochar addition will not only inhibit the absorption of visible light by $g-C_3N_4$, but also reduce the contact interface between biochar and $g-C_3N_4$, thus reducing its photocatalytic activity.

Biochar photocatalyst composites can effectively degrade pollutants through the following ways:

(1) The excellent adsorption performance of biochar provides a good reaction environment for $g-C_3N_4$;

(2) Biochar as an electron transport channel can effectively prolong the lifetime of $g-C_3N_4$ photoexcited electrons;

(3) The mass transfer efficiency and reaction rate of $g-C_3N_4$ in the reaction medium can be significantly improved by the larger specific surface area of biochar;

(4) The oxygen-containing functional groups easily modified on the surface of

biochar effectively enhanced the dispersibility of g-C_3N_4 in the reaction system.

1.4. Biochar clay mineral composite

Clay mineral is a layered structure material composed of oxygen shared by silica tetrahedron and alumina octahedron in different proportions. It has the characteristics of rich resources, large specific surface area, high cation exchange capacity (CEC) and rich surface functional groups. As a new environmentally friendly adsorption material, it is widely used in the removal of heavy metal ions and organic pollutants [30]. Facing the higher requirements of social and economic development for environmental protection and sustainable development, a single adsorption material can not generally meet the high-performance requirements of practical environmental pollution control applications. While preparing adsorption materials with special properties, simultaneously realizing the high-value transformation of natural biological resources is becoming a research hotspot in the field of environmental pollution control.

The source and type of biomass have obvious effects on the morphology, structure and adsorption properties of biochar clay mineral composites. Lignocellulose, as a renewable resource with a wide range of sources, can be prepared into biochar materials, which can be integrated with clay minerals to synthesize biochar clay mineral composite restoration materials with new functions. The irregular porous biochar network structure of lignocellulose hydrothermal carbonization products can be used to prepare composite repair materials with fibrous attapulgite, which can effectively realize the adsorption and removal of phenol [31]. Sugar and starch are used as biomass sources, and their hydrothermal carbonization products are the coexistence of biochar microspheres and fibrous attapulgite. The composite has a good removal effect on organic dye wastewater [32]. In order to improve the adsorption efficiency of dyes in wastewater, Liu et al. [33] prepared a biochar attapulgite composite and applied it to the adsorption of yellow X-GL. It was found that its specific surface area could reach 417 m^2/g, which was 30% and 270% higher than that of biochar and attapulgite respectively. The maximum adsorption capacity of the prepared material for yellow X-GL was 213 mg/g, much higher than that of single biochar and attapulgite.

2. Mechanism of organic pollutants removal from environment by biochar based composite remediation materials

The synthesis of biochar composite restorative materials combines the advantages of biochar and its composites (metal materials, photocatalysts and clay minerals). Generally speaking, biochar has the following three potential effects on its composite materials:

(1) As the substrate of metal materials, photocatalysts and clay minerals, biochar can effectively increase the contact area between its dispersion and pollutants;

(2) Biochar has large specific surface area and rich oxygen-containing functional groups, which can promote the reactivity of metal materials, photocatalysts and clay minerals with target pollutants;

(3) Biochar accelerates the mass transfer process of pollutants from the environmental medium to the composite surface through its own adsorption process

[34].

Loading metal materials, photocatalysts, clay minerals and other particles on biochar, and in turn, the adsorption characteristics of biochar also have the following two advantages:

(1) Metal materials, photocatalysts and clay minerals degrade the adsorbed pollutants, promote the regeneration of biochar and enhance its ability to adsorb organic pollutants;

(2) Metal materials, photocatalysts and clay minerals can improve their adsorption performance for pollutants by preventing the accumulation of pollutants in the biochar matrix [35].
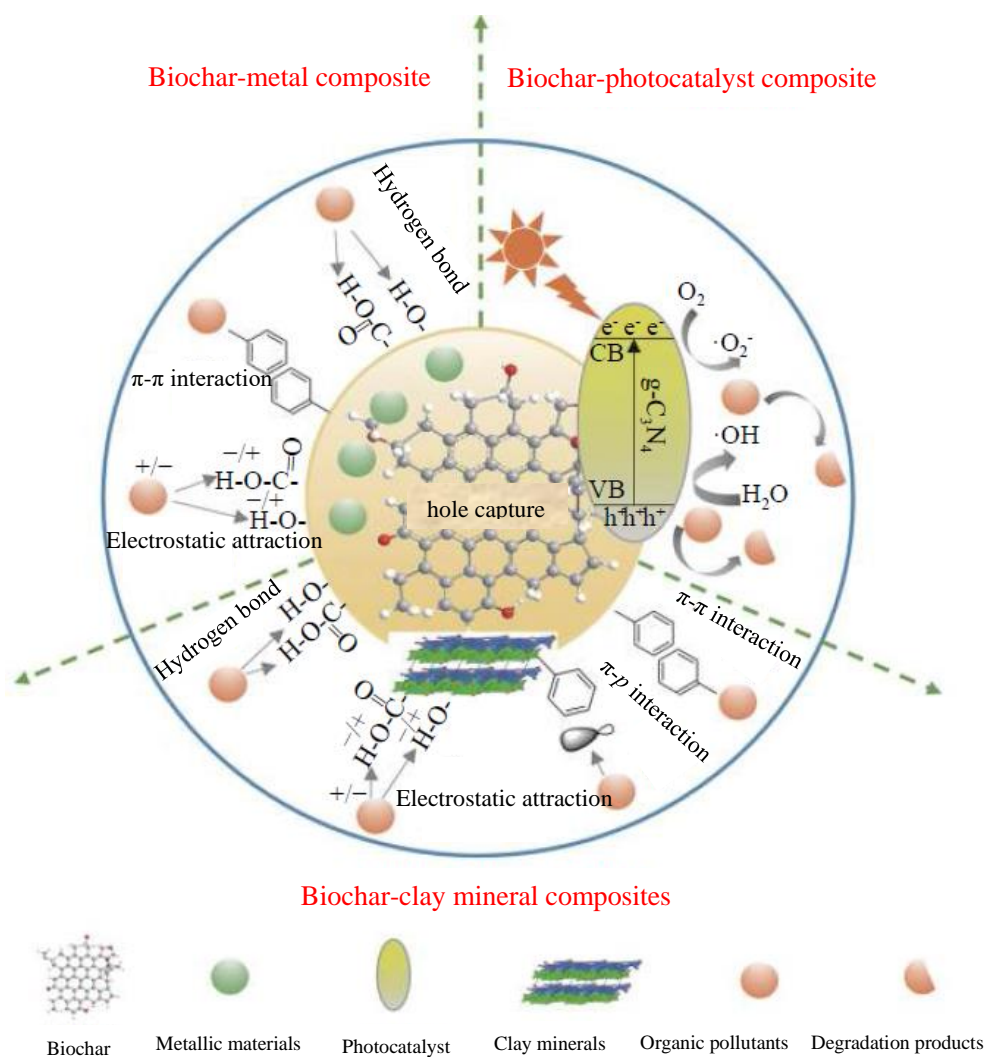
Figure 2. Removal mechanism of organic pollutants by biochar-based composites.

Figure 2 summarizes the various mechanisms of the interaction between biochar based composite remediation materials and organic pollutants.

The interaction mechanism between biochar metal composites and organic pollutants mainly includes π-π interaction, hydrogen bonding and electrostatic attraction [36]. The mechanism of biochar clay mineral composite for removing organic pollutants mainly involves π-π interaction, π-p interaction, hydrogen bonding

and electrostatic attraction [37]. The oxygen-containing functional groups on the surface of biochar matrix composites have lone pair electrons and high electronegativity, which can be used as electron donors; organic pollutants with benzene ring structure (polycyclic aromatic hydrocarbons, sulfonamide antibiotics) have highly delocalized π conjugated systems, and their electronic defects can act as electron acceptors to interact with biochar composites [38]. The p orbitals on heteroatoms (O, n) contained in organic pollutants such as phenol and oxytetracycline can interact π -p with large π bonds in biochar composites [39].

The oxygen-containing functional groups on the surface of biochar composites are negatively charged after deprotonation. They can interact with cationic dyes through electrostatic attraction to achieve the purpose of dye decolorization in wastewater [40]. Hydrogen bonds are covalent bonds formed by hydrogen atoms and atoms with high electronegativity. The pKa value of COOH group on the surface of biochar composites is 3.0~5.0, and that of chloramphenicol is 5.5. Under the condition of pH < 5.5, the free functional groups (mainly –COOH) on the surface of biochar composites can form hydrogen bonds (chloramphenicol-no2-hooc-bc) with nitro groups in chloramphenicol. This chemical bond is also called charge assisted hydrogen bond. At the same time, under this pH condition, the hydrogen bond (chloramphenicol oh HOOC BC) between COOH and chloramphenicol OH on the surface of biochar composite also plays a major role in its adsorption process [41].

The lifetime of electron hole pairs produced by Semiconductor Photocatalysts under visible light conditions is very short, which is so low that if the separation of electron hole pairs cannot be effectively realized, they will be compounded inside or on the surface of semiconductor materials, reducing the photocatalytic activity of semiconductor materials. In biochar semiconductor photocatalyst composites, biochar, as an electron storage body, has a large specific surface area, which can effectively extend the transmission distance of photogenerated electron holes in semiconductor materials, promote their separation efficiency, and further improve the photocatalytic degradation capacity of the composites [42]. Biochar photocatalyst composites participate in the degradation of organic pollutants, mainly including:

(1) The photo excitation on the conduction band of photocatalyst and the reaction in the reaction system generate active groups Participate in the photocatalytic degradation of organic pollutants;

(2) And reaction generation on the valence band of photocatalyst participate in the photocatalytic degradation of organic pollutants;

(3) Photocatalyst valence band directly participates in the photocatalytic degradation of organic pollutants [43].

3. Application of biochar composites in the remediation of organic polluted environment

Biochar based composites combine the unique physical and chemical properties of biochar and metal materials, photocatalysts, clay minerals, etc., and their remediation efficiency for polluted environment is generally better than that of single materials. In recent years, biochar based composites have made a lot of practical application progress in the remediation of organic polluted environment.

3.1. Dyes

At present, the annual output of various dyes in China is about 1.6 million tons, of which 10%~15% of dyes are discharged with wastewater during processing and use. Dye wastewater has the characteristics of large chromaticity, complex composition, high toxicity and difficult biodegradation [44]. After entering the water environment, it is very easy to cause water and soil environmental pollution and great potential harm to human health. Biochar composites have large specific surface area and strong redox capacity, which can effectively adsorb and degrade organic dyes in wastewater, as shown in **Table 1**.

Table 1. Comparison of dye removal from wastewater by different biochar-based composites.

Biochar raw materials	Compound material	Preparation method	Contaminants	Adsorption capacity/removal rate	Ref.
Corn straw	NZVI	Calcination method/500 °C	Malachite green	99.9%	[45]
Empty fruit string	$FeCl_3 \cdot 6H_2O$	Microwave heating method	Methylene blue	$265 \ mg \cdot g^{-1}$	[46]
Peanut shell	Fe_2O_3	Calcination method/400 °C	Methylene blue	$46.2 \ mg \cdot g^{-1}$	[47]
Macroalgae	Fe_3O_4	Calcination method/600 °C	Acid Orange 7	$382 \ mg \cdot g^{-1}$	[48]
Ramie	Mg/Al-LDH	Calcination method/500 °C	Crystal violet	$374 \ mg \cdot g^{-1}$	[40]
Bovine bone	Mg/Al-LDH	Calcination method/600 °C	Methylene blue	$406 \ mg \cdot g^{-1}$	[49]
Corncob	Ni/Al-LDH	Calcination method/700 °C	Acridine orange	$108.6 \ mg \cdot g^{-1}$	[50]
Bagasse	Attapulgite	Calcination method/700 °C	Reactive brilliant red X-3B	$72.2 \ mg \cdot g^{-1}$	[51]
Bagasse	Montmorillonite	Calcination method/600 °C	Methylene blue	84.3%	[52]
Bamboo	TiO_2	Hydrothermal method	Methylene blue	99%	[53]
Chestnut leaf	$G-C_3N_4$	Calcination method/520 °C	Methylene blue	91%	[35]
Agar powder	$N-TiO_2-Fe_3O_4$	Calcination method/800 °C	Methylene blue	94%	[54]
Seaweed	TiO_2	Wet precipitation method	Methylene blue	99.2%	[55]

3.2. Antibiotics

Antibiotics have been widely used in medicine, agriculture, animal husbandry and other fields, but they can induce microorganisms to produce resistance genes in the environment and pose a great threat to human health and ecosystem. The production of antibiotics in China ranks first in the world, and the total consumption of antibiotics in 2013 reached 16×104 T, 150 times the total consumption of antibiotics in the UK [56]. The matrix and metabolites of antibiotics are generally stable and difficult to be completely degraded in natural processes. The traditional bioremediation technology generally has the disadvantage of low treatment efficiency for antibiotic pollutants. The new biochar based composite material has a wide application prospect for the removal of antibiotics, as shown in **Table 2**.

Table 2. Removal effect of different biochar-based composites on antibiotics.

Biochar raw materials	Compound material	Preparation method	Contaminants	Adsorption capacity/removal rate	Ref.
Potato haulm	MnO$_x$	Calcination method/500 ℃	Norfloxacin	6.94 mg·g^{-1}	[57]
			Ciprofloxacin	8.37 mg·g^{-1}	
			Enrofloxacin	7.19 mg·g^{-1}	
Corn straw	MnO$_2$	Calcination method/600 ℃	Oxytetracycline	39.92 mg·g^{-1}	[58]
Walnut shell	Fecu	Oxide pyrolysis and impregnation ciprofloxacin	Ciprofloxacin	100%	[59]
Bagasse	Mg/Al-LDH	Calcination method/475 ℃	Tetracycline	1118.12 mg·g^{-1}	[60]
Pennisetum hydridum	Mg/Al-LDH	Coprecipitation method	Sulfamethoxazole	97%	[61]
Wheat stalk	Montmorillonite	Calcination method/400 ℃	Norfloxacin	25.53 mg·g^{-1}	[37]
Municipal solid waste	Montmorillonite	Impregnation method	Ciprofloxacin	167.36 mg·g^{-1}	[62]
Cauliflower	Montmorillonite	Calcination method/500 ℃	Oxytetracycline	58.85 mg·g^{-1}	[63]
Municipal solid waste	Bentonite	Calcination method/450 ℃	Ciprofloxacin	190 mg·g^{-1}	[64]
Municipal solid waste	Montmorillonite	Calcination method/500 ℃	Tetracycline	77.96 mg·g^{-1}	[65]
Corncob	TiO$_2$	Sol gel method	Sulfamethoxazole	91%	[66]
Reed straw	TiO$_2$	Sol gel method	Sulfamethoxazole	91.27%	[67]
Rice straw	G-MOS$_2$	Hydrothermal method	Tetracycline hydrochloride	70%	[68]
Poplar shavings	G-C$_3$N$_4$	Ball milling method	Enrofloxacin	81.1%	[69]

3.3. Petroleum hydrocarbons and polycyclic aromatic hydrocarbons

Pollution control and environmental control of petroleum hydrocarbons and polycyclic aromatic hydrocarbons have always been an important problem to be solved in the field of water and soil ecological environment restoration. Hydrocarbon pollutants in the environment have the characteristics of stable chemical properties, strong persistence and difficult degradation. Entering the soil environment will directly lead to the destruction of soil physical and chemical structure, reduce soil permeability, oxygen content and water holding capacity, thus hinder the circulation and transfer of nutrients in the plant rhizosphere environment, and reduce the bioremediation effect of petroleum hydrocarbons and polycyclic aromatic hydrocarbons. When hydrocarbon pollutants enter the water environment, they will form a dense oil film on the surface of the water, reduce the transparency and dissolved oxygen of the water, and cause the deterioration of the water [70]. Traditional bioremediation technologies are inefficient, time-consuming and greatly affected by changes in environmental factors. Using biochar materials with good adsorption performance as carriers and combining with other catalytic materials or adsorbents with unique performance can play a key role in improving the remediation efficiency of hydrocarbons in the environment, as shown in **Table 3**.

Table 3. Removal efficiency of hydrocarbons by different biochar-based composites.

Biochar raw materials	Compound material	Preparation method	Contaminants	Contaminated medium	Adsorption capacity/removal rate	Ref.
Wheat straw	NZVI	-	Polycyclic aromatic hydrocarbons	Soil	82%	[71]
Wood	Fe_3O_4	Coprecipitation method	Polycyclic aromatic hydrocarbons	Estuarine sediment		[72]
			6 Ring/5 Ring/4 Ring		90%/84%/87%	
Bagasse	S-NZVI	Impregnation method	Ethylene dichloride	Groundwater	100%	[73]
Corn straw	NZVI	Impregnation method	Ethylene dichloride	Water body	99%	[74]
Pine needle	NFe_3O_4	Calcination/400 ℃	1,4-dioxane	Water body	98%	[75]
Rice husk	NZVI	Impregnation method	Ethylene dichloride	Water body	99.4%	[76]
Bamboo	Fe_3O_4	Wet precipitation method	Polycyclic aromatic hydrocarbons	Marine sediment	86%	[77]
Corn straw	K-g-C_3N_4	High temperature pyrolysis	Naphthalene	Water body	82.19%	[78]
Rice husk/koh	Attapulgite	Calcination/500 ℃	Aniline	Water body	15.21 mg·g^{-1}	[79]
			Pyridine		20.74 mg·g^{-1}	

4. Conclusion and prospect

The application of biological carrier materials in the remediation of organic polluted environment generally has the problems of short carrier time, low efficiency and high product cost. Biochar is a kind of adsorption material with wide sources, simple preparation and relatively low cost. It has the advantages of high surface activity, developed pore structure, good chemical stability and easy modification of functional group structure. The preparation of biochar from agricultural and forestry wastes is not only a very effective way of carbon sequestration, but also has broad application prospects in soil improvement and environmental protection. In the future, in terms of the performance improvement of biochar based composite repair materials and their application in the control of organic pollutants in the environment, the following aspects of research and development need to be paid more attention:

(1) Combining biochar with new catalysts and adsorbents, we developed new biochar based composite remediation materials with high removal efficiency of organic pollutants, and further studied the removal mechanism of organic pollutants by different biochar based composite remediation materials.

(2) In view of the fact that the understanding of the interaction mechanism between microorganisms, soluble organic matter and biochar based composite remediation materials in the soil environment is still vague, combined with the complex characteristics of the soil environment, strengthen the research and development of biochar immobilized microbial composite remediation materials, reveal their synergistic degradation mechanism of organic pollutants in the soil environment, and optimize and determine the key remediation process parameters.

(3) Aiming at the problems of short time, low efficiency and high cost of carrier materials for the remediation of organic polluted environment, we will strengthen the research and development of long-term broad-spectrum biochar based composite remediation carriers with high remediation efficiency for typical organic pollutants

such as petroleum hydrocarbons, halogenated hydrocarbons and polycyclic aromatic hydrocarbons, and effectively give play to the synergistic remediation effect of biochar microorganism plant on organic polluted environment.

References

1. Melia PM, Busquets R, Hooda PS, et al. Driving forces and barriers in the removal of phosphorus from water using crop residue, wood and sewage sludge derived biochars. Science of The Total Environment. 2019; 675: 623-631. doi: 10.1016/j.scitotenv.2019.04.232

2. Chen W, Zhang W, Meng J. Research progress and Prospect of agricultural biochar. China Agricultural Science (Chinese). 2013; 46(16): 3324-3333.

3. Yi Y, Huang Z, Lu B, et al. Magnetic biochar for environmental remediation: A review. Bioresource Technology. 2020; 298: 122468. doi: 10.1016/j.biortech.2019.122468

4. Hu B, Ai Y, Jin J, et al. Efficient elimination of organic and inorganic pollutants by biochar and biochar-based materials. Biochar. 2020; 2(1): 47-64. doi: 10.1007/s42773-020-00044-4

5. Liu S, Xu W hua, Liu Y guo, et al. Facile synthesis of Cu(II) impregnated biochar with enhanced adsorption activity for the removal of doxycycline hydrochloride from water. Science of The Total Environment. 2017; 592: 546-553. doi: 10.1016/j.scitotenv.2017.03.087

6. Ghodake GS, Shinde SK, Kadam AA, et al. Review on biomass feedstocks, pyrolysis mechanism and physicochemical properties of biochar: State-of-the-art framework to speed up vision of circular bioeconomy. Journal of Cleaner Production. 2021; 297: 126645. doi: 10.1016/j.jclepro.2021.126645

7. Fang J, Jin L, Cheng L, et al. Research Progress on the stability of biochar in environment (Chinese). Journal of soil. 2019; 56(5): 1034-1047.

8. Dai Y, Zhang N, Xing C, et al. The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: A review. Chemosphere. 2019; 223: 12-27. doi: 10.1016/j.chemosphere.2019.01.161

9. Peng B, Chen L, Que C, et al. Adsorption of Antibiotics on Graphene and Biochar in Aqueous Solutions Induced by π-π Interactions. Scientific Reports. 2016; 6(1). doi: 10.1038/srep31920

10. Zhu D, Zhou Q. Research Progress on Application of functional nano materials in remediation of heavy metal polluted water (Chinese). Journal of Agricultural Environmental Sciences. 2018; 37(8): 1551-1564.

11. Keiluweit M, Nico PS, Johnson MG, et al. Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar). Environmental Science & Technology. 2010; 44(4): 1247-1253. doi: 10.1021/es9031419

12. Wang S, Zhang H, Huang H, et al. Influence of temperature and residence time on characteristics of biochars derived from agricultural residues: A comprehensive evaluation. Process Safety and Environmental Protection. 2020; 139: 218-229. doi: 10.1016/j.psep.2020.03.028

13. Ameloot N, Graber ER, Verheijen FGA, et al. Interactions between biochar stability and soil organisms: review and research needs. European Journal of Soil Science. 2013; 64(4): 379-390. doi: 10.1111/ejss.12064

14. Feng Z, Yuan R, Wang F, et al. Preparation of magnetic biochar and its application in catalytic degradation of organic pollutants: A review. Science of The Total Environment. 2021; 765: 142673. doi: 10.1016/j.scitotenv.2020.142673

15. Zhu Z, Fan W, Liu Z, et al. Fabrication of the metal-free biochar-based graphitic carbon nitride for improved 2-Mercaptobenzothiazole degradation activity. Journal of Photochemistry and Photobiology A: Chemistry. 2018; 358: 284-293. doi: 10.1016/j.jphotochem.2018.03.027

16. Inyang M, Gao B, Zimmerman A, et al. Synthesis, characterization, and dye sorption ability of carbon nanotube–biochar nanocomposites. Chemical Engineering Journal. 2014; 236: 39-46. doi: 10.1016/j.cej.2013.09.074

17. Yu Z, Huang Y, Lian F. Study on the adsorption properties of biochar manganese oxide composite for arsenic (III) (Chinese). Journal of Agricultural Environmental Sciences. 2015; 34(1): 155-161.

18. Tang Z, Zhao S, Qian Y, et al. Research Progress on the formation mechanism of persistent free radicals in biochar and its environmental application. Progress in chemical industry. 2020; 39(4): 1521-1527.

19. Chakraborty S, Favre F, Banerjee D, et al. U(VI) Sorption and Reduction by Fe(II) Sorbed on Montmorillonite. Environmental Science & Technology. 2010; 44(10): 3779-3785. doi: 10.1021/es903493n

20. Wang S, Zhao M, Zhou M, et al. Biochar-supported nZVI (nZVI/BC) for contaminant removal from soil and water: A critical review. Journal of Hazardous Materials. 2019; 373: 820-834. doi: 10.1016/j.jhazmat.2019.03.080

21. Alagha O, Manzar MS, Zubair M, et al. Magnetic Mg-Fe/LDH Intercalated Activated Carbon Composites for Nitrate and Phosphate Removal from Wastewater: Insight into Behavior and Mechanisms. Nanomaterials. 2020; 10(7): 1361. doi: 10.3390/nano10071361

22. Wu H, Feng Q, Yang H, et al. Enhanced phenanthrene removal in aqueous solution using modified biochar supported nano zero-valent iron. Environmental Technology. 2018; 40(23): 3114-3123. doi: 10.1080/09593330.2018.1549104

23. Zhang Q, Wang Y, Wang Z, et al. Active biochar support nano zero-valent iron for efficient removal of U(VI) from sewage water. Journal of Alloys and Compounds. 2021; 852: 156993. doi: 10.1016/j.jallcom.2020.156993

24. Fan X, Cao Q, Meng F, et al. A Fenton-like system of biochar loading Fe–Al layered double hydroxides (FeAl-LDH@BC)/H2O2 for phenol removal. Chemosphere. 2021; 266: 128992. doi: 10.1016/j.chemosphere.2020.128992

25. Wang X, Maeda K, Thomas A, et al. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. Nature Materials. 2008; 8(1): 76-80. doi: 10.1038/nmat2317

26. Ye S, Wang R, Wu MZ, et al. A review on g-C3N4 for photocatalytic water splitting and CO2 reduction. Applied Surface Science. 2015; 358: 15-27. doi: 10.1016/j.apsusc.2015.08.173

27. Gui M, Li F, Wang Y, et al. Photocatalytic degradation of organic pollutants by modified graphite phase carbon nitride (Chinese). Journal of Liaoning University of petrochemical technology. 2019; 39(2): 1-9.

28. Lam SM, Sin JC, Mohamed AR. A review on photocatalytic application of g-C3N4/semiconductor (CNS) nanocomposites towards the erasure of dyeing wastewater. Materials Science in Semiconductor Processing. 2016; 47: 62-84. doi: 10.1016/j.mssp.2016.02.019

29. Meng L, Yin W, Wang S, et al. Photocatalytic behavior of biochar-modified carbon nitride with enriched visible-light reactivity. Chemosphere. 2020; 239: 124713. doi: 10.1016/j.chemosphere.2019.124713

30. Zong L, Tang J, Mou B, et al. Research progress of attapulgite/carbon composite adsorbents (Chinese). Progress in chemical industry. 2021; 40(1): 282-296.

31. Rozic M, Cerjan-Stefanovic S, Kurajica S, et al. Ammonical nitrogen removal from water by treatment with clays and zeolites. Water Research. 2000; 34(14): 3675-3681.

32. Xu Y, Wu X, Liu C, et al. Effect of biomass carbon source on organic modification and adsorption properties of attapulgite (Chinese). Chemical reaction engineering and process. 2013; 29(2): 119-124.

33. Liu W, Yao C, Wang M, et al. Kinetics and thermodynamics characteristics of cationic yellow X-GL adsorption on attapulgite/rice hull-based activated carbon nanocomposites. Environmental Progress & Sustainable Energy. 2012; 32(3): 655-662. doi: 10.1002/ep.11680

34. Premarathna KSD, Rajapaksha AU, Sarkar B, et al. Biochar-based engineered composites for sorptive decontamination of water: A review. Chemical Engineering Journal. 2019; 372: 536-550. doi: 10.1016/j.cej.2019.04.097

35. Pi L, Jiang R, Zhou W, et al. g-C3N4 Modified biochar as an adsorptive and photocatalytic material for decontamination of aqueous organic pollutants. Applied Surface Science. 2015; 358: 231-239. doi: 10.1016/j.apsusc.2015.08.176

36. Inyang M, Gao B, Zimmerman A, et al. Sorption and cosorption of lead and sulfapyridine on carbon nanotube-modified biochars. Environmental Science and Pollution Research. 2014; 22(3): 1868-1876. doi: 10.1007/s11356-014-2740-z

37. Zhang J, Lu M, Wan J, et al. Effects of pH, dissolved humic acid and Cu2+ on the adsorption of norfloxacin on montmorillonite-biochar composite derived from wheat straw. Biochemical Engineering Journal. 2018; 130: 104-112. doi: 10.1016/j.bej.2017.11.018

38. Ahmed MB, Zhou JL, Ngo HH, et al. Single and competitive sorption properties and mechanism of functionalized biochar for removing sulfonamide antibiotics from water. Chemical Engineering Journal. 2017; 311: 348-358. doi: 10.1016/j.cej.2016.11.106

39. Tang J, Mu B, Zong L, et al. One-step synthesis of magnetic attapulgite/carbon supported NiFe-LDHs by hydrothermal process of spent bleaching earth for pollutants removal. Journal of Cleaner Production. 2018; 172: 673-685. doi: 10.1016/j.jclepro.2017.10.181

40. Tan X, Liu Y, Gu Y, et al. Biochar pyrolyzed from MgAl-layered double hydroxides pre-coated ramie biomass (Boehmeria nivea (L.) Gaud.): Characterization and application for crystal violet removal. Journal of Environmental Management. 2016; 184: 85-93. doi: 10.1016/j.jenvman.2016.08.070

41. Ahmed MB, Zhou JL, Ngo HH, et al. Nano-Fe 0 immobilized onto functionalized biochar gaining excellent stability during sorption and reduction of chloramphenicol via transforming to reusable magnetic composite. Chemical Engineering Journal. 2017; 322: 571-581. doi: 10.1016/j.cej.2017.04.063

42. Shi J. On the Synergetic Catalytic Effect in Heterogeneous Nanocomposite Catalysts. Chemical Reviews. 2012; 113(3): 2139-2181. doi: 10.1021/cr3002752

43. He S, Xiao K, Chen XZ, et al. Enhanced photoelectrocatalytic activity of direct Z-scheme porous amorphous carbon nitride/manganese dioxide nanorod arrays. Journal of Colloid and Interface Science. 2019; 557: 644-654. doi: 10.1016/j.jcis.2019.09.035

44. Li Y, Zhang P, Wang D, et al. Adsorption characteristics of Rhodamine B on magnetic Ginkgo biloba biochar (Chinese). Functional materials. 2019; 50(5): 5121-5127.

45. Eltaweil AS, Ali Mohamed H, Abd El-Monaem EM, et al. Mesoporous magnetic biochar composite for enhanced adsorption of malachite green dye: Characterization, adsorption kinetics, thermodynamics and isotherms. Advanced Powder Technology. 2020; 31(3): 1253-1263. doi: 10.1016/j.apt.2020.01.005

46. Mubarak NM, Kundu A, Sahu JN, et al. Synthesis of palm oil empty fruit bunch magnetic pyrolytic char impregnating with FeCl3 by microwave heating technique. Biomass and Bioenergy. 2014; 61: 265-275. doi: 10.1016/j.biombioe.2013.12.021

47. Qiu Y, Xu X, Xu Z, et al. Contribution of different iron species in the iron-biochar composites to sorption and degradation of two dyes with varying properties. Chemical Engineering Journal. 2020; 389: 124471. doi: 10.1016/j.cej.2020.124471

48. Jung KW, Choi BH, Jeong TU, et al. Facile synthesis of magnetic biochar/Fe3O4 nanocomposites using electro-magnetization technique and its application on the removal of acid orange 7 from aqueous media. Bioresource Technology. 2016; 220: 672-676. doi: 10.1016/j.biortech.2016.09.035

49. Meili L, Lins PV, Zanta CLPS, et al. MgAl-LDH/Biochar composites for methylene blue removal by adsorption. Applied Clay Science. 2019; 168: 11-20. doi: 10.1016/j.clay.2018.10.012

50. Wang H, Zhao W, Chen Y, et al. Nickel aluminum layered double oxides modified magnetic biochar from waste corncob for efficient removal of acridine orange. Bioresource Technology. 2020; 315: 123834. doi: 10.1016/j.biortech.2020.123834

51. Chen S, Zhou M, Wang HF, et al. Adsorption of Reactive Brilliant Red X-3B in Aqueous Solutions on Clay–Biochar Composites from Bagasse and Natural Attapulgite. Water. 2018; 10(6): 703. doi: 10.3390/w10060703

52. Yao Y, Gao B, Fang J, et al. Characterization and environmental applications of clay–biochar composites. Chemical Engineering Journal. 2014; 242: 136-143. doi: 10.1016/j.cej.2013.12.062

53. Wu F, Liu W, Qiu J, et al. Enhanced photocatalytic degradation and adsorption of methylene blue via TiO2 nanocrystals supported on graphene-like bamboo charcoal. Applied Surface Science. 2015; 358: 425-435. doi: 10.1016/j.apsusc.2015.08.161

54. Mian MM, Liu G, Yousaf B, et al. One-step synthesis of N-doped metal/biochar composite using NH3-ambiance pyrolysis for efficient degradation and mineralization of Methylene Blue. Journal of Environmental Sciences. 2019; 78: 29-41. doi: 10.1016/j.jes.2018.06.014

55. Fazal T, Razzaq A, Javed F, et al. Integrating adsorption and photocatalysis: A cost effective strategy for textile wastewater treatment using hybrid biochar-TiO2 composite. Journal of Hazardous Materials. 2020; 390: 121623. doi: 10.1016/j.jhazmat.2019.121623

56. Xu J, Hu P, Lv Ji, et al. Pollution characteristics and control measures of antibiotics and resistance genes in water environment (Chinese). Science and technology Herald. 2018; 36(15): 13-23.

57. Li R, Wang Z, Zhao X, et al. Magnetic biochar-based manganese oxide composite for enhanced fluoroquinolone antibiotic removal from water. Environmental Science and Pollution Research. 2018; 25(31): 31136-31148. doi: 10.1007/s11356-018-3064-1

58. Gao M, Zhang Y, Gong X, et al. Removal mechanism of di-n-butyl phthalate and oxytetracycline from aqueous solutions by nano-manganese dioxide modified biochar. Environmental Science and Pollution Research. 2017; 25(8): 7796-7807. doi: 10.1007/s11356-017-1089-5

59. Mansoori S, Davarnejad R, Ozumchelouei EJ, et al. Activated biochar supported iron-copper oxide bimetallic catalyst for degradation of ciprofloxacin via photo-assisted electro-Fenton process: A mild pH condition. Journal of Water Process Engineering. 2021; 39: 101888. doi: 10.1016/j.jwpe.2020.101888

60. Tan X, Liu S, Liu Y, et al. One-pot synthesis of carbon supported calcined-Mg/Al layered double hydroxides for antibiotic removal by slow pyrolysis of biomass waste. Scientific Reports. 2016; 6(1). doi: 10.1038/srep39691

61. Li G, Huang Z, Chen C, et al. Simultaneous adsorption of trace sulfamethoxazole and hexavalent chromium by biochar/MgAl layered double hydroxide composites. Environmental Chemistry. 2019; 16(1): 68. doi: 10.1071/en18132

62. Ashiq A, Sarkar B, Adassooriya N, et al. Sorption process of municipal solid waste biochar-montmorillonite composite for ciprofloxacin removal in aqueous media. Chemosphere. 2019; 236: 124384. doi: 10.1016/j.chemosphere.2019.124384

63. Liang G, Wang Z, Yang X, et al. Efficient removal of oxytetracycline from aqueous solution using magnetic montmorillonite-biochar composite prepared by one step pyrolysis. Science of The Total Environment. 2019; 695: 133800. doi: 10.1016/j.scitotenv.2019.133800

64. Ashiq A, Adassooriya NM, Sarkar B, et al. Municipal solid waste biochar-bentonite composite for the removal of antibiotic ciprofloxacin from aqueous media. Journal of Environmental Management. 2019; 236: 428-435. doi: 10.1016/j.jenvman.2019.02.006

65. Premarathna KSD, Rajapaksha AU, Adassooriya N, et al. Clay-biochar composites for sorptive removal of tetracycline antibiotic in aqueous media. Journal of Environmental Management. 2019; 238: 315-322. doi: 10.1016/j.jenvman.2019.02.069

66. Kim JR, Kan E. Heterogeneous photocatalytic degradation of sulfamethoxazole in water using a biochar-supported TiO2 photocatalyst. Journal of Environmental Management. 2016; 180: 94-101. doi: 10.1016/j.jenvman.2016.05.016

67. Wang Y, Li F, Rong X, et al. Remediation of Petroleum-contaminated Soil Using Bulrush Straw Powder, Biochar and Nutrients. Bulletin of Environmental Contamination and Toxicology. 2017; 98(5): 690-697. doi: 10.1007/s00128-017-2064-z

68. Ye S, Yan M, Tan X, et al. Facile assembled biochar-based nanocomposite with improved graphitization for efficient photocatalytic activity driven by visible light. Applied Catalysis B: Environmental. 2019; 250: 78-88. doi: 10.1016/j.apcatb.2019.03.004

69. Xiao Y, Lyu H, Yang C, et al. Graphitic carbon nitride/biochar composite synthesized by a facile ball-milling method for the adsorption and photocatalytic degradation of enrofloxacin. Journal of Environmental Sciences. 2021; 103: 93-107. doi: 10.1016/j.jes.2020.10.006

70. Hu X, Sun Y. Oxidative degradation of polycyclic aromatic hydrocarbons in industrial site contaminated soil by chlorine dioxide (Chinese). Journal of applied technology. 2021; 21(1): 88-91.

71. Oleszczuk P, Kołtowski M. Effect of co-application of nano-zero valent iron and biochar on the total and freely dissolved polycyclic aromatic hydrocarbons removal and toxicity of contaminated soils. Chemosphere. 2017; 168: 1467-1476. doi: 10.1016/j.chemosphere.2016.11.100

72. Dong CD, Chen CW, Kao CM, et al. Wood-Biochar-Supported Magnetite Nanoparticles for Remediation of PAH-Contaminated Estuary Sediment. Catalysts. 2018; 8(2): 73. doi: 10.3390/catal8020073

73. Chen J, Dong H, Tian R, et al. Remediation of Trichloroethylene-Contaminated Groundwater by Sulfide-Modified Nanoscale Zero-Valent Iron Supported on Biochar: Investigation of Critical Factors. Water, Air, & Soil Pollution. 2020; 231(8). doi: 10.1007/s11270-020-04797-3

74. Dong H, Zhang C, Hou K, et al. Removal of trichloroethylene by biochar supported nanoscale zero-valent iron in aqueous solution. Separation and Purification Technology. 2017; 188: 188-196. doi: 10.1016/j.seppur.2017.07.033

75. Ouyang D, Yan J, Qian L, et al. Degradation of 1,4-dioxane by biochar supported nano magnetite particles activating persulfate. Chemosphere. 2017; 184: 609-617. doi: 10.1016/j.chemosphere.2017.05.156

76. Yan J, Han L, Gao W, et al. Biochar supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene. Bioresource Technology. 2015; 175: 269-274. doi: 10.1016/j.biortech.2014.10.103

77. Dong CD, Chen CW, Hung CM. Synthesis of magnetic biochar from bamboo biomass to activate persulfate for the removal of polycyclic aromatic hydrocarbons in marine sediments. Bioresource Technology. 2017; 245: 188-195. doi: 10.1016/j.biortech.2017.08.204

78. Li F, Lin M. Synthesis of Biochar-Supported K-doped g-C3N4 Photocatalyst for Enhancing the Polycyclic Aromatic Hydrocarbon Degradation Activity. International Journal of Environmental Research and Public Health. 2020; 17(6): 2065. doi: 10.3390/ijerph17062065

79. Meng F, Song M, Chen Y, et al. Promoting adsorption of organic pollutants via tailoring surface physicochemical properties of biomass-derived carbon-attapulgite. Environmental Science and Pollution Research. 2020; 28(9): 11106-11118. doi: 10.1007/s11356-020-10974-y