Review

Biochar-based composites for removing chlorinated organic pollutants: Applications, mechanisms, and perspectives

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ABSTRACT

Chlorinated organic pollutants constitute a significant category of persistent organic pollutants due to their widespread presence in the environment, which is primarily attributed to the expansion of agricultural and industrial activities. These pollutants are characterized by their persistence, potent toxicity, and capability for long-range dispersion, emphasizing the importance of their eradication to mitigate environmental pollution. While conventional methods for removing chlorinated organic pollutants encompass advanced oxidation, catalytic oxidation, and bioremediation, the utilization of biochar has emerged as a prominent green and efficacious method in recent years. Here we review biochar's role in remediating typical chlorinated organics, including polychlorinated biphenyls (PCBs), triclosan (TCS), trichloroethene (TCE), tetrachloroethylene (PCE), organochlorine pesticides (OCPs), and chlorobenzenes (CBs). We focus on the impact of biochar material properties on the adsorption mechanisms of chlorinated organics. This review highlights the use of biochar as a sustainable and eco-friendly method for removing chlorinated organic pollutants, especially when combined with biological or chemical strategies. Biochar facilitates electron transfer efficiency between microorganisms, promoting the growth of dechlorinating bacteria and mitigating the toxicity of chlorinated organics through adsorption. Furthermore, biochar can activate processes such as advanced oxidation or nano zero-valent iron, generating free radicals to decompose chlorinated organic compounds. We observe a broader application of biochar and bioprocesses for treating chlorinated organic pollutants in soil, reducing environmental impacts. Conversely, for water-based pollutants, integrating biochar with chemical methods proved more effective, leading to superior purification results. This review contributes to the theoretical and practical application of biochar for removing environmental chlorinated organic pollutants.

1. Introduction

With the deterioration of the ecological environment, although the application of persistent organic pollutants (POPs) has long been curbed, there is still a need to adopt certain means to eliminate their adverse effects on the environment [1]. POPs are widely distributed and categorized into pesticides, industrial chemicals, and compounds employed in production and their byproducts [2,3]. Chlorinated organic pollutants (chlorinated POPs) epresent a significant subset of POPs. Consequently, the exploration of removal

methods for these contaminants remains a critical area of research. Organochlorine compounds are a general term for a class of organic compounds in which the hydrogen atom is replaced by a chlorine atom, a series of organic compounds with a carbon or hydrocarbon backbone combined with chlorine. There is a wide range of examples of chlorinated organics, including polychlorinated biphenyls (PCBs), triclosan (TCS), trichloroethene (TCE), tetrachloroethene (PCE), organochlorine pesticides (OCPs), and chlorobenzenes (CBs), which are widely applied in industry, resulting in residues in most environments as persistent organic substances. The transfer pathways of chlorine-containing organic pollutants in the environment are shown in Fig. 1. POPs have high mobility and may be concentrated in snow and water bodies through long-distance atmospheric transport and wet and dry deposition, which pollute clean areas. Part of the POPs are

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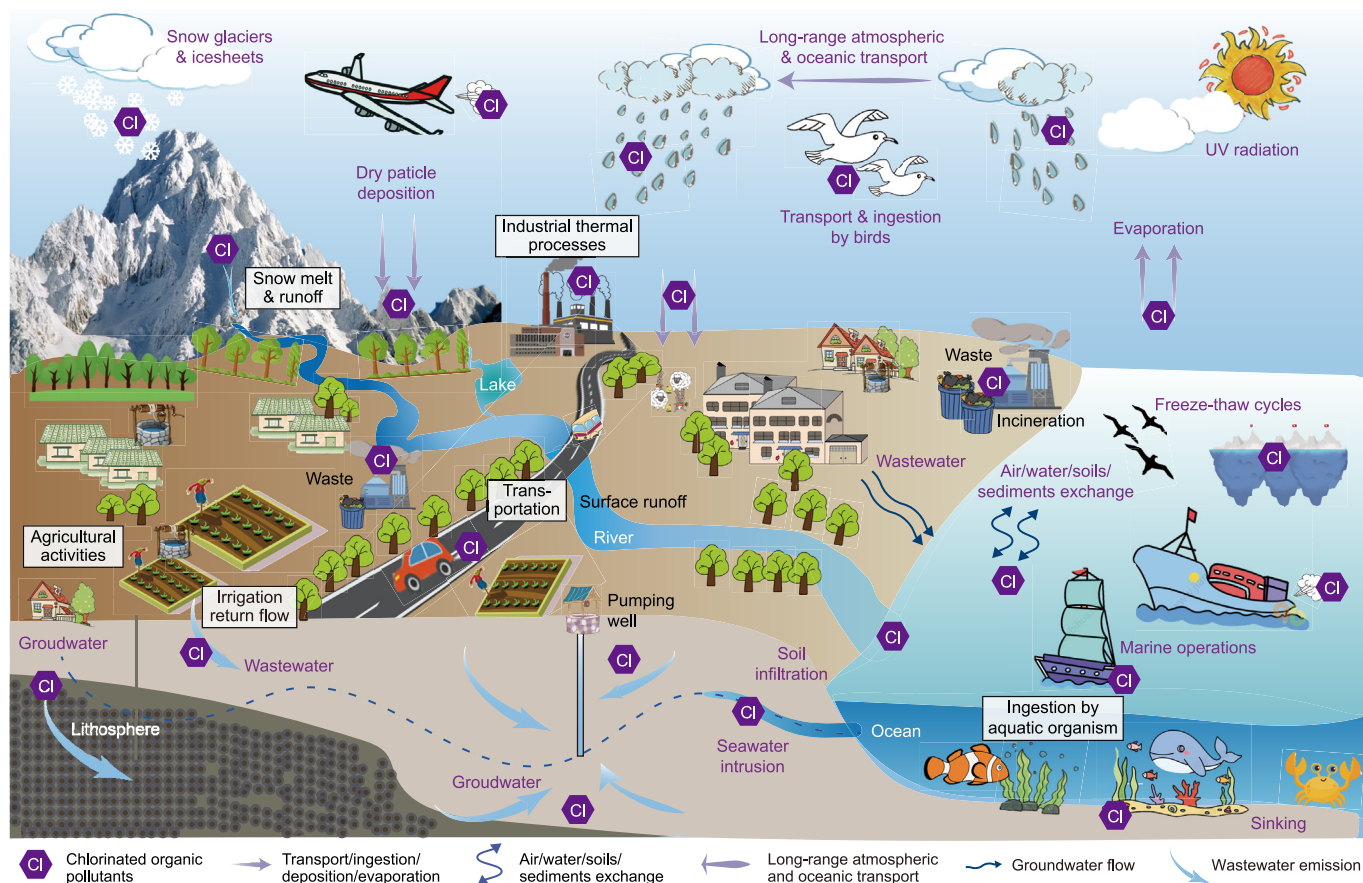[1] Co-first author.

Fig. 1. Distribution migration of organic chlorine-containing pollutants in the environment.

transferred from the aqueous phase to the soil and substrate through physical action and enter into the biological chain along with bioabsorptive transformations, which further threaten the safety of the whole ecosystem [4,5]. With the development of industry, the range of applications for chlorine substitutes has increased accordingly with the emission of large amounts of environmental chlorinated pollutants, which are highly toxic, nonbiodegradable, and carcinogenic, resulting in negative effects on human and wildlife health [6,7]. Therefore, managing chlorinated pollutants is important for protecting against public health issues [8,9]. The methods for treating chlorinated organics are mainly advanced oxidation, electrocatalytic oxidation, photocatalytic oxidation, nano-zero-valent iron treatment, and bioremediation.

Advanced oxidation is a wastewater treatment method that utilizes strong oxidizing substances (hydroxyl radicals, ozone, superoxide radicals, etc.) to react with dissolved pollutants in wastewater to degrade the pollutants [10,11]. Electrocatalytic oxidation refers to the electrode, electrolyte interface charge transfer to accelerate the reaction of catalytic oxidation, which can effectively reduce the activation energy of the interfacial electric field reaction system to promote the reaction so that the organic matter in the anode is rapidly degraded [12]. Photocatalytic oxidation is based on charge separation on the surface of photoconductors. Semiconductors are used as catalysts in the photocatalytic process, whereby electrons are excited from the valence band to the conduction band by absorbing photons with energies greater than or equal to the bandgap of the semiconductor material, producing photoelectrons and holes. The holes c- = onvert water or

hydroxide ions adsorbed on the surface of the semiconductor to ·OH to degrade chlorinated organic pollutants to CO_2 and H_2O [13]. Nano zero-valent iron treatment refers to zero-valent iron particles with particle sizes in the range of 1−100 nm, which are widely utilized for the disposal of organic halides, inorganic salts, and heavy metals in wastewater and soil on account of their large specific surface area and strong reducibility [14]. Biodegradation is a treatment method that utilizes the metabolic action of organisms to remove organic matter from the environment [15,16]. However, in recent years, the coupling of these methods with biochar materials has also gradually gained attention in the study of removing chlorinated organics [17,18].

Biochar is a carbon-rich material produced by biomass pyrolysis under anaerobic conditions [19]. Due to its unique microporous structure, rich functional groups, large specific surface area, and high porosity, biochar is significantly superior in removing pollutants and ecological remediation [20−22]. According to research, biochar has shown excellent performance in pollutant adsorption in the environment [23], remediation of contaminated environments [24], wastewater treatment [25], energy production [26], catalysis [27], climate protection [28], and agricultural soil amendments [29]. It has become one of the main materials for removing environmental pollutants due to its low-cost raw materials, wide range of raw materials, good adsorption properties, large scope for modification, and environmental friendliness [19].

Given the current state of pollution caused by chlorinated organic compounds, cost-effective and efficient approaches for the remediation of chlorine pollutants from the environment are urgently needed [30]. Removing chlorinated organics from the

environment by employing biochar is a promising solution for environmental remediation. In addition to being an environmentally friendly material with strong adsorption capacity, biochar can also be potentially valuable as a source of electron donor, electron acceptor, or electron shuttle for pollutant degradation for microorganisms and coupled with catalytic reactions to achieve the removal of chlorinated pollutants from the environment by various biological or chemical methods [18,31].

Currently, the related reviews on the removal of environmental pollutants by biochar focus on the raw materials, synthesis, modification, process parameters, and activation of biochar, ignoring the nature and characteristics of the pollutants. There is a lack of reviews on the application of biochar in removing chlorinated organic pollutants [30,32]. Consequently, this paper systematically summarizes the latest research progress on removing chlorinated organic pollutants by biochar, expecting to promote the practical application of biochar for removing chlorinated organic pollutants. With this aim in sight, this paper presents a detailed description of the effectiveness of biochar on the removal of several typical chlorinated organic pollutants (PCBs, TCS, TCE, PCE, CBs, OCPs), the application method and the analysis of the removal mechanism to provide a more comprehensive understanding of the removal of organic chlorinated compounds. This study also systematically introduces the link between the properties of biochar and preparation methods, providing a theoretical basis for developing methods for preparing high-performance biochar materials. Additionally, this review discussed the advantages and shortcomings of the treatment of chlorinated organics utilizing biochar and the potential challenges and possibilities for the future, making a theoretical contribution to the realization of biochar applications for removing chlorinated organics.

2. Biochar preparation

Biochar is made from biomass waste, carbonized under non-oxygen or oxygen-limited conditions, and forms a carbonaceous material [33]. Biochar usually exhibits high porosity, aromaticity, multiple anionic functional groups, and a large specific surface area, making it a good adsorbent material for removing environmental pollutants [34]. To date, various kinds of materials, such as sewage sludge [35,36], agricultural biowaste [37], lignocellulosic biomass [38], algae [39,40], coconut shell [41], walnut shell [42], and food waste [43], have been made into biochar, which demonstrates the richness and diversity of raw materials for biochar preparation. In addition to the variety of raw materials used to prepare biochar, there are various methods, including pyrolysis, hydrothermal carbonization, torrefaction, and gasification [44]. The technology of preparing biochar by pyrolysis is relatively mature and convenient to operate, and the pyrolysis process produces fewer pollutants, but the prepared biochar has the disadvantages of uneven pore size distribution, small specific surface area, and poor adsorption selectivity [45]. The hydrothermal carbonization preparation of biochar has a high total carbon conversion rate of nearly 100%, the preparation process is green and environmentally friendly, and the degree of resource utilization of waste is high. However, the process as a whole is immature and strongly influenced by environmental factors, and the specific reaction mechanism still needs to be further explored [46]. The biochar prepared by Torrefaction can be an alternative fuel due to its high calorific value and carbon content and the low energy consumption and cost of the preparation process. However, the performance of the prepared biochar was unstable, and further optimization of the process mode is still needed [47]. Biochar prepared by gasification has a high carbon conversion rate and low manufacturing cost without the requirement of an anaerobic environment, but gasification produces a low yield of

biochar and has more limitations in the operating parameters [44]. As seen from Table 1, biochar can be prepared from various raw materials, mostly from cheap waste biomass, and pyrolysis is the mainstream method for biochar preparation.

Generally, the larger the surface area of biochar, the more favorable it is for the adsorption of pollutants and the enhancement of its ability to remove pollutants. Therefore, the pyrolysis temperature in the preparation process needs special attention, as it will greatly affect the size of the specific surface area of biochar [60]. The escape of volatiles during the pyrolysis process leads to the generation of pores and cracks in the biochar, which results in the generation of a microporous structure containing a large number of adsorption active sites and functional groups (pore sizes <2 nm and the number of micropores is positively correlated with the ability of biochar to adsorb pollutants [61]. The kinds and amounts of functional groups on the surface of biochar affect the removal mechanism of pollutants; for example, -C-H and −OH functional groups can form stable complexes with heavy metals to enhance the adsorption of heavy metals, and the presence of phenolic groups and −COOH can enhance the surface charge and redox properties of biochar to degrade organic pollutants [62]. Accordingly, with the application and development of biochar, a large number of studies have found that certain modifications (metal salt/metal oxide modification, organic modification, acid/base modification, solid waste modification, and other modified materials) of biochar lead to better performances of biochar [63,64] (see Fig. 2). Metal oxides or salts are added to the biochar feedstock and then pyrolyzed to produce modified metal biochar. In this case, the modified biochar doped with metal ions enhances the surface complexation, precipitation, and electrostatic effect between the biochar and the pollutants. Moreover, it enhances the ability to reduce organic pollutants and achieves more effective pollutant removal [65]. Organic modification can compound abundant functional groups (-SH, −NH$_2$, −OH, and −COOH, etc.) of organic matter onto biochar, providing more adsorption sites for pollutants and thus enhancing biochar's removal performance on pollutants [66]. Acid modification can introduce groups from acids into biochar, such as -PO and -POOH from phosphoric acid, −NO from nitric acid, −SO$_3$H from sulfuric acid, and −OH and −COOH groups from organic acids, thus enriching the types of functional groups in biochar [67]. Alkaline modification can change the content of oxygen-containing functional groups and the size of the specific surface area of biochar, modified by NaOH to increase the content of −OH and C=C in biochar, and modified by KOH to increase the specific surface area of biochar [68]. Acid/alkali modification is facile and inexpensive, but it is difficult to obtain uniform modification results due to the diverse conditions of biochar preparation. Biochar modification utilizing carbonaceous materials enhances the adsorption capacity of virgin biochar by increasing its specific surface area and more adsorption sites [69]. Most biochar does have superior performance and a stronger ability to remove pollutants after modification, but different modification methods have various mechanisms and effects on the modification of biochar; therefore, the characteristics of the pollutants, the type of raw materials of biochar, the preparation method of biochar and other factors should be taken into consideration to choose the appropriate modification method. Biochar has a high surface area and abundant functional groups, which can remove pollutants from water and soil through various mechanisms (adsorption, pore filling, ion exchange, and electrostatic interactions), and substances such as heavy metals, pesticides, antibiotics, and dyes can be fixed efficiently [70−72]. Due to its stable carbon frame structure and difficulty in decomposition, biochar can directly form a carbon sink, and its application to agricultural soils can hinder the production and emission of greenhouse gases, thus reducing greenhouse gas

Table 1
Preparation and modification of biochar and its application in the environment.

Raw materials	Preparation method	Mechanism	Application	Reference
Corn straw biochar	300 °C, pyrolysis	Biochar enhances degrading microbial activity and inhibits the activity of pathogenic flora.	2% CB300 increased the dissipation rate of polycyclic aromatic hydrocarbon (PAH) in soil by 31%.	[48]
Wheat straw biochar	400–700 °C, co-pyrolysis	Biochar has a large specific surface area, high aromaticity, and high adsorption capacity.	The phenanthrene (PHE) biodegradation rate showed a u-shaped distribution with increasing pyrolysis temperature.	[49]
Rhombus shell biochar	Chemical precipitation method; Loaded LaFeO$_3$	Interactions between surface oxygen species at LaFeO$_3$ defective sites and the graphitized biochar network	The total PAHs degradation efficiency was 90%.	[50]
Water hyacinth biochar	700 °C, pyrolysis	Highly aromatic, dominated by nitrogen, carbon, and oxygen functional groups.	The removal of PAHs from the sediment reached 74%.	[51]
Bamboo biochar	700 °C, pyrolysis	Physisorption, based on weak forces and electrostatic interactions, and chemisorption, involving stronger bonds through functional groups on biochar.	The biochar-modified electrolytic integrated system achieved 90.3% removal of atrazine.	[52]
Zaoji biochar	500 °C, pyrolysis	Physisorption, based on weak forces and electrostatic interactions, and chemisorption, involving stronger bonds through functional groups on biochar.	Zaoji biochar removed 97.6% of the pesticide Leuco.	[53]
Sludge biochar	500 °C, pyrolysis	Higher adsorption capacity and increased adsorption active sites.	Malathion was degraded by 65–70%.	[54]
Magnetic algal residue biochar	The algal residue and Fe$_3$O$_4$ were mixed in the proportion C:Fe = 4:1; 800 °C, pyrolysis	Pore filling, ion exchange, π-π EDA, surface complexation, and hydrogen bonding.	Atrazine removal by biochar reached 95.5% within 8 h at a concentration of 10 mg L^{-1}.	[55]
Sawdust biochar	600 °C, pyrolysis	Adsorption is enhanced by pore adsorption and hydrophobicity of the biochar surface.	The removal of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) was more than 90%.	[56]
Microalgae *Chlorella*	The hydrothermal liquefaction at 250 °C and 10 MPa	Endothermic physical adsorption and π-π interaction.	The maximum adsorption capacity of tetracycline was up to 25.9 mg g^{-1}.	[57]
Sludge biochar	800 °C, pyrolysis	PMS is activated by C=O, pyridine nitrogen, and graphitic nitrogen on the surface of biochar.	It achieved 99% removal of bisphenol A within 20 min.	[58]
Iron (Fe)-impregnated biochar produced by *Cyperus alternifolius*	500 °C, pyrolysis	Biochar adsorption, plant uptake, and microbial degradation.	Chlorpyrifos, endosulfan, fenvalerate, and diuron were efficiently removed over 99%.	[59]

emissions and slowing global warming [73]. Recently, a variety of biochar materials, such as bamboo biochar [74], pine needle biochar, wheat straw biochar [75], and sludge biochar [76], have been prepared and are capable of removing most chlorinated organic pollutants, such as PCBs, TCS, and TCE. Moreover, many investigations have modified basic biochar, such as KMnO$_4$ and Fe(II)-modified sludge-based biochar [77], Fe–Mn-modified catalytic sludge biochar [77], and composites of bamboo biochar and zero-valent iron [78], with TCS and TCE removal rates close to 100%, improving the removal efficiency of chlorinated organic pollutants during the preparation of biochar. It is clear from the above that the application of biochar to the removal of pollutants has the advantages of accessible raw materials, low cost, and high treatment efficiency, so biochar materials have a broad application prospect for the removal of hard-to-degrade chlorinated organic compounds.

3. Sources and toxicity of organic pollutants containing chlorine

Chlorinated organic pollutants are widely used in industry and are dispersed throughout the ecosphere through transport and transformation, jeopardizing biosafety and disrupting the balance of ecosystems. There are various kinds of chlorinated organic pollutants, which are mainly classified as polychlorinated biphenyls, triclosan, trichloroethene, tetrachloroethylene, organochlorine pesticides, chlorobenzenes, etc.

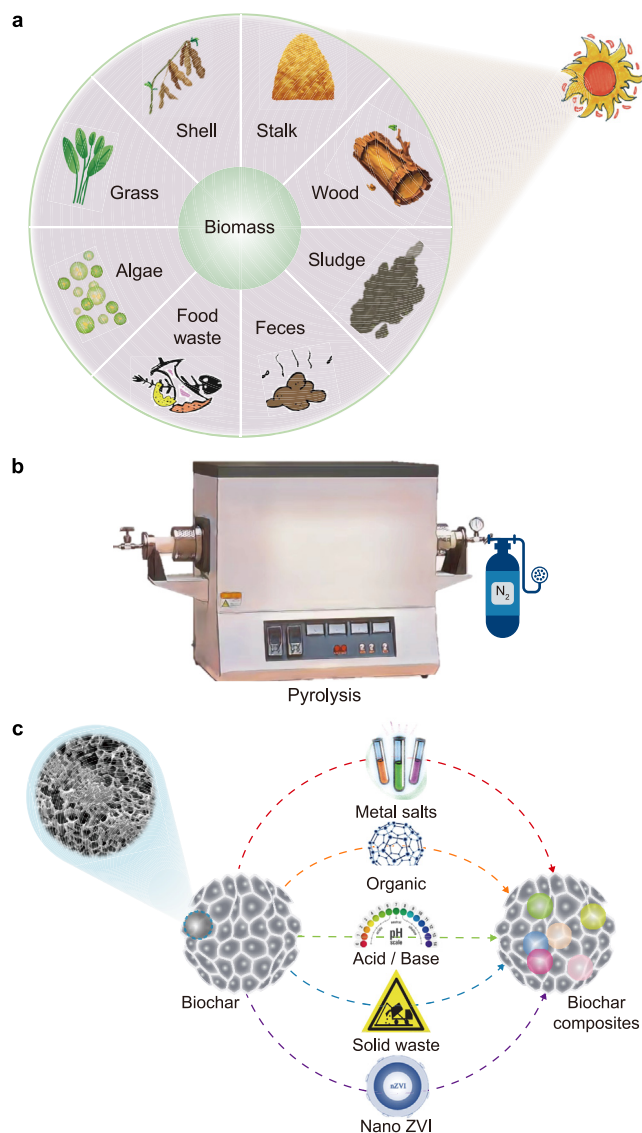### 3.1. Polychlorinated biphenyls

The organic compounds resulting from substituting biphenyls with varying numbers (1–10) of chlorine atoms are collectively called polychlorinated biphenyls (PCBs). Due to the diversity of the

number and position of substitutions of chlorine atoms, the number of PCBs series of substances is up to 209 [79]. The synthesis of PCB originated in the 1880s, mainly for industrial chemicals and then, between 1929 and 1930, for commercial applications [80]. PCBs are widely used as additives in various industrial products such as insulating oil, fireproofing agents, copy paper, rubber, transformer dielectric fluid, plasticizer, lubricant, ceramic glaze, and printing ink [81], owing to their stable physical and chemical properties, resistance to strong acids and bases, and good electrical insulation and heat resistance. However, the application of PCBs has caused water, soil, and sediment contamination in the environment. PCBs enter organisms through dietary intake, skin contact, and respiration, posing a potential risk to the ecological environment and human health [82,83]. Thus, on May 22, 2001, the Stockholm Convention listed PCBs as POPs. In addition, PCBs are chemically stable, biotoxic, and environmentally enriched and are hard to degrade naturally in the environment. Thus, suitable solutions are urgently needed to remediate environmental pollution, and using biochar to treat PCB pollution is a cost-effective and eco-friendly method [84].

3.2. Triclosan

It is well known that pharmaceuticals and personal care products (PPCPs) are of concern as a class of micropollutants with a wide range of usages and relevance to people's lives, with large emissions and highly toxic metabolites, and the presence of PPCPs has been detected in water, soil, sediment, residual sludge, and people's excreta, posing an enormous threat to people's public environmental safety [85]. Triclosan (5-chloro-2-(2′,4′-dichlorophenoxy) phenol, TCS) is a typical PPCP; its basic physicochemical properties are shown in Table 2. TCS is a broad-spectrum antibacterial agent

Fig. 2. Preparation and modification process of biochar: **a**, Types of biomass; **b**, Preparation of biochar by pyrolysis; **c**, Modification of biochar.

that kills and inhibits gram-positive bacteria, negative bacteria, yeast, and viruses [86]. Since its introduction in 1957, TCS has been widely applied in manufacturing soaps, detergents, cosmetics, plastic additives, and other household products [87]. In the 1990s, more than 700 antimicrobial products containing TCS ingredients were on the market [88]. Until October 2010, European Union regulations banned it as a temporary additive for plastic food contact materials. The United States Food and Drug Administration banned TCS as an antimicrobial agent in soap in 2016, but TCS is still detectable in some products [89]. The widespread usage of TCS has led to significant environmental accumulation through various pathways. For example, TCS has been detected in water, soil, sediment, aquatic organisms, and humans, thus arousing health concerns [90]. Many studies have shown that although TCS is not highly toxic to mammals, it can disrupt the endocrine activity of organisms, damage their endocrine and reproductive development systems, and reduce antibiotic resistance [91]. TCS is highly stable due to its low solubility and high internal surface tension, making it difficult to degrade naturally in the environment, especially in

nutrient-poor aquatic or terrestrial ecosystems, so effective methods to remove TCS from the environment are needed to reduce the environmental threat it poses [92]. Presently, TCS is mainly removed by photolysis, advanced oxidation, adsorption, and biodegradation, but most treatment methods are costly, complex, and unsuitable for large-scale applications [93]. In contrast, removing TCS from wastewater by adsorption using biochar prepared from waste biomass reduces infrastructure and operating costs and is one of the current hot spots of interest [94].

3.3. Trichloroethylene

Trichloroethylene (TCE) is a chlorinated aliphatic hydrocarbon with the physical properties shown in Table 2. It is commonly used as an industrial solvent in the direction of chemical cleaning, industrial degreasing, or chemical raw materials [115]. TCE, an organochlorine solvent, was consumed by industry in 2011 at a rate of 428000 tons and was detected at National Priorities List sites in more than half of the countries [116]. TCE is commonly found in water and soil or volatilized into the atmosphere, posing a certain environmental risk [117]. The presence of TCE in the environment has been reported to enter the body through contaminated water or air and subsequently cause specific toxicity to human organs, such as carcinogenicity to the kidneys and liver, and negative effects on the pregnancy response [118]. Consequently, removing TCE from the environment has interested researchers in environmental safety and human health.

3.4. Others

Tetrachloroethylene (PCE), typically used as an industrial chlorinated solvent, degrades slowly, which causes residues in the environment that pose a safety risk to water and soil and may harm human reproduction and health [119]. Among the various organochlorine pollutants, organochlorine pesticides (OCPs) have been one of the key pollutants of concern for environmental pollution. OCPs are intended for agricultural usage as insecticides and were banned many years ago due to their high toxicity, high transmission capacity, and chemical stability [109]. However, OCPs are also a typical group of POPs, and the destruction of OCPs is important for the remediation of the environment, given that they have previously accumulated in large quantities in the environment, causing worldwide soil contamination and adverse environmental effects [120]. Chlorobenzene (CB) is commonly well known as an industrial solvent, insect repellent, and intermediate in the synthesis of pesticides. It is classified as one of the priority pollutants due to its volatility, high toxicity, persistence, ease of migration and biomagnification, which pose a risk to ecological safety and human health [121].

Typically, the strategies for eliminating chlorinated organic pollutants are categorized into three main approaches: physical, chemical, and biological methods [122]. Physical methods cannot effectively remove chlorinated organic pollutants in the environment. They are often applied as a pretreatment technique to enrich and partially treat chlorinated organic pollutants in the environment, mainly by gas extraction, adsorption, and extraction in conjunction with other methods for removing chlorinated organic pollutants in water [123]. Although the physical methods are convenient, economical, and industrialized, the removal effectiveness is often limited. Consequently, these methods are typically complemented by advanced treatment technologies to enhance removal performance. Chemical approaches primarily utilize advanced oxidation, photocatalytic oxidation, supercritical oxidation, microwaves, and electrochemistry to remove chlorinated organic pollutants [124]. Although such methods are widely

Table 2
Basic properties of different chlorinated organics and the effectiveness of biochar in treating chlorinated organic pollutants.

Chlorine-containing organic species	Basic properties	Biochar characteristics	Application effects	Reference
Polychlorinated biphenyls (PCBs)	$C_{12}H_{10-x}Cl_x$, insoluble in water, soluble in most organic solvents, flowing oily liquid or white crystalline solid or non-crystalline resin, chemically stable.	Bamboo biochar; Surface area: 276 $m^2\ g^{-1}$.	Low organic carbon content combined with biochar is more beneficial for PCBs removal.	[95]
		Pine needle biochar and wheat straw biochar; Average pore width: 35.3 and 19.8 Å; Surface area: 5.2 and 128 $m^2\ g^{-1}$; Elemental C content:75.9% and 69.1%.	The biosorption of PCBs by earthworms was reduced by 71.6%.	[75]
		Sludge biochar; The pore structure and the degree of organic matter decomposition of biochar increase with the preparation temperature.	The removal of PCBs from soils reached 99.9%.	[76]
Triclosan (TCS)	$C_{12}H_7Cl_3O_2$, slightly soluble in water, moderately soluble in dilute alkali, soluble in organic solvents, slightly aromatic, and high purity. White crystalline powder, excellent storage stability.	A heat-dried blend of waste-activated sludge and anaerobically digested primary solids; BET surface area:182 $m^2\ g^{-1}$; Average pore radius is 2.83 Å; Total micropore volume: 0.08 $cm^3\ g^{-1}$.	Remove TCS from wastewater in continuous flow-through columns, with a removal rate of 1330 $\mu g\ g^{-1}$.	[96]
		Food waste-750 °C; Specific surface area: 23.08 $m^2\ g^{-1}$; Pore volume: 0.062 $cm^3\ g^{-1}$; Pore size: 10.78 nm.	Removal of TCS was 14.6 mg g^{-1} (for 50 mg L^{-1}) and 55.6 mg g^{-1} (for 200 mg L^{-1}).	[97]
		$KMnO_4$ and Fe (II) -modified sludge-based biochar; It has a cell-like structure surrounded by EPSs with a wide particle size distribution.	Degradation of TCS reached 91.3% within 3 h.	[77]
		Olive oil production waste; Micropore area: 0.796 $m^2\ g^{-1}$; Average pore width: 26.9 nm.	The adsorption rate of TCS reached 98%.	[98]
		Sludge biochar; It possesses a porous and lamellar structure with a specific surface area of 23.7 $m^2\ g^{-1}$ and C=O functional groups.	Biochar degraded TCS by activating sodium persulphate and achieved 32.5% of total organic carbon removal.	[99]
		Fe- and Mn-modified catalytic sludge biochar; It has layered pore structures and a specific surface area of 24.90 $m^2\ g^{-1}$.	TCS was degraded by 91.3% within 180 min.	[77]
		Empty palm bundle biochar; Specific surface area: 60.3 $m^2\ g^{-1}$; Porosity: 0.54 $cm^3\ g^{-1}$.	The maximum adsorption of TCS was 35.4 mg g^{-1}.	[100]
Trichloroethylene (TCE)	C_2HCl_3, slightly soluble in water, easily soluble in organic solvents, slightly sweet, colorless and transparent liquid, and highly stable.	Wheat straw-nZVI; BET surface area: 137.2 $m^2\ g^{-1}$; Average pore diameter: 8.0 nm.	The removal of TCE by loading with zero-valent iron nanoparticles reached 79% within 15 h.	[101]
		Peanut shells; Particle size distribution: 162 μm (D_{50}) and 376 μm (D_{90}).	Complete removal of TCE by biochar in combination with microorganisms within 150 h.	[102]
		Spruce and oak-derived biochar; BET surface area: 39 and 216 $m^2\ g^{-1}$; Pore diameter: 39 and 12 nm.	The removal rate of TCE was greater than 99.5%.	[103]
		Corn straw; BET surface area: 0.79 $m^2\ g^{-1}$; T-plot of micropore volume: $1.06 \times 10^{-4}\ cm^3\ g^{-1}$.	Microbially coupled biochar provided complete TCE removal within four days.	[104]
		Peanut shell biochar modified with 2 M $FeCl_3$ solution; Specific surface area: 88.81 $m^2\ g^{-1}$; Average pore diameter: 1.54 nm; Iron content: $27.4 \pm 0.1\%$.	Magnetic biochar completely removed TCE from water.	[105]
		Biochar coupled with nanoscale zero-valent iron-nickel material; BET surface area: 1153.68 $m^2\ g^{-1}$; Micropore volume: 0.0425 $cm^3\ g^{-1}$; Pore width: 3.03 nm.	Degradation of TCE was higher than 99%.	[78]
Tetrachloroethylene (PCE)	C_2Cl_4, insoluble in water, soluble in organic solvents, colorless liquid, and highly stable.	Alternanthera philoxeroides biochar; C=C, C−O, and C=O were dominant in sorption on BC300.	The biochar prepared at 400 °C had a sorption capacity of 2.83 mg g^{-1} for PCE.	[106]
		Mugwort biochar; BET surface area: 6 $m^2\ g^{-1}$; Mesopore volume: 0.023 $cm^3\ g^{-1}$.	Over 99% of PCE achieved non-toxic conversion at neutral and alkaline pH conditions.	[107]
				[108]

Table 2 (*continued*)

Chlorine-containing organic species	Basic properties	Biochar characteristics	Application effects	Reference
Organochlorine pesticides (OCPs)	Highly lipid soluble and structurally stable.	Peat moss biochar; BET surface area: 294 m^2 g^{-1}.	Biochar had the best removal performance at a pyrolysis temperature of 500 °C.	
		Soybean straw biochar; It has high aromatic organic matter.	The accessibility of OCPs degraded by 14−86%.	[109]
		Nephelium lappaceum biochar composite zero-valent iron nanomaterial; Surface area: 71.98 m^2 g^{-1}; Total pore volume: 0.33 m^2 g^{-1}; weight% of iron: 66.12%.	Removal rates of 96−99% were achieved for six OCPs.	[110]
		Peanut shell biochar-loaded nano-zero valent iron (BC/nZVI) material; Specific surface area: 30.31 m^2 g^{-1}; Presented a chain-like structure.	The degradation of γ-HCH in water by peanut shell BC/nZVI was 91.87% within 24 h.	[111]
Chlorobenzenes (CBs)	$C_6H_xCl_{(6-x)}$, insoluble in water, soluble in organic solvents, colorless and transparent liquid, and stable.	Rice husk biochar; BET surface area: 29.71 m^2 g^{-1}; Ash: 33.96%.	The CB removal rate within 6 h was 59.4%.	[112]
		Composite of bamboo biochar and nZVI; The surface is rough, and small particles are distributed inside the pores.	The CB removal rate was 99.92%.	[113]
		Corn stover biochar; Surface area: 17.5 m^2 g^{-1}; ash: 47.8%; Total volume: 2.67×10^{-2} cm^3 g^{-1}.	The adsorption of higher CB (pentachlorobenzene and hexachlorobenzene) equilibrates faster than the adsorption of lower CB.	[114]

applicable and have excellent effectiveness, the process investment is high and incapable of satisfying the needs of large-scale applications [124]. Bioremediation is the elimination of pollutants from the environment by the absorption, enrichment, transformation, scavenging, or degradation of plants, microorganisms, or protozoa, among others. Among them, the microbial remediation method is more pronounced. Through the metabolic activities of microorganisms, chlorinated organic matter in the environment is transformed into easily degradable substances or even mineralized [125]. Biological methods are convenient and easily treated *in situ* but are highly selective, require the domestication of microorganisms to build a tolerance system for pollutants, and have a long overall technological process [126]. In conclusion, there is an urgent need to develop highly innovative technologies for removing chlorinated organic pollutants, which are widely distributed, stable, and hazardous, and to optimize efficient, economic, and green technologies for removing chlorinated organic pollutants from the environment.

4. Applications and mechanisms of biochar for the removal of chlorinated POPs

In general, biochar adsorbs chlorinated organic pollutants mainly through hydrophobic interactions, electron donor and acceptor interactions, pore filling, electrostatic interactions, and intermolecular forces [127]. It is worth mentioning that different types of biochar have different adsorption mechanisms for different chlorinated organics, as shown in the following section.

4.1. Removal of PCBs

The molecular structure of PCBs is closely related to the adsorption process and effectiveness of biochar. An increase in chlorine atoms within the PCB structure enhances hydrophobicity, facilitating greater adsorption by biochar [128]. In addition, the molecular volume of PCBs increases with the number of chlorine atoms, altering their surface characteristics. This, in turn, impacts the adsorption process and its effectiveness [84].

On the other hand, the preparation of biochar is crucial to the adsorption effects of PCBs since the properties of biochar, such as specific surface areas, pore volumes, particle sizes, surface morphology, nutrient composition, functional group content, hydrophilicity, and interaction exchange capacity, can affect the adsorption of PCBs to different degrees. The pore-filling mechanism is one of the main mechanisms for biochar adsorption of organic pollutants. The roughness of biochar surface particles negatively correlates with their ability to adsorb PCBs. In contrast, the larger pore volume and specific surface area benefit the removal of PCBs, so the ability to adsorb PCBs can be improved by preparing biochar with microstructures such as porous micropores and smooth surfaces [129].

Silvani et al. prepared biochar using rice husk and mixed wood as substrates for *in situ* remediation of contaminated soil. They showed that both biochar reduced the biosorption of PCBs and that the type of biochar was the main influencing factor compared to the amount of biochar [130]. Wang et al. used wheat straw and pine needles as substrates to pyrolyze into biochar for PCB adsorption [131]. The results showed that two kinds of biochar could adsorb PCBs, where the adsorption affinity of wheat straw biochar for PCBs was stronger than that of pine needle biochar because of the larger surface area and higher surface hydrophobicity of wheat biochar. Moreover, the adsorption volume of biochar for PCBs increased with the concentration of PCBs, and this strong adsorption was mainly related to the enhanced π-π electron donor-acceptor interactions and hydrogen bonding on the surface of biochar. In addition, after adding metal cations to the solution, the direct interaction between metal cations and PCBs attenuated the mutual weakening effect of cation-π-bonds, resulting in a decrease in the hydrophilicity of the local area around the cation-complex functional body and the competitive adsorption of water was alleviated, which further enhanced the adsorption capacity of biochar on PCBs [132].

For soils contaminated by PCBs, biochar simultaneously adsorbs PCBs from the soil during the remediation process and reduces the

bioavailability and accumulation effect of PCBs in the soil (Fig. 3), reducing the environmental risk. Huang et al. showed that the low organic carbon capacity in bamboo biochar-amended soils was more favorable for the degradation of PCBs and biochar adsorption, which may be related to the role of soil bacterial communities, where the soil bacterial 16S rDNA abundance increased with the degradation of PCBs [95]. Hayat et al. found that combining biochar, plants, and degrading bacteria achieved up to 85% removal of PCBs from soil. Biochar as a soil amendment promoted the proliferation of soil microbial communities, which increased the activity and number of PCB-degrading bacteria and thus facilitated the removal of PCBs [133]. The large number of active functional groups in biochar can enhance the metabolic action and biomass of microorganisms by promoting the adhesion and proliferation of microbial cells [134]. Denyes et al. added 11.1% biochar to the soil after PCB contamination. After 50 days, the uptake of PCBs by earthworms and plant tissues was reduced by 88% and 89%, respectively. The survival of aboveground plants and animals was improved, indicating that biochar can reduce the bioavailability of PCBs by organisms, suggesting its ability to improve soil quality and reduce environmental hazards [135]. The high water-holding properties and the ability of biochar to provide nutrients (nitrogen, phosphorus, copper, etc.) contributed to the growth of plants, and the carboxyl groups produced by oxidation on the surface of biochar facilitated the improvement of cation exchange capacity, which led to better retention of nutrients in the soil [136]. In addition, the adsorption capacity of biochar for PCBs due to its porous structure and large specific surface area was stronger than its uptake by plants and animals, leading to decreased bioavailability [137].

In summary, the adsorption of PCBs by biochar has great potential for application to reduce its bioaccumulation effect in the environment, remediate the contaminated environment, and reduce the environmental safety risk caused by PCB pollution.

4.2. Removal of TCS

The specific surface area and surface functional groups of biochar were reported to be the main factors affecting the adsorption capacity. Kang et al. demonstrated a direct correlation between the specific surface area of biochar and its adsorption capacity. They found that a larger surface area results in higher adsorption efficiency. Additionally, oxygen-containing functional groups in biochar, such as hydroxyl, carboxyl, and carbonyl groups, facilitate the

Fig. 3. Biochar coupled with biotechnology for remediation of PCBs contaminated soil.

formation of hydrogen bonds with the −OH groups of TCS. This interaction significantly enhances the adsorption effectiveness [97]. Kimbell et al. prepared biochar with a mixture of waste-activated sludge and its anaerobically digested solids as the substrate. They found that the biochar could adsorb TCS from secondary wastewater [96]. The interaction of C−O bonds, hydrogen bonds between π-electrons and π-π bonds on the surface of biochar with the aromatic ring of TCS may be the major adsorption mechanism, but it should be noted that competition for the location of inorganic nutrients, such as ammonia nitrogen and phosphorus and other micropollutants at high concentrations in wastewater, creates a physical barrier to the adsorption sites on the biochar surface, lowering the removal rate of TCS [97,138]. Wu et al. found that the higher the carbonization of biochar was, the higher the adsorption coefficient, π-π interactions were the main mechanism for TCS adsorption by wheat straw biochar, and the high hydrophobicity of TCS itself enhanced its ability to compete for adsorption on the surface of the biochar [139,140]. Consequently, the adsorption efficiency of triclosan (TCS) is markedly influenced by the inherent properties of TCS, the preparation conditions of the biochar, and the presence of coexisting substances in the environment.

While biochar adsorption of biochar is low cost and effective, it has certain limitations, such as low adsorption efficiency and the biotoxicity of TCS not being inhibited; therefore, some biochar modification is needed to improve the degradation efficiency of TCS. It has been shown that a combination of processes such as biochar and advanced oxidation/photocatalysis show excellent performances in removing TCS. Wang et al. utilized sludge to prepare biochar to activate sodium persulfate (PMS) for the degradation of TCS. They showed that the TCS degradation reached 100% within 2 h with biochar and PMS concentrations of 1.0 g L^{-1} and 0.8 mM, respectively [99]. The analysis revealed that the hydroxyl radicals, sulfate radicals, and singlet oxygen generated by the activated PMS play major roles in the degradation of TCS [141]. Hydroxyl radicals can attach to the biochar surface, while sulfate radicals facilitate electron transfer. This interaction generates carbon-centric radicals on the benzene ring, initiating the dechlorination and hydroxylation of TCS. These processes ultimately lead to the mineralization of TCS into carbon dioxide and water [99]. Ma et al. prepared a biochar/Ag_3PO_4/polyaniline (PANI) composite photocatalyst to improve the adsorption capacity, light and utilization, and reaction activity of Ag_3PO_4. The results showed that after modification by biochar and PANI, the separation of photogenerated carriers increased, h^+ was the main ROS, and the removal of TCS reached 85.21% within 10 min with an apparent rate constant 1.38 times higher than that before modification [142]. The degradation of TCS by $BiVO_4$-modified N-doped biochar reached 94.6% within 60 min, simultaneously reducing the biotoxicity of TCS, with the difference that the main ROS were ·OH instead of h^+ [143]. Guo et al. applied $KMnO_4$ and Fe(II)-modified sludge-based biochar (Fe/Mn-SBC) to the electrocatalytic degradation of TCS. Compared with the control group, Fe/Mn-SBC had a higher specific surface area and a rich pore structure, and the addition of metal elements caused structural defects on the surface of the material, which accelerated the electron transfer process and improved the electrochemical activity; consequently, the catalytic performance was significantly improved [77,144]. Fe/Mn-SBC facilitated the heterogeneous Fenton reaction process, producing large amounts of free radicals, such as ·OH, $^1O_2$, and ·O_2^-, for the degradation and biodetoxification of TCS and proposed a possible degradation path for TCS, as shown in Fig. 4 [77]. It is not surprising that biochar modification to improve its catalytic properties for the degradation of TCS has promising applications.
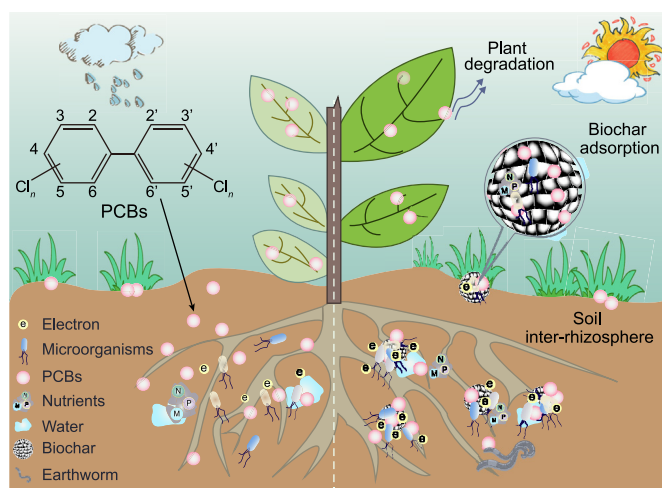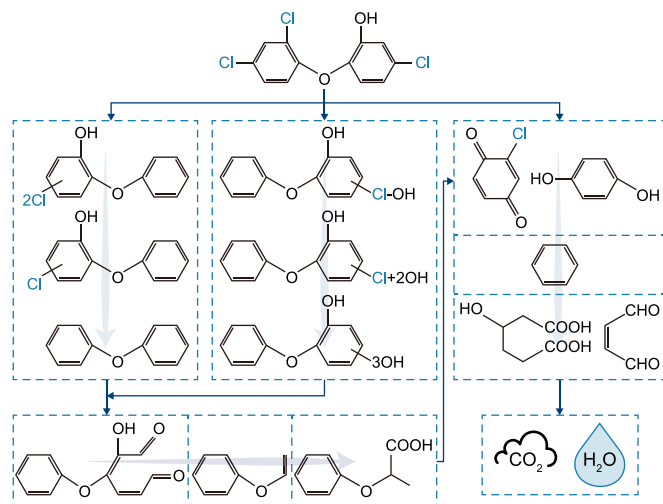
Fig. 4. Possible degradation pathways of triclosan (TCS).

4.3. Removal of TCE

Typically, methods of degrading TCE include advanced oxidation and biodegradation, and using materials such as biochar to remove TCE is also coming to the attention of researchers [145,146]. The removal efficiency of TCE is closely related to the properties of the biochar. Ai et al. prepared animal, plant, and sewage waste biochar at 950 °C. The results showed that animal biochar was the most effective in dechlorinating TCE under the catalytic influence of green rust, which was closely dependent on the high surface area and small pore size of the biochar, the higher number of C−O groups and the high adsorption of TCE [147]. Ahmad et al. found that biochar prepared at 700 °C had a higher degree of carbon enrichment, forming a less polar, more aromatic carbon structure and achieving 88.47% removal of TCE, which was 1.28 times higher than that at 300 °C [148]. Moreover, different sizes of biochar show different properties and adsorption effects. Jin et al. found that biochar with 0−0.75 mu had the highest TCE adsorption efficiency, with a 19.5−62.3% increase in TCE removal compared to biochar with 150−250 and 75−150 mu particle sizes [149]. This enhanced performance is linked to smaller particles offering a larger surface area, more microporous structures, increased electrical conductivity, and a higher density of surface functional groups. Collectively, these attributes boost the biochar's adsorption and catalytic potential. In the preparation of biochar, different elements were added to modify the biochar, and it was found that the catalytic performance of the biochar modified with N and S elements for green rust was greatly improved, and the degradation rate of TCE was increased by 3.5 and 2.5 times, respectively, compared to the raw biochar [150]. It is no wonder that biochar with a large specific surface area, high aromaticity, low polarity, and high adsorption capacity can better remove TCE from wastewater based on chemisorption and pore diffusion mechanisms [151].

In addition to the properties of biochar itself, combining biochar with chemical methods to improve its ability to remove TCE is a competitive approach. Liu et al. synthesized magnetic biochar at 800 °C. They found that pore filling, high hydrophobicity, and reductive degradation with higher reductive iron loading were the main mechanisms for TCE elimination by this biochar [105]. Yan et al. synthesized a biochar composite and nanoscale zero-valent iron (nZVI) to activate peroxynitrite and degrade TCE in water [152]. As shown in Fig. 5a, the experiment showed that the redox effect of nZVI and the oxygen-containing functional groups of

biochar could act as electron transfer mediators, which could provide more $SO_4^- \cdot$ active central sites and promote the degradation of TCE, with 99.4% removal of TCE within 5 min [153,154]. Shan et al. prepared a composite of biochar-nZVI-Ni bimetallic particles to achieve complete removal of TCE from water by activating persulfate and found that $SO_4^- \cdot$ and OH· radicals dominate in degrading TCE in an acidic environment [78]. The more hydrophilic the biochar is, the stronger the adsorption of the BC/nZVI composite, and the more favorable the surface morphology formed and the consequent decay of the passivation process of the nZVI particles for the removal of TCE [155]. In contrast, superoxide radicals and singlet oxygen, mediated by Fe^0 and oxygen-containing groups (C═O), may also be the main reactive oxygen species promoting TCE dichlorination [156,157]. Meng et al. achieved high removal rates of TCE by synthesizing iron-based lignin biochar composites with high specific surface area, uniform nanoparticle distribution, and high iron carbide content. Iron carbide acted as an electron donor for TCE and catalyzed the formation of atomic H· to degrade TCE into 1,2-dichloroethane [158].

On the other hand, combining biochar and biological action for the degradation of TCE is also a better treatment method. Liu et al. added biochar prepared from peanut shells as a substrate to a mixed culture to promote anaerobic biodegradation of TCE. Experimental results showed that adding biochar resulted in a rapid decrease in the concentration of TCE (39.4−88.8%) within 24 h and a 54.5−69.7% reduction in the time to complete removal of TCE [102]. The addition of biochar could shorten the adaptation phase of microorganisms, alleviate the toxic inhibition of TCE, facilitate electron transfer, and increase the abundance of cometabolizing dechlorinating microorganisms while reducing the abundance of competing microorganisms, ultimately establishing
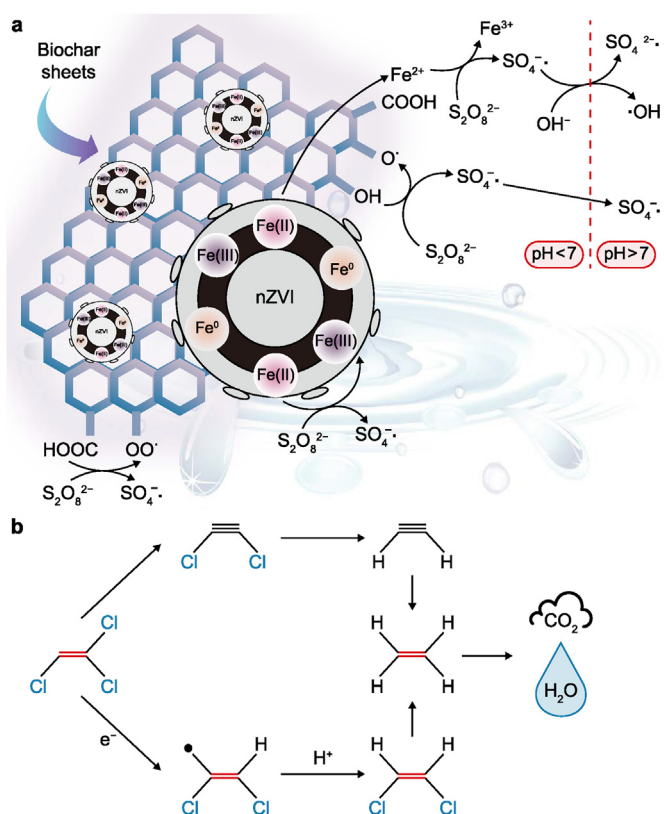

Fig. 5. Degradation mechanisms and possible degradation pathways of trichloroethene (TCE). **a**, Degradation mechanisms; **b**, Possible degradation pathways.

an efficient dechlorination system [102]. Siggins et al. similarly found that biochar prepared from herbal residues and spruce promoted the growth of dechlorinating microorganisms such as *Desulfitobacterium* spp., *Sulfurospirillium* spp., and *Desulfuromonas* spp. and achieved over 99.7% removal of TCE [159]. Biochar could provide nutrients for the growth of microorganisms, and the structure of the material itself increased the contact area with the contaminants and facilitated the electron transfer process, which facilitated the dechlorination process of microorganisms but had no effect on the degradation pathway of TCE [104]. Lyu et al. proposed the efficient degradation of TCE by carboxymethyl cellulose-loaded stabilized iron sulphide nanoparticles in combination with Corynebacterium roqueforti HRJ4, and the degradation pathway of TCE was proposed as shown in Fig. 5b [160]. Rossi et al. showed that the biofilm biochar reactor effectively adsorbed TCE and its intermediate degradation products, and the presence of *Dehalococcoides mccartyi*, a specific microorganism for reductive dechlorination, and the specific genes tceA, bvcA, and vcrA was found, indicating the supportive role of biochar for specific dechlorination microorganisms [161]. Biochar can enhance the growth activity of dechlorinating microorganisms such as *Dehalococcoides* and compounds chemisorption and biodegradation to strengthen its ability to remove TCE [162].

In general, the removal of TCE by biochar is mainly based on the pore-filling mechanism and chemisorption. Consequently, biochar with a larger specific surface area, increased microporosity, higher carbonation level, and more abundant surface functional groups tend to exhibit enhanced TCE adsorption capabilities [163]. Modifying biochar and coupling it with advanced oxidation or biological methods for TCE removal is also gaining attention, offering new pathways for future TCE degradation.

4.4. Removal of other chlorinated POPs

More recently, biochar has also shown superior performance in the remediation of other chlorinated organics, for example, in the removal of tetrachloroethylene (PCE), organochlorine pesticides (OCPs), and chlorobenzenes (CBs), all of which have made some progress.

4.4.1. The removal of PCE

The biodegradation of PCE has been extensively studied, but the slow mineralization rate and long degradation cycles are not conducive to large-scale practical applications [164]. Consequently, research into the rapid degradation of PCE in composite materials based on biochar is also entering the public domain. Schreiter et al. prepared biochar from cow dung, grain hulls, and wood chips yet observed limited PCE adsorption capacity. This limitation may stem from the size exclusion effect of the biochar's micropores, which impedes PCE uptake. Therefore, enhancing the biochar's adsorption properties for PCE may require modifications to its structure [165]. It has been shown that functional groups, such as C$-$O, C$=$O, and C$=$C, in the biochar are crucial factors for the removal of PCE and that acid-modified biochar possesses sufficient functional groups, providing a development direction for the preparation of biochar materials for the removal of PCE [106,166]. Yang et al. prepared wormwood-based biochar for the sulfide-catalyzed degradation of PCE and showed that toxic-free conversion (pH $\geq$ 7) was achieved for over 99% of the PCE, eventually converting to acetylene and chloride ions [167]. Under alkaline conditions, HS$^-$ and S^{2-} are stable in the nature; hence, the pyridine nitrogen structure on the surface of the biochar can nucleophilically react with the adjacent O$-$C$=$O to bond into the sulfur-containing nucleophilic structure, which is more conducive to the catalytic degradation of PCE via sulfides [166]. Furthermore, Kim et al. utilized biochar derived from

peat moss to eliminate a variety of volatile organic compounds (TCE, PCE) from groundwater with positive results, facilitating the remediation of contaminated groundwater [108].

4.4.2. Removal of OCPs

It has been proven that biochar can reduce the active fraction of pesticides in the soil and change the distribution of the soil microbial system, increasing the microbial content and promoting the degradation of pesticides [168]. Ali et al. discovered that biochar changed the composition of the microbial community system in the soil, with an increased abundance of *Proteobacteria* and *Firmicutes* as well as higher total microbial mass, with soybean straw biochar showing better uptake of OCPs in the soil than biochar with peanut shells, rice straw, and sewage sludge as substrates, which lowered the environmental risk posed by OCPs in the soil [109]. Moreover, biochar resulted in reduced vegetable biosorption of OCPs and a consequent reduction in the risk index and hazard quotient index and incremental lifetime cancer risk values associated with vegetable consumption [109]. The nonlinear sorption capacity of biochar for OCPs increased with increasing biochar porosity, and the ratio of biochar to organic carbon was also an overarching factor in the absorption rate of OCPs [169]. Batool et al. synthesized composites by loading nanozero-valent iron on *Nephelium lappaceum* biochar to remove six OCPs from water, achieving 96$-$99% removal of OCPs within 120 min, mainly based on π-π interactions, pore filling, and hydrophobic adsorption mechanisms [110]. Li et al. applied nZVI loaded on peanut shell biochar to remove OCPs from soil and found that the composite had a beneficial effect on eliminating a wide range of OCPs. 92% removal of γ-HCH was achieved within 24 h, and the activity of dehydrogenase and soil microorganisms in the soil was improved to some extent, laterally indicating the improvement of soil quality [111].

4.4.3. Removal of CBs

To reduce the threat posed by residual CBs in the environment, treatment methods based on biochar materials have been progressively applied for CB remediation with good outcomes. Zhang et al. found that hydroquinone-quinone molecules contained in rice husk biochar could induce the production of reactive oxygen species accompanied by the production of hydrogen peroxide and hydroxyl radicals in the Fenton reaction, which in turn promoted the redox degradation of chlorobenzene [112]. Biochar is mainly based on physical adsorption and pore-filling mechanisms for the adsorption of BCs, and the more similar the properties, such as polarity and electrophilicity of biochar versus CBs, the stronger the adsorption capacity, which provides a new idea for the preparation of biochar [114]. Song et al. showed that wheat straw effectively reduced the bioavailability of 1,2,4-CB in the soil, reducing its harmful effects on environmental organisms [170]. It has also been demonstrated that when biochar was added at too high a level, the biosorption of HCB in the soil decreased, but the abundance of dechlorinating bacteria was reduced, which in turn led to a reduction in the dechlorination of HCB [171]. Nevertheless, oxidation on the surface of biochar increases the content of O-containing polar molecules, which reduces the accessibility of aromatic carbon on the surface of the material, thereby inhibiting the adsorption of CBs on biochar [172]. This means that the elemental composition and actual amount of biochar usage should be strictly limited to ensure optimum removal.

Biochar has shown good results in treating other chlorinated organic pollutants and removing organic chlorinated compounds mentioned above. The ball-milled modified hickory biochar prepared by Xiang et al. removed chloroform by a surface adsorption mechanism [173]. Studies have shown that biochar could inhibit the biodegradation of pentachlorophenol (PCP) but could rely on its

strong adsorption to remove PCP [174]. Nitrogen-doped biochar catalyzed the degradation of carbon tetrachloride to Cl^-, trichloromethane, CS_2, and HCO_3^- [175].

Biochar-based methodologies for treating chlorinated organic pollutants vary depending on the type of chlorinated organic pollutant. For PCBs, biochar is mostly available for *in situ* remediation of contaminated soils and combined with soil microorganisms, flora, and fauna to achieve mainly ecological remediation goals. Regarding the removal of TCS, the coupled process of biochar and advanced oxidation/photocatalysis achieved a removal rate of 85.2−100%. Hence, optimizing the oxidation process largely influenced the removal rate of TCS. Further studies focused on combining biochar with nZVI and coupling advanced oxidation for efficient and rapid removal of TCE, and the removal rate could reach 99.4%. In addition, a considerable number of studies have also combined biochar with microorganisms to establish a dechlorination system for TCE, but at this time, the removal process of TCE is more prolonged, but the removal effect is variable, distributed between 39.4% and 99.7%. Biochar-coupled chemical methods are more suitable for PCE degradation while combining biochar and biological systems is more suitable for removing OCPs and CBs from the soil. Interestingly, chlorinated organic pollutants in soil are more suitable for removal using biochar and biology, while for pollutants in water, the combination of biochar and chemical methods is more effective. The effect of methods combined with biochar on the removal of chlorinated organic pollutants is more significant than the effect of the biochar feedstock, so exploring suitable methods based on different pollutant types would be beneficial to promote this research field. It is readily apparent that biochar shows superior performance in the adsorption and degradation of a wide range of organochlorines. Using biochar to eliminate organochlorine pollutants in the real environment is highly promising.

5. Future perspectives

As summarized in Table 2, biochar, as a highly efficient adsorptive catalytic material, can be coupled with chemical or biological methods to effectively remove chlorinated organic pollutants (PCBs, TCS, TCE, PCE, CBs, OCPs, etc.) from the environment to remediate the environment. Based on the current research status of biochar treatment of chlorinated organic pollutants, the following perspectives are summarized for the application of biochar to the efficient and rapid removal of chlorinated organic pollutants in the environment and for engineering applications:

(1) The physicochemical properties of biochar include chemical structures, porosity, specific surface area, and functional group content. All change depending on the preparation method of biochar (raw materials and pyrolysis temperature), which in turn affects the adsorption capacity and catalytic effect of biochar on pollutants. Hence, finding suitable raw materials (waste-based) and developing low-cost preparation methods to prepare biochar materials with excellent performances are the basis for applying biochar to treat organic chlorine pollutants.

(2) It should be noted that the long-term stability of biochar is somewhat controversial, particularly due to concerns over the potential release of organic pollutants with excessive use, which could pose ecological risks. Consequently, attention should be given to the long-term stability of biochar and the transport and storage methods to reduce its negative impact on the environment. Developing easily recyclable biochar formulations can enhance its practical utility. Furthermore, establishing quality standards for biochar's safe ecological

application is crucial. These measures aim to ensure biochar's safe and sustainable use as a long-term environmental solution.

(3) As the nature of organic pollutants varies at different chlorination levels, studies should be carried out on specially formulated biochar suitable for each chlorinated organic pollutant. This approach necessitates optimizing biochar dosage and production methods to enhance its pollutant removal efficacy. The goal is to develop efficient, cost-effective, and environmentally friendly solutions for treating chlorinated organics utilizing biochar.

(4) Biochar can enhance the electrical conductivity among dechlorinating microbial communities and act as a conductive medium in bioremediation systems, but the exact mechanism is still unclear, so further research is warranted to analyze the direct degradation ability of biochar on the degradation of chlorinated organic matter, and the mechanism of promoting the growth of microorganisms and the catalytic effect of cometabolism on the degradation of organic compounds, to realize the practical application of biochar coupled with microorganisms for the degradation of organochlorine pollutants.

(5) Biochar, as a superior catalytic material, can show significant effectiveness in removing chlorine-containing organic pollutants by coupling with advanced oxidation or nZVI, but it is only applied to a relatively small number of activators. The application of activators should be expanded, and the activation mechanism and catalytic mechanism of biochar for advanced oxidation should be further studied to improve the ability of biochar to activate advanced oxidation or nZVI.

(6) Machine learning and artificial intelligence have been combined in the internet era to build models, speculate on pollutant adsorption by biochar, elucidate degradation principles, and optimize experimental parameters to provide a new pathway for future environmental management.

(7) Predominantly, research on pollutants has been conducted in simulated, controlled laboratory settings, which may not accurately reflect the complexities of real-world environmental pollution. Therefore, research should be carried out in real wastewater or environments to overcome the disturbing factors in real environments and improve the efficiency of degrading organochlorine pollutants. Adjusting the conditions or engineering methods based on these findings could significantly advance the industrial application of these solutions.

6. Conclusions

This review summarizes and discusses the methods, action mechanisms, and future directions of biochar in treating chlorinated organic pollutants. Optimizing the combination of biochar and other methods based on the characteristics of organochlorine contaminants can significantly improve the efficiency of removing chlorinated organic pollutants. Biochar's effectiveness largely derives from chemisorption and pore-filling mechanisms. Its integration with biological, advanced oxidation, and nZVI promotes microbial growth, electron transfer rates, and free radical activation, facilitating the rapid and efficient degradation of chlorinated organics. The investigation results show that biochar coupled with advanced oxidation can remove more than 85% of TCS, and sludge biochar combined with PMS can remove 100% of TCS. nZVI and biochar coupled together can remove up to 99.4% of TCE in 5 min. However, the combination of biochar and bioprocessing removes TCE with large variations in the effectiveness of TCE removal

(54.5−99.7%). This approach is also cost-effective, offering significant potential for further development. Applying synthetic biochar materials from waste biomass to remove chlorinated organic pollutants is conducive to achieving sustainable development goals in a circular economy and a green, low-carbon environment. Hence, customizing biochar modifications to pollutant characteristics and optimizing parameters for microbial and advanced oxidation processes can guide biochar's practical application in mitigating the environmental impact of chlorinated organic pollutants.

CRediT authorship contribution statement

Qingqing Song: Methodology, Software, Writing - Original Draft. **Fanying Kong:** Conceptualization, Resources, Writing - Review & Editing. **Bing-Feng Liu:** Project Administration. **Xueting Song:** Validation. **Hong-Yu Ren:** Conceptualization, Investigation, Writing - Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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