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Biochar for the adsorption of endocrine-disrupting chemicals: performance, mechanisms, and strategies

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Endocrine-disrupting chemicals (EDCs) in the environment can interfere with the normal levels of hormones in human bodies, posing threats to human health. Hence, the removal of EDCs is an urgent matter. Biochar, recognized as a low-cost and eco-friendly adsorbent, possesses significant potential for removing EDCs. In recent years, numerous studies have reported on the adsorption of pollutants by biochar. However, a systematic summary specifically addressing the adsorption of EDCs by biochar remains absent. This review addresses this gap by providing the first comprehensive synthesis of biochar applications in the adsorption of EDCs, introducing a novel modular design strategy which is proposed herein for the first time to tailor biochar properties to target EDC structures. This article initially summarizes and analyzes the preparation and modification methods of biochar. Secondly, a discussion is conducted regarding the analysis of various types of EDCs adsorbed by biochar. Based on the mechanism by which biochar absorbs EDCs, a modular design strategy for biochar is first proposed. Additionally, the main influencing factors and economic feasibility of biochar removal for EDCs are deliberated. Finally, prospects for future research on biochar removal of EDCs are presented.

1. Introduction

Endocrine-disrupting chemicals (EDCs) are commonly recognized as one of the most influential pollutants in aquatic environments, and have recently attracted considerable attention as emerging contaminants.[1] EDCs can be broadly grouped into two types: natural and synthetic. Natural EDCs primarily include estrogens, androgens, progestogens, and plant estrogens, while synthetic EDCs typically consist of phthalates, pesticides, phenolic compounds, polyhalogenated compounds,

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drugs, and personal care products.[2] Many consumer products that are commonly used in daily life contain EDCs, including food and beverage packaging, personal care products, cosmetics, pesticides, plastics, adhesives, and plasticizers.[3–6] In recent years, new environmental pollutants have been increasingly identified as EDCs, such as per- and polyfluoroalkyl substances (PFAS), new plasticizers (bis(2-ethylhexyl) terephthalate), and others. Some typical EDCs, like polybrominated diphenyl ethers (PBDEs), nonylphenols, and phthalates (PAEs), are widely used as plastic additives and have long been extensively distributed in the environment.[4] They are now routinely detected in soil matrices,[5] aquatic environments,[6] and the atmospheric compartment. According to reports, surface water and sediment samples were collected in economically developed river basins to detect PAEs. The total concentration (median) of 9 types of PAEs in the water was 5980 ng L^{-1}, and in the sediment was 231 ng g^{-1}. In addition, emerging plasticizer metabolites (such as dibutyl phthalate and di(2-ethylhexyl) phthalate) were also detected.[7] Waniek *et al.*[8] found that in 400 sampling points, 65% of the cumulative risk quotient for natural and synthetic estrogens in global freshwater systems (lakes, rivers, and lagoons), as well as in marine coastal and open ocean environments, was high. Among them, estrone (E1) was detected in most study locations, with concentrations ranging from several to 1000 ng L^{-1}. Moreover, the estrogen levels in rivers of African countries are higher than those in other regions.[9] It is important to note that EDCs may contribute to reproductive and fertility anomalies, endocrine dysfunction, neurological disorders, and various forms of cancer.[10] Furthermore, diseases related to aging (such as atherosclerotic cardiovascular disease, hypertension, diabetes, and chronic kidney disease) have been linked to exposure to EDCs.[11] It is worth noting that even at extremely low concentrations in the range of micrograms per liter (μg L^{-1}) and nanograms per liter (ng L^{-1}), EDCs can have a detrimental effect on the health of both humans and animals.[12] Compared with other pollutants, EDCs have a more extensive source and distribution, their toxicity is exhibited even at very low concentrations, and they can significantly impair reproductive abilities by targeting the endocrine system.[13]

The removal of EDCs is imperative for the preservation of global ecosystems and the well-being of various organisms. Investigation into effective and low-cost technologies for EDCs removal has emerged as a prominent topic of interest in recent years. Currently, the primary methods for removing EDCs include advanced oxidation processes (AOP), membrane separation, membrane bioreactor (MBR), adsorption, and hybrid systems.[14] AOP, such as ozone treatment, can effectively remove EDCs, but this additional treatment increases the cost of wastewater treatment, making it impractical for global application.[15] Recent studies have also employed biochar as a catalyst in AOP for the removal of organic pollutants, demonstrating advantages over traditional AOPs.[16] Membrane separation and MBR systems are prone to high operational costs due to risks associated with membrane contamination and fouling.[17] Hybrid systems (such as those using AOP and membrane separation) are relatively complex, and their operational maintenance costs are also higher.[18] Compared to other removal technologies, adsorption is regarded as the most effective and cost-efficient method for eliminating EDCs.[19]

The adsorbent plays a crucial role in determining the efficiency of the adsorption of EDCs. Activated carbon is a widely utilized adsorbent. However, its associated costs remain comparatively high, and it produces waste that presents significant management challenges.[20] Biochar is a carbon-rich material that can be produced through the thermal pyrolysis of solid waste, such as agricultural residues and sludge from wastewater treatment plants.[21] Due to its exceptional adsorption performance, plentiful availability of raw materials, economic feasibility, and environmental sustainability, it has attracted considerable attention in recent years.[22,23] However, it is undeniable that the adsorption performance of raw biochar still needs improvement. This can be achieved by utilizing modification techniques to further enhance the efficiency of removing EDCs.[24] A recently developed composite material, which features high-performance magnetic biochar enhanced with polyaniline, successfully combines the high adsorption efficiency of biochar with its recoverable magnetism, thereby effectively improving the biochar's adsorption performance.[25] In addition, magnetic biochar has attracted much attention in recent years due to its superior adsorption performance and magnetism as a solid-phase extraction adsorbent for extracting EDCs in the environment.[26] Through ongoing innovations in modification, the adsorption performance of the biochar can be further enhanced, positioning it as a promising area for research.

In contrast to comprehensive reviews on the adsorption of organic pollutants,[27] dyes,[28] and toxic heavy metals,[29] there is a dearth of a comprehensive summary of the latest advancements in the use of biochar for the removal of EDCs. Especially in recent years, with a growing interest in studies on biochar and EDCs, a comprehensive review on the adsorption capacity of biochar for EDCs is now more crucial. Table S2 in the SI compares relevant reviews obtained from searching keywords such as ‘biochar’ and ‘EDCs’ on the *Web of Science* with the current review. In the relevant reviews, most classify EDCs by application into pesticides, pharmaceuticals and personal care products, plasticizers,[20] providing insights into the progress of biochar adsorption of EDCs in different fields. In contrast to other reviews, this paper categorizes EDCs according to their molecular structure characteristics into estrogen-like substances, perfluoroalkyl substances, phthalate esters, polycyclic aromatic hydrocarbons, and organochlorine compounds. It subsequently explores the adsorption performance of various types of EDCs using biochar. This analysis aims to offer valuable insights into the application of biochar for the adsorption of EDCs by focusing on their molecular structures. More importantly, this review, for the first time, proposes a modular design strategy for biochar to adsorb specific structurally characterized EDCs, based on the structural features of different EDCs, offering a unique solution. This paper initially systematically summarizes the preparation and modification methods of biochar. In the modification section, it focuses on the adsorption performance and limitations of biochar-based composites combined with novel nanomaterials such as carbon nanotubes and graphene oxide for EDCs. Subsequently, the adsorption performance of biochar for EDCs with different structures was analyzed in detail, and a modular design strategy for biochar to remove EDCs was proposed based on the adsorption mechanisms. Additionally, the economic feasibility of biochar adsorption for EDCs is also discussed. Finally, this paper presents future development suggestions for the high-efficiency adsorption of EDCs by biochar, thereby providing some reference for tackling the pollution problem caused by environmentally hazardous EDCs.

2. Preparation and modification of biochar for the adsorption of EDCs

The preparation method of biochar plays a crucial role in determining its adsorption performance. The raw biochar obtained may present certain limitations concerning the quantity and diversity of surface functional groups, and a low surface area and insufficient development of pore structure. These factors constrain the adsorption capacity of the raw biochar for EDCs. The modification of biochar can significantly enhance its adsorption performance for EDCs by increasing its surface area, incorporating essential functional groups on the surface, and optimizing its pore structure.

2.1 Preparation of biochar

The preparation methods for biochar mainly include thermal decomposition, hydrothermal carbonization, gasification, baking, and flash pyrolysis carbonization.[30,31] Currently, the preparation method of biochar through anaerobic pyrolysis is more widely accepted, primarily due to its greater economic and environmental sustainability, as well as its ease of operation.[32] To achieve biochar with optimal performance, it is essential to carefully consider the selection of appropriate raw materials, pyrolysis temperature, heating rate, residence time, carbonization atmosphere, and pyrolysis technology. These factors are crucial for determining the properties of biochar.

2.1.1 Raw materials. The raw materials for biochar derived from biomass can be broadly categorized into lignocellulosic biomass (LBM) and non-lignocellulosic biomass (NLBM).[33] LBM can be broadly classified as agricultural residues, forest residues, and herbaceous biomass,[34] mainly consisting of cellulose, hemicellulose, and lignin along with other components.[35] Generally, lignin-rich biomass (such as bamboo and pine) primarily produces biochar with high aromatic carbon content and abundant porosity, while cellulose-rich biomass (such as husks and crop straw) typically produces biochar with a higher surface concentration of oxygen functional groups.[36] Kozyatnyk *et al.*[37] concluded from the Langmuir model that the adsorption of relatively hydrophobic substances, such as BPA and triclosan, on cork biochar is greater than that observed on peach pit and wheat straw biochar. This phenomenon may be related to the highest cellulose content in cork. Consequently, the variations in biomass composition lead to differences in their pore structure and surface area, thereby differing in their adsorption performance for different EDCs. NLBM biochar, primarily composed of animal and poultry manure, sludge from wastewater treatment plants, and insect shells, generally contains varying proportions of proteins and lipids, amongst other components.[33] In terms of structure, the specific surface area (SSA) of fecal biochar is usually smaller than that of plant-based biochar. Li *et al.*[38] discovered that the biochar derived from wheat straw possessed a more developed porosity structure compared to that from cow manure, with its SSA reaching 383 $m^2\ g^{-1}$, over four times higher than that of cow manure biochar, thus rendering it more capable of adsorbing E2. Moreover, the two varieties of biomass biochars show slight variances in elemental composition, as well as in their surface functional groups, providing different benefits for the elimination of various EDCs. For instance, when considering the surface polarity of biochars produced from NLBM (such as pig manure), they exceed those derived from LBM (such as soybeans, rice straw, cotton stalks, and wood chips). Furthermore, as shown in Table 2, NLBM biochar generally exhibits a slightly higher N content compared to that of LBM biochar under identical pyrolysis temperatures. Research has revealed that the N element exerts the greatest influence on the removal of perfluorooctanesulfonic acid (PFOS), due to the positively charged nitrogen-containing groups (such as amine) in biochar attracting negatively charged PFOS *via* electrostatic attraction, thus rendering biochars with higher N content more efficient in removing PFOS.[39] As shown in Table 1, biochar derived from LBM is typically obtained from agricultural residues such as crop stalks, fruit residues (such as peels, shells, and seeds), and trees. Moreover, at the same pyrolysis temperature, LBM biochar generally has relatively smaller pore sizes, larger SSA, and more developed pore structures compared to NLBM biochar, such as those derived from pig manure and cow manure. This usually results in a relatively higher adsorption performance for EDCs. Notably, recent research has shown that co-pyrolysis produces biochars with higher porosity, more functional groups, larger SSA, and greater stability compared to those derived solely from a single feedstock.[40] The co-pyrolysis of various biomass in conjunction with other organic or inorganic raw materials, along with its effects on the properties of biochar, merits investigation, offering new insights and directions for the co-utilization of agricultural, industrial, and domestic waste.

2.1.2 Pyrolysis temperatures. At lower pyrolysis temperatures, the resultant biochars exhibit a higher abundance of oxygen-containing functional groups, thereby showing markedly greater total surface acidity compared to those generated at higher temperatures.[48] Furthermore, with increasing pyrolysis temperature, the carbon content increases, whereas the oxygen and hydrogen contents decline, as do the H/C, O/C, and (O + N)/C atomic ratios. Consequently, biochars produced under higher temperatures exhibit enhanced aromaticity and hydrophobicity, along with reduced polarity.[48,49] Xu *et al.*[50] demonstrated that higher pyrolysis temperatures led to increased internal diffusion rates, enhanced ion-exchange capacities, and relatively larger surface areas, thereby providing more adsorption sites for estrogen. However, certain studies have indicated that

Table 1 The influence of different feedstocks on the properties of biochar[a]

Feedstock	Feedstock category	Pyrolysis temperature (°C)	Element content											
			C%	O%	N%	H%	Ash%	pH	SSA ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Pore diameter (nm)	Pore size (nm)	Target adsorbate	Ref.
Softwood	LBM	700	89.50	5.40	—	2.50	1.60	9.10	204.60	0.12	2.29	—	BPA	37
Peach stones	LBM	700	87.40	10.80	—	1.30	0.60	8.20	309.10	0.16	2.11	—	BPA	37
Cow manure	NLBM	700	58.90	38.20	1.42	1.49	—	10.20	82.70	0.07	—	3.25	E2	38
Wheat straw	LBM	700	58.20	38.50	0.94	1.36	—	10.40	383.00	0.19	—	1.99	E2	38
Cotton straw	LBM	450	71.60	13.30	1.17	3.89	10.10	—	—	0.10	—	4.58	DBP and PHE	41
Soybean straw	LBM	450	70.80	15.60	0.98	3.92	8.70	—	—	0.12	—	4.79	DBP and PHE	41
Rice straw	LBM	450	57.90	11.80	0.83	3.31	26.20	—	—	0.09	—	4.18	DBP and PHE	41
Wood dust	LBM	450	75.90	16.70	0.05	3.66	3.70	—	—	0.17	—	4.18	DBP and PHE	41
Swine manure	NLBM	450	33.70	10.20	2.57	2.55	50.90	—	—	0.05	—	4.79	DBP and PHE	41
Corncob	LBM	500	83.50	12.10	0.68	2.82	4.20	—	134.00	0.04	1.22	—	BPA	42
Pomelo peel	LBM	500	74.00	17.70	1.72	2.74	9.06	—	4.26	0.01	7.75	—	BPA	42
Eucalyptus globulus	LBM	500	64.20	18.00	1.10	2.28	18.50	—	14.00	0.04	10.60	—	BPA	42
Silkworm excrement	NLBM	500	64.30	17.10	3.41	2.08	33.00	—	269.60	0.08	2.33	—	BPA	42
Peanut shell	LBM	600	77.72	7.80	1.38	2.36	10.74	—	71.47	0.08	—	—	DEP	43
Apricot shell	LBM	600	85.53	11.48	0.13	2.46	2.43	—	370.34	0.10	—	—	DEP	43
Coconut shell	LBM	600	89.51	6.18	0.12	2.42	1.78	—	320.42	0.09	—	—	DEP	43
Walnut shell	LBM	600	87.73	7.18	0.14	2.37	2.58	—	329.30	0.10	—	—	DEP	43
Kenaf	LBM	600	64.20	8.00	0.70	1.40	—	10.12	52.8 ± 28.3	0.0439 ± 0.023	—	2.35 ± 0.9	TCS	44
Corn straw	LBM	700	60.40	7.73	1.45	1.12	—	—	289.00	0.15	—	—	PCB	45
Swine bone	NLBM	900	89.63	10.37	—	—	—	—	1024.34	0.81	—	—	MeP	46
Municipal sludge	NLBM	700	68.30	31.70	—	—	—	—	244.30	0.30	—	—	MeP	46
Alfalfa	LBM	650	72.20	8.50	4.60	1.10	13.60	—	405.00	—	—	—	BPA	47

[a] LBM: lignocellulosic biomass, NLBM: non-lignocellulosic biomass, SSA: specific surface area, BPA: bisphenol A, E2: 17β-estradiol, PHE: phenanthrene, DBP: di-*n*-butyl phthalate, DEP: diethyl phthalate, MeP: methylparaben, TCS: triclosan.

high-temperature pyrolysis exerts an inhibitory effect on adsorption, potentially due to the elevated temperatures causing chemical rearrangement and structural degradation of biochar, thereby diminishing its adsorption capacity.[31] Not only that, but the yield of biochar decreases with an increase in pyrolysis temperature. Ban *et al.*[51] found that as the pyrolysis temperature increased, the yield of biochar showed a decreasing trend, which was mainly attributed to the increased decomposition of lignin and cellulose in the raw materials. In summary, pyrolysis temperature significantly affects the pH value, content of carbon elements, surface area, functional groups, and yields of biochar. Therefore, selecting an appropriate pyrolysis temperature is particularly important.

2.1.3 Heating rate and residence time. Depending on the residence time, heating rate, and temperature, pyrolysis can generally be classified into fast, intermediate, and slow pyrolysis.[20] A slower pyrolysis process promotes the formation of micropores within biochar, while a faster heating rate could potentially lead to a more rapid release of volatile components in biomass, resulting in the formation of macroporous structures.[52] Furthermore, an extended residence time can lead to a reduction in the H/C and O/C ratios, indicating a potential increase in the carbon content and aromatic structures of biochar as retention time increases, accompanied by a decrease in oxygen functional groups.[53] Moreover, the longer the residence time, the fewer unstable organic compounds are contained in the biochar.[54]

2.1.4 Carbonization atmosphere. The carbonization atmosphere significantly influences the porosity structure of biochar. Biochar produced in an active atmosphere, such as CO_2 and water vapor, exhibits numerous micropores and a disordered structure. In contrast, biochar produced in inert gases, such as N_2, possesses a more compact structure.[55] Furthermore, the presence of CO_2 in the atmosphere facilitates carbonation, aromatization reactions, and the reduction or conversion of aliphatic functional groups.[56] Some studies have also found that compared to biochar produced under a N_2 atmosphere, biochar prepared in a CO_2 atmosphere contains more oxygen-containing functional groups and exhibits higher aromaticity.[57] Research has demonstrated that biochar produced in a pure N_2 atmosphere exhibits a higher SSA, increased porosity, enhanced polarizability, and reduced aromaticity when compared to biochar prepared in a mixture of 7% O_2 and 93% N_2. It also displays a superior adsorption capacity for BPA, atrazine (ATR), and EE2.[58]

2.1.5 Pyrolysis technology. Microwave-assisted pyrolysis boasts lower energy consumption and higher efficiency compared to traditional pyrolysis.[59] Under certain conditions of pyrolysis temperature, residence time, and atmosphere, an appropriate increase in microwave power can effectively enhance the SSA of biochar. When the microwave power is in a relatively high range, further increases will lead to a continuous decrease in the average pore size of the biochar. At the same time, localized hotspots are easily formed inside the biomass, causing uneven heat distribution, which ultimately results in a reduction in biochar yield.[60] Plasma technology is also a promising new pyrolysis technology, which can efficiently convert raw materials such as agricultural waste into biochar. The application of plasma technology in the preparation of biochar can increase the surface area and surface functional groups such as carboxyl, carbonyl and hydroxyl groups of biochar, thus significantly improving the adsorption capacity of biochar.[61]

It is worth noting that biochar may produce toxic EDCs such as polycyclic aromatic hydrocarbons (PAHs), dioxins, and polychlorinated biphenyls (PCBs) during the pyrolysis stage.[62,63] The pyrolysis temperature, residence time, and raw material characteristics during the preparation process will all affect the production of PAHs.[62] Therefore, increasing the pyrolysis temperature can reduce the production of dioxins. In summary, during the preparation process, it is important to focus not only on the performance of biochar but also on reducing the potential for the generation of pollutants such as PAHs.

2.2 Modification methods of biochar

The adsorption capacity of original biochar is relatively limited. Various modification methods have been developed to improve the adsorption performance of biochar. Common modification methods include steam and ball milling modification, acid and alkaline modification, metal compound modification, and the preparation of biochar-based composites. Table 2 summarizes the effects of different modification methods on the performance of biochar.

2.2.1 Preparation of biochar-based composites. Biochar can also improve its performance through modification using biochar-based composites. Biochar-based composites are primarily produced by impregnating biochar with carbonaceous materials (such as graphene oxide or carbon nanotubes), clay minerals, or organic compounds, with the aim of modifying the properties of the biochar.[71]

For the modification of carbonaceous materials, graphene oxide (GO) and carbon nanotubes (CNTs) are commonly used for soaking and mixing before the pyrolysis of biochar.[72] The pyrolysis of biochar pretreated with GO is an effective method for the production of composite materials of GO-biochar, which exhibit a negative charge increment, retain more oxygen-containing groups, and possess relatively higher polarity and thermostability.[73] Gao *et al.*[69] modified biochar with large-sized (~20 μm), medium-sized (~5 μm), and nanosized GO (~0.2 μm) for the adsorption of bisphenol S (BPS). They observed that the larger the flake diameter, the higher the C/O ratio, potentially resulting in more π–π adsorption sites, which are conducive to BPS adsorption. Furthermore, they found that the large-sized biochar effectively prevented agglomeration and pore structure clogging of the biochar. Furthermore, Abdul *et al.*[74] discovered that the composite material consisting of biochar-graphene nanosheets exhibited higher porosity and surface area, with the primary adsorption mechanism for PAEs being π–π electron donor–acceptor (EDA) interactions. It follows that GO modification significantly increases the SSA of biochar, enhances its chemical stability, and strengthens π–π interactions between biochar and EDCs. Liu *et al.*[75] developed a novel GO supported activated magnetic biochar by grafting GO and magnetite nanoparticles onto the surface of activated biochar. The material effectively removes E2 from aqueous solutions, primarily driven by π–π EDA interactions, electrostatic attraction, and hydrogen bonding. GO is a two-dimensional material, while carbon nanotubes (CNTs) are one-dimensional materials.[76] Inyang *et al.*[77] utilized CNTs to modify biochars, leading to the formation of CNT-biochar composites. It was observed that the physicochemical properties of the biochars, including surface area, porosity, and thermal stability, were significantly enhanced with the incorporation of CNTs. They also used a suspension of CNTs dispersed with sodium dodecylbenzenesulfonate to dip-coat hickory nuts or sugarcane bagasse biomass, followed by slow pyrolysis to produce modified biochar. This modified biochar has good adsorption performance because the surfactant can prevent the aggregation of CNTs, thereby promoting the distribution and stability of individual CNT nanoparticles on the surface of the biochar to adsorb pollutants.[78] Notably, while the study on GO and CNTs as innovative carbonaceous materials for modifying biochar has gradually increased, these are currently hindered by factors such as costs and technology, limiting the full exploitation of the advantages of both biochar and emerging carbonaceous materials. To further develop the modification of biochar with carbonaceous materials, it is necessary to tackle several challenges, including the high cost of nanocarbon materials like CNTs, the tendency of carbon materials to agglomerate with biochar, the weak adhesion between biochar and carbon materials, and the risk of carbon materials detaching from the surface of biochar and subsequently leaching into the environment.

For clay modification, montmorillonite, kaolinite, and vermiculite are commonly used to prepare clay-biochar composites. Different types of clay exhibit distinct effects on the modification of biochar. Liu *et al.*[79] found that the modification of vermiculite can enhance the aromatic stability and chemical oxidation stability of biochar, increase the yield of biochar, and improve the carbon retention rate of biochar. In contrast, modifications using kaolin and $CaCO_3$ have a relatively minimal impact on the carbon retention rate of biochar. Montmorillonite-modified biochar exhibits a larger SSA and highly ordered aromatic structure (C=C) compared to kaolinite-modified biochar.[36] In addition, the same clay has

Table 2 The effect of modification on the performance of biochar for adsorbing EDCs[a]

Feedstock	Modification method	Pyrolysis temperature (°C)	Target adsorbate	SSA (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)	Pore size (nm)	Adsorption capacity (mg g^{-1})	Ref.
Rice husk	—	500	E2	1.39	0.016	8.15	3.52	—	64
Rice husk	H_2SO_4	500	E2	6.85	0.018	6.79	3.05	—	64
Rice husk	H_3PO_4	500	E2	16.80	0.016	6.78	3.83	—	64
Rice husk	NaOH	500	E2	119	0.071	3.40	3.83	34.80–44.93	64
Rice husk	$NaHCO_3$	500	E2	102	0.093	3.42	3.83	36.00–44.40	64
Rice husk	H_2O_2	500	E2	46.70	0.016	3.41	3.42	—	64
Lotus seedpod	—	500	E2	25.21	0.030	—	2.55	147.12	65
Lotus seedpod	KOH	500	E2	364.30	0.390	—	2.17	183.60	65
Burcucumber	—	700	SMZ	2.31	0.008	6.78	—	20.56	66
Burcucumber	Steam	700	SMZ	7.10	0.038	8.39	—	37.73	66
Cow manure	Montmorillonite	450	E2	6.16	0.052	33.54	—	62.89	67
Wheat straw	Montmorillonite	450	E2	4.55	0.020	17.46	—	41.02	67
Coffee grounds	—	600	SMX	2.16	0.006	5.66	—	7.65	68
Coffee grounds	Chitosan	600	SMX	1.78	0.003	3.06	—	14.73	68
Sugarcane	—	600	BPS	5.08	—	—	—	4.00	69
Sugarcane	Graphene	600	BPS	188.90	—	—	—	23.40	69
Sawdust	—	600	PFOS	395.51	—	—	—	178.10	70
Sawdust	Metal oxides	600	PFOS	120.65	—	—	—	194.60	70

[a] SSA: specific surface area, E2:17β-estradiol, SMZ: sulfamethazine, SMX: sulfamethoxazole, PFOS: perfluorooctanesulfonic acid, BPS: bisphenol S.

different modification effects on biochar from different raw materials. Tong *et al.*[67] observed that the montmorillonite-modified manure biochar (CMt) exhibited numerous small particles and micro-pores on its surface, whereas the montmorillonite-modified straw biochar (WMt) displayed large particles, layered structures, and smooth surfaces. The maximum adsorption capacity of CMt for E2 is 41.02 mg g^{-1}, which is lower than that of WMt at 62.89 mg g^{-1}. Nevertheless, the regeneration capability of CMt is slightly superior to that of WMt. In general, clay modification primarily affects surface characteristics (such as SSA, porosity, and functional groups) as well as enhances the stability of biochar (such as thermal stability, chemical oxidative stability, and aromatic stability).

For organic compound modification, a variety of organic compounds (such as chitosan and fulvic acid) have been widely employed in the modification of biochar, effectively providing supplementary functional groups (such as C═O, $-NH_2$, and –OH) to the surface of the biochar.[80] Chitosan, found in nature as the second most abundant biopolymer after cellulose, is recoverable in large quantities from the waste shells of crustaceans.[81] Yavari *et al.*[82] coated the surface of rice husk biochar with chitosan particles. They found that the chitosan modification significantly enriched the functional groups present on the biochar surface, resulting in a 67% increase in its adsorption capacity for imidazolinone herbicides. Organic compounds are often combined with biochar using crosslinking methods to enhance their stability in conjunction. Tran *et al.*[68] prepared chitosan-biochar composites from agricultural waste (including spent coffee grounds, orange peels, and shrimp shells) by loading chitosan onto biochar and cross-linking it with glutaraldehyde. This modified biochar exhibited an adsorption capacity for SMX that was nearly twice that of the original biochar. Wang *et al.*[83] found that after biochar was modified with fulvic acid, –COOH and –OH groups, as well as aliphatic and aromatic ring structures could be introduced on its surface. Furthermore, when this modified biochar was coated with chitosan, this modification method demonstrated enhanced performance in the removal of ciprofloxacin (CIP) compared to biochar modified solely with chitosan. In addition, the preparation of organic compounds and biochar composite materials may face issues such as poor bonding stability and pore blockage. To enhance the adsorption capacity of organic compound modified biochar for EDCs, these issues also need to be further addressed.

2.2.2 Steam and ball milling modification. Common physical modification methods include steam modification and ball milling, both of which mainly enhance the adsorption capacity of biochar by altering its structural characteristics, such as pore volume, pore diameter, and surface area.

Biochar modification *via* steam activation typically is conducted within a temperature range of 500–850 °C, with treatment times ranging from 1 to 7 hours.[84] The introduction of steam can increase the pore volume and surface area, while significantly affecting the pore size distribution of biochar.[66] Lan *et al.*[30] found that performing pure steam modification at 700 °C with the same residence time significantly reduces the microporous structure of biochar while increasing the mesoporous structure. Under the same pyrolysis temperature and residence time, steam-activated biochar has a higher degree of aromatization compared to the original biochar.[85]

Ball milling modification can significantly enhance both the external and internal surface areas of biochar by reducing particle size and expanding the pore network. Additionally, it can improve the dispersion and diffusion rates of biochar in aqueous solutions.[86] As the ball milling time increases, the carbon atom content decreases while the oxygen atom content increases.[87] In contrast to biochar derived from pine sawdust, ball-milled biochar displays enhanced adsorption efficiency for BPA. This may be attributed to the increased oxygen functional groups, defect sites, and SSA resulting from ball milling, thereby providing more adsorption sites.[88]

2.2.3 Acid and alkaline modification. The treatments of acid modification and alkaline modification can improve the surface chemical properties of biochar (hydrophobicity, polarity, and surface functional groups), porosity, and surface area.[89] Currently, acid modification and alkaline modification are usually conducted through post-pyrolysis treatment, which results in more oxygen-containing functional groups (such as –OH, –COOH, C=O). However, some studies have found that pre-pyrolysis treatment has a more abundant pore structure than post-pyrolysis treatment.[90] Therefore, modification with acid or alkali and the pyrolysis sequence has a significant impact on the properties of biochar.

For acid modification, inorganic acids (such as HNO_3, H_2SO_4, H_3PO_4, and HCl)[91] and organic acids (such as oxalic acid, citric acid, *etc.*)[92] have been widely used for the modification of biochar. The main purpose of acid modification is to remove metals and impurities and to increase acidic functional groups.[31] Furthermore, the majority of raw biochars exhibit lower surface areas, which can be significantly altered through acid treatment. For instance, Li *et al.*[42] employed HCl for the post-treatment of biochar derived from silkworm feces that had been pyrolyzed at 500 °C. The surface area of this HCl-modified biochar increased by over 40 times. Studies have revealed that H_3PO_4-modified biochar exhibits a larger hydrophobic surface area and more abundant micropores, thereby demonstrating superior adsorption capability towards BPA.[93] Moreover, during the activation process, H_3PO_4 facilitates dehydration and depolymerization, while simultaneously preventing excessive pyrolysis of lignocellulose and inhibiting the collapse of the carbon skeleton.[94] Saini *et al.*[95] found that the biochar produced from bagasse that underwent post-treatment with HNO_3 after pyrolysis at 600 °C had more acidic functional groups compared to the original biochar. This increase in acidic functional groups influenced the π-electrons present within the biochar matrix, thereby weakening the π–π interactions between adsorbates and adsorbents. Therefore, the benefits of acid modification must be weighed against its potential disadvantages, while considering the properties of the target substance.

In terms of alkaline modification, commonly used alkali-modifying reagents are sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium bicarbonate ($NaHCO_3$), and potassium carbonate (K_2CO_3). Typically, alkaline-modified biochar exhibits a larger SSA and greater hydrophobicity, with alkaline modification also enhancing the presence of oxygen functional groups,[96] thereby enhancing its adsorption capacity. Tang *et al.*[97] modified straw biochar through both acid (HNO_3, HCl) and alkaline treatments. Their findings indicated that the biochar treated with NaOH exhibited a larger SSA and enhanced hydrophobicity, enabling the removal of over 95% of BPA. Zhang *et al.*[64] used acids (H_2SO_4 and H_3PO_4), alkalis (NaOH and $NaHCO_3$), and oxidants (H_2O_2) separately to modify rice husk biochar by microwave-assisted activation, with microwave-assisted alkali modification showing the largest surface area. Furthermore, its removal efficiency for E2 was higher than that of other modified biochars. Liu *et al.*[65] employed KOH to modify lotus biochar, discovering that the post-treatment exhibited superior E2 adsorption capacity compared to direct treatment and pre-treatment biochars. This was attributed to the larger surface area (364.30 $m^2\ g^{-1}$) and pore volume (0.39 $cm^3\ g^{-1}$) as well as the abundance of active sites in the post-treated biochar. Consequently, the sequence of the KOH modification step significantly influences a variety of properties of biochar.

Furthermore, Tang *et al.*[98] found that, due to the synergistic effect of alkaline and acid modifications on porosity, biochar modified through a combined alkaline-acid treatment demonstrated higher rates of SSA and pore volume growth compared to those subjected solely to acid or alkaline treatment. In summary, alkali modification generally demonstrates a superior enhancement of hydrophobicity and SSA compared to acid modification. For the removal of many hydrophobic EDCs, alkali modification tends to be more advantageous.

2.2.4 Metal compound modification. Common metal compound modification reagents include metal oxides and metal salts. Metal oxide modification can facilitate the generation of –OH and –COOH functional groups on the surface of biochar, while also modifying the surface charge characteristics of the biochar.[99] Yang *et al.* modified biochar with Fe_3O_4, enhancing the surface oxygen functional groups on the biochar, thus promoting the formation of hydrogen bonds between hydroxyl groups on the surface with N and O-containing EDCs.[100] Biochar modified with CuO can form a large number of micropores and mesopores, which is beneficial for the removal of PFAS through pore filling.[101] In addition, loading metal oxides such as CuO can promote the removal of PFAS by providing bridging metal cations between PFAS molecules and biochar as intermediate binding sites. However, it is important to note that the majority of metal oxide modifications may result in a reduction of the surface area of biochar, as their precipitates can obstruct the pores of the biochar.[72] Liu *et al.*[102] discovered that the biochar derived from persimmon seeds modified with $ZnCl_2$ exhibited an impressive increase in surface area from 29.7 $m^2\ g^{-1}$ to 2057 $m^2\ g^{-1}$ and pore volume from 0.017 $cm^3\ g^{-1}$ to 0.549 $cm^3\ g^{-1}$ compared to the original biochar. Moreover, the modification with $ZnCl_2$ enhanced electrostatic attraction through surface coordination and charge changes, resulting in a significant enhancement in the removal rate of PFAS. The magnetic biochar, modified with $FeCl_3$, demonstrates a significantly enhanced SSA, hydrophobicity, and aromaticity, which in turn improves the hydrophobic interactions and π–π interactions between the biochar and SMX. Consequently, the removal efficiency of SMX can be increased from 73.86% to 94.06%.[103] Moreover, this magnetic biochar exhibits ease of separation and recovery for recycling, as well as its potential for contaminant removal, making it highly valuable for further research.[25,103]

To address the diverse EDCs pollution in complex environments, it is necessary to rationally select and design biochar modification strategies based on the structure of target pollutants, environmental conditions, and cost. Table 3 provides a systematic comparative analysis of the advantages, limitations, and applicable EDCs types of each modification technology. Overall, the selection of modifications is a decision-making process that seeks the optimal solution among adsorption performance, environmental compatibility, long-term stability, and cost. We must not only focus on whether it can improve the adsorption performance of biochar but also on whether it can be applied on a long-term and large-scale basis to remove various environmental EDCs.

3. Adsorption performance of biochar for different EDCs

To enhance the adsorption efficiency of biochar, its preparation conditions and modification methods should be adapted to the molecular structural characteristics of the target substances. This necessitates a clear elucidation of the relationship between biochar structure and its adsorption performance. The review therefore introduces biochar adsorbents specifically designed for the capture of typical EDCs, including estrogenic compounds, PFAS, phthalate esters (PAEs), PAHs, and organochlorine compounds. The primary focus is on elucidating the adsorption mechanisms to reveal how the structural features of biochar influence its adsorption capacity for EDCs. Accordingly, strategies for the production and modification of biochar are proposed to enhance its efficiency in adsorbing different EDCs.

3.1 Estrogen

Estrogenic EDCs are frequently found in contaminated environments, including natural estrogens such as estrone (E1), 17β-estradiol (E2), and estriol (E3), as well as synthetic estrogens like 17α-ethinylestradiol (EE2) and phenolic xenoestrogens, including nonylphenol (NP) and bisphenol A (BPA).[19,104] As shown in Fig. 1, both natural estrogen and synthetic estrogen EE2 possess four-carbon ring structures,

Table 3 Comparative analysis of biochar modification[a]

Modification category	Representative methods	Key advantages	Major limitations	Suitable EDCs types
Chemical modification	Acid modification (HNO_3, H_3PO_4)	Introduces oxygen-containing functional groups (*e.g.*, –COOH, –OH), low cost	May reduce SSA, limited improvement for non-polar EDCs	Alkaline/polar EDCs (*e.g.*, bisphenols)
	Alkali modification (KOH, NaOH)	Significantly increases SSA and micropore volume, enhances hydrophobicity and π–π interactions	Limited effectiveness for acidic EDCs due to electrostatic repulsion	Hydrophobic/aromatic EDCs (*e.g.*, PAHs)
Physical modification	Steam activation (H_2O, CO_2)	Significantly develops micropores and increases SSA	High energy consumption, high carbon loss, limited ability to regulate surface chemistry	Non-polar/weakly polar EDCs (*e.g.*, PAEs)
	Ball milling	Reduces particle size, increases surface area, and activates the surface	Limited improvement in pore structure, high energy consumption, uncontrollable introduction of functional groups	Various EDCs
Metal and compound modification	*e.g.*, Fe_3O_4	Optimizes the pore structure, enhances specific coordination interactions, enables magnetic separation for easy recovery	Possible pore plugging and SSA reduction, higher cost	EDCs with coordinating groups (*e.g.*, tetracyclines)
Biochar-based composite modification	Clay mineral composites (bentonite, montmorillonite)	Changes the surface characteristics of biochar (*e.g.*, pore structure), enhances structural stability, extremely low cost	Limited improvement in SSA, weak adsorption for non-ionic EDCs	Ionic/polar EDCs (*e.g.*, PFAS)
	Carbonaceous composites (GO, CNTs)	Greatly increases SSA, enhances π–π interactions	Nanoparticles prone to aggregation, potential environmental risks (nanotoxicity), high raw material cost	Electron-rich/aromatic EDCs (*e.g.*, estrogens)
	Organic compound (*e.g.*, chitosan and HA)	Introduces functional groups, low cost	May introduce competitive adsorption, mechanical strength may decrease	Polar and ionizable EDCs (*e.g.*, bisphenols)

[a] SSA: specific surface area, PAHs: polycyclic aromatic hydrocarbons, PAEs: phthalate esters, GO: graphene oxide, CNTs: carbon nanotubes, HA: humic acid.

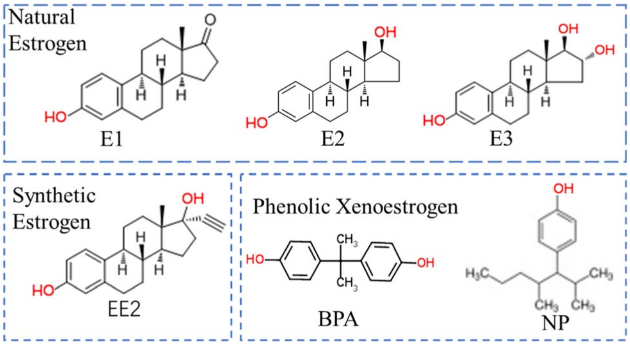

Fig. 1 The structures of some typical estrogenic EDCs.

which are relatively similar, whereas phenolic xenoestrogens have fewer carbon rings, resulting in structural disparities compared to the former two. But nearly all estrogenic EDCs possess at least one benzene ring and a hydroxyl group attached to a cyclic structure. The structural characteristics of estrogenic EDCs facilitate π–π interactions between their benzene rings and the aromatic structure of biochar, while the phenolic hydroxyl groups further enhance hydrogen bonding with biochar. Consequently, the selection of biochar with a structurally compatible design is essential for attaining optimal adsorption efficiency of estrogenic EDCs.

Ahmed *et al.*[105] obtained biochar by pyrolyzing eucalyptus wood particles at 600 °C after activation with phosphoric acid. The average particle size of this biochar fell within the range of 75–600 μm, its pore structure comprising mesopores and macropores, and its surface is rich in different functional groups (such as –COOH, –OH, C=O, and C=C). Its adsorption of hydrophobic organic pollutants such as E1, E2, E3, EE2, and BPA mainly occurs through π–π EDA interactions, hydrogen bonding and hydrophobic interactions. Ding *et al.*[106] synthesized Fe/Mn/N co-doped biochars with a relatively high SSA (247.66 $m^2\ g^{-1}$) while maintaining a high degree of graphitization. This modification makes the biochar more conducive to serving as a π-electron acceptor, with –OH groups present in BPA functioning as π-electron donors, enhancing π–π EDA interactions and thus enhancing adsorption capacity. Gao *et al.*[69] prepared large-sized (∼20 μm) GO-modified biochar, which provided more π–π adsorption sites for BPS. Consequently, this modified biochar has an adsorption capacity for BPS that is approximately 2.8 times higher than that of the original biochar. Moreover, Kasambala *et al.*[107] found that banana peel biochar (BPB) is more conducive to the adsorption of progesterone than mango peel biochar (MPB). This phenomenon can be attributed to the higher aromaticity of BPB relative to MPB, along with its increased oxygen-containing functional groups. These functional groups facilitate interactions with the –OH and C=O moieties of progesterone, thereby enhancing hydrogen bonding and π–π interactions with the biochar. Consequently, progesterone-like EDCs can achieve a removal efficiency of up to 92.8%. The modification of K_3PO_4 on biochar significantly increased the volume and surface area of micropores and mesopores, making pore filling and electrostatic attraction the dominant adsorption mechanisms, thereby enhancing its adsorption capacity for BPA.[108]

In addition to enhancing estrogen adsorption through the preparation and modification of biochar, it is essential to consider the environmental factors that influence adsorption. Ahmed *et al.*[109] discovered that under pH > 9.0 conditions, five phenolic EDCs (E1, E2, E3, EE2, and BPA) may exist in anion form. Furthermore, the electrostatic repulsion between the negatively charged surfaces of biochar and the EDC anions significantly hinders the adsorption process.[110] Consequently, overly elevated pH can reduce the adsorption of estrogens by biochar.[111] In the pH range of 3 to 8, estrogen exists in its undissociated form. Within this pH range, π–π EDA interactions and hydrogen bonding interactions are the main driving forces for the adsorption process, facilitating the adsorption of estrogen from water systems by biochar.[112] The adsorption capacity of biochar sourced from lychees decreases with an increase in HA concentration within the range of 0–50 mg L^{-1}.[113] Therefore, it must also be taken into account that HA in the environment competes with estrogens for adsorption onto the biochar.

In general, the main adsorption mechanisms of biochar for estrogen are π–π-EDA interactions and hydrogen bonding, due to the presence of benzene rings and –OH groups in estrogen. Nevertheless, pore filling continues to play a crucial role in the adsorption mechanism for biochar to adsorb estrogenic EDCs (such as BPA).[114] The preparation and modification of biochar mainly aim to enhance its graphitization level, increase its aromaticity and surface polar functional groups, thereby strengthening the adsorption of estrogen. Moreover, environmental factors such as pH and HA cannot be overlooked in terms of influencing the dominant adsorption mechanism.

3.2 Perfluoroalkyl substances

PFAS, which are widely employed in various everyday products such as food packaging and firefighting foam, have the potential to cause hormonal disruptions, and developmental or reproductive hazards.[115] Therefore, PFAS are also classified as EDCs.[116] PFAS, which consist of hydrophobic perfluoroalkyl tails and hydrophilic ionic heads (either carboxylic or sulfonic acids), mainly include perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA).[117] At the same time, PFAS can also be divided into long-chain PFAS and short-chain PFAS based on the length of the carbon chain, where long-chain PFAS refers to PFCA with eight or more carbon atoms and PFSA with six or more carbon atoms.[118]

As the length of the C–F chain increases, PFAS becomes more lipophilic and more hydrophobic.[70,118] Generally, longer-chain PFAS predominantly rely on hydrophobic interactions, whereas shorter-chain PFAS primarily depend on electrostatic attraction. This distinction renders the adsorption of short-chain PFAS more susceptible to interference from other ions and molecules present in the environment.[115] For PFSA and PFCA, the –OH on biochar can easily form hydrogen bonds with the electronegative O atoms in –COOH and $-SO_3H$, but PFSA has greater hydrophobicity than PFCA.[117]

Research has shown that PFCAs with 4–9 CF_2 moieties range from 0.45 to 0.72 nm in effective cross-sectional diameter. In the case of larger PFCAs possessing a spiral structure, an excessively small pore size of biochar will inhibit the entry of PFCAs.[119] Typically, the pore diameter of biochar needs to be 2–3 times that of PFAS molecules to effectively capture PFAS.[120] Fig. 2 shows the relationship between long-chain perfluorooctanoic acid (PFOA) and short-chain perfluoropentanoic acid (PFPeA) affected by the pore structure of biochar.

Ao *et al.*[121] found that bamboo biochar produced by steam activation has a highly hydrophobic surface and dispersed mesopores (2–10 nm), which is effective for PFAS adsorption. The pores of magnetic bagasse biochar are also mesoporous (3–15 nm), which can capture perfluorooctane sulfonate (PFOS) molecules with lengths and diameters of approximately 1.3 and 0.4 nm, respectively, within the porous structure of the biochar.[122] Liu *et al.*[123] prepared porous Fe-doped graphitized biochar, which improved the adsorption of short-chain PFAS by enhancing electrostatic interactions and pore filling. On one hand, they increase the positive charge of biochar by impregnation with $FeCl_3$, promoting its electrostatic interactions with anionic PFAS. On the other hand, they improved the pore structure of biochar through wet ball milling, facilitating the pore-filling effect during the PFAS adsorption process.

Regarding the impact of environmental factors, when the pH in the environment is high, the adsorption capacity of biochar for short-chain PFAS decreases due to the decreased electrostatic attraction.[102] Moreover, the presence of dissolved organic matter (DOM) in the environment may interfere with the adsorption mechanisms or compete for adsorption sites, clogging the pores of biochar surfaces and thus hindering the removal of PFAS.[120,124]

Overall, biochar demonstrates a greater efficacy in adsorbing long-chain PFAS compared to short-chain PFAS. Short-chain PFAS, due to their relatively weak hydrophobicity and smaller molecular size, make it more difficult for biochar to adsorb them. In the future, it is necessary to further design biochar that efficiently adsorbs short-chain PFAS. This can be achieved by enhancing the pore structure of biochar to better match short-chain PFAS and by promoting electrostatic attraction between the surface of biochar and short-chain PFAS.

3.3 Phthalate esters

PAEs are widely used as plasticizers to improve the flexibility and processability of polymer materials, and many common plastic products contain PAEs. Some PAEs, such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), and *n*-octyl phthalate (DnOP) pose serious hazards to human health and the environment, and are classified as "priority pollutants" by many countries.[125,126]

As depicted in Fig. 3, PAEs structurally contain benzene rings, ester groups, and alkyl chains of varying lengths. Generally, the shorter the alkyl chain, the smaller the PAE molecules

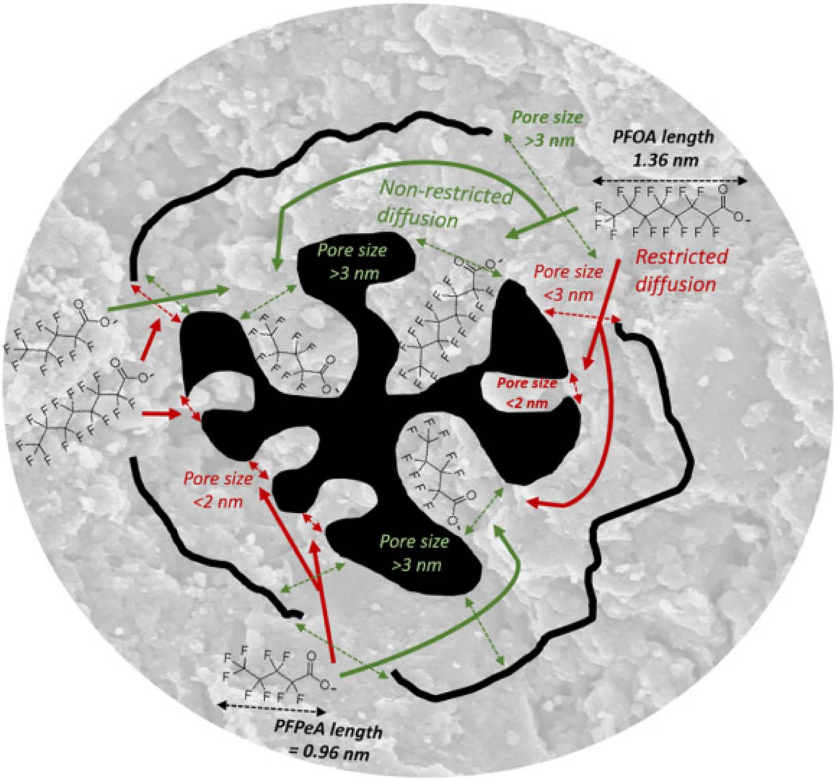

Fig. 2 The diffusion of PFOA and PFPeA into the pores of biochar.[120] (this figure has been reproduced from ref. 120 with permission from, copyright ELSEVIER, 2024).

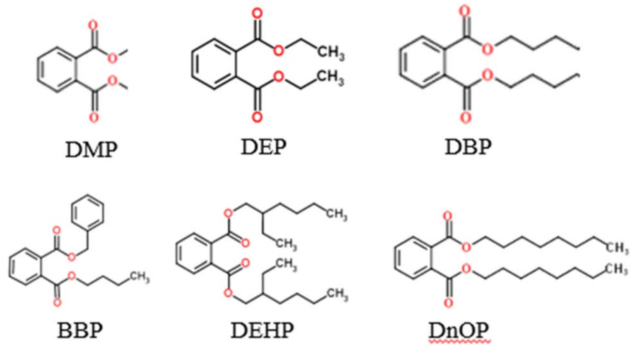

Fig. 3 Structural diagrams of six common PAEs.

will diffuse more quickly into the pores of the biochar, resulting in a faster adsorption rate.[125] As the alkyl chain length increases, its adsorption rate decreases. However, concurrently, a longer alkyl chain increases hydrophobicity, thereby enhancing the hydrophobic interactions between biochar and long-chain PAEs. Moreover, biochar with a hierarchical pore structure can better adsorb PAEs of various molecular sizes present in the environment. Zhang *et al.*[127] first pretreated lotus stems with NaOH and then pyrolyzed them at 600 °C to obtain biochar, whose SSA increased by 125.3 times compared to the original biochar. Additionally, the pore sizes ranged from several dozen to several hundred micrometers, featuring a three-dimensional, porous, irregular honeycomb structure, capable of adsorbing PAEs of different sizes, with an adsorption capacity for DMP of 125 mg g^{-1}. Moreover, NaOH-modified rice husk biochar contains more aromatic structures than the original biochar and has a higher degree of carbonization, which is more conducive to adsorbing PAEs through π–π interactions.[128] As depicted in Fig. 4, Abdul *et al.*[74] modified biochar with graphene nanoplatelet composites to adsorb PAEs. This modified biochar exhibited a higher porosity and SSA, which strengthened the π–π EDA interactions between DMP, while the adsorption of DBP was attributed to their hydrophobicity. Consequently, the biochar that adsorbs long-chain PAEs should have a larger hydrophobic surface area, while the biochar that adsorbs short-chain PAEs should contain more aromatic structures to enhance π–π EDA interactions.

Compared to long-chain PAEs, the adsorption of short-chain PAEs by biochar is more affected by the pH in the environment. Moreover, the adsorption capacity of biochar for PAEs decreases with an increase in pH.[129] This is because pH affects the surface charge of biochar, altering its properties and thereby influencing the adsorption mechanism of biochar with PAEs. DOM will compete with PAEs for adsorption sites and alter the surface properties of biochar.[126] But in some cases, HA and fulvic acid can also partially promote the adsorption of hydrophobic PAEs. The effect of DOM on the adsorption of PAEs by biochar depends on the concentration and composition of DOM.[128]

In summary, the primary adsorption mechanism of biochar for long-chain PAEs is hydrophobic interaction, whereas short-chain PAEs are π–π EDA interactions.[43,74,130] The adoption of biochar characterized by appropriate pore structures, extensive hydrophobic surface areas, and aromatic properties is essential for optimizing its PAEs adsorption capabilities. For example, biochar produced through high-temperature pyrolysis exhibits enhanced hydrophobic surface area, porosity, and a greater degree of aromatization. This not only increases the availability of sites for pore filling and hydrophobic interactions but also reinforces the π–π EDA interactions between the PAE molecules and the biochar.

3.4 Polycyclic aromatic hydrocarbons

Natural wildfires as well as human activities (such as waste incineration and fossil fuel combustion) generate complex mixtures of high molecular weight PAHs, including pyrene, benzo[*a*]pyrene (BaP), dibenz[*a*,*l*]pyrene, and benzanthracene.[131] As shown in Fig. 5, PAHs are characterized by the presence of two or more aromatic rings, primarily composed of carbon and hydrogen, exhibiting very low polarity. Based on their molecular structures, PAHs can be classified into low

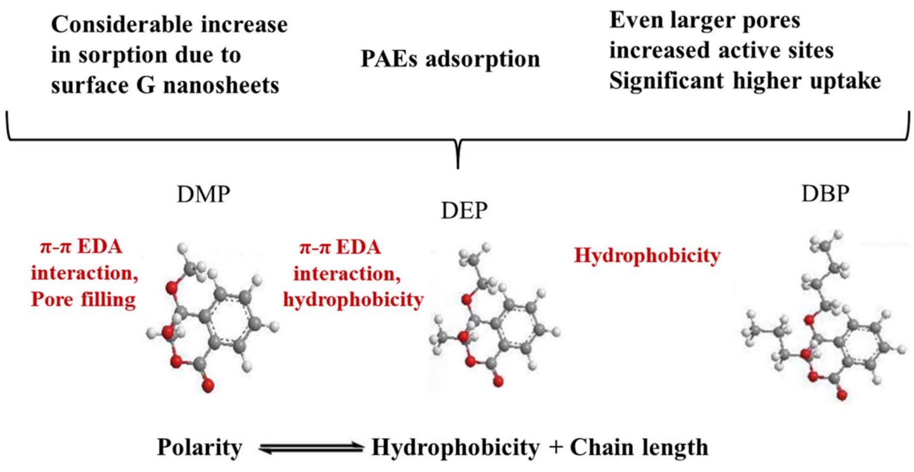

Fig. 4 The interaction mechanism between graphene nanosheet composite modified biochar and PAEs.[74] (this figure has been adapted from ref. 74 with permission from ELSEVIER, copyright 2017).

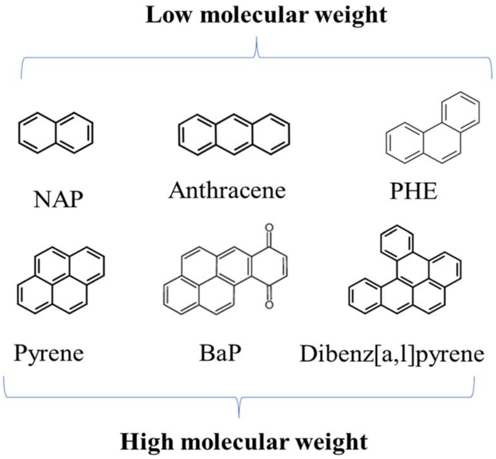

Fig. 5 Some structures of PAHs.

molecular weight (LMW) and high molecular weight (HMW) categories. Low molecular weight polycyclic aromatic hydrocarbons encompass di- and tri-ring structures, including naphthalene (NAP), anthracene, and phenanthrene (PHE), whereas high molecular weight polycyclic aromatic hydrocarbons comprise quadruple rings and structures with a greater number of rings.[132]

Generally, as the number of benzene rings in PAHs increases, their hydrophobicity also increases. The mechanisms of biochar adsorbing PAHs mainly involve pore filling, hydrophobic interactions, π–π interactions, and electrostatic interactions.[133,134] Pathak *et al.*[135] discovered that the CO_2 activation of bagasse biochar could enhance its surface area, functional groups, and exhibit a porous structure, resulting in an adsorption capacity for NAP that was approximately eight times greater than that of the original bagasse biochar. Zhang *et al.*[136] demonstrated that graphene-coated biochar enhanced the π–π interactions with PAHs, thereby exhibiting excellent adsorption capacity for PAHs. Liu *et al.*[137] found that the biochar derived from chicken manure at a pyrolysis temperature of 700 °C has a rich pore structure, which can adsorb 84.3% of NAP from the solution. However, Fabian *et al.*[134] found that biochar prepared at a lower pyrolysis temperature (~300 °C) has a higher adsorption capacity for pyrene, primarily due to its higher hydrophobic interactions and greater cation exchange capacity. The nonlinear relationship between production temperature and the adsorption capacity of biochar may be due to the destruction of aliphatic alkyl and ester groups during biochar production.[138] Therefore, the optimal pyrolysis temperature for the production of biochar adsorbing PAHs still needs further exploration.

Research shows that under low pH conditions, the surface functional groups of biochar become protonated, giving biochar a positive charge, which results in greater electrostatic interactions with PAHs, thereby enhancing adsorption.[135] For instance, PAHs such as PHE and NAP are more favorable for adsorption under acidic pH.[138,139] However, some studies have also shown that the effect of pH on the overall adsorption efficiency of low molecular weight PAHs (such as PHE) can be neglected, while its impact on heavier PAHs (such as BaP) is more pronounced.[139] Further research is needed on the effect of pH on the adsorption of different molecular weight PAHs by biochar, to find the optimal adsorption pH for different PAHs, thus guiding the adsorption of PAHs in the environment.

In general, porous structures of biochar can be obtained through modification methods such as CO_2 activation or by adjusting the pyrolysis temperature, to better adsorb PAHs of different molecular weights. It is also feasible to design biochar that can enhance π–π interactions based on the abundant benzene ring structure of PAHs.

3.5 Organochlorine compounds

Common organochlorine compounds include organochlorine pesticides (OCPs), herbicides (atrazine), antiseptics (triclosan), dioxins, and PCBs.[140,141] As shown in Fig. 6, these chlorinated EDCs, with their benzene rings or other cyclic structures, are connected by one or more chlorine atoms. The adsorption capacity of biochar for such EDCs is largely influenced by the changes in hydrophobicity and polarity brought about by the number of chlorine atoms, as well as the impact of the cyclic structure.

Cho *et al.*[44] used kenaf biochar pyrolyzed at 750 °C for the adsorption of triclosan, with the adsorption mechanism primarily based on hydrophobic interactions and π–π interactions. The adsorption of triclosan by this biochar is less influenced by ionic strength, and HA has a negligible inhibition effect on it. For DDT-like aromatic ring-containing pesticides, when the aromatic ring of the pesticide molecule approaches the aromatic ring present on the surface of biochar, the π electron cloud engages in π–π stacking interactions.[142] This phenomenon enhances the affinity between the pesticide and biochar, consequently improving both the adsorption capacity and efficiency. In addition, Song *et al.*[143] found that biochar from soybean straw has better absorption of OCPs in soil compared to biochar from peanut shells and rice husks. And the nonlinear adsorption capacity of biochar for OCPs increases with the increase of biochar porosity. It is reported that the adsorption capacity of biochar derived from agricultural waste for atrazine is related to the SSA of the biochar. Generally, the larger the hydrophobic surface area of the biochar, the better its adsorption performance for atrazine.[34] Dioxins mainly include

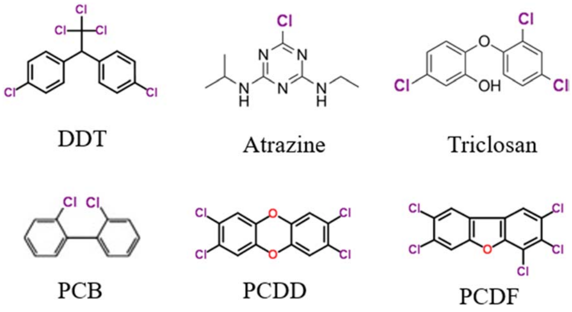

Fig. 6 Structures of typical organochlorine compounds.

polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).[144] Xiong *et al.*[145] discovered that N doping into biochar could enhance π–π electronic and electrostatic interactions, and adding pyridine N-functional groups was found to be most effective in enhancing the adsorption capacity of N-doped biochar for PCDDs and PCDFs.

For PCBs, their hydrophobicity depends on the number of Cl atoms attached to the biphenyl rings. That is, the more Cl atoms attached, the higher the hydrophobicity and the lower the water solubility.[141] The hydrophobicity and planarity of PCBs are the primary characteristics influencing their adsorption onto biochar. Planarity refers to the coplanar arrangement of the benzene ring structures in PCB molecules, typically observed in homologs with no substituent steric hindrance or with substituents located at para-positions. Non-planarity, on the other hand, refers to the distortion of benzene rings caused by steric hindrance from *ortho*-chlorine substituents, which disrupts molecular coplanarity and results in a non-planar molecular configuration. When PCBs exhibit non-planar configurations, the spatial steric hindrance diminishes pore filling and surface π–π EDA interactions, thereby leading to a reduced adsorption capacity of biochar.[45] Wang *et al.*[146] prepared pine needle biochar, which has a high adsorption affinity for PCBs. However, due to dispersive interactions and separation, the non-planar PCBs adsorbed by pine needle biochar are fewer than the planar PCBs. In addition, the study also showed that the co-existence of HA and metal cations increased the adsorption of PCBs on biochar. For PCBs with non-planarity due to an excessive number of Cl atoms, biochar can be designed utilizing the higher number of Cl atoms. Additionally, attention should be paid to how their irregular non-planar structure affects the interaction mechanisms and the demand for the porous structure of biochar.

3.6 Practical application

Biochar has become an efficient adsorbent material for removing EDCs in aquatic environments due to its wide range of raw material sources, low cost, and significantly improved adsorption performance through modification. It has demonstrated important application potential in actual wastewater treatment and environmental remediation. Many studies simulate real aquatic environmental systems to explore the adsorption capacity of biochar, yet the conditions in real water bodies are more complex and there is a certain gap between them and simulated systems.

3.6.1 Application examples. Yuan *et al.*[147] applied crayfish shells and waste activated sludge to prepare biochar, which was used to remove tetracycline and other antibiotics from aquaculture wastewater, achieving an adsorption efficiency of up to 77.1%. Ponnuchamy *et al.*[148] produced biochar from agricultural waste, with the biochar derived from sugarcane bagasse attaining an adsorption efficiency of up to 64% for the removal of BPA from wastewater at a pH of 6.0. Furthermore, in the pilot study, biochar produced from agricultural residue waste using batch and fixed-bed methods exhibited effective adsorption performance for estrogenic EDCs in water.[149] Research on the adsorption of EDCs using biochar is relatively extensive. However, it predominantly remains confined to laboratory, small pilot, and pilot-scale stages, with a limited number of cases demonstrating large-scale practical applications. The large-scale application of biochar in complex environments remains constrained primarily by insufficient long-term performance stability, the competitive effects of coexisting substances, and the cost of modification. Furthermore, the lack of relevant engineering application standards has also delayed its industrialization process.

3.6.2 Challenges faced. Biochar has great potential to restore water environments contaminated with EDCs. However, there are still significant challenges in using biochar for the remediation of complex aquatic environments, such as changes in water quality, pH fluctuations, and the presence of competing ions and coexisting pollutants, all of which can affect the performance of biochar.[150] Biochar still faces significant challenges in the remediation of complex aquatic environments. Factors such as water chemistry fluctuations, the presence of competing ions, and variations in pH can all impact its performance.[151] Jin *et al.*[103] found that when SMX and BPA coexist in aquatic environments, there is competitive adsorption between them, which inhibits their diffusion on the surface of iron-modified biochar. In environments where multiple EDCs coexist, competitive adsorption sites may appear, and the adsorption affinity of EDCs may also change. In such environments, adsorption sites are preferentially occupied by those EDCs with higher adsorption affinity, thereby reducing the ability of other EDCs to compete for adsorption sites.[152] In addition, Table S1 in the SI provides a detailed summary of the effects of various factors on the adsorption of EDCs by biochar under real environmental conditions. Currently, there is limited research on the complexity of biochar adsorption of multiple EDCs coexisting, mostly limited to simulating biochar adsorption in the laboratory with a few mixed EDCs. Future research on biochar adsorption of EDCs should focus more on practical large-scale applications rather than merely simulating adsorption scenarios.

4. Modular design strategies for biochar utilization in the adsorption of EDCs

Based on the rapid development of the research on the preparation and modification of biochar, as well as the continuous discovery of new EDCs in the process of human industrialization, this paper proposes a modular design strategy for biochar adsorption of EDCs for the first time. The modular design strategy entails initially observing the adsorption mechanisms associated with the structural unit modules of the target EDCs during the biochar design process. Subsequently, the biochar structure that can effectively interact with these mechanisms is determined. Ultimately, based on this structure, a comprehensive preparation and modification plan for the biochar is formulated. It is important to note that for EDCs with more complex structures, this strategy should be based on their primary adsorption mechanisms when designing biochar; otherwise, the design of biochar will become very complicated and difficult to implement. In this process, it is crucial to summarize the corresponding adsorption mechanisms of different structural unit modules.

4.1 Adsorption mechanism of various structural modules of EDCs

As shown in Table 4, biochar can interact with a type of EDCs in different ways. The main interactions include hydrophobic interactions, π–π interactions, hydrogen bonding, electrostatic interactions, and pore filling.[22,107] And ion bonds, covalent bonds, and coordination bonds that belong to chemical adsorption are almost absent.[153]

4.1.1 Hydrophobic interactions. The most typical structures that can interact hydrophobically with biochar are alkyl chains, especially long chains with 4 or more carbon atoms. Next are benzene rings and polyhalogenated structures. Generally, among the homologs of the same type of EDCs, molecules with longer molecular chains are more likely to adsorb through hydrophobic interactions. The majority of EDCs exhibit varying degrees of hydrophobicity, so hydrophobic interactions are a common mechanism for the adsorption of EDCs onto biochar.

4.1.2 π–π Interactions. π–π Interactions mainly include π–π stacking and π–π EDA interactions. π–π Stacking typically occurs between the aromatic structures of biochar and the benzene rings of EDCs. In π–π EDA interactions, the electron-withdrawing polar groups on EDCs (such as C═O, –COOH, *etc.*) usually serve as π electron acceptors, while the π electrons on biochar typically act as π electron donors. The electron-withdrawing chlorine substituents in organic chlorinated compounds such as atrazine can also enhance adsorption through π–π EDA interactions with the aromatic carbon of biochar.[160] Higher pyrolysis temperatures produce stronger π electron accepting biochar, primarily interacting with EDCs containing π electron donors through π–π EDA interactions.[161] Due to the generally aromatic structure of biochar, its π electron cloud is delocalized, making π–π interactions one of the important mechanisms for the adsorption of EDCs on biochar.

4.1.3 Hydrogen bonding. Hydrogen bonding interactions often occur between polar groups on biochar (such as –OH, –COOH, and C═O) and polar groups on EDCs (such as –COOH, –SO_3H, and –COOR). Therefore, to enhance the hydrogen bonding interaction between biochar and EDCs, it is often approached from the perspective of preparation and modification to ensure that biochar contains rich oxygen-containing functional groups. Biochars derived from rice husks, soybean stalks, and peanut shells, with their abundance of oxygen functional groups, can enhance hydrogen bonding interactions with EDCs.[162] Hydrogen bonding is typically not the dominant mechanism for the adsorption of EDCs onto biochars, as the proportion of polar functional groups in most EDC molecules is limited across their entire structure. However, for EDCs with shorter chain lengths, the proportion of polar components will be larger, and hydrogen bonding may play a very important role in adsorption.

Table 4 Comparison of the mechanisms of biochar adsorption of different EDCs

EDCs	Feedstock of biochar	Pyrolysis temperature (°C)	Mechanisms	Ref.
Estrone	Walnut shell	700	Hydrophobic effect, hydrogen bonding and π–π interactions	50
17β-Estradiol	Wheat straw	450	Hydrogen bond, electrostatic, π–π interactions	81
Estriol	*Eucalyptus globulus* wood	400	Hydrogen bonding and π–π EDA interactions	109
17α-Ethynylestradiol	Poultry litter and wheat straw	400	Hydrophobic effect, pore-filling and hydrogen bonding	154
Bisphenol A	Corn straw	600	Pore-filling, hydrogen bonding and π–π interactions	154
Nonylphenols	Sawdust	650	Hydrophobic and π–π interactions, electrostatic, hydrogen bonding	155
4-*Tert*-octylphenol	Poplar wood	850	Hydrophobic interaction, hydrogen bonding, π–π interactions and pore-filling	156
Perfluorooctane sulfonic acid	Sawdust	600	Hydrophobic, electrostatic interaction, and pore-filling	70
Perfluorooctanoic acid	Sludge	800	Pore-filling, hydrophobic, and electrostatic interactions	157
Diethyl phthalate	Bamboo	820	Pore-filling, π–π interactions, and electrostatic interaction	158
Di-*n*-butyl phthalate	Rice straw	600	Pore-filling, hydrophobic interaction, π–π interactions, and hydrogen bonding	130
Dimethyl phthalate	Lotus stem	600	Pore-filling, π–π EDA interactions, and hydrogen bonding	127
Sulfamethoxazole	Orange peel	350	Ion exchange, π–π interactions, hydrogen bonding, and pore-filling	68
Ciprofloxacin	Potato stems and leaves	500	Hydrophobic interaction, π–π EDA interactions, hydrogen bonding, and electrostatic interactions	54
Norfloxacin	Coffee ground	500	Pore-filling, electrostatic interaction, and hydrophobic interaction	159
Triclosan	Peach stones	700	Hydrophobic interaction and pore-filling	37
Atrazine	Pig manure	700	Hydrophobic interaction, pore-filling, and π–π EDA interactions	154
Naphthalene	Bagasse	600	Electrostatic attraction, hydrogen bonding, and π–π interactions	135

4.1.4 Electrostatic interactions. The electrostatic interactions between biochar and EDCs mainly depend on the surface charge of biochar and the charge of the EDCs. Unlike the three types of interactions mentioned above, the mechanism of electrostatic adsorption is greatly influenced by external environments, such as pH. Furthermore, attraction that favors adsorption only occurs when the charges of biochar and the target EDCs are opposite.[161] Therefore, when EDCs have obvious charge characteristics, such as acids, they can be considered to enhance the adsorption performance of biochar by utilizing electrostatic attraction. However, with the change in solution pH, the weight of electrostatic attraction in adsorption will change.

4.1.5 Pore filling. The porous structure of biochar is crucial for pore filling. Generally, the pores of biochar are classified into three types based on their pore size, namely micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm).[130] First, biochar must have a sufficiently high specific surface area to provide enough adsorption sites. Secondly, the pore size capable of achieving effective adsorption must be at least larger than the size of the target substance. This is to ensure that during the adsorption process, the target substance can enter the pores based on the four types of interactions described above. Many literatures suggest that the size of the pole matches the size of the target object, but there is no absolute definition of what matching means. As long as the aperture is close to the size of the target object, generally within 2–3 times,[120] pole-matched adsorption can be achieved. In addition, Jia *et al.*[163] summarized that for biochar itself, if no additional modifications are made, the pore size distribution can be either wide or narrow. Pore filling is essentially based on the fact that smaller molecules tend to enter the pores and adsorb due to size effects more easily. However, the influence of pore filling is generally only observable among smaller molecules. In larger EDC homologs, typically, due to the dominance of hydrophobic interactions, biochar achieves higher adsorption amounts for larger EDC molecules compared to smaller EDC molecules, thereby not demonstrating the effects of pore filling.

In addition, under various complex environmental conditions, the interactions and influences among different pollutants, ions, and biochar often lead to changes in the dominant adsorption mechanisms. Li *et al.*[164] found that the main adsorption mechanism of corn cob biochar for sulfa methoxypyridazine is pore filling, with π–π EDA dominating under acidic conditions, while hydrogen bonding interactions dominate under alkaline conditions. Therefore, the adsorption mechanisms of biochar with different EDCs are influenced by many environmental conditions, which also poses a challenge to the efficient removal of EDCs. When designing biochar for the adsorption of EDCs, it is necessary to consider in advance the effects of environmental conditions such as pH on its adsorption performance and mechanism. Table 5 summarizes the structures of biochar and EDCs related to the adsorption mechanisms, laying the foundation for the upcoming modular design strategy.

4.2 Modular design strategies for biochar adsorbing EDCs

Based on the analysis of the adsorption mechanism above, we can relate the structural characteristics of EDCs to the preparation and modification methods of biochar. Therefore, when facing new EDCs, suitable biochar can be prepared to efficiently adsorb the target EDCs. Regardless of any biochar, having a high SSA is essential. As depicted in Table S2, it can be observed that the typical structure of EDCs comprises alkyl chains, benzene rings, halogen atoms, and polar groups. Consequently, when encountering novel EDCs, one can design the biochar structure from the perspectives of preparation and modification by simply analyzing its structural units and relying on its primary adsorption mechanism.

4.2.1 The structure of alkyl chain. If EDCs consist primarily of alkyl chains with a chain length of four or more carbon atoms, priority should be given to enhancing the hydrophobicity of biochar. In terms of preparation, elevated pyrolysis temperatures and lignin-rich feedstocks such as bamboo, wood, *etc.*, can enhance the hydrophobicity and increase surface area of biochar.[38,94,165] In terms of modification strategies, alkali modification can enhance the SSA and hydrophobicity of biochar. In terms of modification strategies, by alkali modification, biochar can possess a larger SSA and stronger hydrophobicity,[64,96] thereby enhancing the hydrophobic interaction between biochar and long-chain EDCs. It is important to note that the modification should not sacrifice a lot of the porous structure.

4.2.2 The structure of benzene ring. If the structure of EDCs mainly contains many benzene ring structures, priority should be given to utilizing π–π interactions to achieve adsorption. For instance, lignin-rich raw materials and higher pyrolysis temperatures can lead to the production of more aromatic structures in biochar.[38,166] In terms of modification strategies, using steam activation and NaOH modification can also enhance the aromaticity of biochar.[85,128] In addition, graphene is proposed to be used to modify biochar, which can enhance π–π interactions with EDCs containing benzene rings, while also providing higher SSA and porosity.[69]

4.2.3 The structure of halogen atoms. If the molecules are not large and contain only a small number of halogen atoms, it may be possible to utilize hydrogen bonding for adsorption. By increasing the oxygen-containing functional groups on the surface of biochar, the hydrogen bonding interactions between biochar and EDCs can be enhanced. During the preparation of biochar, it is important to note that excessively high pyrolysis temperatures and prolonged residence times can reduce the number of oxygen-containing functional groups. Therefore, it becomes particularly important to control the pyrolysis temperature and residence time to retain a substantial amount of oxygen-containing functional groups on the surface of the biochar. In terms of raw material, choosing biomass with a high content of hemicellulose and cellulose is more conducive to the production of biochar with oxygen-containing functional groups.[35] From the perspective of modification, acid–base treatment after pyrolysis enables biochar to possess more oxygen-containing functional groups.[90] In addition, the

Table 5 Mechanism of EDCs adsorption by biochar, corresponding structures, and typical EDCs[a]

	Corresponding structure		
Mechanism	EDCs structure	Biochar structure	Typical EDCs
Hydrophobic interactions	Long alkyl chains, hydrophobic groups	Hydrophobic surface, low-polarity functional groups, high carbon content	Estrogenic EDCs (BPA), long-chain PAEs and PFAS
π–π Interactions	Aromatic ring (benzene ring)	Aromatic structure, graphitized carbon layers, high specific surface area	Estrogenic EDCs (BPA, E2, EE2, E1), short-chain PAEs, PAHs
Hydrogen bonding	Polar groups (phenolic hydroxyl), halogen atom	Surface functional groups such as hydroxyl (–OH), carboxyl (–COOH), and carbonyl (C=O)	Estrogenic EDCs (BPA, E2, EE2), OCPs
Electrostatic interactions	Charged groups	Oppositely charged groups	Short-chain PFAS (perfluorobutanoic acid)
Pore filling	Molecular size and conformation	Porous structure, high specific surface area and pore volume	PAEs (DMP)

[a] BPA: bisphenol A, PFAS: perfluoroalkyl substances, PAEs: phthalate esters, PAHs: polycyclic aromatic hydrocarbons, E2: 17β-estradiol, EE2: 17α-ethinylestradiol, E1: estrone, OCPs: organochlorine compounds, DMP: dimethyl phthalate.

modification of organic compounds (such as chitosan) can directly or indirectly introduce polar functional groups (such as $-NH_2$ and –OH) onto the surface of biochar.[80,82] If the molecule is large and contains many halogen atoms, consider using hydrophobic interactions for adsorption.

4.2.4 **The structure of polar functional group.** Biochar can enhance hydrogen bonding interactions with EDCs containing polar groups by increasing the oxygen-containing functional groups on its surface. For EDCs containing acidic or basic polar groups, attention should be paid to their charge under environmental pH conditions. Based on this, the suitable isoelectric point of biochar should be designed to allow it to have an opposite charge to the EDCs in this environment, thus enhancing the electrostatic attraction. For instance, the isoelectric point can be adjusted through acid or base modification.

4.2.5 **Regulation of pore size.** In general, preparing biochar with a hierarchical porous structure can achieve better adsorption performance. Macro-pores can reduce diffusional resistance, while micro-pores or mesoporous structures that match the target can accurately capture it. In terms of preparation, cellulose-rich materials are beneficial for the production of microporous biochar, while lignin-rich materials favor the production of macroporous biochar. Additionally, higher pyrolysis temperatures can promote the development of the pore structure of biochar, especially facilitating the formation of micropores.[38,94] In terms of modification, alkaline modification can endow biochar with a richer pore structure, while phosphoric acid modification can increase the appropriate micropore volume.[64,96]

Based on the analysis above, the optimal preparation and modification conditions for the biochar that can achieve effective adsorption of target substances can be preliminarily determined. However, the structures of biochar and EDCs are diverse. When considering the design of biochar structure, it is necessary to focus on the possible main adsorption mechanism for designing.

5. Economic feasibility of biochar in removing EDCs

The cost of biochar is primarily determined by the production costs of biochar (the accessibility and ease of obtaining biomass raw materials, as well as the preparation and modification of biochar), and the costs associated with its regeneration. The sources of raw materials for biochar are diverse, and cost-effective feedstocks—such as agricultural and forestry residues, industrial by-products, and municipal waste—can be utilized in its production, thereby yielding substantial economic benefits. According to studies, the average energy requirement for producing biochar (6.1 MJ kg^{-1}) is approximately 15 times lower than that for activated carbon (97 MJ kg^{-1}).[167] Biochar energy consumption is relatively low, which can reduce production costs by reducing energy consumption during production. The modification of biochar leads to increased costs for modified equipment, reagents, and energy consumption. Low-cost modifiers such as clay, scrap steel slag, among others, can also be applied for modification, with the aim to minimize the cost of modification. In addition, through innovative technologies and enhancements in the modification process, it is possible to lower the cost of modified biochar. For instance, the use of microwave treatment as a novel physical modification method can mitigate the issue of high energy consumption associated with steam modification. Despite this, modified biochar, due to its superior adsorption performance, still offers considerable economic benefits compared to other adsorbent materials. According to research, the price of biochar is considered reasonable when it is approximately sixteen times cheaper than activated carbon, thereby rendering it competitive against commercial activated carbons.[117]

Table 6 Regeneration method of biochar adsorbing different EDCs

Biochar	Target adsorbate	Eluent	Regeneration process	Usability level of biochar	Ref.
Apple tree branches biochar	Bisphenol A	Methanol	The desorption time for methanol elution was 60 min	The adsorbent maintained 90% adsorption capacity after five cycles	106
Cow manure/wheat straw biochar	17β-Estradiol	Ethanol and deionized water	Mt-biochars were washed several times with ethanol and deionized water and then dried at 80 °C	After four adsorption–desorption cycles, their adsorption efficiency decreased by 14.3% and 19.2%	81
Peanut shell biochar	Diethyl phthalate	Methanol	Washing with methanol and drying in vacuum oven at 60 °C for 8 h	More than 80% removal efficiency remained after five cycles	126
Maize straw biochar	Polyfluorinated substances	Methanol	—	After four consecutive recycling processes, the PFAS by Fe–M–BC900 still averaged up to 94.7% of the initial sorption values	123
Dawn redwood and bridal wreath biochar	Pyrene	Acetonitrile	Solvent regeneration was performed using acetonitrile as a medium-polarity solvent that is miscible with water and organic compounds	—	134
Palm kernel shell biochar	Phenanthrene and benzo (a)pyrene	DI water and acetone	Regeneration *via* a facile approach of mild rinsing with DI water and acetone, and the sorbents were filtered and washed using vacuum filtration	The sorption efficiency of AB-PMS was in the range of 99.4–85.5% over the five cycles of adsorption–regeneration	139
Rice husk and chicken manure biochar	Dimethoate	—	Hydrothermal regeneration	At the end of the fifth cycle, the adsorption efficiency of DT decreased by only 3.09%	169
Wheat straw biochar	Norfloxacin	Methanol	—	After five cycles of regeneration, the removal percentage of NOR was 86.5%	126
Peels of pomelo (yuzi) biochar	Ciprofloxacin	NaOH	—	Adsorption capacity remained >64 ± 0.68% in the sixth cycle	170
Bamboo biochar	Bisphenol a and sulfamethoxazole	NaOH and DI water	By washing the biochar with 0.1-M NaOH and DI water with the aid of ultrasonication and oven-drying at 60 °C for 24 h after magnetic separation	After four cycles of regeneration, the removal efficiencies of BPA and SMX were only reduced by 7.6 and 8.2%	171

The regeneration process of biochar involves both adsorption and desorption processes.[168] The regeneration methods for biochar include solvent regeneration, thermal regeneration, microwave radiation regeneration, and supercritical fluid regeneration.[15] The most commonly used regeneration method is solvent regeneration. In the process of adsorbent regeneration, critical factors encompass the composition of the eluent, the duration of contact time, and the number of cycles over which the adsorbent can be effectively regenerated and reused.[126] Concerning regeneration, as demonstrated in Table 6, biochars that adsorb EDCs exhibit satisfactory adsorption performance upon solvent regeneration. The advantageous regeneration properties of biochars increase the number of cycles for reuse, thereby significantly lowering their costs. This highlights the economic viability of utilizing biochars for the removal of EDCs. However, it is still necessary to further optimize the regeneration methods of biochar and reduce the impacts of factors related to the desorption suppression process. For solvent regeneration methods, the types and ratios of eluent, contact time, and other parameters need to be optimized, while for thermal regeneration, the pyrolysis conditions also need further optimization.

6. Conclusions and perspectives

Currently, EDCs are widely distributed in the environment, causing serious harm to humans, animals, and even the entire ecosystem. Due to its high adsorption capacity, economic benefits, and environmental advantages, biochar has great potential for application in the adsorption of EDCs. This review focuses on the adsorption performance of biochars for different structure characteristics of EDCs and proposes a modular design strategy for biochars. Future research on the use of biochar for adsorbing EDCs should focus on the following aspects:

(1) In terms of biochar preparation, future efforts should focus on the selection of raw materials, the optimization of preparation conditions, and the development of preparation technologies. The selection of LBM and NLBM requires careful consideration beforehand. The preparation conditions,

particularly the pyrolysis temperature, exert a significant influence on various properties of biochar, including carbon content, surface area, functional groups, and numerous other characteristics. Furthermore, the current yield of biochar is not high. Therefore, in the future, it is necessary to further optimize the preparation conditions and develop new preparation techniques (such as microwave-assisted pyrolysis) to enhance the performance and yield of biochar.

(2) In terms of biochar modification, suitable modification methods need to be chosen for different types of biomass biochar. In future research, firstly, the modification of biochar should be based on the adsorption mechanism and the structural requirements of the targeted EDCs for the structure of biochar, rather than blind modifications. Secondly, biochar can be combined with other emerging technologies in various ways. For example, enhancing the integration of nanotechnology with biochar can enable novel nanocomposite materials (such as GO and CNTs) to better assist biochar in adsorbing EDCs. At present, biochar-based composites show good adsorption performance for EDCs, but technical issues such as the stability of their combination urgently need to be resolved. Moreover, the modification of biochar with nanomaterials increases the cost of biochar, limiting its large-scale production and application. Therefore, the development of multifunctional, low-cost biochar-based nanocomposite materials is urgently needed. Furthermore, the combination of biochar and biotechnology also holds great potential. Biochar, through the mediation of immobilized functional microorganisms, can achieve a synergistic integration of adsorption and degradation processes, while concurrently enhancing its performance and regenerative capacity, thereby facilitating more effective removal of target EDCs from environment. Thirdly, biochar should be modified to enhance its adsorption performance while minimizing the loss of its cost advantage. The cost of modification agents should be minimized to the greatest extent feasible. Furthermore, the modification procedures ought to be streamlined, with an emphasis on identifying simple yet efficient processing techniques. In addition, the development of modified biochar with high recoverability and regenerability is essential to facilitate effective recycling and reuse.

(3) In the future, emphasis should be placed on in-depth research into mechanisms such as competitive adsorption under the coexistence of various EDCs, as well as strengthening the integration of artificial intelligence (AI) with biochar applications. By combining AI and fully utilizing machine learning algorithms, the preparation and modification conditions can be optimized, enabling intelligent design of the surface properties of biochar to achieve high adsorption performance and high yield. Make full use of AI to predict the changes in biochar's adsorption behavior toward multiple coexisting EDCs under different environmental conditions. Through data analysis, adjust the design of biochar to reduce the impact of environmental factors on its adsorption of EDCs.

The advantages and economic advantages of biochar properties (such as high specific surface area, abundant pore structure and functional groups) make it have great potential as a solid phase extraction adsorbent, especially magnetic solid phase extraction. This review provides a reliable basis for the application of biochar in the field of solid phase extraction. Biochar has potential applications in the removal of EDCs, and further development is needed in its preparation and modification. In the future, the utilization of biochar for the removal of EDCs from the environment is expected to be more economical, environmentally sustainable, and safer.

Author contributions

Xin Gao: data curation, formal analysis, editing writing original draft, and review. Ruobing Jia: validation, formal analysis. Yingying Zhang: validation, formal analysis. Jun Kang: validation, formal analysis. Lifei Zhang: validation, formal analysis. Hong Ren: supervision, visualization and validation. Hong Ye: conceptualization, investigation, methodology, supervision, and validation.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Supplementary information (SI): analysis of influencing factors for the adsorption of various EDCs by biochar, the summary of characteristics of some common EDCs, the full-text abbreviation table, relevant literature data diagrams, and the summary diagram of adsorption mechanisms. See DOI: https://doi.org/10.1039/d5ra08986g.

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