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Review Article

Progress on the adsorption characteristics of nZVI and other iron-modified biochar for phosphate adsorption in water bodies

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Abstract: The issue of water body eutrophication induced by phosphorus is escalating, and there is an urgent need for materials that can control phosphate in water bodies. Biochar is often used as an adsorption material for phosphate removal from water bodies because of its high efficiency, strong stability, and low cost. However, the phosphate adsorption capacity of pristine biochar is limited, and iron and its compounds are often loaded to overcome this limitation and improve the adsorption effect. The current status of the use of nanoscale zero-valent iron (nZVI) and other iron-modified biochar in the treatment of eutrophic water is summarized. The preparation process of nanoscale zero-valent iron-modified biochar was introduced. The adsorption mechanism of nZVI and other iron-modified biochar in phosphorus removal from water was explained (mainly related to the roles of electrostatic, precipitation, complexation, ion exchange, etc.); the effects of factors such as dosage, pH value, and initial phosphate concentration on the adsorption of phosphate by iron-modified biochar were analyzed; and the possibility of reusing iron-modified biochar after adsorbing phosphate was pointed out. Based on the above research, the problems and future development directions of nZVI and other iron-modified biochars were proposed. This study provides a theoretical basis for the treatment of eutrophication in water bodies and the utilization of solid waste resources.

Keywords: Biochar; nZVI; Iron modification; Phosphate; Adsorption

1 Introduction

In recent years, with the rapid development of the world's economy, the eutrophication of water bodies, a global surface source of pollution caused by human activities and industrial production, has become increasingly serious (Zou et al., 2020). Research has shown that phosphorus (P) is one of the main factors inducing eutrophication in water bodies (Lu et al., 2023), and water bodies with total phosphorus (TP) concentrations of 0.02 mg/L or more or a trophic state index (TLI (TP), China) > 50 are regarded as experiencing eutrophication in water bodies (Melia et al., 2017). Waterbody phosphorus typical representative removal technology includes

chemical, biological, and adsorption methods (Pan et al., 2021). The chemical method involves adding chemical reagents to the phosphorus removal water body to achieve chemical precipitation to remove phosphorus, the operation is simple, and the effect is stable, but it produces a large amount of sludge, which can easily lead to secondary pollution (Huang et al., 2017). The biological method utilizes the life activities of special microorganisms (aerobic respiration, anaerobic respiration, etc.) to achieve phosphorus fixation and removal in water bodies, while also removing other water pollutants such as nitrogen, sulfur, and organic matter; however, the stability of this treatment method is poor, and the influence of this method on the outside world is big (Robinson et al., 2023). At the same time, adsorption methods with high efficiency, strong stability, and low-cost features are widely used in the removal of phosphorus from the water body (Li et al., 2020).

Biochar is a solid product formed by high-temperature cracking and carbonization of biomass under low-oxygen or completely oxygen-isolated conditions (Yi et al., 2024). It is selected as the adsorbent in the adsorption method because of its wide range of sources (agricultural, forestry, industrial, and municipal solid wastes, etc.) (Feng et al., 2024), unique physical structure (high porosity, high specific surface area, etc.) (Feng et al., 2024), and special chemical properties (high degree of unsaturation and rich content of functional groups) (Lu et al., 2023), it has been selected as a commonly used adsorbent in adsorption methods and widely used for phosphorus removal in eutrophication of water bodies. To further improve the phosphorus adsorption performance of biochar, researchers have prepared modified biochar with metals and their compounds to increase the types and number of their metal functional groups (Li et al., 2020), increase the degree of unsaturation, and thus achieve efficient and stable phosphorus removal (Ajmal et al., 2020). Among them, the metal iron element (Fe) and its compounds have the advantages of easy accessibility, low cost, and a very strong affinity for phosphate (Palansooriva et al., 2021). Thus, it is the most commonly used metal-loading element in metal-modified biochar (Li et al., 2023), and the modified biochar has more stable, efficient, and complex adsorption mechanisms (ion exchange, complexation, etc.) for phosphate (Lu et al., 2023).

2. Research on phosphate adsorption by nano zero-valent iron and other iron-modified biochar

According to the “2023 China Ecological Environment Status Bulletin” (MEE, 2024), among the 205 important lakes (reservoirs) undergoing nutrient status monitoring, 8.3% are in Oligotropher, 64.4% are in Mesotropher, and 27.3% are in Eutropher (23.4% for Light eutropher and 3.9% for Middle eutropher), China still faces a relatively severe situation of water eutrophication (Fig. 1) and reducing the phosphorus content or bioavailability of phosphorus in water bodies is one of the key strategies for achieving sustainable development of water resources. At present, the main remediation methods for water body eutrophication include adsorption, chemical, and biological methods (see Table 1) (Huang et al., 2017).

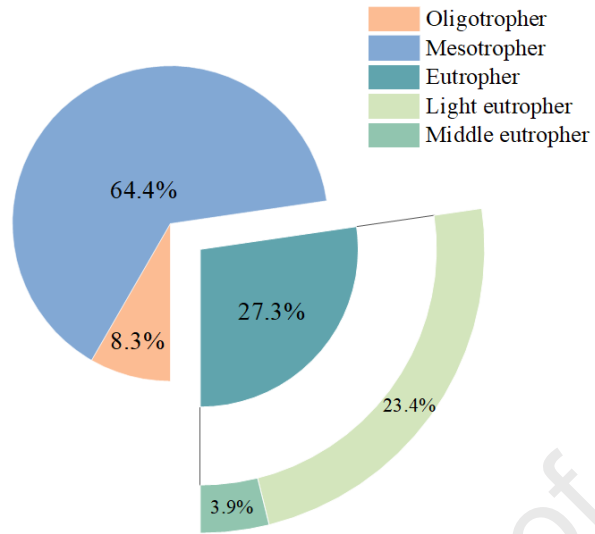


Fig. 1 205 lakes (reservoirs) undergoing nutrient status testing (MEE, 2024).

Table 1

Eutrophication water restoration methods

Category	Material	Suitability	Advantage	Limit	Reference
Adsorption method	Natural materials	Medium	Widely sourced	Poor adsorption effect	(Dai et al., 2019)
	Industrial waste residue	Medium	High yield and good adsorption effect	It has environmental toxicity and is non renewable	(Dai et al., 2019)
	Artificial synthetic materials	High	Widely sourced, low-cost, environmentally friendly, high adsorption performance	The adsorption stability of the raw material is poor and requires modification treatment	(Kavitha et al., 2018)
Chemical method	Flocculent settling	Medium	The use of chemical flocculants and ions to undergo chemical precipitation in water results in high removal efficiency	High cost and risk of secondary pollution	(Ranzinger et al., 2022)
	Crystallization precipitation	Medium	Generate magnesium ammonium phosphate crystals, which contain a large amount of nutrients	The amount of chemical reagents used is large, and the difficulty of recovery is high	(Zhang, Teng et al., 2021)
Biological method	Microbiological method	Medium	Utilizing polyphosphate accumulating bacteria to achieve phosphorus removal in an alternating aerobic and anaerobic cycle, with low cost and simple operation	High requirements for water quality, strict environmental requirements, and relatively poor selectivity	(Ayushman et al., 2014)
	Artificial floating island system	Low	Fill composite media materials and plant aquatic plants, with good removal effect and green and beautiful appearance	The repair time is relatively long, the anti-interference ability is poor, and the construction period is long	(Wang et al., 2008)
	Biological retention facilities	Low	Utilizing aquatic plants with high environmental adaptability and strong adsorption capacity,	The process is complex and lengthy, constrained by various environmental	(Alikhani et al., 2020)

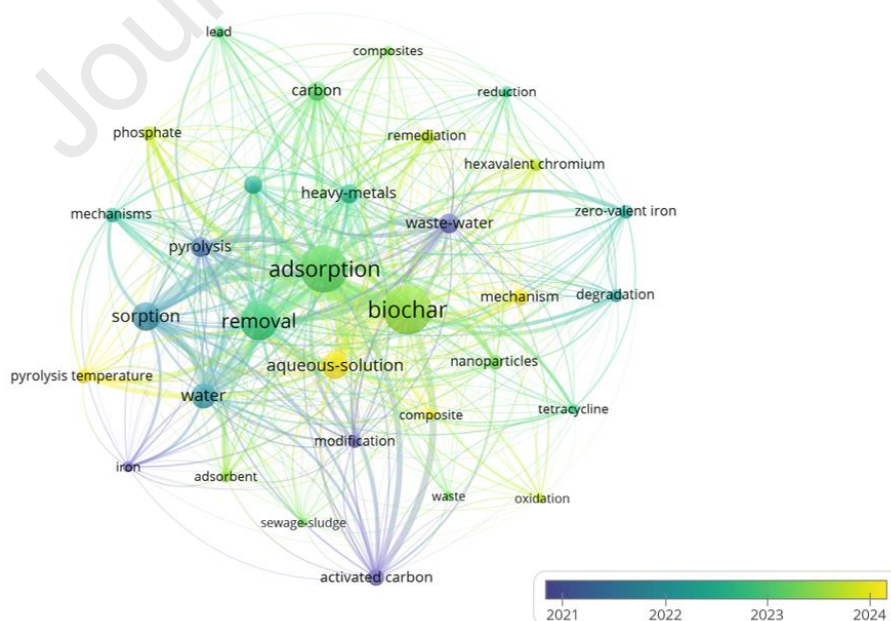
resulting in better ornamental performance factors

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Metal modification is a type of biochar modification that has attracted much attention in recent years (Ajmal et al., 2020). The loading of biochar with iron and its compounds is one of the most effective means to overcome the limitation of phosphate adsorption on biochar (Palansooriva et al., 2021). Metal modification loads iron and its compounds onto biochar in a variety of forms (particles, flowers, sea urchins, and even nanosized), which increases the specific surface area and provides more adsorption sites for phosphate (Li et al., 2020), and the rich pore structure of biochar makes the iron and its compounds uniformly distributed on the surface and in the pore channels, which reduces the phenomenon of agglomeration and improves the stability, and the two synergistically work together to further overcome the adsorption limitations and enhance the adsorption of phosphate (Kang et al., 2021).

Further bibliometric analysis of the studies on modified biochar for water eutrophication is shown in Fig. 3. Fe-modified biochar has been widely used in water eutrophication treatment because of its high Fe content (Wei et al., 2024), low environmental risk, high reactivity, etc., and among them, nano zero-valent iron (nZVI)-loaded biochar has attracted much attention (Wang et al., 2019). To meet the requirements of phosphorus removal from water under different conditions, researchers have developed composite metal-modified biochar (LDHs, hydrotalcite-type intercalation materials) with “Fe + other metals” (Rahman et al., 2021) and even magnetic biochar for the convenience of recycling modified biochar (Xu et al., 2023). Iron-modified biochar can overcome the phosphate adsorption limitation of biochar to a greater extent and significantly improve the phosphate adsorption effect, which has become a popular research direction in the field of phosphate removal by biochar in the eutrophication of water bodies.

Fig. 3 Bibliometric analysis of modified biochar based on the Web of Science Core Collection database.



3. Preparation of nano zero-valent iron-modified biochar and mechanism of phosphate adsorption

Biochar loaded with nano zero-valent iron is a composite material that uniformly disperses

nanoiron particles on the surface of biochar. In the process of removing pollutants, both biochar and nano zero-valent iron play a role (Wang et al., 2019). Compared with other loading materials, biochar has a rich pore structure, multiple functional groups on its surface, and strong modifiability (Feng et al., 2024). Moreover, biochar is more economical and environmentally friendly, providing benefits for reusing raw biomass materials (Feng et al., 2024). Therefore, loading nano zero-valent iron onto biochar can effectively improve the specific surface area and dispersibility of the composite (Palansooriva et al., 2021) while combining the strong adsorption of biochar with the strong reducibility of nano zero-valent iron, making it a promising water remediation technology.

3.1. Zero-valent iron nanoparticles

Nano zero-valent iron particles (nZVIs) are nanoscale solid particles with high reactivity, high surface area, and high surface energy and have a typical core-shell structure of Fe⁰ and iron oxide layers (Mao et al., 2023), which makes them have a relatively significant removal effect on various pollutants (heavy metals, organic substances, inorganic substances, antibiotics, etc. (Kang et al., 2022) in the water body. However, since nZVI is prone to agglomeration (nZVI particles aggregating with each other due to magnetic or other strong forces) in the environment (Liu et al., 2020), which leads to a significant decrease in its important physicochemical properties, such as specific surface area, reactivity, and surface energy, the study of how to limit the agglomeration phenomenon of nZVI is imminent. Currently, porous materials can be used as nZVI carriers to alleviate or reduce their aggregation (Premarathna et al., 2019). Among the porous material carriers with high surface areas and ion exchange capacities, biochar has become one of the most widely used nZVI-loaded materials (Kang et al., 2022). nZVI oxide shells on the outside of the core can react with the surface functional groups of biochar to form stable chemical bonds (Song et al., 2020). Moreover, the loading of nZVI onto the surface of biochar can also help improve the surface properties of biochar (e.g., specific surface area, pore structure, and the type and number of functional groups (Mao et al., 2023)) and add more stable and efficient adsorption mechanisms for pollutant removal (precipitation, complexation, ion exchange, etc.) (Wang et al., 2020).

3.2. Application of conventional biochar for phosphate adsorption

Conventional biochar may have different internal and external characteristics (physical structure and chemical properties (Lu et al., 2023)) because of its different carbon sources (agricultural and forestry solid waste, industrial solid waste, urban solid waste, etc. (Pan et al., 2024)) and preparation methods (pyrolysis, hydrothermal, activation, microwave, etc.) (Table 2); however, it is rich in pore structure and has a large specific surface area. The oxygen-containing functional groups and unsaturated bonds carried on their outer surface and inner pores can provide binding sites for adsorbing phosphates (Zeng et al., 2013). Therefore, in the selection of raw biochar materials, researchers tend to prefer agricultural and forestry solid waste because of its low cost, simple synthesis, wide range of sources, and low environmental toxicity (Zhou et al.,

2024). Moreover, high porosity and other characteristics can not only improve the basic adsorption capacity of biochar but also provide possibilities for loading metals and their compounds (Ma et al., 2020).

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Table 2

Effects of raw materials and preparation methods on the structure of biochar

Classification	Raw material	Preparation method	Preparation temperature (°C)	Specific surface area (m ² /g)	Average pore diameter (nm)	Morphology	Reference
Agricultural and forestry solid waste	Corn cob	Pyrolysis	400	17.53	—	Uneven micropores and protrusions	(Li et al., 2024)
	Tobacco straw	Pyrolysis	550	53.16	3.93	—	(Hu et al., 2024)
	Peanut shell	Activation-pyrolysis	60/600	17.75	3.11	Honeycomb structure	(Zhao et al., 2024)
	Kenaf	Hydrothermal	200	36.46	5.32	Spherical particles	(Rajendran and Dhandapani, 2024)
Animal solid waste	Pig manure	Hydrothermal	220	14.96	9.76	Loose and porous surface structure	(Feng, Fang et al., 2024)
	Sheep manure	Pyrolysis	600	63.91	2.79	Irregular loose particles	(Li, et al., 2023)
	Cow dung	Hydrothermal	220	15.87	3.66	—	(Zhao et al., 2016)
	Sheep manure	Pyrolysis	600	76.20	9.10	Uneven and porous structure	(Tang et al., 2022)
Industrial solid waste	Oil shale	Pyrolysis	550	98.81	9.72	—	(Lu et al., 2024)
	Alkali lignin	Pyrolysis	500	1.32	4.17	A large number of needle shaped crystals	(Chen et al., 2023)
	Printing and dyeing sludge	Pyrolysis	900	140.65	6.50	Mesoporous proportion>90%	(Jiang et al., 2022)
	Industrial hemp	Pyrolysis	600	129.44	8.06	Layered structure with clear boundaries	(Yuan et al., 2022)

Urban solid waste	Municipal sludge	Pyrolysis	500	5.26	16.75	Structural uplift and collapse, with obvious cracks	(Ma et al., 2024)
	Municipal sludge	Hydrothermal	170	29.39	7.77	—	(He-Li et al., 2023)
	Coffee grounds	Pyrolysis	600	55.06	6.27	Uneven pores and particles	(Zhang et al., 2023)
	Kitchen waste	Hydrothermal	260	5.54	7.14	Many small protrusions	(Chen, Chen et al., 2023)
Composite solid waste	Wine lees/sludge	Activation-pyrolysis	110/450	287.88	4.84	Granular protrusions of varying sizes	(Wu et al., 2022)
	Corn stover/aluminum ash	Hydrothermal	150	30.19	6.81	Surface roughness and uniform particle distribution	(Lu, Li et al., 2024)
	Rice husks/MOFs	Pyrolysis	700	581.85	3.60	Uniform distribution of octahedral nanoparticles	(Zhou, Zhu et al., 2024)
	Fly ash/corn stover	Pyrolysis	800	44.29	0.45	—	(Zheng et al., 2023)

Note: “—” is an expression not provided in the literature.

After biochar is added to eutrophic water bodies, under the effects of electrostatic attraction and liquid concentration, anions such as phosphate will approach it continuously and fill the rich pore structure of biochar through van der Waals forces and electrostatic forces, and physical adsorption will occur (Zeng et al., 2013). Moreover, the abundant functional groups (-OH, -COOH, -ROH, -NH₂, etc.) and unsaturated bonds of biochar capture anions such as phosphate (Yao et al., 2011) and replace the original anions of biochar through ion exchange, ligand exchange, hydrogen bonding, anions, etc., to form products with hydrogen bonding connections or more stable chemical bonding connections (Zhang et al., 2018). Although other anions (SO₄²⁻, OH⁻) in the water body will also be adsorbed by such mechanisms, the higher phosphate concentration in eutrophic water bodies inhibits the competitive adsorption of other anions to a certain extent (Jung et al., 2016). Biochar carries a small number of metal elements (Ca, Fe, Mg, etc.) after high-temperature pyrolysis of biomass (Yao et al., 2011), and the metal cations are easily adsorbed with phosphate by precipitation, complexation, and other types of chemisorption. The amount of adsorption is greater than that of the above adsorption mechanisms (Kang et al., 2021). Moreover, biocarbons have high modifiability (Oliveira et al., 2017), which allows the targeted loading of metal elements to further increase the adsorption of phosphate by conventional biochar.

3.3. Preparation of nano zero-valent iron-modified biochar

The main metal nano- or metal nano-oxide particles modified on the surface of biochar that have been reported thus far include Fe⁰, Fe₂O₃, Fe₃O₄, Al₂O₃, CaO, La₂O₃, ZnO, etc. (Wang et al., 2019). Compared with other metals, Fe is not only abundantly stored in nature but also has matured processes for purification and enrichment, and it is less toxic to the environment with less toxicity from metal leaching (Liu et al., 2020). Biochar loaded with iron-based materials has been found to effectively immobilize phosphate in water through adsorption and chemical precipitation (Liu et al., 2015). nZVI has the advantage of being nanometal compared to ordinary zero-valent iron particles (Wang et al., 2019), whereas biochar can improve the reactivity of nZVI by increasing its electron transfer capacity because of its good electrical conductivity (Mao et al., 2023). At the same time, biochar provides a good carrier for nZVI to minimize its aggregation, so loading nZVI onto biochar and using it to remove phosphate from water bodies has a greater advantage (Song et al., 2020). Table 3 shows some common means of preparing nZVI from biochar and their advantages and disadvantages. At this stage, the best preparation method is selected according to different application scenarios and conditions to fulfill the purpose of greening the environment. Ren et al. (2021) prepared biochar loaded with nZVI using reed as a raw material at different temperatures (300, 500, 700, 900 °C) that was able to adsorb elemental phosphorus from the water body, and the highest phosphate adsorption capacity of nZVI-BC was achieved at 700 °C. The maximum P adsorption of nZVI-loaded biochar prepared by Ma et al. (2020) with rapeseed straw reached 13.64 mg/g, which was 3.5 times greater than that of unloaded nZVI-loaded rapeseed straw biochar.

Table 3

Nano zero-valent iron-modified biochar preparation methods and comparison

Preparation method	Raw material	Advantage	Disadvantage	Size (nm)	Reference
Ball milling	Metal nanoparticles/metal oxide particles	Controlled particle size and high activity	Mechanical action, high energy consumption, high losses	1–100	(Zeng et al., 2022)
liquid-phase reduction	NaBH ₄ , Fe ²⁺ /Fe ³⁺ salt solution	Homogeneous structure, high product purity, rapid reaction	Byproducts are toxic	1–100	(Djebbi et al., 2022)
Carbothermal reduction	Gas-reducing agent, Fe ²⁺ /Fe ³⁺ salt solution	Low cost and easy access	Enormous energy consumption and strict reaction conditions	20–150	(Karunaratne et al., 2022)
Gas-phase thermal reduction	Hematite, pyrite particles	Fewer and less toxic byproducts	The preparation process has a high threat factor and requires high energy	10–100	(El-Temsah et al., 2016)
Ultrasound auxiliary equipment	NaBH ₄ , Fe ²⁺ /Fe ³⁺ salt solution	Uniform particle size, small particle size, large surface area	Byproducts are toxic	10	(Jamei et al., 2014)
Electrochemical method	Fe ²⁺ /Fe ³⁺ salt solutions/electrodes	Simple and inexpensive to operate	Nanoparticles are easily aggregated and less active	1–20	(Yoo et al., 2007)
Green synthesis	Plant extracts, Fe ²⁺ /Fe ³⁺ salt solution	Environmentally friendly and green, no secondary pollution	Difficult to produce, difficult to control shape	20–120	(Ningthoujam et al., 2023)

3.4. Mechanism of phosphate adsorption by the nano iron-modified biochar

After nano zero-valent iron (nZVI) was loaded onto the surface of the biochar and with the rich pore structure of the biochar, the agglomeration of the nZVI particles, owing to their own magnetic properties, was greatly improved (Wang et al., 2018). At the same time, nZVI also introduced a variety of stabilizing adsorption mechanisms for phosphate adsorption on the biochar (Fig. 4).

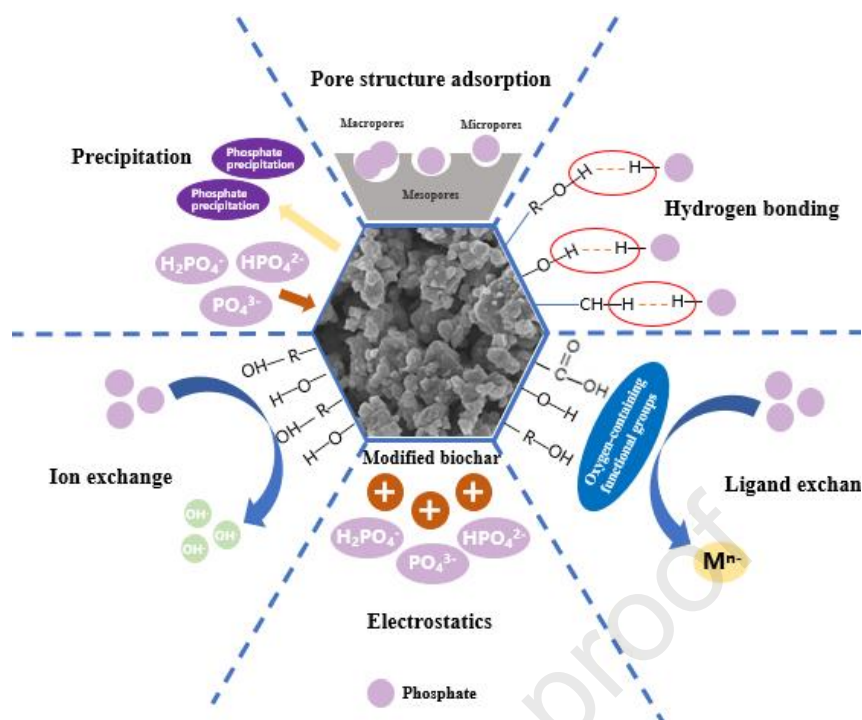


Fig. 4 Mechanism of phosphate adsorption by nZVI-loaded biochar.

The nZVI-loaded biochar had more obvious -OH vibrations at approximately 3420 cm^{-1} and 1630 cm^{-1} in the FTIR pattern (Deng et al., 2021), and after the adsorption of phosphate, the transmittance significantly increased. The -OH band shifted to a lower wavelength, and the spectral band broadened, which indicated that the nZVI on the surface of the biochar was transformed into hydroxylated iron oxides (Sheng et al., 2014). At the same time, obvious characteristic peaks were observed at approximately 1016 cm^{-1} and 470 cm^{-1} , corresponding to the P-O and Fe-O peaks, respectively, which were attributed to the asymmetric vibration of Fe-O-P (He et al., 2018), indicating that chemisorption between nZVI and phosphate occurred. By XPS analysis, nZVI-modified biochar usually shows characteristic peaks of P2p3/2 and P2p1/2 at binding energies of 134.0 eV and 135.3 eV (Li and Zhang, 2006), representing P=O and P-O, respectively, which further suggests that phosphate is removed from the water column by nZVI-modified biochar in the form of adsorption (Ma et al., 2020) and that nZVI will be present in the biochar, suggesting that multiple oxidation states exist. The signal peak of Fe(0) (approximately 707.0 eV) disappears after the adsorption of phosphate (Li et al., 2019), and the characteristic peaks of multiple oxidation states of nZVI are shifted toward higher binding energies because of electron transfer between valence bands due to the formation of Fe-O-P inner-sphere complexes (Liu et al., 2022), suggesting that nZVI is involved in the adsorption of phosphate at higher binding energies (711.0 eV, 725.0 eV, etc.) and produces more stable substances (Lu et al., 2020). Notably, XRD analysis also revealed that the crystal surface diffraction peaks of Fe⁰(110) were significantly weakened after the adsorption of phosphate on nZVI-modified biochar (Wu et al., 2021), and the crystal surface diffraction peaks of substances such as FePO₄·2H₂O, Fe(H₂PO₄)₃, and Fe₄(PO₄)₃(OH)₃ could be detected (Ma et al., 2020), which indicated that the nZVI on the surface of nZVI-modified biochar underwent a redox

reaction and removed phosphate from the water column via precipitation (Wang et al., 2019).

4. Mechanism of phosphate adsorption by iron-modified biochar

Conventional unmodified biochar has a simple pore structure, small specific surface area, and low content of oxygenated or metal functional groups, which leads to unsatisfactory selectivity and adsorption of phosphate in water bodies (Feng et al., 2024) and may even be interfered with by other coexisting ions or release its own elemental phosphorus in complex water environments (Kang et al., 2013), which exacerbates eutrophication of water bodies. Biochar modified with iron can improve the surface characteristics (specific surface area, pore size, etc. (Yao et al., 2011)) of pristine biochar to a greater extent; at the same time, it also introduces many metal functional groups (Fe-O-, FeO_x-, etc. (Zeeshan et al., 2021)), which limits phosphate adsorption by pristine biochar and improves the surface activity, reaction speed, etc., which improves the adsorption capacity of phosphate (Table 4).

Table 4

Adsorption effects of biochar and iron-modified biochar on phosphate in water

Note: “—” is an expression not provided in the literature; the adsorption capacity is based on Langmuir model fitting.

Modification method	Raw material	Fe morphology	Preparation temperature (°C)	SSA (m ² /g)	ADP (nm)	pH	Adsorption capacity (mg/g)	Reference
Unmodified	Flos farfarae	—	600	17.53	—	10.49	4.79	(Zeng et al., 2013)
	Sludge	—	690	40.916	4.510	—	3.18	(Yao et al., 2011)
	Beet residue	—	600	—	—	7	4.34	(Zhang et al., 2018)
Conventional iron modification	Food waste	FeOH	600	100.42	1.25	—	31.83	(Kang et al., 2021)
	Corn stalks	Fe ₂ O ₃	550	—	—	9.5	98.0	(Li et al., 2020)
		Fe(OH) ₃						
	Activated sludge	Fe(OH) ₂ Fe(OH) ₃	550	254.4	0.887	—	111.0	(Yang et al., 2018)
Layered double hydroxides (LDHs)	Douglas-fir	α-FeOOH FeOOH	—	267.3	13.2		1588.9	(Irfan et al., 2023)
	Corn stalks	—	500	51.46	3.62	8.94	73.28	(Bian et al., 2023)
	Corn stalks	Fe ₂ O ₃	600	—	—	9.3	222.9	(Bolbol et al., 2019)
Magnetically modified	Date palm leaf	α-Fe ₂ O ₃	700	—	—	7.93	174.5	(Zubair et al., 2022)
	Crab shell	LaFeO ₃	700	26.72	—	—	65.62	(Xu et al., 2023)
	Litchi skin	CaFe ₂ O ₄	500	5.98	—	4.17	57.4	(Thanh Le et al., 2023)

4.1. Mechanism of phosphate adsorption by iron-modified biochar

Owing to its rich pore structure and high specific surface area (Ajmal et al., 2020; Li et al., 2020; Lu et al., 2023), biochar can be loaded with a large amount of Fe by various means (impregnation, coprecipitation, redox, ball milling, etc.). Fe and its compounds can coexist in the internal and external structures of biochar in various forms (FeO , Fe_2O_3 , Fe_3O_4 , $\text{Fe}(\text{OH})_3$, etc.) (Ajmal et al., 2020; Palansooriva et al., 2021; Lu et al., 2023). After loading Fe and its compounds on biochar, the pore structure also changes (either larger or smaller), the types and numbers of metal functional groups and unsaturated bonds greatly increase, and more phosphate adsorption sites are present (Li et al., 2020). At the same time, in a variety of adsorption mechanisms (Fig. 5), chemical adsorption, such as complexation, precipitation, and ion exchange, plays a dominant role in the adsorption of phosphate (Lu et al., 2023), and phosphates are immobilized in a more stable form on Fe-modified biochar (Palansooriva et al., 2021).

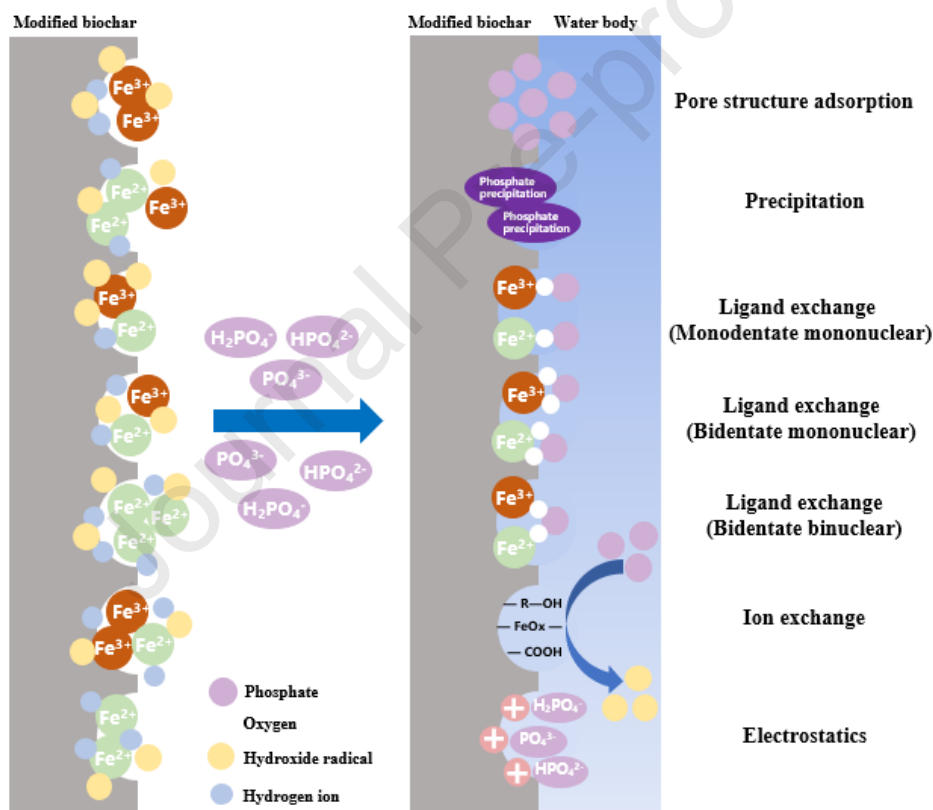


Fig. 5 Mechanism of phosphate adsorption in water by iron-modified biochar.

Phosphate in eutrophic water bodies under the action of a concentration gradient force and electrostatic force, from the high concentration or negatively charged aggregation area continuously and spontaneously migrates to the surface of the iron-modified biochar (low concentration, positive charge), the metal functional groups in the modified biochar capture the free state of the phosphate, replacing the hydroxyl group carried by itself or in other parts of the body, and a large amount of phosphate is adsorbed through ligand exchange, ion exchange, and

precipitation (Yang et al., 2018). Li et al. (2020) prepared iron-modified biochar via the impregnation method, and after the adsorption of phosphate on modified biochar, the intensity of the absorption peak at 570 cm^{-1} (Fe-O) decreased, the intensity of the absorption peak at 1000 cm^{-1} (P-O) increased, using FTIR analysis, indicating that the Fe-OH groups interacted with the phosphate to form a complex. Irfan et al. (2023) also came to the same conclusion experimentally: the high adsorption performance of iron-modified biochar for phosphate is attributed to its porous structure and abundance of iron compounds (Fe-OH, FeC, etc.).

4.2. Mechanism of phosphate adsorption by the LDH biochar composites

Layered bimetallic hydroxides (LDHs), a class of layered materials (hydrotalcite, hydrotalcite-like) with two-dimensional nanolayered structures, mainly consist of positively charged lamellae formed by OH-octahedrally coordinated metal cations (divalent and trivalent) and interlayer anions (Fig. 6(a)) (Bukhtiyarova, 2019). Researchers often load "Fe + other metals" onto the surface of biochar to achieve efficient adsorption of phosphates. (Mishra et al., 2018).

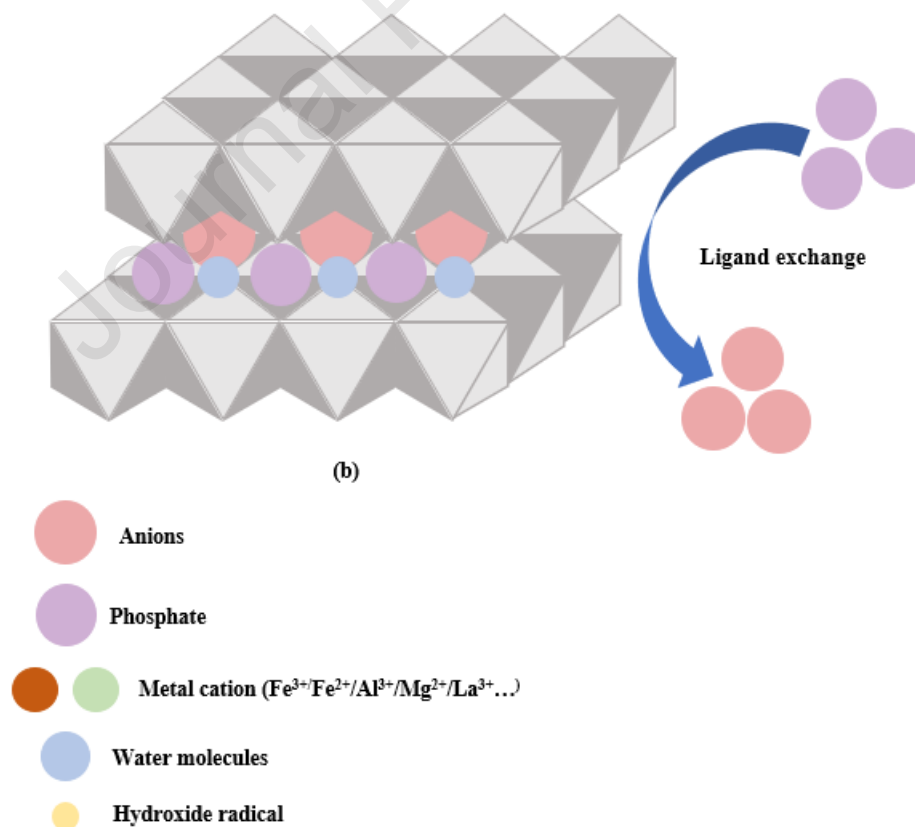


Fig. 6 (a) Structure of LDHs. (b) Main adsorption mechanism of LDHs.

The mechanism of phosphate adsorption by LDH biochar composites mainly involves

electrostatic attraction, ion exchange, and ligand exchange (Bukhtiyarova, 2019), where the two lamellar host plates are connected with interlayer anions by weak interaction forces, and in eutrophic waters, negatively charged phosphate carries negatively charged phosphate under electrostatic attraction and diffusion forces (concentration differences) to form complexes with Fe^{3+} /other metal cations on the surface of LDH biochar (Mishra et al., 2018); alternatively, phosphate disrupts the octahedral structure with stronger forces to replace -OH and generate complexes with Fe^{3+} /other metal cations (Irfan et al., 2023); or the weak interlayer interaction force is interrupted, and some of the metal cations of the LDHs disintegrate and dislodge, combine with the free phosphate and attach to the pore structure of the biochar in the form of precipitation (Bolbol et al., 2019). Moreover, the interaction between phosphate and interlayer anions is also an important part of the adsorption mechanism, as the adsorption system should spontaneously change from chaotic to stable, while high-valence phosphate can replace some low-valence interlayer anions, which makes the lamellar mother plate and the interlayer anions stabilize with a stronger interaction force (Bian et al., 2023; Bukhtiyarova, 2019). Rahman et al. (2021) used loaded Fe/Mg-LDHs treated with a high-concentration phosphate solution and reported that not only the characteristic peaks of modified biochar successfully loaded with Fe/Mg-LDHs but also specific Fe/Mg-phosphate compounds (FePO_4 and $\text{Mg}_3(\text{PO}_4)_2$) generated after the adsorption of phosphate were detected via X-ray diffraction (XRD). Bolbol et al. (2019) also confirmed that biochar loaded with Fe-containing LDHs strongly affects the phosphate solutions via precipitation, complexation, etc., and other effects on phosphate adsorption.

4.3. Mechanism of phosphate adsorption by other metal-modified biosorption

Biochar can be loaded not only with Fe and its compounds but also with other metals with strong adsorption properties for phosphates, such as Mg, La, etc. (Zhao et al., 2021). Some slightly inferior metals (Ca, Al, etc.) are also options for loading onto biochar (Thanh Le et al., 2023). In practical applications, different metals can be either loaded individually or coloaded to prepare modified biochar composites, involving the same adsorption mechanisms, including precipitation, complexation, ion exchange, and other chemical adsorption mechanisms (Table 5), but whether these metals will interact (synergistically or antagonistically) with each other and adsorb other anions in eutrophic waters still need to be thoroughly explored and investigated.

Table 5

The mechanism of phosphate adsorption by other metal modified biochar

Load metal	Adsorption mechanism	Reference
La	$\text{La}^{3+} + \text{PO}_4^{3-} \rightarrow \text{LaPO}_4$ $\text{La}(\text{OH})_3 + \text{PO}_4^{3-} \rightarrow \text{LaPO}_4 + 3\text{OH}^-$ $\text{La}^{n+} + \text{PO}_4^{3-} \rightarrow \text{LaOPO}_3^{n-3}$	(Zhao et al., 2021)
Mg	$3\text{Mg}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Mg}_3(\text{PO}_4)_2$ $\text{Mg}^{2+} + 2\text{H}_2\text{PO}_4^- \rightarrow \text{Mg}(\text{H}_2\text{PO}_4)_2 \rightarrow \text{MgHPO}_4 + \text{H}_3\text{PO}_4$	(Chen et al., 2018)
Ca	$5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3(\text{OH})$ $5\text{Ca}^{2+} + 3\text{HPO}_4^{2-} + 4\text{OH}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3(\text{OH}) + 3\text{H}_2\text{O}$	(Wang and Kong, 2018)

	$5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + 7\text{OH}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3(\text{OH}) + 6\text{H}_2\text{O}$	
Al	$\text{Al}^{3+} + \text{PO}_4^{3-} \rightarrow \text{AlPO}_4$	(Elkhlifi et al., 2023)
	$\text{Al}(\text{OH})_2^+ + \text{H}_3\text{PO}_4 + \text{OH}^- \rightarrow \text{AlPO}_4 + 4\text{H}_2\text{O}$	
	$\text{AlPO}_4 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Al}(\text{H}_2\text{PO}_4)_3$	

5. Influencing factors of modified biochar adsorption of phosphate

Nano zero-valent iron- and other iron-modified biochars have significant advantages in the adsorption of phosphate in water due to their unique physical and chemical characteristics (Pan et al., 2021), such as complex pore structure, rich functional group content, and multiple adsorption mechanisms, such as high adsorption capacity, high removal rate, and low dosage (Huang et al., 2017). Notably, the phosphate removal ability of modified biochar is jointly influenced by the adsorbent itself and the water environment (dosage, pH, concentration) (Table 6).

Table 6

Main factors influencing adsorption performance of modified biochar

Modification method	Raw material	Fe morphology	Dosage (g)	pH	Initial concentration (mg/L)	Adsorption capacity (mg/g)	Reference
					①	②	
Conventional iron modification	Food residues	FeOH	0.10	7.0	500	31.83	(Kang et al., 2021)
	Straw/sludge	FeC	0.20	7.0	10	5.23	(Irfan et al., 2023)
	Corn straw	Fe ₂ O ₃	0.01	4.5	30	32.40	(Dong et al., 2023)
	Activated sludge	Fe(OH) ₃	0.10	7.0	20	111.0	(Yang et al., 2018)
LDHs	Coconut husk	—	0.10	7.0	0.5	4.55	(Su et al., 2023)
	Corn straw	Fe ₂ O ₃	0.05	7.0	28	206.20	(Liu et al., 2021)
	Corn straw	—	0.04	—	1000(biogas slurry)	73.28	(Bian et al., 2023)
	Pinecone	Fe(OH) ₃	-	7.0	50	160.80	(Huang et al., 2024)
Magnetically modified	Crab shell	LaFeO ₃	0.05	7.0	-	65.62	(Xu et al., 2023)
	Chrysanthemum	Fe ₃ O ₄	0.20	—	50	37.37	(Pu et al., 2023)
	Litchi peel	CaFe ₂ O ₄	0.20	5.0	30	57.40	(Thanh Le et al., 2023)
	Rice straw	Fe ₃ O ₄	0.10	7.0	-	-	(Long et al., 2023)
nZVI	Corn cob	nZVI	0.03	3.0	20	82.78	(Huang et al., 2022)
	Corn straw	nZVI	0.05	6.0	5	25.00	(Ai et al., 2022)
	Reed straw	nZVI	0.05	—	23	95.20	(Ren et al., 2021)
	Rapeseed straw	nZVI	0.05	7.0	20	12.14	(Ma et al., 2020)

Note: “—” is an expression not provided in the literature; ①The initial phosphate concentration is the lowest concentration set in the isothermal adsorption experiment; ②The adsorption capacity is fitted according to the Langmuir model.

5.1. Dosage

The metal leaching toxicity of Fe-modified biochar is an important parameter that cannot be ignored in the removal of phosphorus from eutrophic waters because of the loading of Fe and its compounds. A low dosage of modified biochar can maximize the utilization of active sites on the modified biochar. However, other anions in eutrophic waters compete with phosphate for adsorption, thereby resulting in lower removal rates (Luo et al., 2021). Excessive dosage of modified biochar can indeed eliminate a considerable amount of phosphate from eutrophic waters. However, the active sites of the modified biochar do not fully maximize its adsorption performance, and its overall utilization is low and prone to agglomeration (Haddad et al., 2018), increasing the risk of Fe and its compounds derived from biochar, which will cause secondary pollution to eutrophic waters.

5.2. pH

Changes in the pH of eutrophic water bodies directly affect the distribution of the surface charge of modified biochar, resulting in a low-pH environment, a decrease in the number of positive charges on the surface of modified biochar, and a decrease in the attraction of negatively charged phosphate. Phosphate to migrate to the surface of the biochar needs a greater difference in concentration generated by diffusion force to make up for the lack of electrostatic force of attraction (Yin et al., 2017), so lower phosphate concentrations and pH, lead to a decrease in the adsorption performance of modified biochar. Moreover, in different pH environments, phosphate exists in the form of a variety of structural bodies ($2 < \text{pH} < 7$, H_2PO_4^- ; $7 < \text{pH} < 12$, HPO_4^{2-} ; $12 < \text{pH}$, PO_4^{3-}), which indirectly affects the binding energy of modified biochar and phosphate (Zheng et al., 2020), resulting in a large difference in adsorption capacity.

5.3. Initial phosphate concentration

The diffusion force, one of the pulling forces for phosphate to migrate to the modified biochar in the water body continuously, is strongly affected by the initial phosphate concentration in eutrophic water. The high initial concentration is conducive to accelerating the adsorption process of the modified biochar, thereby enabling it to achieve adsorption equilibrium more rapidly (Zhu et al., 2018). The large amount of phosphate ions increases the chance of phosphate adsorption on the active sites carried by the modified biochar and, to a certain extent, inhibits the competitive adsorption of coexisting ions (Zhang et al., 2022). At low concentrations, the traction of phosphate in the water body is insufficient, less phosphate can be bound to the active sites of modified biochar, and even the phosphate groups generated by pyrolysis of the modified biosalt itself release phosphate into the water body, exacerbating the degree of eutrophication (Sang et al., 2023).

5.4. Other influencing factors

The complex environment of the water body constantly affects the physicochemical properties of modified biochar, and in addition to the several factors mentioned above, researchers have found that coexisting ions (Liu et al., 2019), biochar species, etc., also affect the adsorption performance of adsorption-modified biochar for phosphates. In eutrophic water bodies, a certain amount of SO_4^{2-} , CO_3^{2-} , NO_3^- , etc. (Kang et al., 2021) is also often present, which affects the pH of the water body while also competing with phosphate ions for adsorption, resulting in a lower adsorption capacity of modified biochar than the theoretical value. Notably, the various influencing factors mentioned above can also have a superimposed effect, resulting in a chain reaction that significantly alters the various physicochemical properties of the modified biochar, with threats such as the risk of detachment of the loaded Fe and its compounds or disintegration of the octahedra in the LDHs (Rahman et al., 2021).

Therefore, the process of phosphate adsorption by nano zero-valent iron and other iron-modified biochar in eutrophic waters is opaque, asynchronous as well as uncontrollable, and the influence of various factors on the adsorption mechanism needs to be further investigated.

6. Application prospects and directions of modified biochar

Biochar has become a widely studied adsorbent material after modification with nano zero-valent iron and other iron (Pan et al., 2024). Moreover, it is also highly favored in the field of repairing eutrophic water bodies because of its unique physical structure and chemical properties (Ajmal et al., 2020). The development of technology in today's world is "green, environmentally friendly, and circular" (Long et al., 2023), which poses new challenges to the research and application of biochar and modified biochar. Therefore, the use of zero-valent iron and other iron-modified biochar is urgently needed to achieve positive responses in this situation.

6.1. Analysis of the recycling performance of modified biochar

Fe-modified biochar has high reusability. When it reaches adsorption equilibrium for phosphate, it can be eluted by using NaOH and other substances as the eluent, which results in the adsorbent falling off the modified biochar and restoring its adsorption performance for phosphate (Table 7) (Zhang et al., 2021). Even the SiO_2 and other substances in the biochar dissolve in the eluent, which to some extent increases the specific surface area and porosity (Wang et al., 2016). Yang et al. (2021) conducted adsorption-desorption experiments on Fe-modified biochar using NaOH as the eluent. Although some sites were deeply bound and the desorption efficiency failed to reach 100%, the modified biochar still had high adsorption performance for phosphate (only a 15% decrease) after the experiment was repeated five times. Dong et al. (2024) confirmed the high reutilization rate of Fe-modified biochar.

Table 7

Main mechanisms of phosphate resolution by Fe-modified biochar

Adsorption mechanism	Reference
$\text{FePO}_4 + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3 + \text{H}_3\text{PO}_4$	(Shepherd et al., 2017)
$\text{Fe}_2\text{HPO}_4 + 2\text{H}_2\text{O} + \text{OH}^- \rightarrow 2(\text{O}_x)\text{FeOH} + \text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$	(Dong et al., 2024)
$\text{Fe}_2\text{HPO}_4 + 2\text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2(\text{O}_x)\text{FeOH} + \text{HPO}_4^{2-} + 2\text{H}_2\text{O}$	(Bian et al., 2018)

Iron-modified biochar can be used as a phosphate fertilizer for improving soil nutrient levels in addition to being desorbed for reuse. Phosphate in the adsorbed form is affected by the complex environment of the soil (aging effects, cation exchange capacity, microorganisms, etc.) and is shed from modified biochar (Mishra et al., 2018), which is more beneficial for the utilization of plants and animals. Irfan et al. (2023) reported that the addition of soil containing adsorbed phosphate-modified biochar to plant roots, stems and leaves resulted in greater growth and heavier fresh and dry weights than those of the unamended group. Similarly, Bian et al. (2018) reported that soil fertility significantly increased and that the plant yield increased to 139.3% after the soil application of Fe-modified biochar with adsorbed phosphates. Fe-modified biochar not only is widely used in the management of eutrophic waters but also has potential value in the direction of agricultural production (Shepherd et al., 2017).

6.2. Research directions for modified biochar

Biochar and modified biochar, under the development concept of being “green, environmentally friendly, and circular” (Sah et al., 2024), have been continuously studied and analyzed for their preparation methods, modification methods, and adsorption characteristics of phosphates in water, which has greatly inspired the research direction of biochar and modified biochar (Fig. 6).

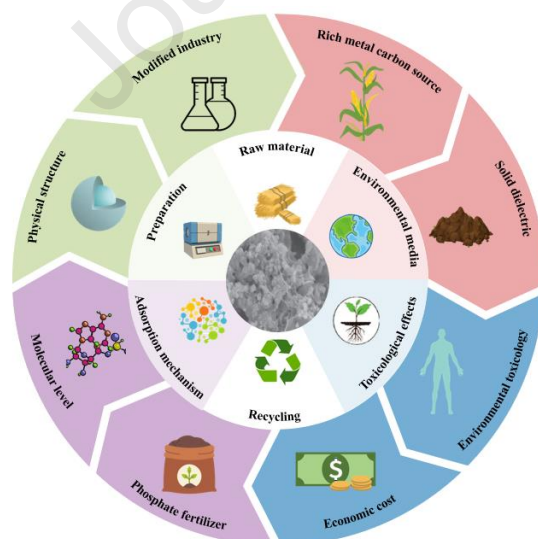


Fig. 6 Research directions for zero-valent iron and other iron-modified biochar.

From the perspective of carbon source selection, solid waste that is easily enriched in metals or contaminated with metals can be used as a carbon source to reduce the use of modifiers and

reuse highly environmentally toxic solid waste (Ravindiran et al., 2024). This type of metal modification method has a relatively high utilization rate and is relatively environmentally friendly, which is in line with current technological development goals (Xiao et al., 2024). From the perspective of preparing iron-modified biochar, modified biochar is strongly influenced by the carbon source and preparation conditions (Ma, Zhao et al., 2024). The characterization of modified biochar (pore size distribution, specific surface area, etc.) varies greatly under different preparation methods and conditions, which in turn affects its adsorption performance; the exploration of the optimal conditions for the preparation of modified biochar should be strengthened to summarize a scientific and green preparation process (Li et al., 2023). From the perspective of the mechanism of action of iron-modified biochar, on the one hand, in-depth research should be conducted on the adsorption mechanism of iron-modified biochar for phosphate, using more advanced detection methods to achieve molecular and atomic level mechanism analysis (Lu et al., 2020). On the other hand, iron-modified biochar should consider the treatment effect in a composite system with multiple interferences coexisting and determine its treatment capacity in the field of environmental remediation (Ma, Zhao et al., 2020). From the perspective of environmental media, modified biochar has a relatively efficient adsorption effect on phosphates in water bodies, but sediment and soil often contain excessive phosphorus (Lu, Zhao et al., 2023), which enters natural water bodies through rainwater runoff, underground seepage, and other means, leading to eutrophication of water bodies (Ma, Song et al., 2024). Therefore, its adsorption performance in solid- or liquid–solid-phase environments is worth paying attention to. From the perspective of environmental impact after the application of iron-modified biochar, it is necessary to explore the binding stability between iron-modified biochar, modified biochar and phosphate after the addition of iron-modified biochar for remediation in the environment (Wang et al., 2024) to determine the stability and persistence of modified biochar in environmental remediation and evaluate the long-term impact of the application of modified biochar on the natural environment (He et al., 2023). From the perspective of recycling, after adsorption equilibrium, modified biochar accumulates a large amount of phosphorus (Irfan et al., 2023), which can be used as a high-quality slow-release phosphate fertilizer to transfer excess phosphorus from water to barren soil (Bian et al., 2018), alleviating the dilemma of the uneven distribution of global phosphorus resources.

7. Conclusions

Native biochar is successfully loaded with iron (Fe) and its compounds by means of metal element loading modification, which can increase the specific surface area and number of adsorption sites, as well as the number and types of surface functional groups, and can enhance the adsorption effect of modified biochar on phosphate through electrostatic adsorption, ligand exchange, complexation, etc., which can effectively solve or overcome the drawbacks of the lower adsorption capacity and poorer removal effect of native biochar.

In the future, further research is needed on carbon source selection, preparation optimization,

mechanism of action, environmental media, environmental toxicity, and recycling of nano zero-valent iron and other iron-modified biochar to achieve widespread application in the field of environmental remediation.

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Declaration of competing interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of the data; in the writing of the manuscript; or in the decision to publish the results.

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