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Modified biochar: synthesis and mechanism for removal of environmental heavy metals

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Abstract

With social progress and industrial development, heavy metal pollution in water and soils environment is becoming more serious. Although biochar is a low-cost and environmentally friendly adsorbent for heavy metal ions, its adsorption and immobilization efficiency still need to be improved. As an upgraded version of biochar, modified biochar has attracted extensive attention in the scientific community. This review summarized the recent research progress on the treatment methods on heavy metal pollutants in water and soils using biochar. The features and advantages of biochar modification techniques such as physical modification, chemical modification, biological modification and other categories of biochar were discussed. The mechanism of removing heavy metals from soil and water by modified biochar was summarized. It was found that biochar had better performance after modification, which provided higher surface areas and more functional groups, and had enough binding sites to combine heavy metal ions. Biochar is a very promising candidate for removing heavy metals in environment. Furthermore, some high valent metal ions could be reduced to low valent metals, such as Cr(VI) reduction to Cr(III), and form precipitates on biochar by in-situ sorption-reduction-precipitation strategy. However, it is still the direction of efforts to develop high-efficiency modified biochar with low-cost, high sorption capacity, high photocatalytic performance, environmentally friendly and no secondary pollution in future.

Highlights

1. Efficient elimination of heavy metal ions by biochar from wastewater was summarized.
2. Immobilization of heavy metal ions in soil by biochar through sorption-reduction-precipitation was reviewed.
3. The interaction mechanism of heavy metal ions with biochar was discussed in details.

Keywords: Modified biochar, Environmental heavy metals, Synthesis, Mechanism, Pollution management

1 Introduction

With the rapid development of industry and the increase in the types and quantities of agricultural chemical products, the pollution of heavy metals in natural water and soils caused by industrial wastes, pesticides, and fertilizers has become increasingly serious. The pollution by heavy metals is a serious threat to environmental ecosystem and human health because of its persistence and concealment. Therefore, the efficient elimination of heavy metals from water and soil has been a hot issue of the public for many years (Wang et al. 2019a; Zhang et al. 2021a; Yu et al. 2021; Liu et al. 2021). Because heavy metals are difficult to be biodegraded or transformed, adsorption and immobilization have become the focus of researchers as the most promising treatment methods in recent years (Liu et al. 2022a). Under the

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dual pressure of social development and environmental protection, biochar has attracted great attention because of its wide application in environmental pollution control and its environmental and economic benefits (Liang et al. 2021).

Biochar is a kind of solid biofuel with high carbon and hydrogen contents and large specific surface areas. It usually refers to converting biomass (e.g., plants, industrial wastes, agricultural wastes, sludge and livestock manure, etc.) in anoxic or anaerobic environment and pyrolyzed at a temperature not higher than 1000 °C (Wardle et al. 2008; Amusat et al. 2021), as shown in Fig. 1. Waste-based biochar is considered an environmentally friendly material, and it's easy to be obtained with low cost. Biochar can adsorb and fix organic contaminants and heavy metals in water and soils (Gao et al. 2019; He et al. 2019), and has a wide application in environmental protection, agricultural production and other fields.

Biochar is rich in stable carbon and contains a large number of nutrient elements. It is widely used in carbon sequestration and soil improvement due to its rich surface micropore structures and the resulting huge surface areas, as well as rich functional groups. Biochar can be used as adsorbents and passivators to remove heavy metals from water and fixed heavy metals in soils (Qiu et al. 2022). This is a win–win strategy for the recycling and utilization of biomass waste as well as environmental remediation. However, the removal and fixation efficiency in water and soils of biochar to heavy metals is relatively limited. The modification of biochar is a suitable method to improve its removal efficiency of heavy metals.

In the database of Web of Science (SCIE only, from 2008), papers with the topic of "modified biochar" or "biochar modification" or "engineered biochar" or "designer biochar" were searched on April 22, 2022, and a total of 3310 papers were found. The retrieved articles were saved as plain text files, including full records and cited references, and were converted into executable formats using Citespace's "Data/Import/Export" function to visualize the retrieval records (Panahi et al. 2020; Chen et al. 2012). After statistical analysis of the publication years of the papers, it is found that the related papers have been increased year-by-year since 2009, and have shown a rapid growth especially in recent five years (2017 to present), as shown in Fig. 2. Hence, modification of biochar for its removal ability improvement is a hot research issue at present. Citespace was used to analyze the keyword co-occurrence of the articles, setting the time slicing from January 2009 to April 2022, one year per slice, choosing "Keyword" as the node type, setting the selection criteria to TOP 5.0% and the maximum number of selected items per slice to 50. It is found that 12 keywords co-occurrence more than 300 times are as follows: sorption/sorption (1312), aqueous solution (838), removal (779), activated carbon (559), biochar (502), water/waste water (836), heavy metal (425), soil (344), carbon (343), and mechanism (320). Therefore, it can be inferred that the study on modified biochar is closely related to the treatment of heavy metal pollution in soils and water, and the researches are focusing on the mechanisms of sorption and removal, as shown in Fig. 3.

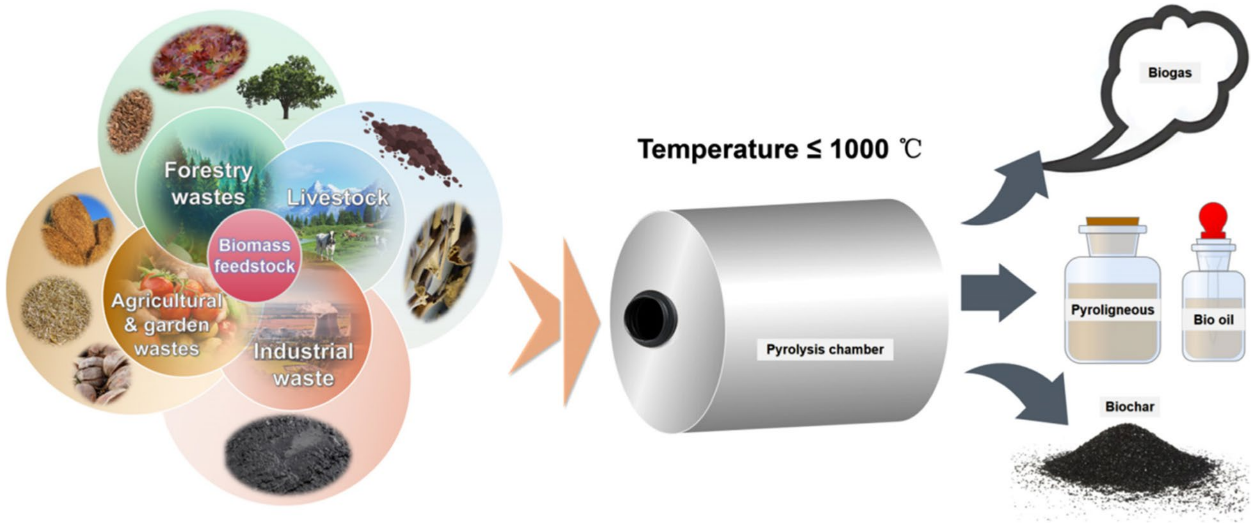

Fig. 1 Raw materials and pyrolysis products of biochar

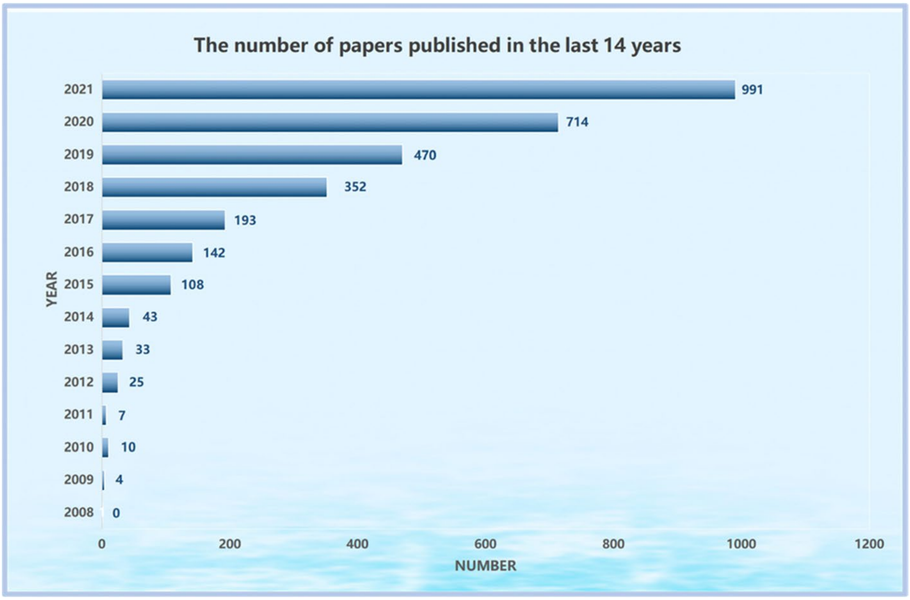

Fig. 2 The number of papers with the topic of "modified biochar" in 2008–2022

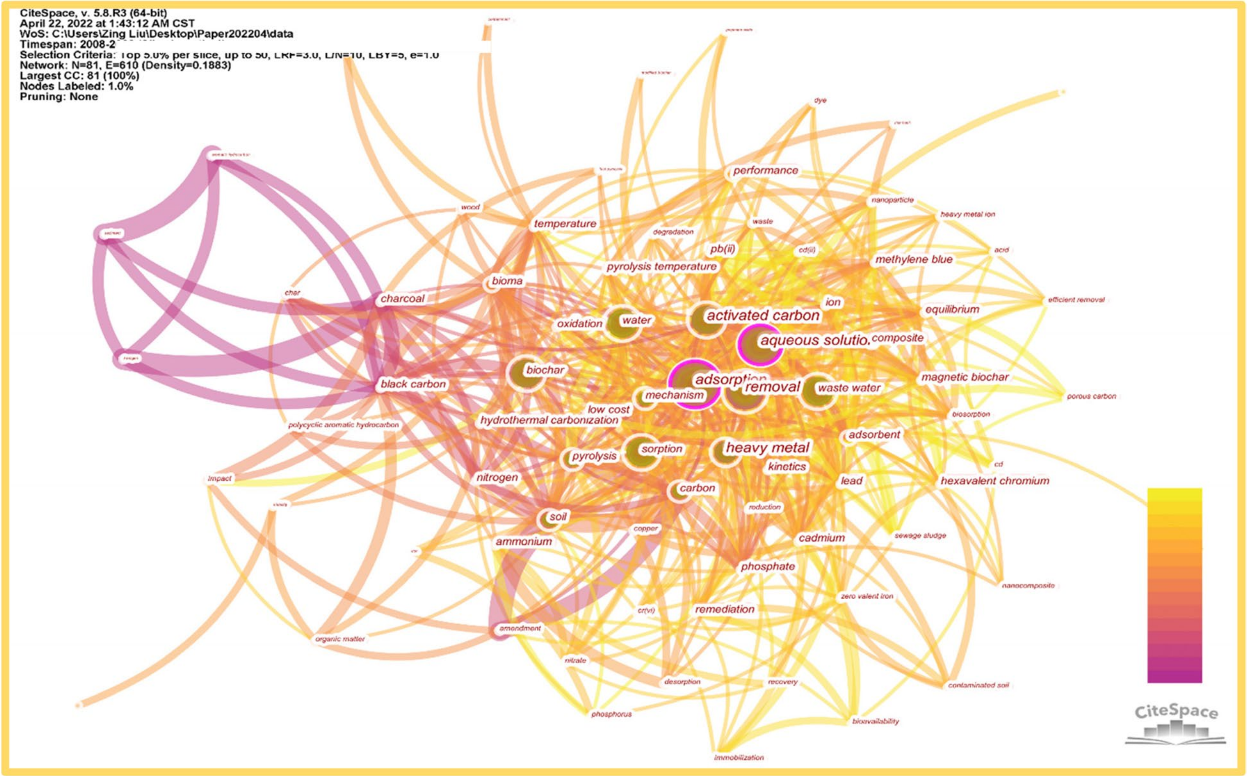

Fig. 3 Keywords co-occurrence analysis of the articles on "modified biochar", the font size corresponds to the number of co-occurrence times

1.1 Heavy metals

Heavy metals generally refer to metals whose density is greater than 5.0 g·cm^{-3}, and there are about 45 kinds of heavy metals in a general sense. According to the World Health Organization (WHO), common toxic and harmful "heavy metals" in environmental pollution include chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb), etc. (WHO, Adverse Health Effects of Heavy Metals in Children 2011, Wan Ngah and Hanafiah 2008). Among them, Cr(VI), As(III), Cd(II), and Hg(II) are the most important heavy metal pollutants, which are found in water and soils that need attention. At the same time, due to the development of nuclear energy industry, uranium (U(VI)) as; a radioactive heavy metal has also attracted great research interest (Chen et al. 2022).

1.1.1 Chromium

Chromium (Cr) is mainly produced in leather tanning, metal electroplating, metal finishing, textile dyeing and other industrial processes, and is widely distributed in wastewater, surface water and groundwater. In nature, chromium occurs mainly in trivalent (III) and hexavalent (VI) forms. Cr(III) is an essential trace element for organisms with low solubility because it can easily form stable and insoluble precipitates (hydroxides, oxides or hydroxides). However, Cr(VI) is more toxic, and chronic exposure to Cr(VI) can lead to cellular mutations that lead to cancer and other diseases (Su et al. 2021).

1.1.2 Arsenic

Arsenic is a kind of heavy metal, which is widely distributed in natural environment. In the natural environment, arsenic rarely exists in the form of elementary substance, but mostly exists in the form of compounds. The classification of arsenic in nature is mainly divided into organic arsenic (mainly include MMA, DMA and TMA), which is less toxic, and inorganic arsenic (mainly include AsH_3, arsenate and arsenite), which is more toxic but less mobile (Srivastav et al. 2022; Nguyen et al. 2019). Arsenic has closely relationship with human life, and is used widely in more than 50 industries such as medicine and health, metallurgy, pesticide, silicate industry, semiconductor, for processing, feed, anticorrosion, cosmetics and military. In the agricultural production, in addition to the widely used defoliants, arsenic-containing herbicides, arsenic-containing pesticides, male insecticides in hybrid rice have been widely used. Meanwhile, arsenic is also the most serious carcinogenic pollutant that threatens human health. The arsenic pollution can cause chronic and subacute acute arsenic poisoning, and can also induce lung cancer, skin cancer and bladder cancer (Asere et al. 2019; Wu et al. 2020a; Yu et al. 2022; Beesley and Marmiroli 2011). Therefore, it is urgent to explore low-cost and efficient methods to remove arsenic from the environment.

1.1.3 Cadmium

Cadmium is a toxic trace element of heavy metals and is a non-essential element for humans, animals and plants, but it is very important in the metallurgy, plastics, electronics and other industries (Cuypers et al. 2010). Cadmium usually enters the soil through the exhaust gas, wastewater and residue discharged from the industrial production process. Cadmium mainly exists in soils in water-soluble, exchangeable, carbonate, silicate, organically bonded, iron and managanese oxidized forms. Cadmium is soluble and exchangeable in water, and can be absorbed by plants and enriched in animals and human body through food chain (Jarup and Akesson 2009). Cadmium enrichment in animals and plants to a certain extent will cause serious harm to animal and plant health, resulting in various diseases and even death of animals, plants and human body (Satarug et al. 2010; Singh et al. 2011). The damage caused by cadmium accumulation has the characteristics of long-term, concealment and irreversibility. Therefore, research on the removal of cadmium in water and soils is of great importance for the protection of the environmental ecosystem and human health (Cuypers et al. 2010; Satarug et al. 2010).

1.1.4 Mercury

As a toxic heavy metal, mercury is listed as one of "Top 10 Major Chemicals of Concern" by WHO. Mercury pollution mainly comes from coal burning, mining or metallurgy, chlor-alkali processing, chemical production and other industries. The United Nations Environment Programme estimates that anthropogenic releases of mercury into the environment are about 2 gigatons per year, and that surface soil mercury pollution has increased by about 86 gigatons due to human activities. Soil pollution causes mercury to be adsorbed by crops, including rice, and mercury is found in human hair. The Minamata Convention on mercury was launched by the United Nations in 2013 to protect human health and the environment, and 128 countries have so far signed the convention. However, while atmospheric mercury levels may decline rapidly after emissions stop, it will take decades for mercury-contaminated soils to reach harmless levels. Therefore, it is necessary to study the effective remediation technology of mercury contaminated soil (O'Connor et al. 2018).

1.1.5 Uranium

Uranium is the heaviest element found in nature and is radioactive. After the fission reaction of uranium atoms, large amounts of energy are released which can be used for nuclear weapons, power generation, and other fields. As a common radioactive pollutant, U(VI) has metabolic toxicity and chemical toxicity to different organisms including human beings. With the continuous development and utilization of nuclear energy, uranium (U(VI)) is inevitably discharged into natural water bodies. With the announcement of Japan's Fukushima nuclear effluent into the sea plan, nuclear pollution in the world has been concerned. Nowadays, nuclear pollution, which poses a serious threat to soil and water, is now common around the world. In order to restore the polluted water bodies and reduce its environmental risk, the efficient removal of U(VI) technology has attracted the attention of researchers (Wang et al. 2020a).

1.2 Preparation and modification of biochar

Biochar is extensively used as an adsorbent for the removal of heavy metals from water (Gao et al. 2019) and as a passivator for the heavy metals in soils (He et al. 2019). In addition, the raw biochar materials could be found from variety of sources, the preparation method is simple, and the waste recycling can be realized. Therefore, the application of biochar for environmental heavy metal remediation is a win-win strategy. However, the fixation ability of original biochar for heavy metals is relatively limited. In order to enhance the fixation ability of biochar for heavy metals and to promote the real application of biochar in environmental heavy metal remediation, modification of biochar through different methods (acid-base modification, nano-material loading/composite, etc.) have been studied all over the world (Ahmed et al. 2016; Liu et al. 2020a).

Currently, the commonly used biochar modification techniques mainly include physical, chemical and biological modifications, as shown in (Figs. 4 and 5) Rajapaksha et al. 2016). Generally, physical method is more suitable for real applications as it is easy to operate on large scale. Chemical modification could change the surface properties according to the application of biochar, but it may need chemicals which are pollutants themselves, or are costly. Biological method can be applied on large scale, but it generally needs relative long contact time to change the structures and surface properties.

1.2.1 Physical methods

Internally modified pyrolysis Internally modified pyrolysis can significantly increase the porosities and surface areas of biochar, thereby enhancing the sorption ability of biochar. Suwunwong et al. (2020) synthesized corn cob biochar using internally modified pyrolysis under the heating rate of 10 °C·min^{-1} and maintained it at 500 °C for 2 h. The yield of corn cob biochar was 24.43 ± 5.28%. It was found that without any chemical treatment, the maximum sorption ability of methylene blue by the biochar was 16.50 mg·g^{-1} at 25°C. The physical properties and chemical compositions of the biochar were measured by elemental analysis, N_2 adsorption-desorption, FT-IR and SEM images, and it was found that the biochar yield and volatile substance composition were higher for low temperature pyrolysis at 400-500°C compared with high temperature pyrolysis. It was found that the pyrolysis temperature was inversely proportional to the biochar yield and volatile substance content. Ammonia ambiance pyrolysis can make efficiently surface modification, increase magnetism and activate N-functional groups. Mian et al. (2018) prepared nitrogen-mixed magnetic biochar containing agar biomass under NH_3 ambiance pyrolysis, and found that the product had the maximum sorption capacity of Cr(VI) up to 142.9 mg·g^{-1}, higher than magnetic biochar and other reported materials. Ammonia environmental pyrolysis improved the magnetism of the biochar, making it easy to separate from the solution and collect after Cr(VI) treatment. Pyrolytically modified urban organic waste (UOW) biochar was considered carbon sink for long-term immobilization of heavy metals in soil (Nair et al. 2020).

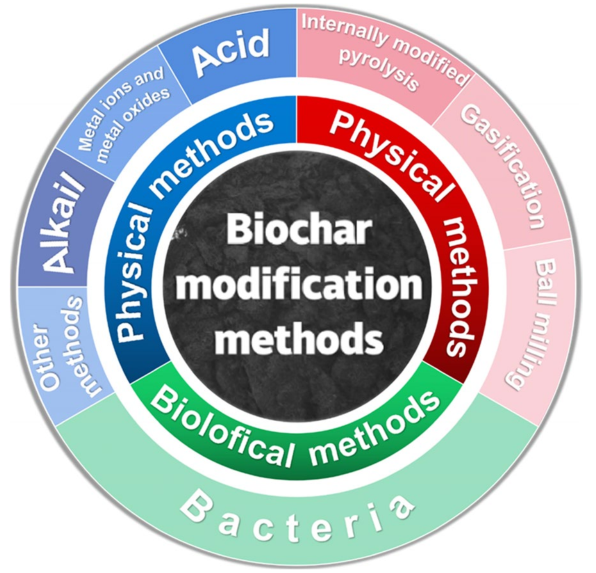

Fig. 4 Modification methods of biochar

Microwave pyrolysis is one widely used technique in the last decade. Microwave heating can increase the heating rate and reduce energy consumption without direct contact with the heated material. This technique is more environmentally friendly than traditional heating methods and has become the most commonly used conventional pyrolysis method. Using K_3PO_4 and clinoptilolite or bentonite as microwave absorbers and catalysts, the low microwave absorption rate and the quality of biochar can be improved during switchgrass pyrolysis. The microwave heating of 10 wt.% K_3PO_4 + 10 wt.% bentonite reached 400°C after 2.8 min, while the conventional heating was 28.8 min, the heating time of adding microwave was reduced to less than 1/10 of the conventional heating time. Compared with the specific surface area of biochar prepared by conventional heating method ($0.33\ m^2 \cdot g^{-1}$), the specific surface area of biochar prepared by microwave heating method ($76.3\ m^2 \cdot g^{-1}$) increased by more than 230 times (Mohamed et al. 2016). Song et al. (2020) developed a nano-magnetite-modified biochar material (m-biochar) using microwave in-situ rapid synthesis method, and systematically studied the removal ability and mechanism of Cr(VI) from polluted groundwater by m-biochar. The maximum sorption capacity of m-biochar was $9.92\ mg \cdot g^{-1}$, which was significantly higher than that of the original biochar ($8.03\ mg \cdot g^{-1}$). It can be concluded that the surface modification of biochar can increase the amount of surface functional groups and make them combine with metal ions, thus improving the sorption capacity of biochar.

Gasification Gasification is the partial oxidation of raw materials by gasification agents (air, oxygen, steam, etc.), and the temperature of the gasification process is usually higher than 700 °C and a small amount of steam and oxygen is required (Hansen et al. 2016). The biochar can form solid, liquid and gas products, but the yield of biochar is lower than that of pyrolysis because gasification tends to focus more on gaseous products (Wang and Wang 2019). The main purpose of steam modified biochar is to increase the specific surface areas, pore volumes and surface morphologies of biochar by reducing the aromatics and polarity of biochar. The surface areas of biochar by steam-modification were increased, which was attributed to corrosion of the biochar surface and the release of additional syngas (mainly in the form of hydrogen) (Vijayaraghavan 2019). The basic mechanism of H_2O vapor modification is described in Eqs. (1) and (2) (Amusat et al. 2021):

$$C + H_2O = H_2 + CO \tag{1}$$

$$C + 2H_2O = 2H_2 + CO_2 \tag{2}$$

The advantage of water vapor modification is that it is environmentally friendly and does not produce secondary pollution, but it also has the disadvantages of high temperature and energy requirements and relatively low carbon yield, which limit the wide application of this method (Amusat et al. 2021).

In addition, water vapor modification can remove the particles or volatile gases trapped on the surface of biochar, thus increasing the pore volume of biochar and making the internal pores of biochar develop (Rajapaksha et al. 2014). Rajapaksha et al. (2015) studied the effects of invasive plant Sicyos Angulatus L. biochar that was steam modified on enhancing the removal of sulfamethazine (SMT) from water, and found that steam activated biochar produced at 700 °C showed the highest sorption capacity at pH 3 ($37.7\ mg \cdot g^{-1}$), increasing sorption capacity by 55% compared to non-activated biochar produced at the same temperature.

Steam modified biochar also performed well in the removal of heavy metals. Wang et al. (2020b) treated biochar by steam activation (SBC) at the temperature of 500 °C for 45 min, and applied it to the effective elimination of Cu^{2+} and tetracycline (TC). The pyrolytic biochar of wood chips, rapeseed, manure particles and wheat straw at 300, 500 and 700 °C was studied, and the difference between steam-activated biochar and non-activated biochar was compared. It was found that steam activation increased Pb(II) sorption capacity of most biochars, mainly due to the increase in surface area. The Pb(II) sorption capacity of rapeseed straw biochar was $195\ mg \cdot g^{-1}$ at 700 °C, nearly 2 times compared with the uptake of wheat straw–based and non–steam activated canola biochars with $109\ mg \cdot g^{-1}$ and $108\ mg \cdot g^{-1}$, respectively (Kwak et al. 2019). The effect of steam modified biochar on the removal of drug compounds in water was studied. Chakraborty et al. (2018) studied the sorption

(See figure on next page.)

Fig. 5 **A**. The process for biochar without and with treatment in descriptive manner. The diagram for different bioreactor types. (Sutar et al. 2022) "Reproduced with permission from Elsevier, Copyright ©2022." **B**. N-doped magnetic biochar preparation via one-step under NH3 environment. (Mian et al. 2018) "Reproduced with permission from Elsevier, Copyright ©2018." **C**. Thiol-modified RS biochar prepared with β-mercaptoethanol for Cd and Pb remediation from polluted soils. (Fan et al. 2020) "Reproduced with permission from Elsevier, Copyright ©2020." **D**. Schematic illustration of fabrication for ZnO/biochar composites. (Chen et al. 2019b) "Reproduced with permission from Elsevier, Copyright ©2019." **E**. Description of various synthesis methods for NMOBCs preparation. (Zhao et al. 2021) "Reproduced with permission from Elsevier, Copyright ©2021." **F**. Schematic diagram of magnetic biochar embedded g-C3N4 nanosheets. (Karpuraranjith et al. 2021) "Reproduced with permission from Elsevier, Copyright ©2021."

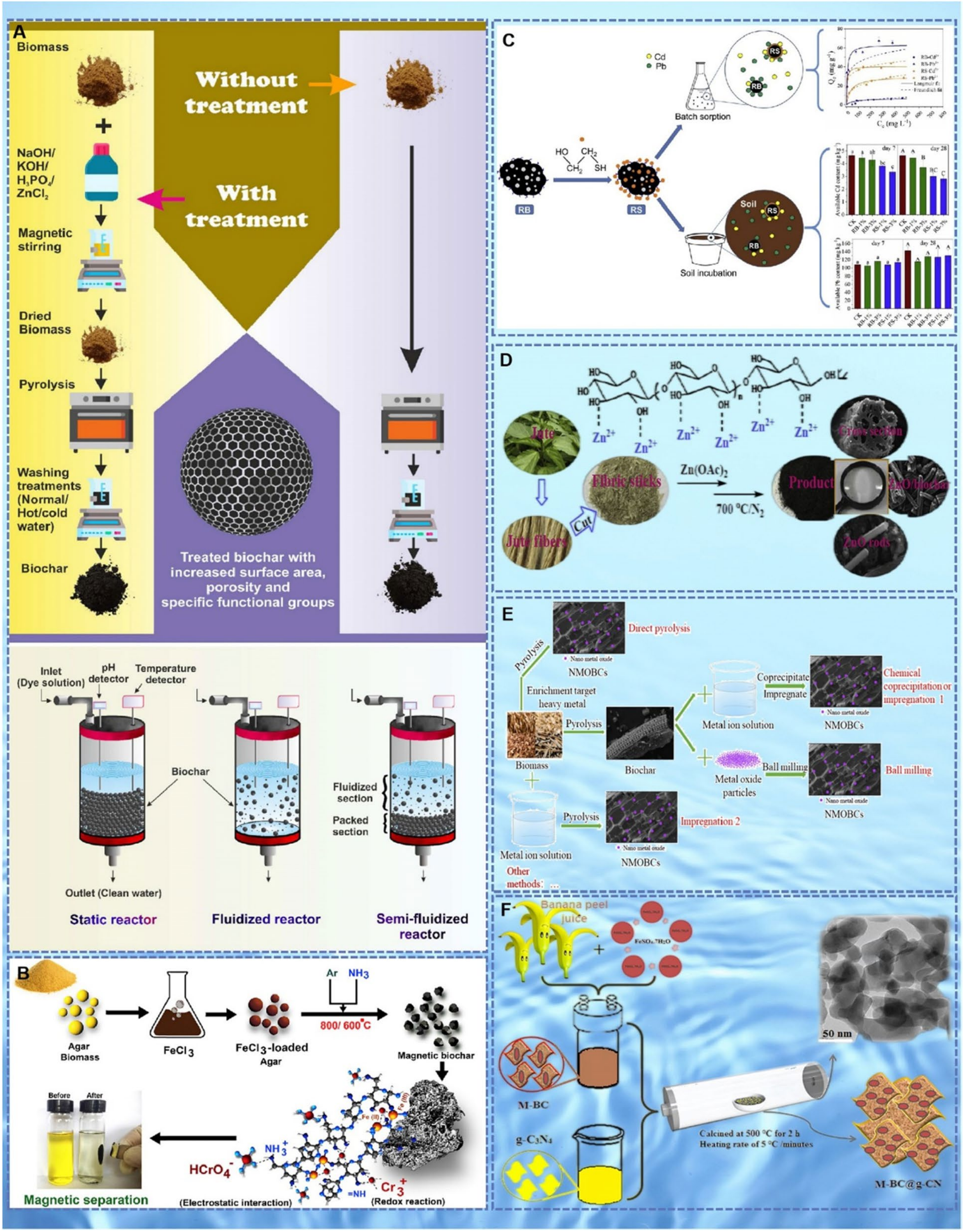

Fig. 5 (See legend on previous page.)

capacities of ibuprofen by protobiochar and steam activated biochar made from Aegle marmelos shell from aqueous solution. Under the optimal removal conditions, Aegle marmelos biochar (WAB) and Aegle marmelos steam activated biochar (WASAB) showed the removal efficiencies of 90% and 95%, respectively. Morphological analysis showed that the active adhesion sites increased after biochar modification. In addition, they compared the sorption abilities of physically (using steam) activated Cocos biochar (CPBC) and chemically (using H_3PO_4) activated Cocos biochar (CCBC) to remove IBP from simulated water, and found that the sorption capacities of IBP by CCBC and CPBC were 12.2 $mg·g^{-1}$ and 9.7 $mg·g^{-1}$, respectively. The total pore volumes of CCBC and CPBC were calculated to be 0.552 $cm^3·g^{-1}$ and 0.417 $cm^3·g^{-1}$, respectively. CCBC had higher pore volume and surface area than CPBC, which confirmed that CCBC had higher sorption ability and microporous characteristics. This may be due to the coconut shell chemical activation by H_3PO_4, which formed porous structures on the surface of the adsorbent (Chakraborty et al. 2019). The conditions of gasification could provide different kinds of active species, which can interact with biochar and thereby change the surface functional groups, pore volumes and surface areas. According to the application requirement, one can select different gasification system to change the biochar surface properties and structures, which is helpful to improve the sorption selectivity and ability.

Ball-milling Ball-milling (solid-phase synthesis) is a common synthesis process of nanomaterials, which has been widely used in industry. As a kind of solvent-free technique, it has widely been used to construct biochar-based materials with well dispersion and high porosities to enhance the environmental pollution treatments. The Ball-milling process produces nanoparticles as small as 10 microns in size and can be operated continuously. Ball-milling of carbon-based composites is a new low-cost method to prepare nano-composites with good surface properties. The physicochemical properties of biochar and its nanocomposites are improved by Ball-milling, such as the total pore surfaces and micropore surfaces of biochar, thus enhancing the sorption capacities of biochar. Due to the interaction of biochar and nanoparticles, biochar nanocomposites can effectively adsorb heavy metals, dyes and emerging organic pollutants in water. The sorption capacity of the original biochar can be improved in the range from several times to more than 200 times. The sorption mechanisms of biochar modified by Ball-milling include physical adsorption, chemical sorption, ion exchange, pore filling, hydrophobic effect and π-π electron donor-acceptor (π-EDA) interaction (Fig. 6) (Amusat et al. 2021), just the same as unmodified biochar.

Ball-milling modified biochar has a good performance in removing environmental heavy metals. Cui et al. (2021) prepared Ball-milling LDHs-biochar composites (B-LDHS-BC) with Ball-milling technique for sorption of Cd(II), studied the influence of Ball-milling on the structures and properties of LDHS-BC, and found that the removal of Cd(II) by B-LDHs-BC included physical adsorption and chemical sorption processes. It was proved that BM successfully removed LDHs from the surface of B-LDHs-BC. Although the N_2-BET surface area (226 $m^3·g^{-1}$) of B-LDHs-BC was a little lower than that of Ball-milling BC, the B-LDHs-BC contained much more oxygen-containing groups and much higher sorption capacity (119 $mg·g^{-1}$). The Cd(II) sorption performance of B-LDHS-BC was enhanced by inducing more active sorption sites and acidic groups (Fig. 7 A and B) (Cui et al. 2021).

Meanwhile, Ball-milling magnetic modified biochar can synergistically remove heavy metal ions and drug compounds in aqueous solution. Li et al. (2020) studied the sorption of TC and Hg(II) from aqueous solution using Ball-milled magnetic nanobiochars (BMBCs) (Fig. 6b). This demonstrated a significant improvement in the removal efficiency of TC and Hg(II) by BMBCs. It was shown that ≥ 99% of TC and Hg(II) were adsorbed to BMBCs at optimal preparation (700 °C, 12 h). The sorption efficiency was negatively correlated with the ionic strength of the solution, but positively correlated with the solution temperature in the temperature range of 25°C ~ 45°C. The results showed that the sorption of TC was mainly dominated by electrostatic interaction, hydrogen bond and Cπ-Cπ interaction, whereas the sorption of Hg(II) ions was mainly controlled by the electrostatic attraction, the formation of Hg–Cπ bond and surface complexation. In addition to excellent removal capability, BMBC700 also showed good recyclability and magnetic separation advantages (Li et al. 2020).

In addition, Ball-milling modified biochar can improve the removal ability of dyes and organic pollutants in aqueous solution. In the work of Zhang et al. (2021b), $BMHCH_2O_2$ was modified by Ball-milling and 10% hydrogen peroxide (H_2O_2) solution in two steps at different pyrolysis temperatures. It was found that the specific surface area (SSA) of biochar significantly increased after Ball-milling, and the hydroxyl groups and carboxyl groups on biochar further increased after the H_2O_2 modification. Therefore, the sorption efficiency of MB on biochar was further improved by two steps of modification. Among

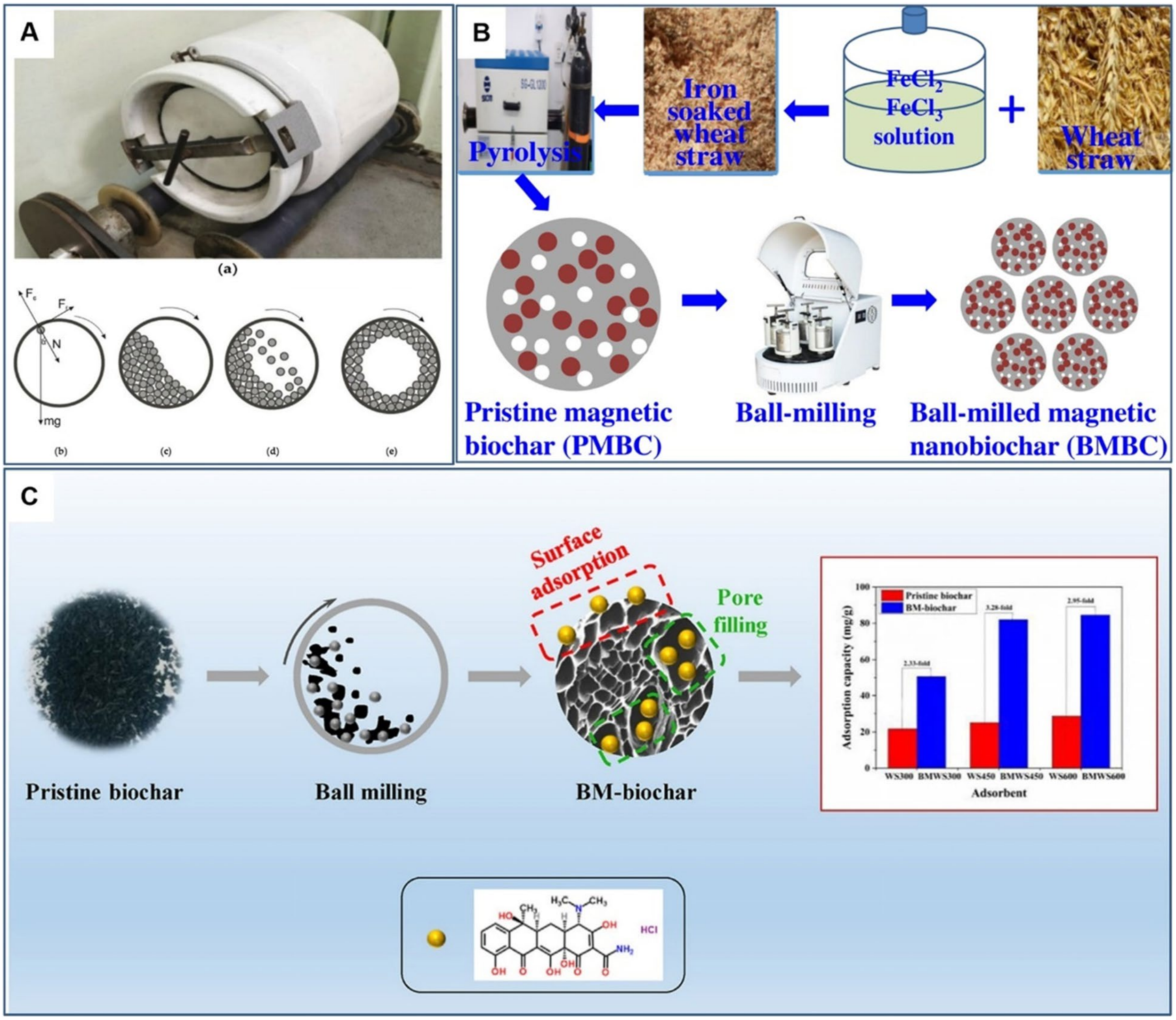

Fig. 6 Preparation and adsorption mechanism of Ball-milling biochar. **A**. A real–world example (**a**), the impact of forces (**b**) and the types of motion of grinding balls in a Ball mill: (**c**) rolling over; (**d**) falling; (**e**) rolling. (Amusat et al. 2021) "Reproduced with permission from Elsevier, Copyright ©2021." **B**. Schematic illustration of BMBC preparation (Li et al. 2020) "Reproduced with permission from Elsevier, Copyright ©2020." **C**. Ball-milling of pristine wheat stalk biochar for adsorption of tetracycline hydrochloride (TCH) (Xiang et al. 2020) "Reproduced with permission from Elsevier, Copyright ©2020."

the tested adsorbents, BMHCH$_2$O$_2$-450 had the largest sorption capacity for MB (310 mg·g^{-1}) (Zhang et al. 2021b). Xiang et al. (2020) investigated the sorption property of tetracycline hydrochloride (TCH) by pyrolytic straw raw and Ball-milled biochar (BM-biochar) at 300 °C, 450 °C and 600 °C. The surface properties of BM-biochar were obviously improved as compared with the original biochar. TCH sorption occurred mainly on the outer spherical surface of biochar and was carried out by filling holes. The sorption capacity was positively correlated with external surface areas, total microporous or mesoporous volumes of biochar (Fig. 6c). The presence of Na$^+$, K$^+$, Mg^{2+} and TCH in the solution produces competitive sorption, while the presence of Ca^{2+} promotes the sorption of TCH by forming tetracycline-Ca^{2+} complexes. BM-biochar pyrolyzed at 600°C has the best adsorption performance, and TCH sorption capacity is 84.54 mg·g^{-1} at pH = 6-8 (Xiang et al. 2020).

In conclusion, Ball-milling modified biochar has the potential to improve the sorption capacity of biochar because the surface areas and the surface sites are increased after Ball-milling, thereby improving the removal of pollutants from aqueous solutions. The study

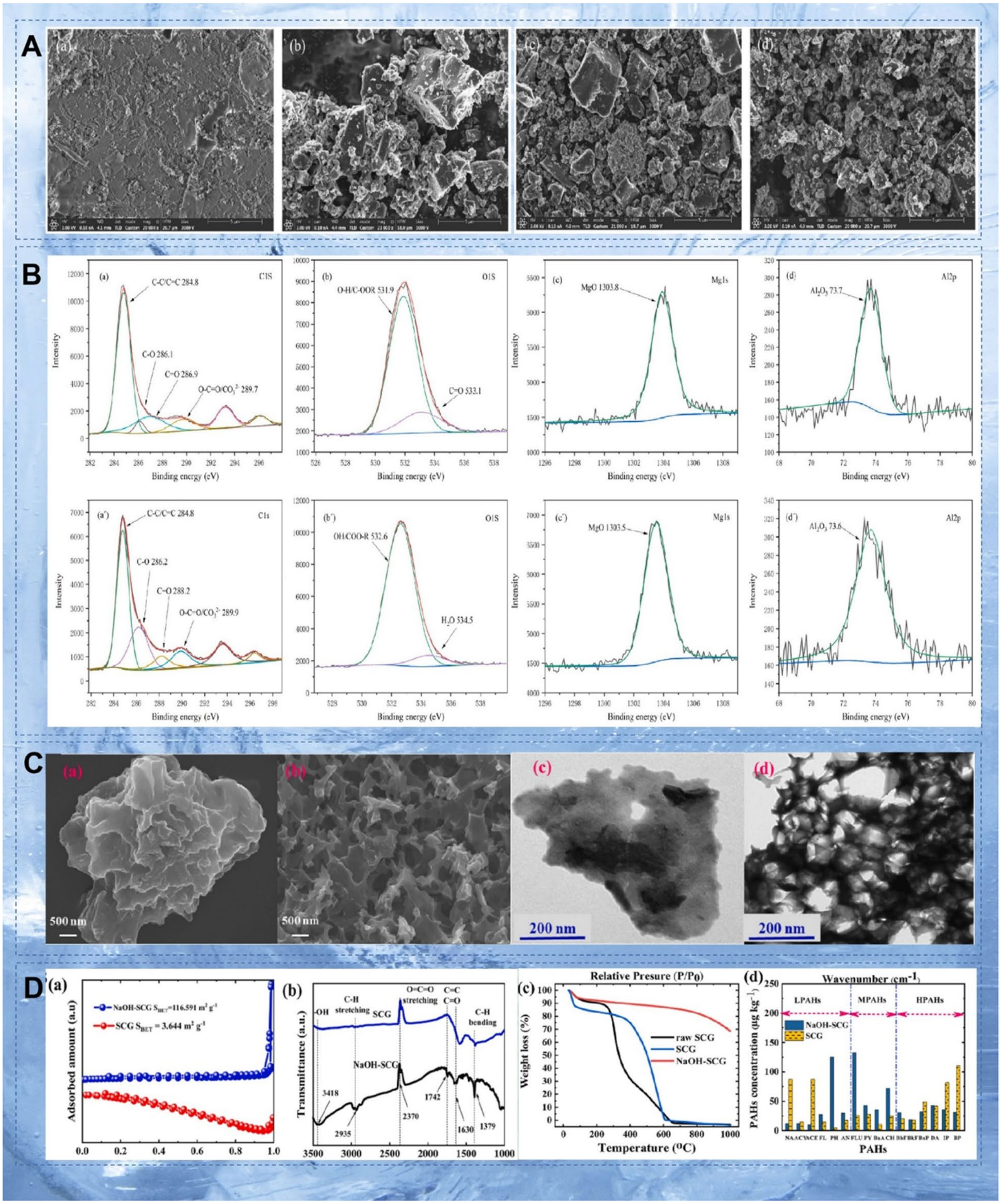

Fig. 7 **A**. SEM images of (**a**) BC, (**b**) B-BC, (**c**) B-LDHs-BC, and (**d**) B-LDHs-BC (Cd(II))."Reproduced with permission from Elsevier, Copyright ©2021." **B**. High resolution XPS spectra for C 1 s, O 1 s, Mg 1 s, Al 2p of B-LDHs-BC (**a**-**d**) and M-BLDHs-BBC (**a**´–**d**´). (Cui et al. 2021) "Reproduced with permission from Elsevier, Copyright ©2021." **C**. The SEM analysis of SCG (**a**) and NaOH-SCG (**b**); The TEM images of SCG (**c**) and NaOH-SCG (**d**)."Reproduced with permission from Elsevier, Copyright ©2021." **D**. (a) N2 adsorption–desorption isotherms, (**b**) FTIR spectra, (**c**) TGA curve, and (**d**) PAHs concentration of SCG and NaOH-SCG. (Nguyen et al. 2021) "Reproduced with permission from Elsevier, Copyright ©2021."

of biochar modified by Ball-milling is of great significance for the elimination of heavy metals from wastewater. Ball-milling is the most commonly used method to modify biochar in really applications because it is easy to operate on large scale. More importantly, the Ball-milling modification could be finished in short time. There are also some disadvantages on this kind of biochar as it only has efficiency on increasing the surface areas, and does not change other functions. Therefore, the combination of Ball-milling method with chemical or biological methods will have a wider application prospect.

1.3 Chemical methods

Chemical technique is one most commonly used method at present, usually includes acid, alkaline, oxidizing-agents, metal salts or metal oxides, and other modifications, etc. (Wang and Wang 2019). Using different kinds of chemicals, the surface properties such as the concentrations of functional groups, the kinds of functional groups, the surface defects etc. could be changed, which is helpful to change the sorption property of biochar.

1.3.1 Acid modification

The improvement of biochar by acid treatment includes removing metals and other impurities on biochar surface, and increasing acid functional groups on biochar surface. Meanwhile, acid treatment can also change the surface areas of biochar, and the effect varies with types and concentrations of acids (Wang and Wang 2019). Acidified biochar is the most suitable soil improver (Panwar and Pawar 2020). Wibowo et al. (2007) modified biochar with HNO_3, after the modification, a large number of oxygen-containing acidic surface groups were introduced on the surface of biochar, and the specific surface areas were increased. Compared with the biochar before oxidation, the O/C ratio of biochar after oxidation with concentrated HNO_3/H_2SO_4 and 30% HNO_3 increased by 10 times (flax), 5 times (CH800), 7 times (flax) and 4 times (CH800), respectively. The total acidities of flax increased from 0 to 3.3 (HNO_3/H_2SO_4) and 1.2 (30% HNO_3) after oxidation. The CH800 had a similar trend (Table 1). Therefore, acid oxidation of biochar increases the O/C ratio and total acidities of biochar (Uchimiya et al. 2012). Liu et al. (2020a) obtained primitive biochar (CSBC) from pyrolysis of corn straw in a finite oxygen condition and modified it with H_3PO_4-CSBC and KOH, respectively. The sorption capacities of CSBC, H_3PO_4-CSBC and KOH-CSBC to MB were 43.1 $mg{\cdot}g^{-1}$, 230.4 $mg{\cdot}g^{-1}$, and 406.4 $mg{\cdot}g^{-1}$, respectively. The chemical treatment significantly improved the sorption ability of MB on biochar, especially for KOH-CSBC. Therefore, the KOH-CSBC has the potential to remove dyes from textile wastewater (Liu et al. 2019). Walnut shell biochar (WSC) and wood powder biochar (WPC) prepared by limited oxygen pyrolysis were modified by $ZnCl_2$, KOH, H_2SO_4, and H_3PO_4. Experimental results showed that the specific surface area of modified biochar after KOH treatment was the highest. Acid modification increased a large number of oxygen-containing functional groups on biochar. These functional groups provided more sorption sites for pollutants, which are conducive to bind the pollutant molecules. The sorption capacities of MB on different treatment reagents were $ZnCl_2 > KOH > H_3PO_4 > H_2SO_4$. The maximum sorption capacities of WPC and WSC by the two biomass treatments were 850.9 $mg{\cdot}g^{-1}$ and 701.3 $mg{\cdot}g^{-1}$, respectively (Liu et al. 2020b). He et al. (2021) prepared rice straw biochar by anaerobic pyrolysis and modified the biochar with 15% H_2O_2 and 1:1 HNO_3/H_2SO_4 mixed acid, respectively. The results showed that the oxidation modification with 15% H_2O_2 and 1:1 HNO_3/H_2SO_4 acid significantly increased the carboxyl functional groups on the biochar surface. The carboxyl functional groups on the surface of biochar were enhanced more effectively by acid modification than by oxidant modification. Cd(II) forms surface complexes through coordination between functional groups and biochar, which is the main mechanism of Cd(II) specific sorption on biochar surface. After modification, the number of carboxyl groups on the surface of rice straw biochar increased significantly, thus improving the specific sorption capacity of Cd(II) on biochar (He et al. 2021). In conclusion, the surface charge and functional groups could be changed obviously after acid modification. The point of zero charge is decreased and the surface purity is increased. The change of surface properties is critical for the application of biochar.

1.3.2 Alkali modification

The main purpose of alkali modification is to increase surface area, pore volume and oxygen-containing functional groups. Common alkali modification reagents are potassium hydroxide and sodium hydroxide (Wang and Wang 2019). Potassium hydroxide modification increases the surface area of biochar prepared by pyrolysis from 14.4 to 49.1 $m^2{\cdot}g^{-1}$, and increases the oxygen-containing functional groups, thus enhancing the sorption capacity of As(V) from 24.49 $mg{\cdot}g^{-1}$ for the original biochar to 30.98 $mg{\cdot}g^{-1}$ (Jin et al. 2014). Sodium hydroxide is less corrosive and less costly than potassium hydroxide (Cazetta et al. 2011). NaOH modified coconut biochar increased its surface area significantly from 1940 $m^2{\cdot}g^{-1}$ to 2885 $m^2{\cdot}g^{-1}$ compared with KOH modified coconut (Cazetta et al. 2011; Tan et al. 2008).

Nguyen et al. investigated the feasibility of TC removal from different aqueous solutions using alkaline treated

Table 1 Raw materials, modification methods and removal effect of heavy metals of modified biochar

Adsorbent	Pyrolysis temperature (°C)	Modification method	Target contaminant	Main results	Reference
Reed residues	650°C	Nano-magnetite + microwave	Cr(VI)	Synthesized m-biochar enhanced Cr(VI) removal ability from contaminated groundwater as compared to pristine biochar	Song et al. 2020
Sawdust and switchgrass	650°C	Triple superphosphate (TSP) and bone meal (BM)	Pb(II), Cu(II), Cd(II)	The biochar copyrolysized with phosphate fertilizers had high metals stabilization in soils	Zhao et al. 2016
$MgCl_2$	400–600°C	Fast pyrolysis	Pb(II), Cd(II) and tetracycline	The MgO@N-biochar had high ability for binding Pb(II) with high sorption capacity of 893 $mg·g^{-1}$ and short equilibrium time (< 10 min)	Ling et al. 2017
Broiler litter manure	350°C, 700°C	Pyrolysis, steam-activated	Cu(II), Ni(II), Cd(II), Pb(II)	Both in soils and water, the addition of biochar increased pH and enhanced heavy metals immobilization	Wang et al. 2019b
β-cyclodextrin functionalized biochar (β-BC)	500 °C	Pyrolysis + mixing	Heavy metals and dye	β-BC possessed the ability to promote the removal of antibiotic resistance genes in wastewater treatment	Wu et al. 2020b
Pine bark waste	950°C	Magnetic($CoFe_2O_4$)	Pb(II) and Cd(II)	MBC showed efficient ability for Cd(II) and Pb(II) removal from aqueous solutions	Reddy and Lee 2014
Waste marine macro-algae	500°C	Iron oxide particles (e.g., magnetite, maghemite)	Heavy metals	Magnetic biochar had high sorption ability for heavy metals than other reported biochar	Son et al. 2018
Walnut shells	249.85°C	Nano FeS and starch (or chitosan)	Pb(II)	Biochar loaded with nano-FeS, starch or chitosan showed much higher sorption ability for Pb(II) than the bare biochar	Liu et al. 2022b
Microcystis biomass	200°C	Fe_3O_4	U(VI)	The Fe_3O_4/biochar had high sorption ability in the removal of U(VI)	Wang et al. 2020a
Cottonseed hull and flax shive	700 °C	Concentrated H_2SO_4/HNO_3 and 30% HNO_3	Pb, Cu, and Zn	Oxidized biochar has rich carboxyl groups which enhanced the sorption ability for Pb, Zn and Cu as compared to unoxidized biochar	Uchimiya et al. 2012

biochar (NaOH-SCG) prepared by pyrolysis of coffee grounds. The results showed that the sorption capacity of NaOH-SCG biochar (113.6 mg·g^{-1}) was 2.9 times higher than that of unmodified SCG (39.2 mg·g^{-1}). The alkaline treated biochar has high sorption capacity for TC and has broad application prospect in the separation of hazardous chemicals in different wastewater (Fig. 7 C and D) (Nguyen et al. 2021). Tang et al. (2022) used alkali-modified straw biochar to remove the emerging contaminants (ECs) in kitchen wastewater, such as bisphenol A (BPA), TC and ofloxacin (OFL). They found that the alkali-modified straw biochar had larger specific surface area, stronger hydrophobicity and higher sorption capacity, and the removal rate of ECs reached 95%-100%. Under static operation mode, the maximum sorption capacities of alkali-modified biochar for BPA, TC and OFL were 71.43, 101.01 and 54.05 mg·g^{-1}, respectively (Tang et al. 2022). Chen et al. (2021) used KOH to modify N-enriched biochar (KNB) from waste chicken feathers. They found that the sorption rates of Cd(II) (2 h to reach equilibrium) and Pb(II) (1 h to reach equilibrium) by KNB were fast. The sorption capacities of Cd(II) and Pb(II) by KNB were 22.32 mg·g^{-1} (Cd(II)) and 119.65 mg·g^{-1} (Pb(II)), which increased by 7.07 and 26.52 times compared with the original biochar, respectively. The main sorption mechanisms of KNB for Cd(II) and Pb(II) included electrostatic interactions, cation-π interactions, complexation and K$^+$ exchange (Chen et al. 2021). Hafizuddin et al. (2021) used sodium hydroxide (NaOH) to modify palm kernel shell (PKS) and coconut shell (CS), and found that the surface modified biochar had high specific surface areas (CS: 356.9 m^2·g^{-1}, PKS: 427.6 m^2·g^{-1}), small pore sizes (CS: 2.2 nm, PKS: 2.0 nm) and large pore volumes (CS: 0.34 cm^3·g^{-1} (Yu et al. 2021), PKS: 0.30 cm^3·g^{-1} (Yu et al. 2021). The results indicated that NaOH modification could effectively improve the surface characteristics of biochar. In addition, the surface modification of 25% NaOH greatly increased the active functional groups of biochar, which directly improved the sorption capacity of biochar (CS: 527.4 mg·g^{-1}, PKS: 627.0 mg·g^{-1}). Compared to acid modification, the alkali modification can also change surface areas, pore volumes and functional groups. After alkali modification, the point of zero charge and oxygen-containing groups are generally increased as compared with the pretreated biochar.

1.3.3 Metal ions and metal oxides-modified biochar

The sorption, catalytic performance and magnetic property of biochar can be changed by modification with metals or metal oxides. Metal modification can improve the biochar sorption capacity for heavy metals and their oxides by increasing the exchange of ions and nitrogen-containing functional groups. The modification with metals or metal oxides are mainly as follows: (1) the metals or metal oxides are firstly mixed with raw materials and then pyrolyzed to synthesize biochar; (2) biochar is prepared by pyrolysis of raw materials, and then soaked with metal ions or metal oxides under certain conditions (Tan et al. 2016). After medication with metals or metal oxides, the properties of biochar could be changed obviously, such as photocatalytic ability, magnetic property, oxidation/reduction property, etc.

Karimnezhad et al. (2014) studied the modification of walnut shell biochar with different concentrations of $ZnCl_2$, and found that the specific surface area of the modified biochar increased with the increase of impregnation ratio. Wang et al. (2015) studied the effect of biochar modified by hematite at 600°C on the removal of As(V) in the soil, and found that the maximum sorption capacity of modified biochar for As(V) could reach 429 mg·kg^{-1} due to the effect of electrostatic sorption and surface functional groups. However, the removal of heavy metals by the original biochar was only 265 mg·kg^{-1}, and the difference was about 2 times before and after modification. O 'Connor et al. (2018) found that sulfur modified rice husk biochar had a higher removal rate of Hg(II) from soil than unmodified biochar, and the removal rate increased with the increase of sulfur addition amount. Wan et al. (2018) impregnated hydrated manganese oxide (HMO) nanoparticles into a peanut shell-derived biochar (BC), and obtained a nanocomposite adsorbent HMO-BC, which showed better sorption capacity than bare BC in actual heavy metal containing wastewater treatment. HMO-BC can effectively remove Pb(II) from the actual lead plating wastewater to the discharge limit (0.2 mg·L^{-1}), the treatment volume of 525BV, much higher than bare BC (60BV), as shown in Fig. 8. Furthermore, the HMO-BC can be reused and has no observed capacity loss. Nitrogen-mixed biochar was modified with magnesium oxide nanoparticles (MgO@n-biochar), and it was found that the MgO@n-biochar had a large sorption capacity for Pb(II) (893 mg·g^{-1}), a short balance time (< 10 min), and a large handling volume (~ 4450BV). Meanwhile, this excellent sorption performance can be maintained with various environmentally relevant interferences, such as pH, natural organic matter and others. It is interesting to note that the material may be suitable for the treatment of wastewater, natural water and even drinking water (Ling et al. 2017).

A method to produce zinc-biochar nanocomposites from bagasse was studied, and the removal of Cr(VI) was 1.2 ~ 2.0 times higher than that of original biochar (Gan et al. 2015). New types of biochar, namely FeS@WNS, Chitosan-FeS@WNS, and Starch-FeS@WNS were constructed by loading FeS, starch or chitosan with WNS. FeS nanoparticles can effectively improve the removal of

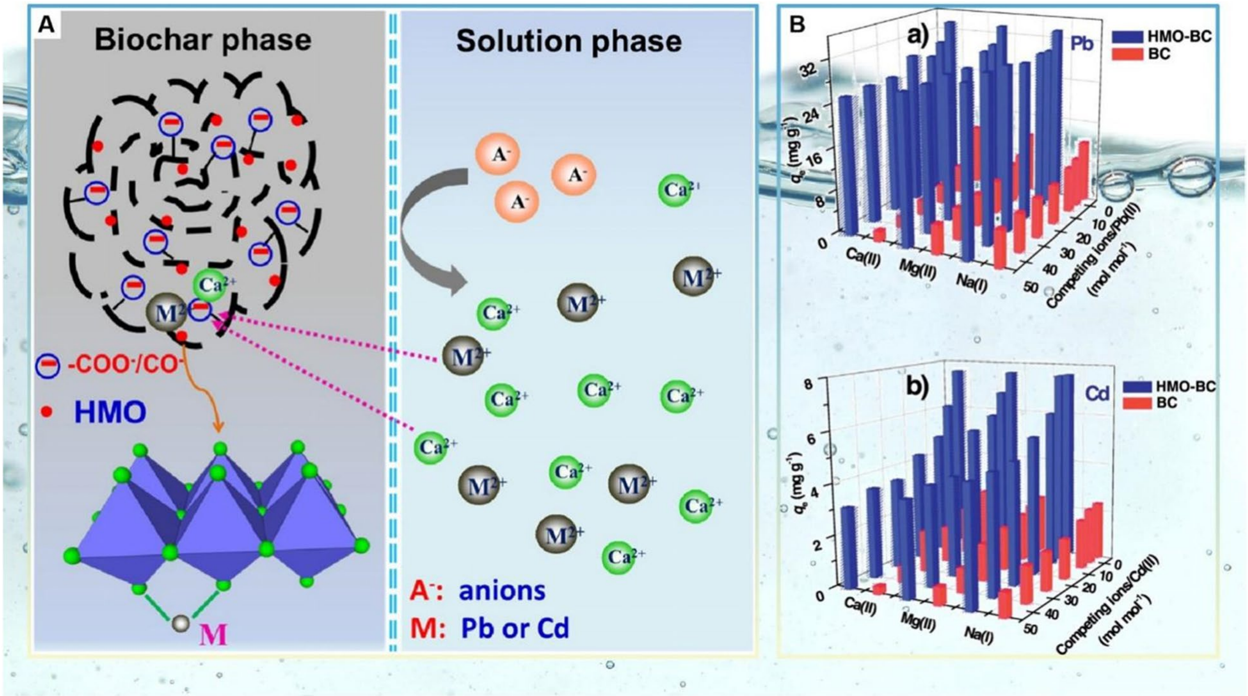

Fig. 8 **A**. Schematic illustration of the enhanced heavy metal sequestration by HMO-BC. **B**. Influence of competitive ions, Ca(II), Mg(II) and Na(I) on sorption of Pb(II) and Cd(II) onto HMO-BC and BC. Conditions: C0 (Pb(II)) = 10 mg L−1, C0 (Cd(II)) = 5 mg L−1, Sorbent dose = 0.2 g L−1, pH = 6.0 ± 0.2, and Temperature = 298 K. Lower Pb(II) and Cd(II) concentrations were chosen to better show the adsorption preference of HMO-BC toward target metals. (Wan et al. 2018)"Reproduced with permission from Elsevier, Copyright ©2018."

Pb(II), while chitosan or starch can improve the stability and easy agglomeration of FeS. The removal mechanisms of Pb(II) in aqueous solution include the electrostatic attraction, H-bonding, ion exchange, physical sorption, and oxidation/reduction. In addition, the three composites are stable and reusable, and can be applied for the treatment of Pb(II) polluted wastewater (Liu et al. 2022b). In terms of increasing magnetism, the combination of biochar and magnetic adsorbents (such as magnetic nano-ferric oxide, zero-valent iron, Co Fe_2O_4, etc.) to generate magnetism can increase the convenience of biochar recovery and improve the sorption capacity for heavy metals (Karunanayake et al. 2018; Reddy and Lee, 2014; Son et al. 2018). Song et al. (2020) found that the sorption capacity of the synthesized magnetic biochar was significantly increased from 8.0 $mg \cdot g^{-1}$ to 9.9 $mg \cdot g^{-1}$ as compared to the original biochar.

1.3.4 Other methods

As for the chemical modification methods, in addition to the above-mentioned categories, there are some other modification methods. Modified methods with materials such as oxidants (containing hydrogen peroxide) (Wang and Wang 2019; Qin et al. 2019), carbonic acid materials (Wang and Wang 2019), inorganic materials (such as montmorillonite, superphosphate, etc.) (Zhao et al. 2016), organic compounds (mercaptan (Lyu et al. 2020), thiourea (Zhu et al. 2020) and so on. Low-temperature plasma method has become one of the research hotspots in recent years due to its low cost, environmentally friendly and good performance.

Fan et al. (2020) prepared a thiol-modified straw biochar (RS), which increased the thiol groups on the biochar surface, complexed with Pb(II) and Cd(II) effectively (61 and 45 $mg \cdot g^{-1}$, respectively), and it was shown that RS selectively adsorbed Cd(II) than Pb(II) in binary-metal systems. The results suggested that the biochar modified by ethanol-activated could be a useful strategy for heavy metal pollution treatment in soils and water and therefore was a promising research material for environmental governance applications. Chen et al. (2022) successfully modified o-PEA on porous carbon by low-temperature plasma method. Cafe/O-PEA has a good sorption capacity for U(VI). The maximum sorption capacity of Cafe/O-PEA is 648.54 $mg \cdot g^{-1}$ at T = 298 K and pH = 6.0 at 1 h, which is much higher than that of most carbon matrix composites. Experimental results show that the sorption of U(VI) is related to the complexation of Cafe/O-PEA with $-NH_2$, phosphate and -OH groups. Therefore, low temperature plasma method is an efficient, environmentally friendly and low-cost material surface modification method, which can effectively enrich U(VI) in aqueous solution, and has positive significance for the treatment of wastewater pollution.

1.4 Biological modification methods

The use of microorganisms to adsorb heavy metals from aqueous solutions has proven to be very promising, low-cost, easy to operate and efficient, especially in the treatment of low concentration heavy metal wastewater. Residual biomass of industrial microorganisms, including bacteria, algae, fungi, and yeast, is able to efficiently accumulate heavy metals. The biological sorption process includes the following mechanisms: cross-cell membrane transport, complexation, ion exchange, precipitation, and physical adsorption. The microbial surface contains large amounts of functional sites such as amino, carbonyl, carboxyl, and hydroxyl groups etc. This may help to improve the sorption effect of biochar by surface grafting and / or functional group exchange (Zilouei et al. 2014; Wang et al. 2021).

Under certain conditions, bacteria have a good sorption effect on different toxic heavy metals (Chakravarty and Banerjee 2012). Due to the lack of long-term stability of biochar in heavy metal remediation, phosphate-solubilizing bacteria (PSB) can increase the release of phosphorus and react with Pb(II) to form stable molybdenite. Chen et al. prepared an alkaline biochar produced from rice husk (RB) and a slightly acidic biochar produced from sludge (SB) as raw materials, and modified them with PSB. The results showed that Pb(II) concentration in water decreased by 18.61 and 53.89% after adding RB and SB, respectively. PSB modification improved Pb(II) removal rates of the two biochar to 24.11 and 60.85%, respectively. The results showed that the uniform distribution of PSB enhanced the release of phosphorus on the surface of biochar, regulated the surface pH value of biochar, and significantly promoted the formation of stable pyroxenite on the surface of biochar. Therefore, the combination of biochar and PSB is a promising candidate for heavy metal remediation (Chen et al. 2019a). The dynamic effects of maize biochar and a heavy metal-resistant pseudomonas on the stability of soil contaminated with mixed Cd(II) and Cu(II) and its potential mechanisms were investigated (Tu et al. 2020). The results showed that the biochar of the inoculated strains increased the soil pH, reduced the exchange and bio-utilization of Cd(II) and Cu(II), improved the soil enzyme activity, and improved the soil microbial community. After biological modification, the biochar could adsorb metal ions more efficiently and fix the adsorbed metal ions more strongly. The soil quality can be improved at the same time.

1.5 Mechanism of pollutants removal from water and soil by modified biochar

The anaerobic heating process increases the specific surface areas and pore volumes of biochar, which is conducive to pore filling, thus improving the sorption capacity of pollutants. There are a large number of O-containing groups on the surface of biochar, such as hydroxyl groups and carboxyl groups, which can make surface complexation, ion exchange, and the electrostatic attraction with heavy metal ions. The specific mechanism of the binding action can be judged by the changes of biochar functional groups before and after the sorption of metal ions, such as the movement, increase or disappearance of the peak. The specific sorption mechanism of different heavy metal ions is also different, which affects the properties of biochar, vice-versa.

1.5.1 Mechanism of heavy metals removal from water by modified biochar

Heavy metal pollution in environmental water, including heavy pollutant metals (such As(III), Cr(VI), Ni(II), Zn(II), Cu(II), Cd(II), Hg(II), U(VI), Pu(IV) etc.) and metal-like metals (such As(III), Se(IV) and As(V)), has become a serious challenge (Schwarzenbach et al. 2010; Yang et al. 2021; Cheng et al. 2021; Li et al. 2021). Heavy metal intake can cause a variety of human diseases, even cancer. Biochar is an efficient, and ecological adsorbent for water purification. After surface modification, the porosity, reactivity and sorption capacity of biochar are increased significantly. The mechanisms of biochar elimination of heavy metals from wastewater mainly include complex formation, electrostatic behavior and ion exchange (Fig. 9). Therefore, using biochar to remove heavy metals is a promising strategy (Liu et al. 2022a; Liang et al. 2021; Srivastav et al. 2022; Chen et al. 2021; Wang et al. 2019b).

Different modification methods lead to different removal mechanisms of heavy metals (Cai et al. 2022). Therefore, if the modification method is correctly conducted, the biochar will have sufficient heavy metal removal capacity, and the heavy metals will be more stable in biochar, thus enhancing the chemisorption and removal mechanism. For example, the pyrolyzed sulfate lignin biochar modified with CO_2 at 800 °C and impregnated with FeO_x improved the sorption efficiency of arsenic in an aqueous solution (Cha et al. 2021). The sorption capacity of the modified reed straw biochar prepared by microwave treated nano-magnetite was $9.92\ mg{\cdot}g^{-1}$, significantly higher than that of the original biochar ($8.03\ mg{\cdot}g^{-1}$) (Song et al. 2020).

On the other hand, it is an effective way to recycle biochar from water by adding magnetism to biochar through modification. Liang et al. (2022) prepared magnetic

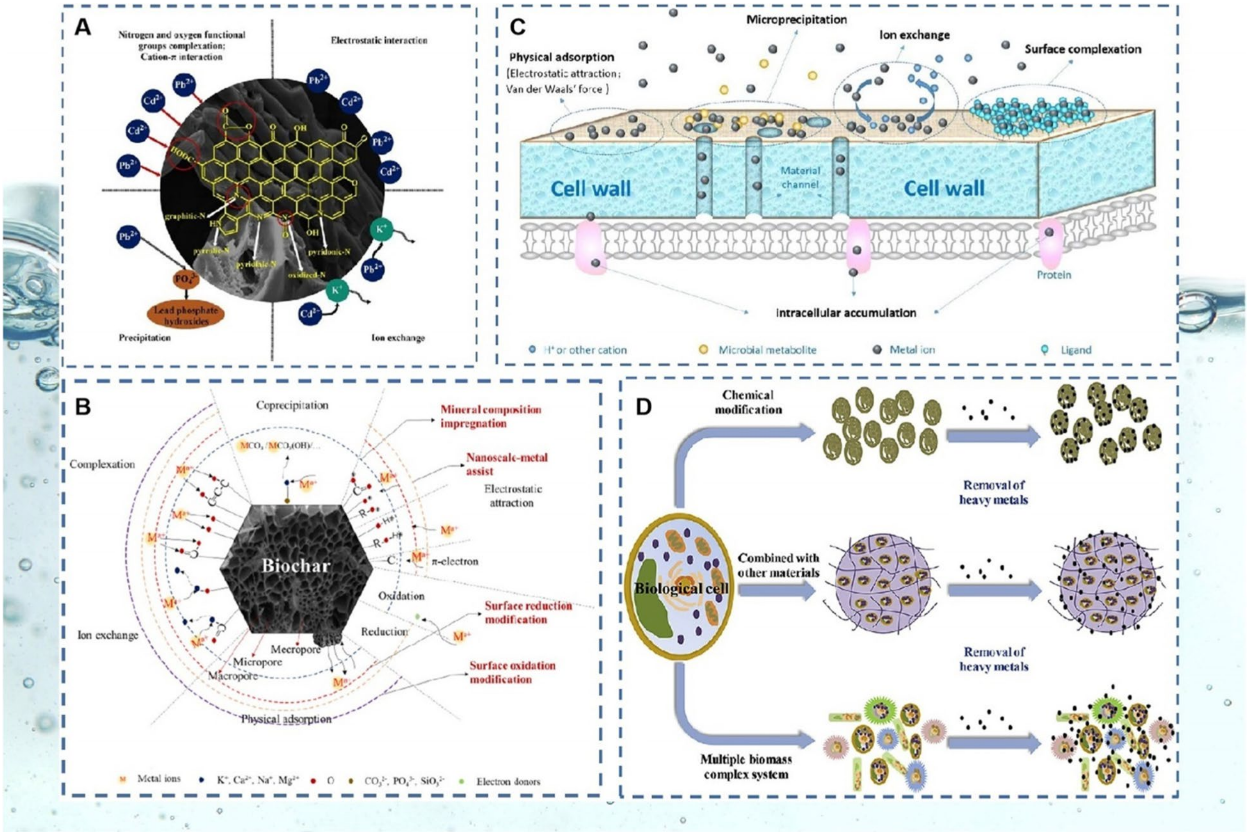

Fig. 9 **A**. **B**. The main mechanisms of biochar adsorption of heavy metals in water (Chen et al. 2021; Wang et al. 2019b) Reproduced with permission from Elsevier, Copyright ©2021,2019. **C**. Adsorption mechanism of biological cells for heavy metals removal."Reproduced with permission from Elsevier, Copyright ©2020." **D**. Three novel methods for heavy metals' removal: chemical modified biomaterial; chemical and biomass material composites; multiple biomass system. (Qin et al. 2020) "Reproduced with permission from Elsevier, Copyright ©2020."

poplar sawdust biochar by co-pyrolysis of $FeCl_3/CaCl_2$ mixed molten salt. Fe_2O_3 generated in-situ made biochar superparamagnetic, which was beneficial to biochar recycling. The results showed that the low-cost and reusable Fe_2O_3/biochar had the potential for efficient and fast removal of antibiotics in water. The efficient elimination of metal ions from wastewater using biochar is generally attributed to the high sorption ability. The surface functional groups form strong inner-sphere surface complexes with metal ions. Some kinds of modified biochar could reduce the metal ions from high valent to low valent, and thereby can form solidification on biochar. The magnetic biochar could be separated from a large volume of aqueous solutions easily using magnetic separation method. Overall, the biochar is a promising material in wastewater treatment in real applications. Biochar could not only preconcentrate metal ions, but also solidify the metal ions and thereby immobilize the movement of metals in environment.

1.5.2 Mechanism of soil heavy metal pollution treatment by modified biochar

As the most common soil pollution problem, heavy metal pollution has attracted wide attention all over the world. A large number of studies showed that biochar could effectively fix metals in contaminated soils due to its large surface areas, rich binding sites and functional groups. Therefore, the use of biochar in soil remediation has become the consensus of more scientists and environmental remediation enterprises. The characteristics of biochar are restricted by the raw materials in production or source of raw materials, as well as the pyrolysis conditions, resulting in differences in pH values, organic carbon contents, cation exchange capacities (CEC), microporous structures, SSA, mineral contents, active sites and functional groups. These differences, combined with the differences in soil properties, will affect the metal mobility and bioavailability of metals by biochar. This

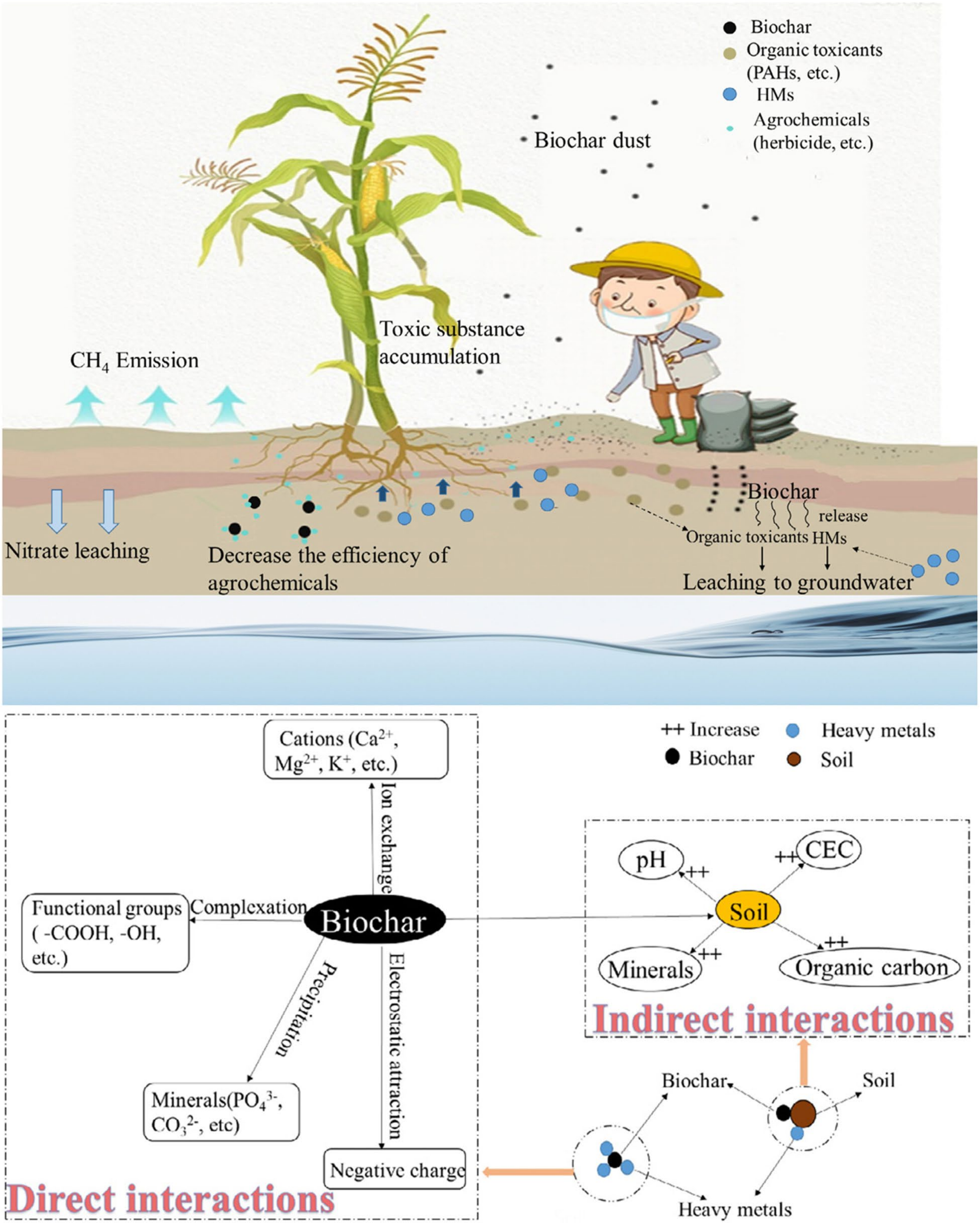

Fig. 10 Biochar-heavy metal interaction mechanism in soil (He et al. 2019) "Reproduced with permission from Elsevier, Copyright ©2019."

makes it difficult to predict and understand the mechanism of metal-biochar interaction in different soils. The effects of biochar on the mobility and bioavailability of metals in soils are as follows: (1) direct interactions between metals and biochar, including electrostatic attraction, ion exchange, complexation and precipitation; (2) affecting soil properties, thereby indirectly affecting the availability of metals in soil, that is, indirect interactions (Fig. 10) (He et al. 2019).

The mechanism and function of biochar sorption and fixation of heavy metal ions (Cd(II), Pb(II), Cu(II) and Ni(II)) in acid soil were studied. It was found that the fixation ability of biochar to soil heavy metals was related to the surface functional properties and structures of biochar and soil. The content and type of surface functional groups of biochar are the key factors for the fixation of heavy metals (Uchimiya et al. 2010). When biochar was added to alkaline soil with high clay content and acidic soil with erosion, it showed that the sorption mechanism of Cu(II) ions in the soil by biochar was mainly electrostatic sorption, and the mechanism of action was the surface complexation and precipitation of functional groups and free π electrons on the surface of carbon materials and Cu(II) ions (Uchimiya et al. 2012). 3% and 5%(W/W) rice biochar were mixed with soil, and it was found that the amount of negative charge in soil increased with the addition of biochar, and the surface complexation of rice biochar increased the sorption capacity of soil to Pb(II) ions (Jiang et al. 2012). For Cr(VI) ions, the key factor of Cr(VI) sorption by biochar is that the oxygen-containing functional groups reduce Cr(VI) to Cr(III). The positively charged Cr(III) ions form a strong electrostatic bond with the negatively charged active sites of biochar, hence achieving the in-situ fixation of Cr(III). In conclusion, the biochar could adsorb Cr(VI) ions with high sorption ability. The Cr(VI) is reduced to Cr(III) and then Cr(III) could form precipitate easily (Qiu et al. 2021). The sorption-reduction-solidification strategy is a suitable method to immobilize heavy metal ions in pollution treatment (Hu et al. 2020; Hao et al. 2022). The mechanisms of heavy metal sorption by bacteria include intracellular, extracellular and cell surface sorption (Fig. 11). Intracellular sorption occurs when heavy metal ions are transferred onto certain organelles to form precipitates or other bioaccumulation. Extracellular sorption is mediated by exopolysaccharides (EPSs) such as glycoproteins, lipopolysaccharides, and soluble polypeptides. Cell surface sorption is generated through the interaction of heavy metal ions with negatively charged groups on EPSs or peptide / protein functional groups on the cell wall. Among the above methods, cell surface sorption is considered the most promising heavy metal sorption technique (Wang et al. 2021).

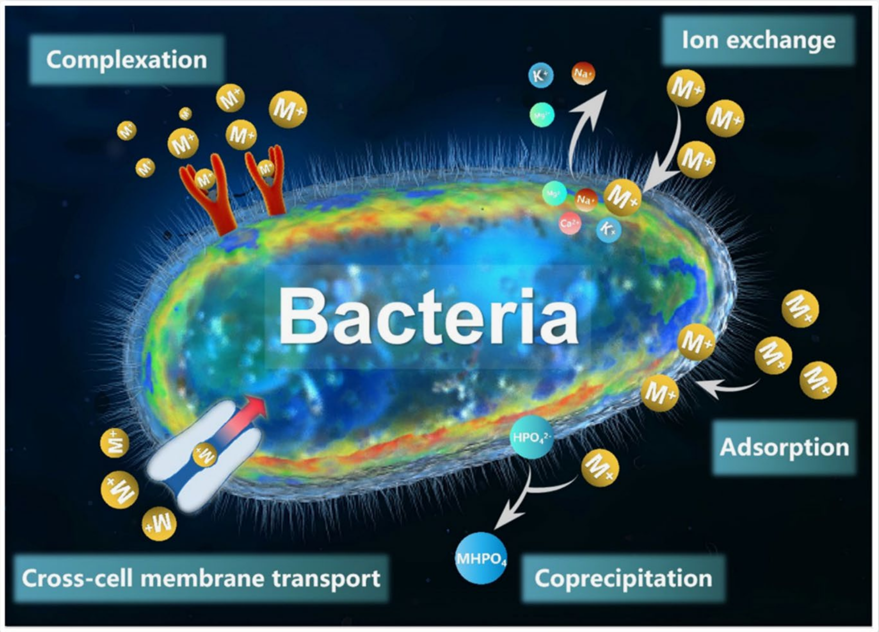

Fig. 11 The mechanisms of microbial adsorption of heavy metals. (Wang et al. 2021)

2 Conclusion and perspective

In conclusion, physical, chemical and biological modifications can increase the specific surface areas, active sites, pore volumes and functional groups of biochar, thereby enhancing the sorption and fixation, and catalytic reduction/degradation of heavy metals and organic contaminants in the environment, as tabulated in Table 1. It is of great significance to construct new modified biochar with environmental protection and strong sorption capacity, and to study its fixation ability of heavy metals in soils, water and its mechanism for the remediation of heavy metals in the environment and the application of biochar. Although a large number of researches have been carried out on the sorption of heavy metals in water and soil by modified biochar, they are usually limited to laboratory studies. The complex raw materials and high production cost limit the large-scale application of modified biochar. Due to the high cost of synthesis and the possibility of secondary pollution caused by the use of chemical products, the current modification methods are difficult to be popularized and have low practical application value. Therefore, to find an efficiency modified biochar with low cost and low secondary pollution is a problem to be solved in the industrialization of modified biochar.

Supplementary Information

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Additional file 1. TOC.

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Authors' contributions

Zhixin Liu: investigation, writing original draft; Ziyi Xu: Investigation; Linfeng Xu: Investigation; Faeiza Buyong: review & editing; Tay Chia Chay: review, investigation; Zhuang Li: investigation; Yawen Cai: investigation; Baowei Hu: investigation; Yuling Zhu: investigation; Xiangke Wang: writing, review & editing. All authors read and approved the final manuscript.

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Availability of data and materials

Authors can confirm that all relevant data are included in the article.

Declarations

Ethics approval and consent to participate

No.

Consent for publication

Agree.

Competing interests

Xiangke Wang is an editorial board member for Carbon Research and was not involved in the editorial review, or the decision to publish, this article. All authors declare that there are no competing interests.

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