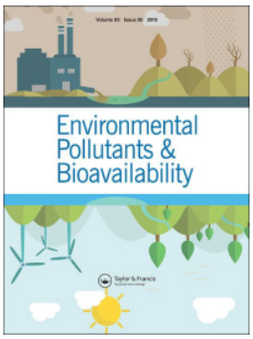

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REVIEW ARTICLE

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Biochar-based materials for the adsorption of phosphorus: a review

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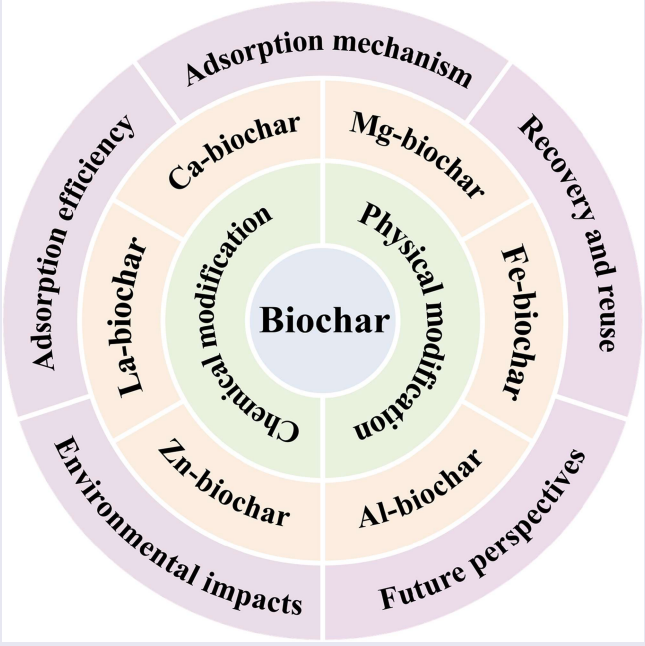
ABSTRACT

Phosphorus pollution is a major driving force of aquatic eutrophication, and its non-renewable nature further highlights the necessity for efficient removal and recovery strategies. Biochar-based materials have attracted considerable attention for phosphorus adsorption due to their low cost and environmental friendliness. This review summarizes recent advances in biochar-based adsorbents, with emphasis on the effects of metal modification on adsorption performance. Key removal mechanisms, including electrostatic attraction, ligand exchange, surface complexation, and precipitation, are discussed. The application of metal-modified biochar in real wastewater treatment and phosphorus recovery is also evaluated, particularly the potential of phosphorus-loaded biochar as a slow-release fertilizer. In addition, phosphorus release behavior, environmental risks, and emerging machine learning approaches for material optimization are reviewed, and future research directions are proposed.



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Biochar; modification; phosphorus recovery; adsorption mechanisms

1. Introduction

Phosphorus, an indispensable life element, exerts a crucial function in numerous vital biochemical processes [1]. Specifically, during plant growth, phosphorus is deeply involved in essential physiological

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processes such as photosynthesis, playing a pivotal role in promoting crop yield and quality [2]. Waterborne phosphorus pollution has emerged as a severe global environmental problem, bringing serious risk to both ecosystems and human health [3]. Owing to agricultural nonpoint source pollution, municipal sewage and other factors, discharged phosphorus causes serious problems such as water eutrophication and disrupts the balance of ecosystems [4]. Meanwhile, phosphate rock resources are nonrenewable. As global agriculture and industry have developed rapidly, the demand for phosphate rock resources continues to grow, rendering the scarcity of such resources increasingly prominent. Consequently, the advancement of green, low-cost and effective phosphorus recovery technologies is imperative [5]. In recent years, various technologies have been studied to address this issue, such as biological treatment, chemical precipitation, adsorption, membrane separation, coagulation-filtration, etc. Among these methods, adsorption has been widely applied because of its simplicity, high efficiency and environmental compatibility [6].

Biochar is a low-cost, porous and carbon-rich material obtained by chemically converting biomass at 200 °C–900 °C in an oxygen-limited environment [7,8]. A variety of raw materials, including agricultural waste, forestry waste and sewage sludge, can be used to prepare it [9]. There are various preparation methods, with commonly used technologies including pyrolysis (fast pyrolysis and slow pyrolysis), gasification, hydrothermal carbonisation and flash carbonisation [10,11]. During the preparation of biochar, the escape of volatile components inside the biomass promotes the formation of a well-developed porous structure [12]. In addition, biochar surface is rich in functional groups, including carboxyl and hydroxyl groups [13]. These functional groups can adsorb phosphorus through ion exchange, complexation and other processes [14]. Owing to these distinctive properties, biochar exhibits enormous application potential in the field of phosphorus recovery from wastewater.

In recent years, the application of biochar in environmental remediation has attracted considerable attention, and existing review articles have focused mainly on its preparation methods [15,16], modification strategies [17–19] and applications in pollutant removal [20]. These studies have summarised the performance advantages of biochar in the removal of both organic and inorganic contaminants [21,22]. Accumulating evidence indicates that biochar exhibits significant potential for phosphorus removal and recovery, particularly in agricultural nutrient management and wastewater treatment [2,23]. However, there is still a lack of systematic analysis focused on phosphorus adsorption on biochar-based materials. Moreover, insufficient attention has been given to the underlying mechanisms, performance differences and potential environmental risks associated with biochar-based materials during phosphorus adsorption. Discussions of real water matrices and long-term operational behaviour remain limited.

This review focuses on the effects of modification strategies on biochar and their influence on phosphorus adsorption performance. Particular attention has been given to the adsorption behaviours and mechanisms of biochar modified with Ca, Mg, Fe, Zn, Al and La, with an emphasis on dominant mechanisms such as electrostatic attraction, ligand exchange, complexation and precipitation. This review aims to systematically summarise recent advances in biochar-based materials for phosphorus adsorption and recovery while comprehensively evaluating their application potential in real water treatment systems, potential environmental risks and long-term environmental behaviour. In addition, in light of recent emerging research trends, the potential application of machine learning in predicting phosphorus adsorption performance and optimising biochar-based materials is briefly discussed. This review is expected to provide systematic support for the rational design and sustainable application of biochar-based phosphorus adsorbents.

2. Surface modification methods of biochar

Insufficient surface functional groups and surface area often limit the performance of pristine biochar [1,24]. Surface modification has emerged as a key strategy to improve the overall properties of biochar by tailoring its surface characteristics. This section provides an overview of common biochar modification methods, including chemical and physical approaches, highlighting their potential to enhance biochar functionality. Meanwhile, the physicochemical properties of biochars derived from different biomass feedstocks after surface modification are summarised in Tables 1 (chemical modification) and 2 (physical modification).

Table 1. Characteristics of biochar modified by chemical methods.

Feedstock	Modification agents	Pyrolysis temperature (°C)	Pore diameter (nm)	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	C(%)	H (%)	O (%)	N (%)	Refs.
Municipal sewage sludge	HNO_3	800	3.88	102.39	0.15	/	/	/	/	[25]
Municipal sewage sludge	CH_3COOH	800	3.87	58.92	0.11	/	/	/	/	[25]
Rice husk	HNO_3	700	14.53	3.94	0.01	42.97	1.26	13.72	1.79	[26]
Willow	HNO_3	700	9.28	2.37	0.01	77.96	1.41	19.54	1.93	[26]
Corn stalk	HCl	700	2.11	219.8	0.12	60.42	1.39	6.03	0.87	[27]
Straw biomass	HNO_3	400	/	31.08	/	50.73	10.12	34.01	5.14	[28]
Wheat straw	HNO_3	700	/	15.52	0.012	86.41	/	13.59	/	[29]
Rice husk	H_2SO_4	500	6.79	6.85	0.018	/	/	/	/	[30]
Rice husk	H_3PO_4	500	6.78	16.8	0.016	/	/	/	/	[30]
Municipal sewage sludge	NaOH	800	3.9	141.78	0.21	/	/	/	/	[25]
Rice husk	KOH	700	6.4	115.5	0.18	71.81	1.71	9.43	0.86	[26]
Willow	KOH	700	31.8	0.84	0.01	84.53	1.3	10.11	1.2	[26]
Corn stover	KOH	500	/	359.1	0.19	75.1	1.88	8.45	1.10	[31]
Corn stalk	KOH	700	2.32	328.02	0.19	65.88	1.42	5.96	0.91	[27]
Algal powder	KOH	800	/	487.55	0.35	/	/	/	/	[32]
Hardwood	NaOH	500	/	62.45	0.12	69.71	4.12	29.49	0.33	[33]
Straw biomass	KOH	400	/	6.59	/	73.9	3.64	20.47	1.99	[28]
Rice straw	KOH	500	2.91	1492.69	1.08	/	/	/	/	[34]
Rice husk	NaOH	500	3.40	119	0.071	/	/	/	/	[30]
Rice husk	$NaHCO_3$	500	3.42	102	0.093	/	/	/	/	[30]

Table 2. Characteristics of biochar modified by physical methods.

Feedstock	Modification methods	Pyrolysis temperature (°C)	Pore diameter (nm)	Specific surface area (m^2/g)	Total pore Volume (cm^3/g)	C (%)	H (%)	O (%)	N (%)	Refs.
Apricot pits	Steam activation	900	/	697	/	95.3	0.77	3.36	0.6	[35]
Walnut shells	Steam activation	900	/	686.5	/	95.6	0.81	3.2	0.42	[35]
Wheat straw	Steam activation	350–650	/	246.2	0.16	/	/	/	/	[36]
Coconut	Steam activation	350–650	/	626.8	0.34	/	/	/	/	[36]
Willow	Steam activation	350–650	/	840.6	0.58	/	/	/	/	[36]
Sewage sludge	Steam activation	600	3.64	123.2	0.11	/	/	/	/	[37]
Sewage sludge	CO_2 activation	600	3.35	113.5	0.095	/	/	/	/	[37]
Wheat straw	CO_2 activation	550	2.28	493.3	0.28	68.3	0.7	7.3	1.1	[38]
Softwood	CO_2 activation	550	2.34	530.3	0.31	93.3	0.9	4.3	/	[38]
Peach stones	CO_2 activation	550	2.14	457.7	0.25	93	0.8	5.5	/	[38]
Waste palm shell	Microwave steam activation	700	1.85	539.8	0.25	81.9	3.6	14	0.7	[39]
Biosolids	Microwave modification	700	8.07	53.55	0.14	/	/	/	/	[40]
Apple tree branches	Ball milling	550	/	102.8	/	81	1.73	8.7	1.18	[41]
Cotton stalk	Ball milling	500	/	351.6	/	/	/	/	/	[42]
Maize stalk	Ball milling	500	/	231.6	/	/	/	/	/	[42]
Rice husk	Ball milling	500	/	253.3	/	/	/	/	/	[42]
Pinecones	Ball milling	300	2.17	20.65	0.011	/	/	/	/	[43]
Corn stalk	Ball milling	550	5.03	393	0.49	/	/	/	/	[44]

2.1. Chemical modification

2.1.1. Acid modification

Acid modification serves dual purposes: removing impurities and introducing acidic functional groups onto the biochar surface [45,46]. Acid treatment can effectively promote the development of the pore structure of biochar. Yin et al. [47] compared the phosphorus adsorption performance of sludge biochar prepared via two methods: acid treatment followed by carbonisation and carbonisation followed by acid treatment. Experiments have shown that two different acid treatment sequences can both optimise the pore structure and increase the specific surface area, thereby increasing the number of adsorption sites. Moreover, the acid treatment after carbonisation significantly enhanced phosphorus adsorption, which was 134% higher

than that of the sample calcined at the same temperature of 750 °C. Specifically, the biochar prepared by carbonisation at 550 °C followed by acid treatment (Zn550-H) achieved a phosphate adsorption capacity of 95.69 mg/g. Compared with other treatment methods, acid treatment can enhance phosphorus adsorption. Park et al. [48] evaluated the phosphorus adsorption behaviour of sesame straw biochar modified with different activating agents. The results indicated that pristine biochar exhibited inorganic phosphorus release, whereas biochar activated with HCl and H_2SO_4 showed enhanced phosphorus adsorption performance, outperforming the unmodified sample.

2.1.2. Alkali modification

Alkali modification contributes to increasing the specific surface area as well as oxygen-containing functional groups of biochar [45,46]. Liu et al. [49] reported that the specific surface area of walnut shell biochar modified with KOH increased from 116.63 m^2/g to 983.75 m^2/g. Fourier transform infra-red spectroscopy (FTIR) analysis revealed that the intensity of the characteristic peak of the hydroxyl groups increased after modification, indicating an increase in oxygen-containing functional groups on the biochar surface. Liu et al. [50] prepared alkaline sludge biochar by grinding KOH and biochar at different mass ratios and impregnating the mixture in water. For the 5/1 KOH-biochar, a notable increase in the specific surface area (from 64.21 m^2/g to 82.90 m^2/g) was observed, along with a remarkably enhanced adsorption performance. Fitting with the Langmuir model showed that the phosphorus adsorption capacity of the 5/1 KOH-biochar reached 42.51 mg/g, surpassing the raw biochar (27.83 mg/g).

2.2. Physical modification

2.2.1. Gas activation

Gas activation typically employs steam or CO_2 as the activating agent to effectively regulate the pore structure and surface properties of biochar under high-temperature conditions. Compared with chemical activation, this approach does not require the introduction of chemical reagents and therefore exhibits environmental friendliness [18,38]. During steam activation, water vapour reacts with carbon to produce CO and H_2. The carbon in the precursor is gradually consumed, and the pores expand over time with increasing oxidation intensity, increasing the porosity and specific surface area of the material [51]. Meanwhile, steam activation can introduce oxygen-containing functional groups, such as carbonyl and hydroxyl groups, onto the biochar surface, thereby enhancing its adsorption performance [52]. In addition to steam, CO_2 can also serve as an important activating gas, primarily facilitating the formation of microporous structures in biochar [53]. Studies have shown that introducing a CO_2 atmosphere during the pyrolysis stage can significantly increase the specific surface area of biochar. For example, CO_2-activated barley straw-derived biochar prepared by Pallarés et al. [54] achieved a specific surface area of nearly 800 m^2/g. Overall, gas activation enhances the adsorption performance of biochar by synergistically regulating its pore structure and surface properties.

2.2.2. Microwave modification

Microwave modification is a physical modification technique based on high-frequency electromagnetic radiation (0.3–300 GHz) [55]. This method can rapidly and efficiently heat biomass without direct contact. Microwave-assisted modification can markedly enhance the properties of biochar. For instance, Shan et al. [56] reported that after microwave modification of cotton straw-derived biochar, the specific surface area increased from 57.05 m^2/g to 189.8 m^2/g, and the total pore volume increased from 0.057 cm^3/g to 0.135 cm^3/g, accompanied by increased formation of oxygen-containing functional groups. Xiang et al. further demonstrated that microwave power exerted a significant influence on the properties of corn stalk-derived biochar, with the specific surface area, total pore volume and micropore volume reaching their maximum values at approximately 500 W, followed by a slight decline at higher power levels [57]. Therefore, microwave modification can improve the pore structure and specific surface area of biochar.

2.2.3. Ball milling

Ball milling has attracted increasing attention as a method for fabricating advanced nanomaterials because of its high efficiency and eco-friendliness, but the current ball milling process may damage the original

structure of biochar [18,20]. Ball milling is an economical and efficient method that uses mechanical energy to grind raw materials into nanoscale particles, thereby enhancing their physicochemical properties [58]. For instance, the specific surface area of corn straw-derived biochar increased dramatically from an initial value of 34.5 m^2/g to 393 m^2/g after ball milling treatment, with a significant increase in the exposure of oxygen-containing functional groups on the biochar surface [44].

3. Metal-modified biochars

Compared with unmodified biochar or conventional adsorbent materials, metal-modified biochar exhibits significant advantages in phosphate adsorption. Metal modification markedly enhances the phosphate adsorption capacity of biochar. In contrast, unmodified biochar shows a limited ability to adsorb phosphate [59]. After metal modification, new chemical adsorption sites can be formed, thereby increasing the phosphorus removal efficiency through ligand exchange, precipitation and complexation [60,61]. Metal modification also helps to improve the specific surface area and pore structure of biochar, further enhancing its overall adsorption performance [62,63].

Metal-modified biochar retains a highly porous structure and low cost while providing metal-based adsorption sites with high affinity, making it superior to most traditional adsorbents in both economic feasibility and adsorption efficiency [64,65]. Moreover, nontoxic or plant-beneficial metal elements (e.g. Ca) can be selected according to specific application requirements, enabling good adaptability in both water treatment and soil remediation [66,67]. More importantly, modified biochar not only enables efficient phosphorus adsorption but also can serve as a slow-release phosphorus fertiliser, thereby achieving resource recovery and circular utilisation [68,69]. The phosphorus adsorption performance of metal-modified biochar and the associated mechanisms are summarised in Table 3.

3.1. Ca-modified biochar

The key to the improved adsorption performance of Ca-modified biochar lies in the chemical adsorption mechanisms involving ligand exchange between Ca^{2+} and phosphate on the adsorbent surface, as well as surface precipitation [82]. The total pore volume of the $CaCl_2$ modified corn stover biochar CaBC800 (prepared via pyrolysis at 800 °C) increased from 0.033 cm^3/g (BC800) to 0.133 cm^3/g, with its specific surface area rising from 30.55 cm^2/g to 238.30 cm^2/g [70]. Compared with unmodified biochar, CaBC800 contained more mesopores, which may stem from the decomposition of $Ca(OH)_2$. This study showed that its phosphate adsorption primarily relies on chemical precipitation as well as ligand exchange between the —OH of the CaBC800 surface and phosphate. CaBC800 exhibits an equilibrium phosphate adsorption capacity of 25.78 mg/g, whereas unmodified biochar has almost no ability to adsorb phosphate. Liu et al. [83] prepared $CaCl_2$-modified biochar (1.5-MBC), which exhibited higher specific surface area and pore volume than pristine biochar. Phosphate adsorption was enhanced through surface precipitation, complexation and ligand exchange, and the Langmuir model predicted an adsorption capacity of 70.26 mg/g (Figure 1a). Liu et al. [84] prepared CaO-biochar by ball milling and pyrolysis of the mixture of eggshell and rice straw powder. The incorporation of eggshells into rice straw elevated the biochar composite's specific surface area and the loading of Ca species, resulting in the optimal phosphate adsorption performance at an adsorption capacity reaching 231 mg/g, indicating a significant improvement compared to 5.58 mg/g of pristine biochar (Figure 1b). In addition, Cao et al. [71] reported that, for $CaCO_3$-modified rape straw biochar (CRS), although it had a smaller specific surface area than raw biochar, mechanisms such as Ca–P precipitation, electrostatic attraction and hydrogen bonding significantly increased its phosphate adsorption capacity from 3.10 mg/g to 96.56 mg/g.

3.2. Mg-modified biochar

Mg modification optimises the specific surface area and pore structure of biochar, supplying extra adsorption sites. Additionally, it strengthens the phosphate adsorption capacity via mechanisms such as electrostatic attraction and surface precipitation with phosphate [24]. MgO-modified biochar was derived from waste woody biomass precursors (pine wood, red oak and hard maple) [90]. The phosphorus

Table 3. Experimental conditions, isotherm data and removal mechanism of phosphorus by modified biochar.

		Experimental conditions				Langmuir isotherm fitting constants			
Adsorbents	Modification agents	Adsorbent dosage (g/L)	Initial concentration (mg/L)	pH	Temperature (°C)	K_L (L/mg)	Q_m (mg/g)	Mechanisms	Refs.
Ca-modified corn stover biochar	$CaCl_2$	1	10–100	6	Room temperature	0.26	33.94	Chemical precipitation, ligand exchange	[70]
Ca-modified rape straw biochar	$CaCO_3$	1	10–200	/	25	0.019	96.56	Chemical precipitation, electrostatic attraction and hydrogen bonding	[71]
Ca-modified wood biochar	$Ca(OH)_2$	1	100–400	9	20	0.13	125.6	Chemical precipitation, electrostatic attraction	[72]
Mg-modified bamboo biochar	$MgCl_2{\cdot}6H_2O$	2	15–1000	8.2	Room temperature	0.027	121.8	Chemical precipitation, electrostatic attraction	[73]
Mg-modified corn straw biochar	$MgCl_2{\cdot}6H_2O$	1	5–500	/	25	0.0016	271.08	Chemical precipitation, electrostatic attraction	[24]
Mg-modified sludge biochar	$MgCl_2{\cdot}6H_2O$	2	25–500	/	25	0.23	120.9	Chemical precipitation, complexation reaction and electrostatic attraction	[74]
Fe and Ca co-modified bamboo biochar	$FeCl_3$, CaO	2.5	2–900	7	25	0.0065	70.8	Chemical precipitation, electrostatic attraction	[75]
Fe-modified rice straw biochar	$FeCl_2$	4	20–200	4.6	25	2.08	39.2	Electrostatic attraction, ligand exchange	[76]
Fe-modified rice straw biochar	$FeCl_3$	4	20–200	4.6	25	0.55	32.6	Electrostatic attraction, ligand exchange	[76]
Fe and La co-modified coffee ground biochar	$FeCl_3{\cdot}6H_2O$, $LaCl_3{\cdot}7H_2O$	0.4	5–175	/	40	3.67	76.58	Chemical precipitation, complexation reaction, electrostatic attraction, ligand exchange	[4]
Fe and Mn co-modified rice straw biochar	$KMnO_4$, $FeSO_4{\cdot}7H_2O$	4	15–500	6	25	0.65	12.74	Complexation reaction, electrostatic attraction	[77]
Al-modified poplar chips biochar	$AlCl_3{\cdot}6H_2O$	2	/	6	25	5.2	47.84	Chemical precipitation, complexation reaction, and electrostatic attraction	[78]
Al-modified food waste biochar	$AlCl_3$	10	10–700	/	25	0.039	197.8	Electrostatic attraction, ligand exchange	[79]
La-modified wood brash biochar	$LaCl_3{\cdot}H_2O$	1.5	0.1–500	7	20	0.02	121	Complexation reaction, electrostatic attraction, and ligand exchange	[80]
La-modified lotus seedpods biochar	$La(NO_3)_3{\cdot}6H_2O$	1.67	5–500	7	25	0.025	52.23	Complexation reaction, electrostatic attraction, and ligand exchange	[81]

adsorption capacity of the pristine biochar ranged from 1.88 to 2.78 mg/g, while that of the MgO-modified biochar reached 28.20–29.22 mg/g, representing an 11-fold increase over pristine biochar. After MgO modification, significant enhancements were observed in the specific surface area, pore volume and cation exchange capacity (CEC) of the biochar. As reported by He et al. [85], the phosphate adsorption capacity of Mg-modified corn stalk biochar (MgB) reached 73.29 mg/g (Figure 1c), with dominant mechanisms including precipitation, ion exchange and electrostatic attraction. Zheng et al. [86] demonstrated that Mg and Al co-modified biochar (MABC) exhibited a phosphate adsorption capacity of 153.4 mg/g (Figure 1d), which

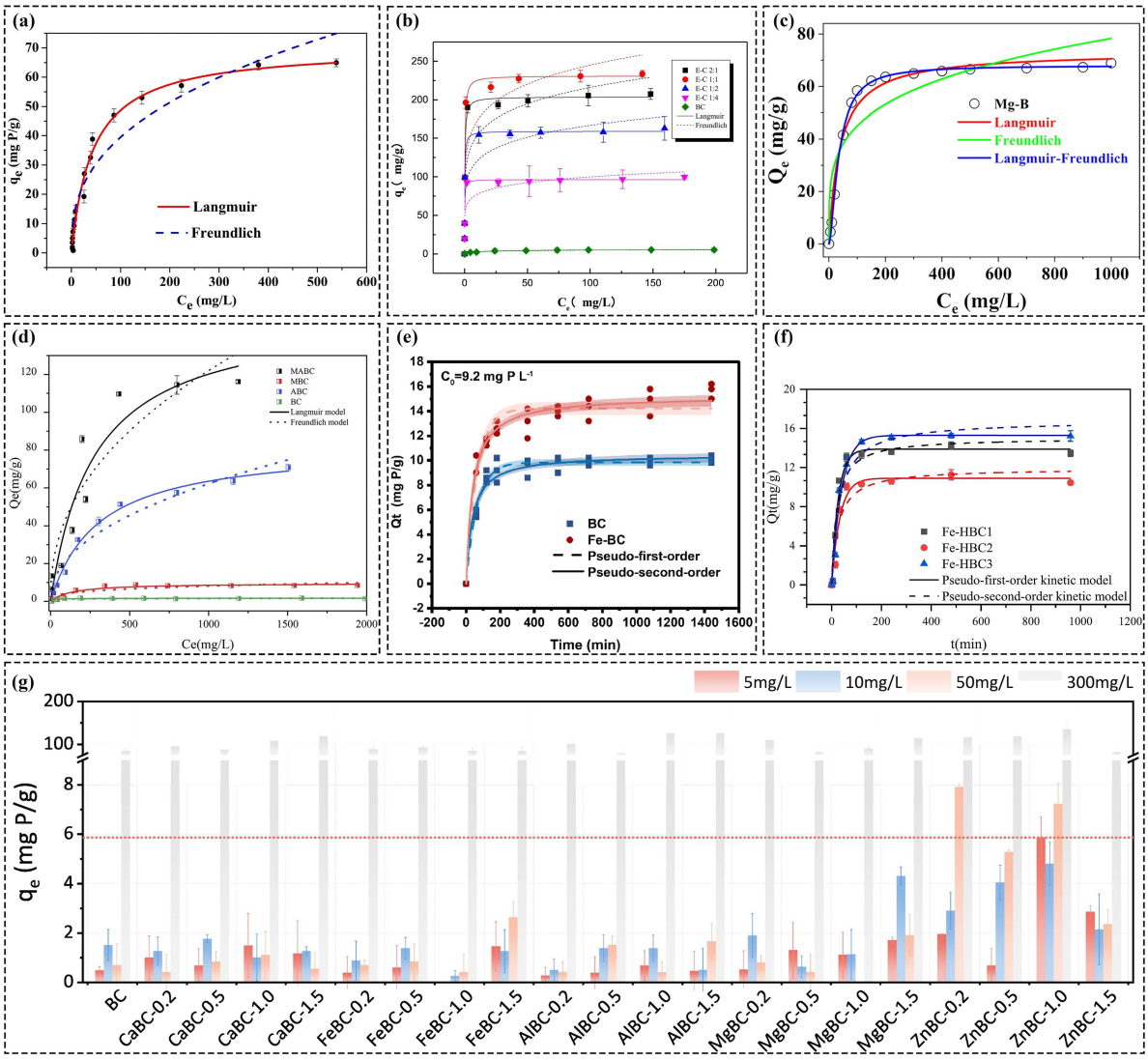

Figure 1. (a) Phosphorus adsorption isotherms on 1.5MBC [83]. Copyright 2024 Elsevier. (b) Adsorption isotherm of phosphate on different CaO-biochar composites and pristine biochar [84]. Copyright 2019 Elsevier. (c) phosphate adsorption isotherm of the Mg-modified corn stalk biochar [85]. Copyright 2022 Springer Nature. (d) Phosphate adsorption isotherms of various biochars, including Mg–Al-modified biochar, Mg-modified biochar, Al-modified biochar and pristine biochar [86]. Copyright 2020 Elsevier. (e) Phosphate adsorption kinetics of biochar and Fe-biochar under 9.2 mg P/L initial phosphorus concentration [87]. Copyright 2024 Elsevier. (f) Adsorption kinetic model fitting for phosphate adsorption onto Fe-modified biochar [88]. Copyright 2024 Elsevier. (g) Phosphate adsorption screening for metal-modified biochar produced through metal-mediated biomass pyrolysis from real wastewater [89]. Copyright 2024 Elsevier.

was 15.91 times higher than Mg-modified biochar, 1.85 times higher than Al-modified biochar and 93.54 times higher than unmodified biochar. Following phosphate adsorption, diffraction peaks of $AlPO_4$ (PDF No. 76-0226) and Mg_3 $(PO_4)_2$ (PDF No. 35-0134) were observed in MABC's XRD pattern, demonstrating that MABC adsorbs phosphate through co-precipitation. Guo et al. [91] demonstrated that the specific surface area of Mg-modified algal biochar (Mg@ABB) boosted from 14.55 m^2/g (unmodified biochar) to 108.30 m^2/g, providing more phosphate adsorption sites. The phosphate removal rate of Mg@ABB can reach 100%, with the adsorption capacity reaching 39.20 mg/g under specific conditions.

3.3. Fe-modified biochar

Fe-modified biochar exhibits several distinct advantages in phosphate adsorption. The Fe species (e.g. Fe^{2+}, Fe^{3+}) introduced onto biochar surfaces provide abundant active sites, enabling interactions with phosphate

through mechanisms such as ligand exchange, surface precipitation and electrostatic attraction. Xiong et al. [87] prepared wheat straw biochar modified with $FeCl_3 \cdot 6H_2O$ (Fe-BC). Compared with pristine biochar, Fe-BC had an increased number of micropores, with its specific surface area increasing from 127.70 m^2/g to 369.97 m^2/g, and was capable of forming bidentate Fe–phosphate surface complexes with PO_4^{3-}. According to the pseudo-second-order kinetic model, the equilibrium adsorption amount of Fe-BC reached 15.25 mg/g at an initial phosphorus concentration of 9.2 mg/L, which was higher than that of pristine biochar (10.47 mg/g), as shown in Figure 1e. As reported by Huang et al. [88], biochars derived from apple branches, rice straw and kiwi branches were modified via HCl soaking followed by $FeCl_3$ treatment, named Fe-HBC1, Fe-HBC2 and Fe-HBC3. Their equilibrium adsorption amount, as derived from the pseudo-first-order kinetic model, was measured as 13.88 mg/g, 10.91 mg/g and 15.31 mg/g, respectively (Figure 1f). Fe modification resulted in higher specific surface area and average pore size relative to unmodified biochar: the increased specific surface area was due to Fe particle deposition on the biochar surface, which increased surface roughness. Meanwhile, HCl-induced acidification and $FeCl_3$ modification caused the filling or etching of some micropores and mesopores, increasing the average pore size. These modifications significantly restructured the biochar surface, creating more adsorption sites and improving the pollutant adsorption capacity. Ajmal et al. [92] employed the coprecipitation of Fe(II) and Fe(III) to magnetically modify wood and rice husk biochar. Although the specific surface area of the biochar decreased after Fe modification, its adsorption capacity for PO_4^{3-} (25–28 mg/g) was nearly twice that of unmodified biochar (12–15 mg/g). The underlying removal mechanisms are primarily electrostatic attraction, surface precipitation and ligand exchange.

3.4. Zn-modified biochar

Among various metal-modified biochars, Zn-modified biochar exhibits excellent phosphorus adsorption activity. Rice straw biochar was modified using $FeCl_3$, $MgCl_2$, $ZnCl_2$, $AlCl_3$ and $CaCl_2$ to prepare Fe-, Mg-, Zn-, Al- and Ca-modified biochar [89], which were designated sequentially as FeBC, MgBC, ZnBC, AlBC and CaBC. CaBC, AlBC, MgBC and ZnBC showed approximate maximum phosphate adsorption capacities of 140 mg/g at an initial phosphate concentration of 300 mg/L, significantly exceeding those of FeBC and unmodified biochar (Figure 1g). Nevertheless, when the initial phosphate concentration of wastewater was ≤50 mg/L, the phosphate adsorption capacity of ZnBC notably exceeded those of other metal-modified biochar. This phenomenon could stem from the capacity of ZnBC to strike an optimal balance between the Gibbs free energy of formation of Zn phosphate and the solubility product constant.

3.5. Al-modified biochar

Al-modified biochar is one of the primary phosphorus-adsorbing materials studied by researchers. Al-modified biochar was produced from Korean pine residue as the raw material, with Al ions obtained from water treatment sludge [93]. The phosphate adsorption capacity of the biochar impregnated with recovered Al ions reached 11.9 mg/g, similar to that of $Al_2(SO_4)_3$ impregnated biochar (14.39 mg/g). Yin et al. [78] prepared four types of Al-modified poplar chips biochar with Al loadings of 5%, 10%, 15% and 20%, respectively. The Langmuir–Freundlich model could well describe the adsorption of PO_4^{3-} by the biochar. The 20 wt% Al-modified biochar exhibited the best adsorption performance for PO_4^{3-} (57.49 mg/g) according to the Langmuir–Freundlich model.

3.6. La-modified biochar

In the Shang et al. experiment, the phosphate adsorption kinetic curve of the La-ammonium-modified hydrothermal biochar (La-A-HC) exhibited good fit with the pseudo-second-order kinetic model, demonstrating that chemical adsorption was the dominant mechanism [94]. Platanus biochar modified with La exhibits a similar mechanism: as the initial phosphorus concentration increases to 30 mg/L (from 10 mg/L), its adsorption saturation capacity increases to 75 mg/g (from 25 mg/g), with the adsorption efficiency reaching 100% in both concentration ranges [95].

4. Mechanisms of phosphate removal by biochar-based materials

For phosphate removal by biochar-based materials, the mechanisms involve multiple aspects, such as electrostatic attraction, ligand exchange, precipitation, complexation, etc.

4.1. Electrostatic attraction

Electrostatic attraction refers to the interaction between positively charged adsorption sites and negatively charged phosphate ions [96]. In aqueous solutions, phosphate predominantly exists in the forms of PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$. When positively charged sites are introduced onto the biochar surface through metal ions or metal oxides, the enrichment and removal of phosphate can be achieved via electrostatic attraction, as shown in Figure 2a [16,97]. This process is strongly influenced by the solution pH and the point of zero charge (pH_{pzc}) of the biochar. When $pH < pH_{pzc}$, surface functional groups are protonated, rendering the adsorbent positively charged and facilitating phosphate binding [98]. For example, under low pH conditions, MgO on the surface of MgO@MBC is readily protonated, which renders the MgO@MBC surface positively charged and thereby facilitates phosphate adsorption via electrostatic attraction [99]. Moreover, electrostatic attraction can act synergistically with ligand exchange and complexation, promoting the

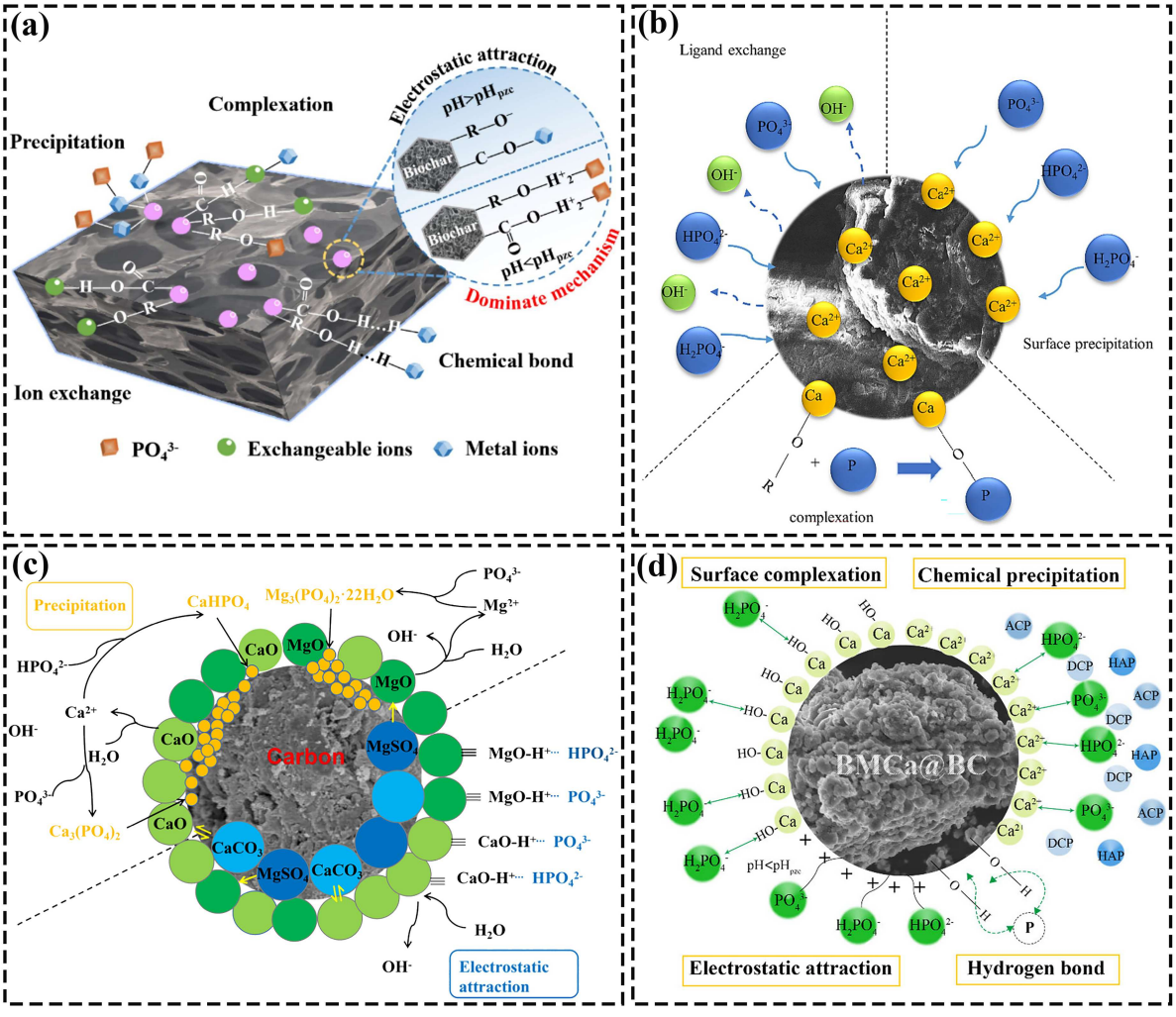

Figure 2. (a) Mechanistic overview of phosphate adsorption on biochar-based adsorbents [16]. Copyright 2025 Elsevier. (b) Schematic illustration of phosphate adsorption by Ca-modified biochar [83]. Copyright 2024 Elsevier. (c) Schematic diagram of phosphorus adsorption mechanisms on sludge-derived biochar [101]. Copyright 2022 Elsevier. (d) Schematic diagram illustrating the phosphate adsorption mechanism of ball-milled Ca-loaded biochar [102]. Copyright 2023 Elsevier.

formation of diverse surface complexes, thereby increasing the capacity of phosphate removal systems [100].

4.2. Ligand exchange

Ligand exchange is one of the important mechanisms for phosphate removal by biochar-based materials, with its core principle involving the substitution of surface hydroxyl groups by phosphate ions, followed by the formation of stable inner-sphere complexes through metal active sites, as shown in Figure 2b [83,103]. During this process, phosphate ions can react with metal–oxygen bonds (M–OH) to form monodentate or bidentate coordination structures [23]. Compared with reversible ion exchange, the inner-sphere complexes formed via ligand exchange are more stable and therefore more suitable for long-term phosphorus removal applications [16]. Metal or metal oxide modifications can provide abundant active sites on biochar surfaces, thereby enhancing ligand exchange interactions. For example, Ajmal et al. reported that magnetic modification significantly increased the adsorption capacity of biochar for PO_4^{3-} to approximately twice that of the unmodified material, which was attributed to the hydroxyl active sites introduced by modification that strengthened the binding between phosphate and the material surface [92]. Overall, ligand exchange effectively enhances phosphate adsorption performance by forming stable metal–phosphorus inner-sphere complexes.

4.3. Precipitation

Surface precipitation originates mainly from chemical reactions between phosphate ions and metal species on the biochar surface, resulting in the formation of insoluble precipitates that are immobilised on the material surface (Figure 2c) [101,104]. Metals such as Ca, Mg, Fe and La that are introduced or enriched in biochar can serve as active sites for precipitation reactions, reacting with phosphate ions in solution to form stable precipitated phases. For example, Mg-modified biochar can generate $Mg_3(PO_4)_2$ precipitates during the adsorption process [105]; CaO-biochar composites tend to form hydroxyapatite ($Ca_5(PO_4)_3OH$) [84], whereas La-modified biochar mainly achieves efficient phosphorus immobilisation through the formation of $LaPO_4$ [106]. Surface precipitation is influenced by the solution pH. Luo et al. [107] reported that the formation of $LaPO_4$ in $La(OH)_3$ nanorod/walnut shell biochar is highly pH dependent, with acidic conditions (pH = 3) favoring precipitation, while the process is inhibited at pH = 11. Therefore, surface precipitation plays an important role in phosphorus removal by metal-modified biochars.

4.4. Complexation

When phosphate ions come into contact with metal oxide sites on the biochar surface, such as Mg–O, Ca–O and Fe–O, surface complexation reactions readily occur, leading to the formation of stable chemical bonds (Figure 2d) [23,102]. Surface complexation mainly includes two forms: outer-sphere complexation and inner-sphere complexation. The former typically exhibits no bond breaking or formation, whereas the latter forms covalent bonds and is sometimes accompanied by bridging ligands [23]. In the La-modified sludge biochar, X-ray photoelectron spectroscopy (XPS) results indicated that phosphate could form inner-sphere La–O–P complexation structures with the metal species [65]. In addition, La/Al co-modified biochars are capable of forming both La–O–P and Al–O–P inner-sphere complexes, thereby achieving synergistic phosphorus immobilisation [108].

5. Recovery and reuse of phosphate

5.1. Reuse of phosphate-loaded biochar-based materials as fertilisers

Phosphate-loaded biochar-based adsorbents can be reutilised as soil amendments. Owing to its high carbon and nutrient contents, biochar enhances soil fertility and facilitates plant growth [87]. The phosphate-loaded Ca/Mg co-modified coffee ground biochar (CMBC-P) mitigated the negative impact of CMBC on plant germination (Figure 3a), exhibiting good biocompatibility and plant growth-promoting

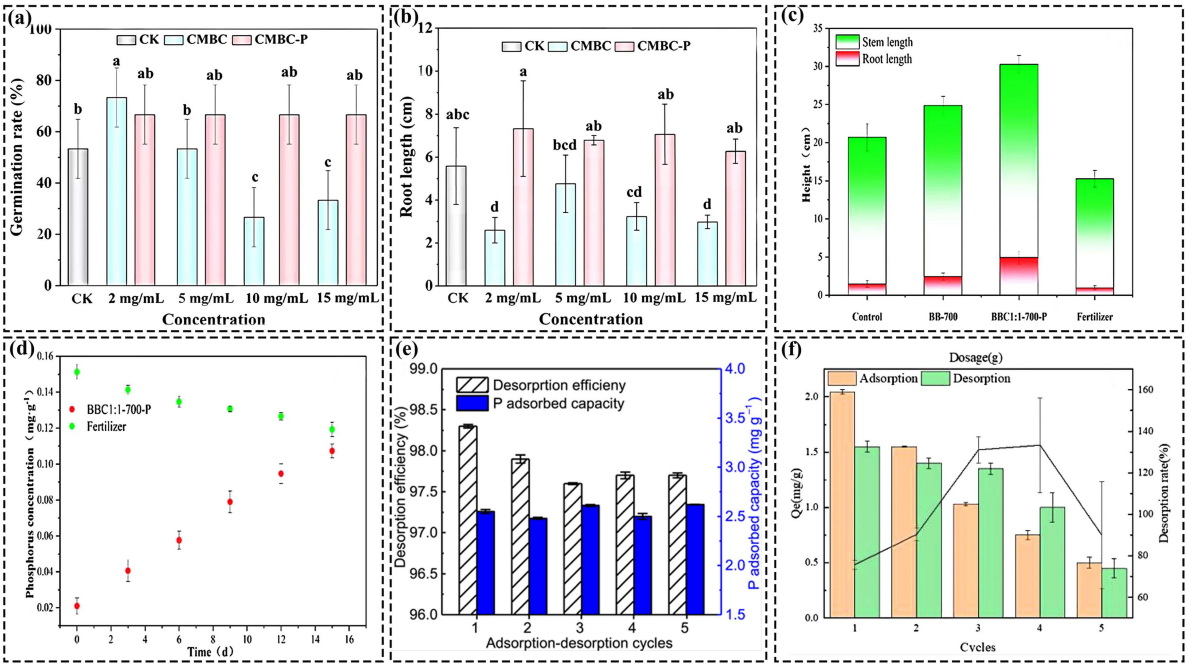

Figure 3. (a) Seed germination rate of cucumber seedlings under CMBC and CMBC-P treatments [109]. Copyright 2024 Elsevier. (b) Root length of cucumber seedlings under CMBC and CMBC-P treatments [109]. Copyright 2024 Elsevier. (c)Root and stem lengths of BB-700 group and BBC1:1-700-P group [59]. Copyright 2024 Elsevier. (d) Variation in the phosphorus content of the fertiliser group and BBC1:1-700-P group [59]. Copyright 2024 Elsevier. (e) Fe-300 biochar desorption efficiency and phosphorus adsorptive capability in KH_2PO_4 solution over five successive adsorption–desorption cycles [110]. Copyright 2020 Elsevier. (f) Desorption and recycling of Fe-modified maize straw biochar [111]. Copyright 2024 Frontiers.

ability (Figure 3b) [109]. For $CaCl_2$-modified buckwheat hull biochar (BBC), the root and stem lengths of buckwheat treated with BBC 1:1-700-P were superior to other treatments, attributed to its slow phosphate release (Figure 3c) [59]. A comparison of the soil phosphate content between the BBC 1:1-700-P application group and the chemical fertiliser group showed that the phosphate release in the BBC 1:1-700-P group increased slowly within 15 days, while that in the chemical fertiliser group decreased gradually (Figure 3d). Thus, BBC 1:1-700-P overcomes the drawbacks of traditional phosphate fertilisers, prevents excessive phosphate from entering water bodies, and serves as a novel soil phosphate fertiliser. However, the risk of phosphorus release remains a concern. The feedstock and preparation methods of biochar can significantly influence its phosphorus binding capacity; if the binding strength is insufficient, phosphorus may be readily released, leading not only to resource loss but also to the potential exacerbation of aquatic eutrophication.

5.2. Phosphate desorption and precipitation

Phosphate desorption from biochar surfaces can be achieved using eluents such as acids, alkalis, or salts. The choice of eluent depends on the desorption efficiency, regeneration cycles and its impact on doped elements in modified biochar [59]. To evaluate the recycling and regeneration performance of Fe-300 biochar for phosphorus removal efficiency, phosphorus desorption tests were conducted. It is worth noting that after five consecutive adsorption/desorption cycles in KH_2PO_4 solution, the phosphorus adsorption capability of Fe-300 biochar showed indistinct changes, with the desorption efficiency in the fifth cycle still exceeding 97% of the adsorption capacity (Figure 3e) [110]. After five regeneration cycles in NaOH solution (Figure 3f), the phosphate adsorption capacity of Fe-modified biochar decreased to 24%, indicating a significant decline in the recyclability of the adsorbent. Adsorbent dissolution and incomplete desorption may account for the reduced P recovery rate [111].

Although chemical desorption can effectively achieve phosphorus release and biochar regeneration, this process for metal-modified biochar is often accompanied by the disruption of metal–phosphorus bonds and metal leaching, which may pose potential risks to aquatic and soil environments [23]. In addition, ions introduced by the desorbing agents may induce soil salinization and groundwater contamination. Therefore, future studies should focus more on systematically assessing and mitigating ecological risks from regeneration processes while preserving high phosphorus recovery efficiency.

6. Application potential, environmental impacts and emerging research methods of phosphorus adsorption on biochar-based materials

6.1. Practical applications of phosphorus adsorption by biochar-based materials

In recent years, related studies have gradually extended from laboratory-scale synthetic solution systems to conditions that more closely resemble real water environments, thereby preliminarily validating the application potential of biochar-based materials for phosphorus removal. Sun et al. [112] reported in column experiments that eggshell-modified biochar maintained 100% phosphorus removal efficiency for 586 min when treating simulated wastewater with a phosphorus concentration of 200 mg/L under continuous-flow conditions, demonstrating excellent dynamic stability. Qin et al. [113] found that in column adsorption experiments, the breakthrough time for phosphorus in real wastewater (25 h) was significantly longer than that in synthetic wastewater (20 h), which was attributed to the presence of coexisting Ca^{2+} and Mg^{2+} ions in real wastewater that promoted phosphorus immobilisation on the adsorbent surface. To meet the demands of rural wastewater treatment, oyster shell-rice husk biochar achieved total phosphorus removal efficiencies of 93.9%–99.4% in actual rural domestic wastewater, with the effluent quality stably meeting current discharge standards, providing direct evidence for its engineering applicability [114].

However, from an overall perspective, the engineering-scale application of biochar-based materials for phosphorus adsorption remains limited, which has to some extent constrained their large-scale deployment. At present, most studies are still conducted in synthetic solution systems, while long-term operational validation in real wastewater and natural water bodies remains insufficient [115]. Interference from coexisting anions and dissolved organic matter (DOM) in real water matrices may weaken the phosphorus adsorption selectivity of biochar-based materials, leading to discrepancies between laboratory results and practical performance [102,116]. Therefore, future efforts are needed to promote large-scale application by enhancing the interference resistance of materials.

6.2. Environmental risks and potential impacts of phosphorus adsorption by biochar-based materials

The environmental stability of biochar is one of the key factors determining its potential environmental risks and is generally closely related to the aromaticity of its carbon structure and the degree of aromatic condensation [117]. The feedstock type and pyrolysis conditions strongly influence the physicochemical properties of biochar, and its long-term environmental stability, therefore, requires careful evaluation. Higher pyrolysis temperatures are conducive to increasing the degree of biochar aromatisation, thereby increasing its structural stability; however, excessively high temperatures (>600 °C) may induce pore structure collapse, thereby reducing the adsorption efficiency [20]. In addition, during practical applications, the release of DOM from biochar may have a significant impact on its application potential in the environment [118].

Meanwhile, metal-modified biochar often contains certain amounts of metal elements, which may pose potential risks of metal ion leaching during water and wastewater treatment processes [20]. The long-term release of metal components can not only lead to secondary pollution but may also disrupt the existing ecological balance in soils or aquatic systems. In addition, the potential toxicity of biochar-based materials to biological systems warrants attention. Previous studies have shown that the effects of biochar on microorganisms exhibit a clear dose–response relationship: low doses of biochar generally promote microbial enzyme activity [119]; in contrast, high doses of tobacco stem-derived biochar may induce the generation of reactive oxygen species, leading to cytotoxicity and genotoxicity [11]. Therefore, it is particularly important to establish a systematic and comprehensive environmental risk assessment framework to balance adsorption performance with environmental safety. Recent studies have proposed

multiscale risk assessment strategies for the systematic monitoring of the environmental impacts of biochar, including laboratory-scale toxicity and metal leaching tests, performance decay evaluations during pilot-scale operation, and the integration of life cycle assessment to evaluate overall environmental benefits and potential risks [20].

6.3. Application of machine learning in phosphorus adsorption by biochar-based materials

As phosphorus pollution becomes increasingly complex, traditional biochar design approaches relying on one factor at a time experiments are no longer sufficient to systematically elucidate the relationships among material structure, preparation conditions and adsorption performance [120]. Against this backdrop, machine learning has been gradually introduced, providing a new paradigm for the design and performance prediction of phosphorus adsorbents. Recent studies have demonstrated that machine learning can quantitatively analyse the 'structure–performance' relationships of biochar by integrating large datasets. Zhang et al. [16], based on over 50 studies, found that pyrolysis temperatures below 600 °C and appropriate metal modification strategies are beneficial for enhancing phosphorus adsorption performance, whereas excessively high metal loading exhibits a plateauing effect. Lu et al. [121] further revealed the dominant factors through machine learning analysis: the influence of the specific surface area on phosphorus adsorption was limited, while the combined importance of the operational conditions reached 35.1%; simultaneously, the metal composition was identified as a key structural factor with a feature importance of 31.7%, highlighting the critical role of metal modification in enhancing phosphorus adsorption. Fu et al. [122] compared six machine learning models and achieved predictions of the adsorption capacity and residual phosphorus concentration of metal-modified biochar. Their results showed that Mg-modified biochar exhibited the highest adsorption capacity (387–396 mg/g), while La-modified biochar could reduce residual phosphorus to 0 mg/L, enabling customised preparation tailored to different water quality targets.

At the mechanistic level, machine learning combined with characterisation analyses has indicated that metal-modified biochar primarily adsorbs phosphorus via surface complexation at low phosphorus concentrations, whereas precipitation reactions gradually dominate under high loading conditions [16], providing a basis for understanding adsorption behaviours across different application scenarios. However, machine learning methods cannot accurately predict the long-term environmental impacts of biochar, and future studies should integrate them with life-cycle assessment methods for a systematic evaluation.

6.4. Future perspectives

Despite the significant potential of biochar-based materials for phosphorus removal, several research gaps still exist, mainly in the following aspects.

(i) Biochar-based materials may pose potential ecological risks during application, including metal ion leaching, the inhibition of microbial activity and long-term effects on soil and aquatic ecosystems. Moreover, current ecological risk assessments lack a systematic framework, and studies on long-term toxicity effects are clearly insufficient.
(ii) The selective removal mechanisms of different phosphorus species by biochar-based materials, as well as their phosphorus release kinetics when used as a slow-release fertiliser, still require further investigation.
(iii) Most existing studies are limited to laboratory-scale experiments under idealised conditions, which fail to reflect the complex water quality and operating conditions of actual wastewater and natural waters, leading to significant differences between laboratory adsorption performance and field application outcomes.

To promote the application and development of biochar-based materials in phosphorus removal and resource recovery, future research should focus on the following aspects:

(i) It is essential to systematically evaluate the long-term operational performance and structural stability of biochar in real wastewater and multicontaminant coexisting systems. Pilot-scale and field-scale

studies can clarify the engineering applicability of these materials under complex environmental conditions.

(ii) Future studies should aim to reveal the mechanisms of phosphorus binding, transformation and release on the surfaces of biochar-based materials. The integration of machine learning and artificial intelligence to establish quantitative relationships between biochar structure and performance can provide new pathways for the precise design and intelligent manufacturing of biochar.

(iii) Long-term ecological monitoring should be conducted to systematically assess metal leaching, changes in microbial communities and potential ecological risks.

(iv) Attention should be given to the phosphorus release kinetics of biochar-based materials and their potential phytotoxicity. Establishing dose–response relationships will help determine appropriate application rates to maintain the soil ecological balance.

7. Conclusion

This review summarises the research progress of biochar-based materials in the phosphorus adsorption and recovery, with a particular focus on the role of metal-modification strategies in enhancing phosphorus removal performance. Existing studies indicate that the incorporation of metals such as Ca, Mg, Fe, Zn, Al and La can significantly improve the phosphorus adsorption capacity of biochar, demonstrating promising potential for both phosphorus pollution control and resource recovery. Phosphorus removal by metal-modified biochar is generally driven by a combination of electrostatic attraction, ligand exchange, surface complexation and precipitation. Relevant studies have gradually expanded from laboratory systems to real wastewater conditions, preliminarily confirming the feasibility of engineering applications for biochar-based materials.

However, environmental safety remains a critical factor limiting the large-scale application of biochar-based materials. Risks such as metal leaching and potential ecological toxicity highlight the need for systematic long-term environmental behaviour and risk assessments alongside performance evaluations in order to balance pollutant removal efficiency with environmental safety. In addition, machine learning offers a novel approach for elucidating the structure–performance relationships of biochar and guiding material optimisation, but its effective application still depends on the continuous accumulation of high-quality data. Overall, biochar-based materials hold great promise for phosphorus removal and resource recovery. Future research should further strengthen long-term validation under realistic water conditions and integrate artificial intelligence approaches to develop rational material designs and safe applications.

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Author contributions

None.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Data availability statement

Data will be made available upon request.

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