



REVIEW

Removal performance, mechanisms, and influencing factors of biochar for air pollutants: a critical review

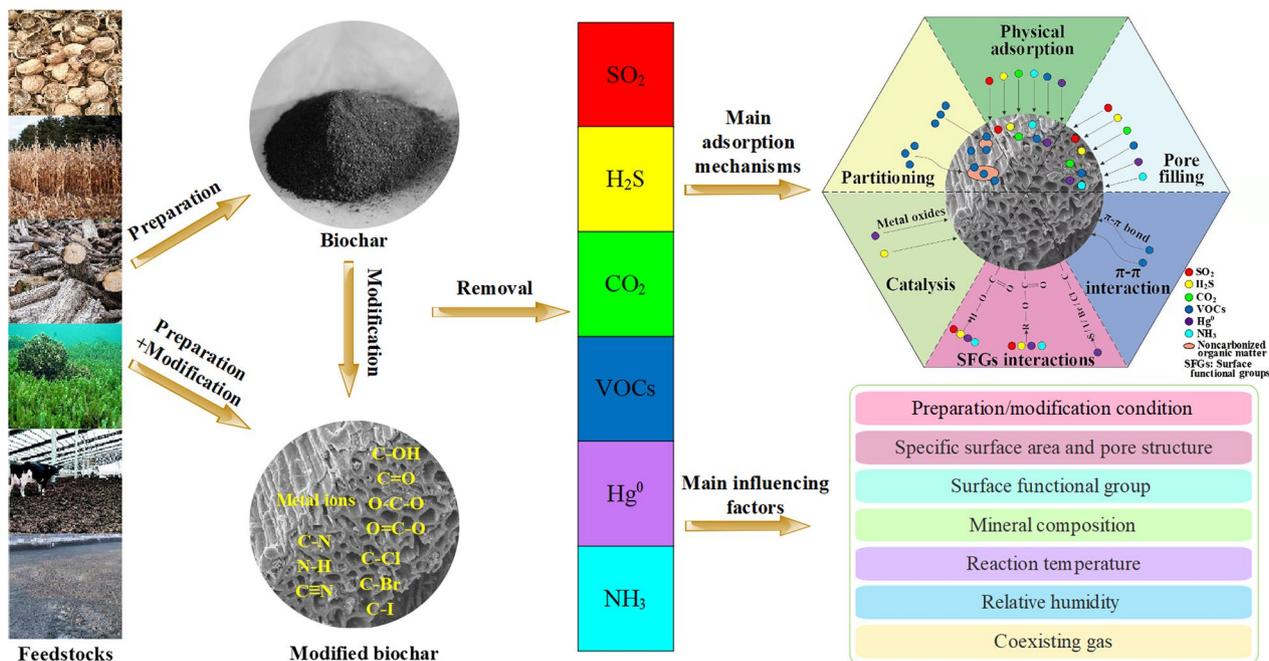
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Abstract

The emission of air pollutants from various industries is a major contributor to environmental pollution. The removal of these pollutants before they are discharged into the environment has become an important means of controlling air pollution. Biochar has attracted increasing attention because of its low cost, high porosity, large specific surface area, abundant surface functional groups, and high removal capacity. The physicochemical properties of biochar are greatly affected by feedstock types, preparation, and modification conditions. For this reason, the capacity and propensity of biochar for removing air pollutants are rather variable. To understand the existing research status and grasp the latest research progress, a systematic review on the removal of different air pollutants by biochar is highly needed. Based on the recent research, this paper systematically analyzes and summarizes the preparation and modification methods of biochar commonly used for the removal of six air pollutants (SO₂, H₂S, CO₂, Hg⁰, VOCs, and NH₃), as well as the removal performance and mechanisms. Then, the potential influencing factors (preparation parameters, physicochemical characteristics of biochar, and removal conditions) are discussed. Finally, the regeneration of biochar, suggestions, and future perspectives are proposed.

Graphical Abstract



Extended author information available on the last page of the article

Highlights

1. Common preparation and modification methods of biochar for removing air pollutants are introduced.
2. Removal performance and mechanisms of biochar for air pollutants are discussed.
3. The influencing factors and regeneration methods of biochar for the removal of air pollutants are explored.

Keywords Biochar · Modification · Air pollutants · Removal performance · Removal mechanisms · Influencing factors

1 Introduction

The large-scale exploitation and combustion of fossil fuels, as well as agricultural and animal husbandry production, have produced a variety of air pollutants that are harmful to the global environment and human health. Carbon dioxide (CO₂), sulfur dioxide (SO₂), hydrogen sulfide (H₂S), elemental mercury (Hg⁰), volatile organic compounds (VOCs), and ammonia (NH₃) are common air pollutants emitted in large quantities, mainly from industrial production, which not only pollute the environment, but also threaten human health (Niu et al. 2017; Vikrant et al. 2017; Zhang et al. 2017a; Kung et al. 2019; Kumar et al. 2020). Thus, a variety of measures have been developed to control and mitigate pollution by the aforementioned gases. In the case of SO₂, the removal methods include flue gas desulfurization (Abdulrasheed et al. 2018) and wet washing (Illingworth et al. 2019). H₂S can be treated by wet oxidation, scrubbing (Liu and Wang 2019), biological oxidation (Peluso et al. 2018), and adsorption (Sahota et al. 2018). CO₂ can be removed by adsorption (Mohd et al. 2013). As regards VOCs, the commonly used methods are biodegradation and oxidation technology (Shen and Zhang 2019). Besides, some general methods are used to remove different air pollutants, such as membrane separation method for removing H₂S and CO₂ (Rezazakemi et al. 2014; Peluso et al. 2018), absorption method for removing CO₂ and VOCs (Li and Kang 2019; Shen and Zhang 2019), and catalytic method for removing H₂S, CO₂, Hg⁰, and NH₃ (Zhang et al. 2014a, 2020a; Vikrant et al. 2017; Sahota et al. 2018; Xiong et al. 2018). Adsorption method is widely used in the removal of air pollutants. The use of chemicals and catalysts, however, can increase costs and lead to secondary pollution and equipment corrosion. Biological control processes are slower to operate than their chemical equivalents, and often require elevated environmental conditions. In this respect, adsorption techniques have attracted a great deal of attention because of their relatively low cost and energy requirement, simple and clean operation (Du et al. 2019), as well as the good removal efficiency under low air pollutant concentration (Vikrant et al. 2017).

Air pollutants can be removed by adsorption to activated carbon, activated carbon fibre, carbon nanotubes, graphene

and its derivatives, nanomaterials, polymers, metal–organic frameworks, and biochar (Liu et al. 2020; Wang et al. 2020b). Among these adsorbents, activated carbon is the most widely used, but its large-scale application can still be limited by high cost (\$1100–1700/t) (Li et al. 2016a; Fdez-Sanromán et al. 2020). It is necessary to develop low-cost adsorbents that can efficiently remove air pollutants from the environment.

Biochar is a porous and carbon-rich material obtained by pyrolysis of biomass under limited oxygen supply conditions (Lehmann 2007; Gaunt and Lehmann 2008). Due to its desirable properties, such as low cost (\$90–1200/t) (Fdez-Sanromán et al. 2020), potential high adsorption capacity, enriched surface functional groups (SFG), large porosity and specific surface area (SSA) (Sun et al. 2017), biochar has been widely used for soil amendment (Yang et al. 2017a; Wang et al. 2019), nutrient recovery and heavy metal removal (Wang et al. 2015, 2018a, 2020a; Lian et al. 2019; Lucaci et al. 2019), and cultivation of microorganisms (Yang et al. 2015; Igalavithana et al. 2017).

With the aggravation of air pollution, the application of biochar in the removal of industrial air pollutants has attracted increasing attention. At present, the main research focuses on sulfur-containing gases (SO₂, COS, CS₂, and H₂S) (Song et al. 2017b; Zhang et al. 2020c), CO₂ (Igalavithana et al. 2020), toxic and harmful gases (Hg⁰, NH₃, and VOCs) (Shan et al. 2019; Krounbi et al. 2020; Xiang et al. 2020), and there are few studies on other air pollutants (e.g., NO_x and ozone). However, the removal capacity of biochar for air pollutants of different properties is quite different, as well as the factors affecting the removal performance. Previous studies on the removal of biochar for some air pollutants have been summarized by several reviews (Zhang et al. 2017b; Bamdad et al. 2018b; Dissanayake et al. 2020b; Liu et al. 2020; Gwenzi et al. 2021). However, due to the differences in the properties of different gases, it is necessary to compare and summarize the general regulations for the removal by biochar. Since the actual industrial waste gas contains a variety of complex components, interactions between these components may occur, which can inevitably affect the removal capacity and mechanisms of biochar. Besides that, many factors can also affect its removal

performance. However, most of the previous reviews only discussed the influence of the physicochemical properties of biochar on the removal of one or several air pollutants with similar properties, and lacked the comparison of gases with different properties. Besides, removal conditions (e.g., reaction temperature, relative humidity, and coexisting gases) are rarely discussed and compared. Therefore, based on the recent research, this review systematically summarizes the application of biochar in the removal of six common industrial air pollutants (SO_2 , H_2S , CO_2 , Hg^0 , VOCs, and NH_3). The purposes of this review are to (1) introduce the common preparation and modification methods of biochar commonly used for air pollutants removal; (2) analyze the removal performance and mechanisms of biochar for six air pollutants with different properties; (3) discuss the factors affecting the removal of air pollutants by biochar; (4) summarize the regeneration methods of adsorbed saturated biochar; (5) put forward the perspectives for future research. This review tries to outline the entire life cycle of biochar from the perspective of biochar preparation–removal application–regeneration–waste biochar reuse, which is helpful to accelerate the industrial application of biochar in flue gas terminal treatment.

2 Methods of literature search

The current research mainly searched the literature published in the Web of Science and Google Scholar. Search keywords were mainly “biochar”, “gas”, “gas pollutant”, “acid gas”, “greenhouse gas”, “flue gas”, “metals”, “ CO_2 ”, “ SO_2 ”, “ H_2S ”, “(element) mercury”, “ Hg^0 ”, “volatile organic compounds”, “VOCs”, “ammonia”, “ NH_3 ”, and “review”, using the combination of “and” and “or”, and manually screening the searched literature. Besides that, the references of searched literature were also consulted. Figure 1 shows that from 2014 to 2021, the numbers of literature on biochar and its removal of six air pollutants have shown a gradual increase. It is also found that the number of literature on SO_2 and NH_3 is less than that of other air pollutants, which requires more in-depth research.

3 Preparation and modification of biochar for the removal of air pollutants

3.1 Preparation

The feedstocks of biochar usually include agricultural waste, food residue, sludge, animal manure, invasive plants, and seaweed (Ahmed et al. 2016; Liu et al. 2018b; Feng et al. 2021c). The common preparation methods of biochar include pyrolysis, gasification, hydrothermal carbonization,

or microwave pyrolysis (Sajjadi et al. 2019) (Fig. 2). Differences in feedstocks and preparation methods can directly affect the physicochemical properties, and hence the adsorption capacities of biochar (Cha et al. 2016).

Gasification generally refers to the partial oxidation and combustion of biomass materials in the presence of a specific gas (air, oxygen, or steam) at a temperature of 600–1200 °C (Bamdad et al. 2018b; Wang and Wang 2019). Since the main product is gas, the yield of biochar is very small (Cha et al. 2016).

Hydrothermal carbonization refers to the process of immersing biomass materials in water under a certain pressure at 175–300 °C. Biochar produced by hydrothermal carbonization has relatively high SFG and acidity, while the presence of water during the process gives rise to materials with high moisture content (Ahmed et al. 2016; Rangabhashiyam and Balasubramanian 2019).

Microwaves are electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz (Huang et al. 2016). Since microwave pyrolysis can transfer energy to biomass materials quickly and evenly, the process is more efficient, easier to control, and more economical of time and energy than other carbonization methods (Huang et al. 2015; Wahi et al. 2017; Wang et al. 2017). Biochar prepared by microwave pyrolysis is also more porous and has a higher SSA (Wahi et al. 2017) and stability (Wang et al. 2017) than the material obtained by conventional pyrolysis.

Pyrolysis is a process of thermal decomposition of biomass in the absence of oxygen or at low oxygen concentration (Rangabhashiyam and Balasubramanian 2019). There are two categories of pyrolysis: fast and slow. The former is used for bio-oil and syngas production, while the latter process is conducive to biochar synthesis (Igalavithana et al. 2020). Slow pyrolysis is characterized by a relatively slow heating rate, long residence time, wide temperature range, and high product yield (Neves et al. 2011; Lian and Xing 2017). In addition, according to the pyrolysis temperature, the pyrolysis can be divided as low-temperature pyrolysis (300–400 °C), medium-temperature pyrolysis (400–500 °C), and high-temperature pyrolysis (> 500 °C) (Ahmad et al. 2021). Generally, biochar prepared under medium or low-temperature pyrolysis has hydrophobicity and contains more SFG, however, its SSA and porosity are usually low (Das and Sarmah 2015; Usevičiūtė and Baltrėnaitė-Gedienė 2020). With the increase of pyrolysis temperature, the SSA of biochar increases, the pore structure and hydrophilicity improve, but it may lead to the loss of some SFG (Usevičiūtė and Baltrėnaitė-Gedienė 2020; Ahmad et al. 2021; Song et al. 2022). Considering the yield and physicochemical properties of biochar (e.g., SSA, pore structure, and SFG), as well as cost and operating conditions, pyrolysis seems to be the most commonly used preparation method (Rangabhashiyam and Balasubramanian 2019).

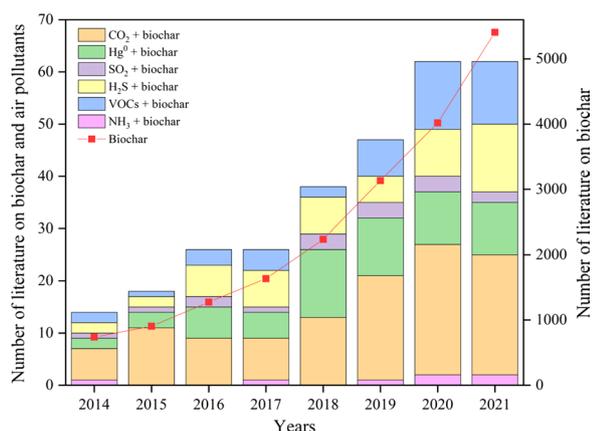


Fig. 1 The numbers of literature on biochar and its removal of six air pollutants from 2014 to 2021 (Data come from Web of Science)

3.2 Activation/Modification

To optimize the physicochemical properties of biochar to improve its removal capacity for air pollutants, it is necessary to modify biochar in a targeted manner. The commonly used modification methods include physical activation and chemical modification (Fig. 3).

Physical activation can increase the SSA, improve pore structure, and change the SFG and polarity of biochar (Wang et al. 2017; Rangabhashiyam and Balasubramanian 2019). Various processes may be used, such as gas and plasma activation, as well as ball milling (Bae and Su 2013; Sajjadi et al. 2019). Gas (steam, O₂, and CO₂) activation introduces oxygen-containing functional groups (Feng et al. 2017) and produces a large number of pores, especially CO₂ activation mainly produces micropores. But it may decrease the

polarity and aromaticity of biochar (Bae and Su 2013; Sajjadi et al. 2019; Singh et al. 2019). Gas activation has cost advantages but also some shortcomings, such as difficulty in regulating the activation temperature and insufficient activation (Wang et al. 2017). The two-step activation was used to explore the effect on the physicochemical properties of biochar. The results showed that the one-step method was conducive to the formation of SFG and chemical adsorption sites, and the two-step method was conducive to improving the pore structure of biochar (especially the formation of micropores) and promoting its aromatization (Feng et al. 2021a). On the other hand, plasma activation increases energy density and distribution, as well as enhances activation efficiency (Karim et al. 2017; Niu et al. 2017; Xu et al. 2018b). In a plasma environment, gas is ionized and recombined on the material surface, generating new chemical bonds (Zhang et al. 2020b), and causing little damage to the surface texture of the adsorbent. Moreover, plasma activation is simpler to perform than chemical impregnation, reducing cost and time, and avoiding secondary pollution (Xu et al. 2018b). Different types of gases can be used in accordance with the requirement for increasing the numbers of specific SFG (Sajjadi et al. 2019), for example, the following gases were used in Hg⁰ removal: O₂ (Luo et al. 2017), H₂O (Zhang et al. 2019b), HCl (Luo et al. 2019), Cl₂ (Wang et al. 2018b), and H₂S (Zhang et al. 2019b). Ball milling is also a good activation method capable of reducing particle size and increasing SSA (Wang et al. 2017). The ball-milled biochar can then be chemically modified to open the pore structure and supplement the SFG (Shen and Zhang 2019; Lyu et al. 2020).

Chemical modification, using acid, alkali, metal, or metal oxide, is also widely practiced (Wang and Wang 2019). The

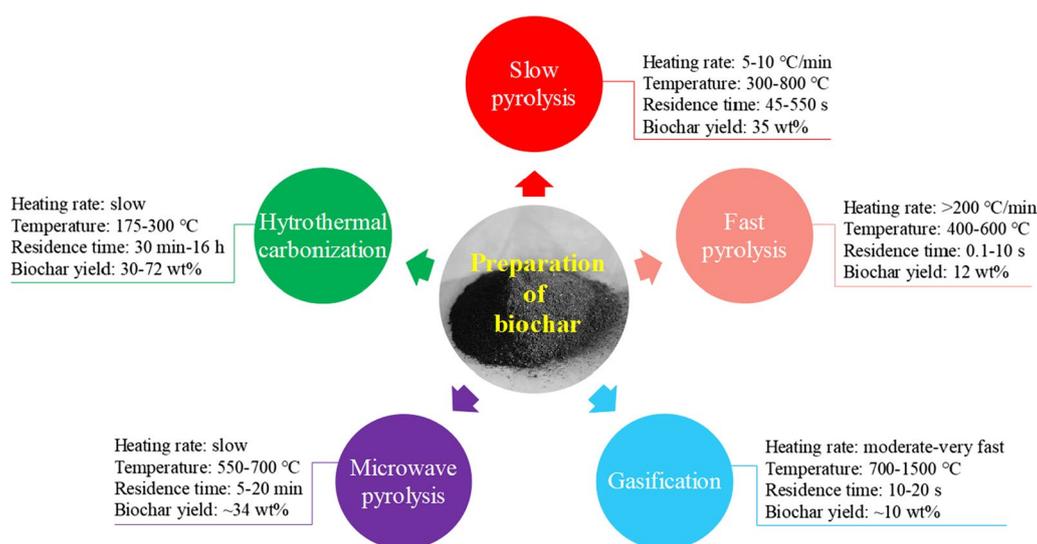


Fig. 2 Main preparation methods of biochar for air pollutants removal

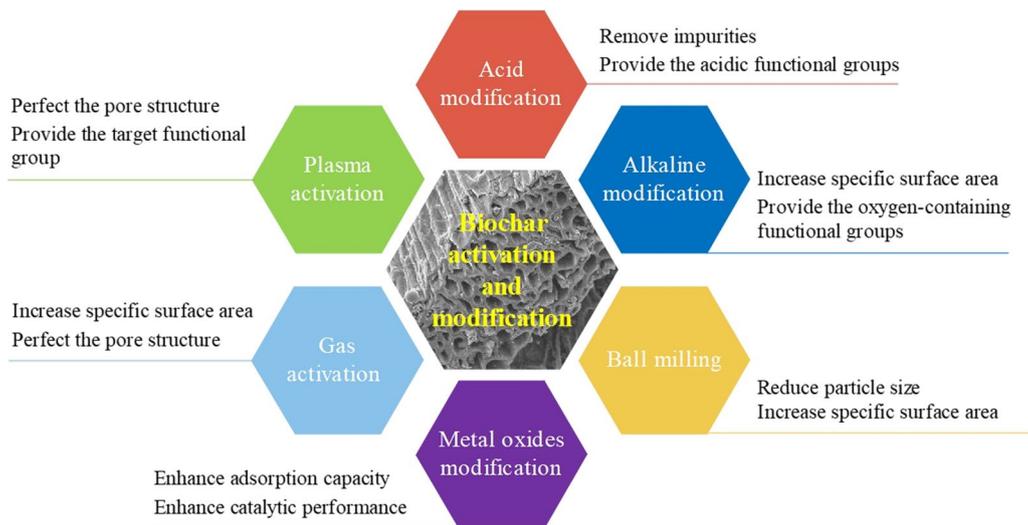


Fig. 3 Main modification methods of biochar for air pollutants removal

process promotes the formation of micropores and improves the pollutant removal performance of biochar (Song et al. 2017a). Besides increasing the numbers of acidic or basic groups on the biochar surface, acid or alkali modification changes the SSA and pore structure (Rajapaksha et al. 2016; Wang and Wang 2019). For example, KOH modification of wood chips biochar led to a ten-fold increase in SSA (Dissanayake et al. 2020a). Metal or metal oxide modification can also increase the numbers of active sites on the surface of biochar, thereby enhancing its catalytic activity (Wang and Wang 2019). However, the chemical modification does not always have a positive outcome. Al-Wabel et al. (2019), for example, found that the maximum capacity of *Conocarpus* biochar for removing CO₂ decreased from 197 to 9.17 mg/g after modification with K₂CO₃. This finding may be ascribed to pore blocking and the resultant decrease in SSA. It is therefore advisable to control modifier dosage and duration of treatment.

Physical activation usually represents low cost and simple operation, while chemical modification usually improves pore structure, increases the SSA and SFG content of biochar significantly, and is more targeted for the removal capacity, which comes with cost and additional treatment to eliminate excess chemicals (Plaza et al. 2014; Xu et al. 2016b). In brief, the relationship between cost and performance needed to be balanced when choosing the modification methods.

4 Removal performance and mechanisms of air pollutants

4.1 SO₂

SO₂ is involved in the formation of sulfuric acid smoke and acid rain. By decreasing the pH of soil and water, acid rain is deleterious to animal and plant growth (Iberahim et al. 2018). SO₂ mainly comes from the oxidation of organic matter, volcanic eruptions, as well as the combustion of sulfur-containing biomass and fossil fuels (Roy and Sardar 2015). The removal of SO₂ to biochar has attracted a great deal of attention. Table S1 shows the content and types of SFG of biochar used to remove SO₂, and Table S2 shows the physicochemical properties of biochar and its removal capacity for SO₂.

The capacity of biochar for removing SO₂ can be greatly increased by modification. Iberahim et al. (2019), for example, reported that the optimum capacity of palm oil sludge biochar for SO₂ removal increased from 9.75 to 16.65 mg/g after activation with CO₂. They suggested that the mechanism was mainly physical adsorption. Earlier, Xu et al. (2016b) measured a removal capacity of 8–16 mg/g for unmodified biochar prepared from dairy manure, sewage sludge, and rice husk. The removal performance of biochars was related to the presence of K, Ca, Fe, and other mineral species, capable of promoting the conversion of SO₂ to sulfite and sulfate. Subsequently, biochar prepared from forest wood residues removed up to 77 mg/g of SO₂ after

modification with KOH, CO₂, or steam which enhanced the concentration of SFG (C–OH, C=O, O–C–O, and O=C–O), and the removal capacity was related to the ability to oxidize SO₂ to SO₃ (Braghiroli et al. 2019).

The capacity of biochar for removing SO₂ can also be enhanced by nitrogen doping (Sun et al. 2016). Nitrogen-containing functional groups can enhance physical adsorption (van der Waals and electrostatic interactions) (Sun et al. 2016; Qu et al. 2018) as well as chemical oxidation of SO₂ (Shao et al. 2018; Zhang et al. 2020c). For corncob biochar modified with CO₂ and methyl-diethanolamine, Shao et al. (2018) found that pore structure played a crucial role in physical adsorption, while nitrogen-containing functional groups (C–N and N–H) were involved in chemical oxidation. The best removal capacity reached 156 mg/g. Subsequent XPS analysis by Zhang et al. (2020c) indicated that the adsorbed SO₂ was converted through the following sequence: SO₂ → SO₃ → SO₄²⁻.

In short, the removal of SO₂ by biochar is effected through a combination of oxidation and physical adsorption (electrostatic and van der Waals interactions) (Fig. 4), and its dominant mechanism depends on the SSA, SFG, and pore structure of biochar (Fig. 5).

4.2 H₂S, COS, and CS₂

H₂S is mainly generated during biogas production, fossil fuel combustion, and landfill (Peluso et al. 2018; Li et al. 2019; Liu et al. 2019). H₂S is highly toxic, which may corrode equipment and deactivate industrial catalysts, and has adverse effects on human health (Shang et al. 2016b; Zhang et al. 2017a). The use of biochar as an adsorbent of H₂S has been widely reported. Table S2 gives a summary of the removal data.

COS and CS₂ are toxic and harmful air pollutants generated during the production and transportation of fossil fuel and calcium carbide (Sun et al. 2014; Song et al. 2017b). Besides polluting the environment, these gases can poison the catalyst used in the industrial production (Sun et al. 2014). COS and CS₂ are commonly removed by adsorption (Xie et al. 2011) and catalysis (Zhou et al. 2020). Since the latter process gives rise to H₂S, there is a need to develop a biochar-based adsorbent capable of removing the three gases simultaneously (Song et al. 2017b).

Raw or physically activated biochars have been used to remove H₂S. For sludge biochar activated by CO₂, Papurello et al. (2020) reported that pyrolysis temperature, residence time, and filter bed height effected removal capacity. They suggested catalytic oxidation and sulfur deposition as the underlying mechanisms. In the case of *Enteromorpha* and *Sargassum* biochar, Han et al. (2020) postulated that functional groups (C=O, C–O, and –COO) were involved in removing H₂S through acid–base

neutralization and oxidation. Earlier, Shang et al. (2013) reported that H₂S removal by biochar followed pseudo-first-order kinetic model, involving a combination of physical and chemical removal.

Shang et al. (2016b) used rice hull biochar, prepared by pyrolysis at 500 °C to remove H₂S, reporting a maximum removal capacity of 382.70 mg/g. Subsequently, Ayiania et al. (2019) used biochar which was prepared from anaerobically digested dairy fibre to remove H₂S from biogas. Removal capacity was influenced by ash content, SSA, porosity, alkalinity, nitrogen content, SFG, and mineral elements (Ca, Al, Fe, and Mg). H₂S was apparently adsorbed into micropores and catalytically oxidized to sulfur and sulfate by mineral elements and nitrogen-containing functional groups. Similar findings have been reported on the removal of H₂S from biogas and syngas (Hervy et al. 2018; Pelaez-Samaniego et al. 2018; Sahota et al. 2018). A mixture of woodchips and anaerobic digester residue was used to prepare biochar, which was then used as a filler to remove H₂S from biogas in a continuously stirred tank reactor. Relatively high pH (7.98) and humidity (80–85%) improved the removal capacity of H₂S, reaching a maximum removal capacity of 273.2 mg/g. FTIR analysis indicated that carboxyl and hydroxyl radicals were the main functional groups involved (Kanjanarong et al. 2017), and this was similar to the early research results (Shang et al. 2012). Besides that, S⁰ was formed in the oxygen-poor pores, while SO₄²⁻ was mainly associated with biochar surface sites. S⁰ may be further oxidized to SO₄²⁻ in an oxygen-rich environment (Xu et al. 2014; Kanjanarong et al. 2017), but this requires more in-depth research.

The removal of H₂S can be enhanced by increasing the surface alkalinity of biochar through alkaline metal modification. When corn stover and maple biochars were modified with FeCl₃, their H₂S removal capacities increased by 22 and 1.23 times, respectively, with the modified maple biochar showing an optimum removal capacity of 269 mg/g. This observation might be ascribed to the addition of positive charge, the increase in SSA, and the enhancement of catalytic oxidation (Choudhury and Lansing 2020). The effect of nitrogen-doping on H₂S removal was assessed by measuring the removal of waste gases from urban landfills to biochar. A maximum removal capacity of 332 mg/g was measured for the modified biochar due to an increase in SSA and SFG coupled with microbial proliferation, as well as the synergistic effect of removal and biodegradation (Qin et al. 2020). Sun et al. (2017) prepared biochar by pyrolysis of potato peel waste in a fluidized bed reactor at 8000 L/min kg and 500 °C for 5 min. In addition to significantly reducing pyrolysis time and carbon loss, H₂S was adsorbed into the biochar pores and reacted with SFG.

Besides being a good adsorbent, biochar can also be used as a carrier to catalyze the hydrolysis of COS and CS₂. Sun

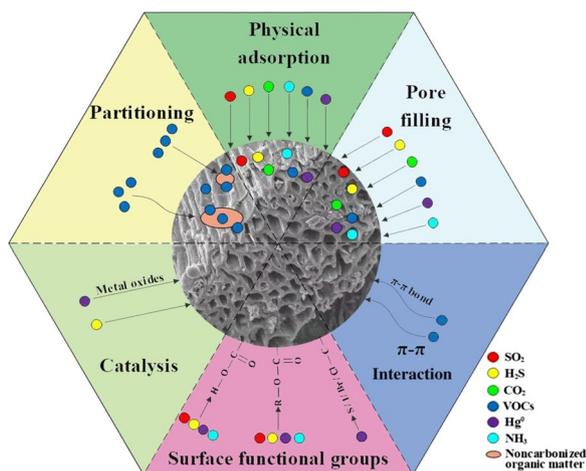


Fig. 4 Main removal mechanisms of different air pollutants by biochar

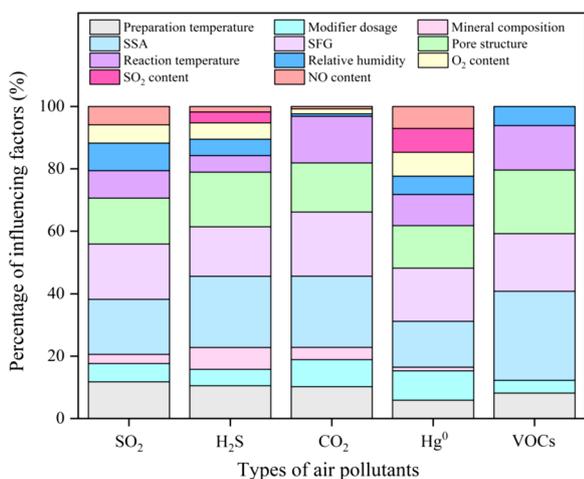


Fig. 5 Main factors affecting the removal of air pollutants by biochar and their proportions (Data come from 98 literature. There are few studies on NH₃ removal by biochar, and the data are not enough to be summarized)

et al. (2018) removed COS, CS₂, and H₂S simultaneously using a tobacco stem biochar that had been modified with CuO and Fe₂O₃, giving a maximum sulfur removal capacity of 231.28 mgS/g. They proposed that COS and CS₂ were catalytically converted to H₂S, which was then oxidized to sulfur and sulfate. Song et al. (2017b) further suggested that the C–OH promoted the removal and hydrolysis of COS and CS₂, while C=O and –COOH promoted the oxidation of H₂S. Similarly, Song et al. (2017a) investigated the catalytic hydrolysis of CS₂ and COS by walnut shell biochar after modification with four alkaline agents, reporting that hydrolysis efficiency decreased in the order: KOH > NaOH > KHCO₃ > NaHCO₃. They suggested that

KOH and NaOH reacted with biochar carbon, generating micropores while KHCO₃ and NaHCO₃ decomposed to CO₂, increasing the total pore volume (TPV) of biochar.

The H₂S removal by biochar is controlled by both physical and chemical removal (Fig. 4 and Fig. S1). The principal underlying mechanism is the conversion of H₂S into sulfur and sulfate through catalytic oxidation of SFG. The removal process is influenced by the physicochemical characteristics of biochar (SSA, micropore, and SFG) and removal conditions (humidity and oxygen) (Xu et al. 2014; Kanjanarong et al. 2017; Ayiania et al. 2019).

4.3 CO₂

The rising concentration of CO₂ in the atmosphere as a result of fossil fuel burning and land-use change is a key driver of global warming and climate change (Tate and Theng 2014; Tiwari et al. 2017). Therefore, the development of technologies for CO₂ capture and storage has become necessary (Huang et al. 2015; Chatterjee et al. 2018; Hussin and Aroua 2020).

Biochar for CO₂ removal has been synthesized using common feedstocks, such as agricultural or wood residues (Zhang et al. 2014b, 2016; Huang et al. 2015; Shahkarami et al. 2015; Creamer et al. 2016; Madzaki et al. 2016), and daily wastes (Ello et al. 2013; Lahijani et al. 2018; Wu et al. 2018). Pristine biochar has a low CO₂ removal capacity, and hence needs to be modified. The modifying agents include metal salts (Creamer et al. 2016; Lahijani et al. 2018), gases (Shahkarami et al. 2015; Zhang et al. 2016), acids (Karimi et al. 2020), and alkalis (Li et al. 2016b; Ismail et al. 2020). The research on the CO₂ removal data by different biochars has been summarized (Jung et al. 2019; Kua et al. 2019; Singh et al. 2019; Zhang et al. 2019d; Dissanayake et al. 2020b).

The capacity of carbon materials for removing CO₂ may be enhanced by alkali treatment (Chiang and Juang 2017; Ahmed et al. 2020). For example, Igalavithana et al. (2020) reported that the capacity of food waste/wood biochar for removing CO₂ increased from 114 to 141 mg/g after modification with KOH. The removal isotherm was of the Freundlich type, indicative of physical and chemical processes. In the study of CO₂ removal using coconut shell biochar, Du et al. (2019) found similar mechanisms.

The incorporation of metals or metal hydr(oxides) into biochar can also enhance its capacity for removing CO₂. Xu et al. (2020) found that incorporation of iron oxyhydroxide into ball-milled hickory chip biochar increased CO₂ removal and formation of carbonate and bicarbonate. When walnut shell biochar was impregnated with various metals, its CO₂ removal capacity was enhanced in the order: Mg > Al > Fe > Ni > Ca > Na with the Mg-loaded sample showing a capacity of 80 mg/g. Kinetic analysis indicated

that physical adsorption was the main mechanism, while the MgO formed reacted with adsorbed CO₂ to yield carbonate (Lahijani et al. 2018). More recently, Zubbri et al. (2020) used rambutan peel biochar, modified with different magnesium salts, as adsorbents of CO₂. A maximum removal capacity of 76.80 mg/g was measured and physical adsorption was suggested as the dominant mechanism.

When biochar is modified with amino compounds, its CO₂ removal capacity is enhanced through the addition of nitrogen-containing functional groups. At the same time, the surface polarity, microporosity, and alkalinity of the biochar increase (Chiang and Juang 2017; Yaumi et al. 2017; Hu et al. 2020). Xu et al. (2019b) reported that the CO₂ removal capacity of bagasse biochar, modified by ammonium hydroxide, was nearly 130% higher than that of the unmodified material. This finding was ascribed to the increased content of C≡N and –NH₂ groups, and the enhancement of SSA. Bamdad et al. (2018a) prepared biochar with sawmill residues and modified it by nitration and aminopropyl triethoxysilane. The modified biochar had a nitrogen content of 0.24 wt% and a CO₂ removal capacity of 162.8 mg/g. Similarly, Liu and Huang (2018) ascribed the high removal capacity of coffee grounds biochar, modified with KOH-treated melamine, to the increase in microporosity, and the formation of more nitrogen-containing (mainly pyrrole nitrogen) active sites.

It is generally accepted that the microporosity, SSA, and pore structure (Figs. 5 and 6) of biochar are the dominant factors affecting CO₂ capture and removal through van der Waals force, electrostatic interactions, and pore-filling (Fig. 4) (Huang et al. 2015; Bamdad et al. 2018b; Wu et al. 2018; Du et al. 2019). Even so, chemical removal through covalent bonding may occur (Ahmed et al. 2020), especially for biochar that has been modified with alkali metals, and acid–base neutralization reactions occur to produce carbonate and bicarbonate (Al-Wabel et al. 2019).

4.4 Hg⁰

Hg⁰ is released into the environment through volcanic eruption, rock weathering, and other natural phenomena. It is also emitted through coal combustion and incineration of mercury-containing waste (Johari et al. 2016). Because Hg⁰ tends to accumulate in the biosphere and is very toxic to humans, its emission needs to be controlled (Shi et al. 2020).

Biochar has great potential for removing Hg⁰. Unmodified biochars can remove a small amount of Hg⁰ through physical adsorption (Zhang et al. 2019a). On the other hand, biochars that have been modified with metal oxides and halides are good adsorbents of Hg⁰, capable of oxidizing Hg⁰ to Hg²⁺ (Yang et al. 2018b). Table S2 shows the physicochemical properties of biochar and its removal capacity for Hg⁰, and

Table S3 shows the changes in SFG of biochar before and after the removal of Hg⁰.

Metal oxide-modified biochar can remove Hg⁰ through catalytic oxidation and charge transfer (redox) reactions in which metal oxides and ions, lattice oxygen, and chemisorbed oxygen play an active role (Xu et al. 2018b, 2019c; Yi et al. 2018; Zhao et al. 2019). For example, pinecone biochar impregnated with Cu–Mn oxide can promote electron transfer between Mn⁴⁺ and Mn³⁺, and between Cu⁺ and Cu²⁺ in which adsorbed Hg⁰ is oxidized to HgO by lattice oxygen, chemically adsorbed oxygen, and oxygen in the flue gas (Yi et al. 2018). Similar mechanisms were reported by other scholars (Yang et al. 2017b; Shan et al. 2019). Zhao et al. (2019) used walnut shell biochar that has been modified with FeCl₃ alone, or in combination with CuSO₄ and KMnO₄, to remove Hg⁰ through physical adsorption and chemical oxidation, involving C=O, –COOH, metal oxides, metal ions, lattice oxygen, chemically adsorbed oxygen, and Cl[–] as well as the synergistic effect between Fe₂O₃ and CuO or CuFe₂O₄. The proposed mechanism needs to be checked as with other synergistic effects involving MnO₂ and CeO₂ (Yang et al. 2017b), CuOx and CeO₂ (Xu et al. 2018a), and MnO₂ and Fe₂O₃ (Jia et al. 2018). More recently, Shi et al. (2020) prepared biochar by co-pyrolysis of rice straw and CaCO₃, the ‘hierarchical’ biochar was not only more effective than the conventional one but also showed a better anti-interference ability against SO₂ and H₂O. To solve the problem of adsorbent separation and recovery, Xu et al. (2019c) synthesized magnetic biochar by one-step pyrolysis of Fe(NO₃)₃, loaded wood, and polyvinyl chloride. Besides having good magnetic properties, the product had a large SSA and contained more C=O groups.

Halide modification can generate covalent-bonded halide on the biochar surface which can function as active sites in the oxidation of adsorbed Hg⁰. The underlying mechanism is the conversion of adsorbed Hg⁰ to HgX, which is then oxidized to HgX₂, where X denotes Cl, Br, or I (Xu et al. 2018b). Using *Sargassum* biochar, modified with NH₄Br, Yang et al. (2018d) showed the existence of C–Br, C=O, and Hg²⁺. In the meantime, Xu et al. (2019a) investigated the removal of Hg⁰ by *Enteromorpha* biochar modified with NH₄Cl and NH₄Br. The NH₄Br-modified biochar was a better adsorbent of Hg⁰ than that modified with NH₄Cl. The performance of halide-modifying agents with respect to Hg⁰ removal decreases in the sequence: I > Br > Cl, presumably because the formation and content of carbon–halogen groups are influenced by the size and reducibility of the respective halide ion (Li et al. 2016a, 2017a; Liu et al. 2018b; Xu et al. 2018b; Yang et al. 2018c). Earlier, Shen et al. (2015) used HCl, ZnCl₂, and NH₄Cl to modify medicinal residue biochar. The NH₄Cl-modified biochar was a better adsorbent of Hg⁰ than its ZnCl₂[–] and HCl-modified counterparts. They

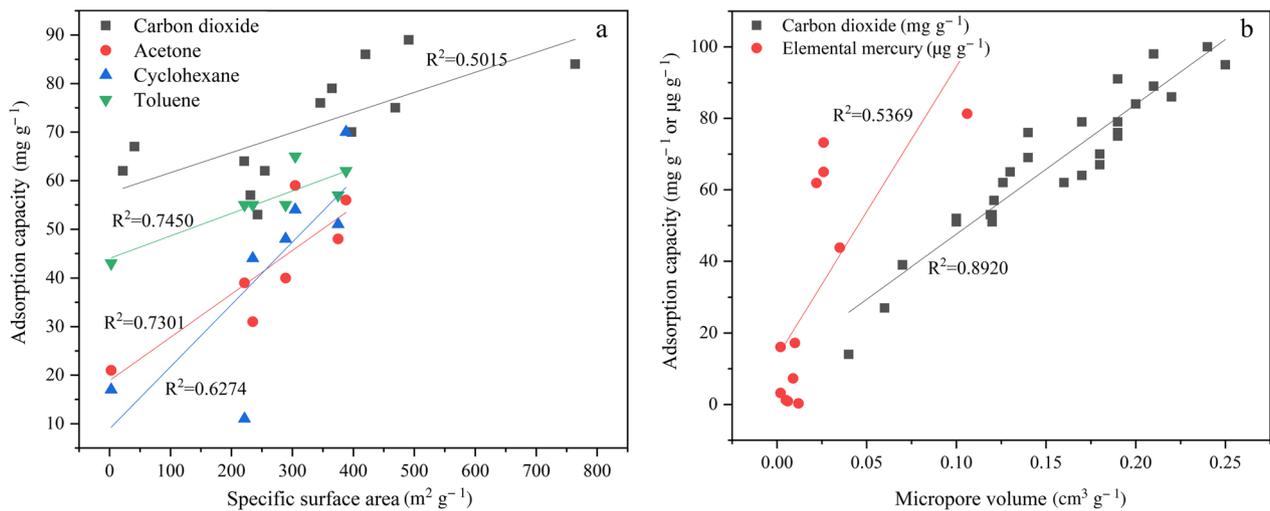


Fig. 6 a Relationship between SSA (600 °C) of biochar and its capacity for removing various air pollutants; b relationship between micropore volume of biochar and its capacity for removing CO₂ and

Hg⁰. Data from Zhang et al. 2014b, 2015b, 2016, 2017c, 2020d; Shang et al. 2016a, 2016b; Wang et al. 2018b, 2018c

suggested that the smaller particle size of NH₄Cl and the presence of N–H groups were conducive to Hg⁰ removal.

The effect of plasma modification and microwave-assisted modification on the capacity of biochar to remove Hg⁰ has also been investigated. Using H₂S plasma-modified wheat straw biochar, Zhang et al. (2019b) found that removal efficiency was greatly enhanced at 30 °C when the removal process followed both pseudo-first-order and pseudo-second-order kinetics. At 150 °C, neither model could accurately describe the removal process due to the decrease in physical and chemical removal, and the onset of partial oxidation in the gas phase. The results indicated that C–S and carboxyl groups were the main SFG involved in the oxidation of Hg⁰ to HgS and HgO. Experiments using Cl₂ plasma modification gave similar results. The number of active sites and functional groups on the surface of biochar was affected by discharge time, voltage, gas flow rate, and chlorine concentration. Besides that, the removal process conformed to pseudo-first-order, pseudo-second-order, and Elovich kinetic models, indicating that the removal process was affected by both physical and chemical removal (Zhang et al. 2019a).

To assess the similarities and differences between gas- and plasma-modified biochar to remove Hg⁰, Luo et al. (2019) prepared sorghum straw biochar modified with HCl gas and HCl plasma. Both types of biochar were able to oxidize Hg⁰ to Hg⁺, but the removal capacity of the HCl plasma-modified material was four times that of the HCl gas-modified sample. Shan et al. (2019) used microwave activation and Mn–Fe oxides to modify cotton straw biochar which was then treated with ultrasound. Microwave activation promoted pore structure development and increased SSA, while ultrasonic treatment caused the active ingredients of Mn and

Fe to disperse, yielding biochar with an optimal removal capacity of 531 µg/g.

In brief, catalysis and oxidation play an important role in the Hg⁰ removal by biochar (Fig. 4 and Fig. S2). Biochar can be modified by various means, giving rise to a variety of active sites on its surface, such as SFG, lattice oxygen, chemically adsorbed oxygen, halide ions, and metal ions, and yielding different end products (Jia et al. 2018).

4.5 VOCs

VOCs may be divided into eight categories: alkanes, aromatic hydrocarbons, alkenes, halogenated hydrocarbons, esters, aldehydes, ketones, and others. Most anthropogenic VOCs are generated during the use of fossil fuels. VOCs are important precursors in the formation of fine particulate matter, ozone, and other secondary pollutants. These substances, in turn, can cause atmospheric pollution by forming smog and photochemical smog (Ojala et al. 2011).

The removal by biochar of acetone, cyclohexane, and toluene, representing polar, non-polar, and weakly polar VOCs, respectively, has been the subject of many investigations. The physicochemical properties of biochar and its removal capacity for VOCs are shown in Table S2. For example, Zhang et al. (2019c) prepared hickory wood and peanut hull biochar to remove acetone and cyclohexane. After H₃PO₄ modification, the SSA of the two biochars increased by 155 and 180 times, respectively, and the hickory wood biochar had the largest capacity for removing acetone (147.77 mg/g) and cyclohexane (159.66 mg/g). Modification of hickory wood and peanut shell biochar with CO₂ was also conducive to acetone and cyclohexane removal because of the

accompanying increase in the SSA of the treated materials. Kinetic analysis indicated that physical adsorption played a dominant role in the VOCs removal (Zhang et al. 2020d). Using a factory-produced biochar to remove acetone, Lamplugh et al. (2020) noted that removal capacity was influenced by the SSA and average pore size of biochar, as well as the flow conditions of acetone. Kumar et al. (2020) used non-activated neem, sugarcane, and bamboo biochars to remove six different VOCs. The removal capacity was dependent on pyrolysis temperature, feedstocks, and contact time. The process followed pseudo-second-order kinetic model, suggesting that it was more consistent with chemical removal. Yang et al. (2020) used H_3PO_4 and K_2CO_3 to jointly modify waste bovine bone biochar and found that the co-modification formed a hierarchical pore structure, and greatly increased the SSA and TPV.

Regarding the removal mechanisms (Fig. 4), it is reported that physical adsorption is the main mechanism of VOCs removal on biochar, while some studies suggest that polar VOCs (acetone, ethanol, and chloroform) are physically adsorbed to the biochar surface, while non-polar and weakly polar VOCs (cyclohexane and toluene) are removed by surface adsorption and partitioning (Zhang et al. 2017c; Xiang et al. 2020). Other studies show that π - π interaction is an important biochar removal mechanism for VOCs as well, especially the removal of benzene VOCs (Sun et al. 2020; Zhang et al. 2020d; Feng et al. 2021b). Due to the variety and different properties of VOCs, the removal mechanisms of VOCs onto biochar still needs further research.

4.6 NH_3

NH_3 is a highly reactive and corrosive gas, which can damage human respiratory system. It is easy to cause serious harm when exposed to high concentration NH_3 environment for a long time (Vikrant et al. 2017). NH_3 may also be transferred to land or water through sedimentation, aggravating eutrophication (Ramlogan et al. 2020). Thus, reducing the concentration of NH_3 in the environment is conducive to human health and environmental quality. Table S2 shows the removal capacity of NH_3 on biochar.

The molecular particle size of NH_3 is about 0.3 nm, and the adsorbent with a large pore size has a weak retention effect on it (Han et al. 2021). Therefore, reducing the pore size of the adsorbent and increasing the proportion of biochar micropores are conducive to improving its removal capacity. However, studies have pointed out that, the content of acidic functional groups (such as $-SO_3H$, $-COOH$, and $-OH$) rather than the pore structure of the adsorbent plays a leading role in the removal process (Jasuja et al. 2015; Mochizuki et al. 2016; Han et al. 2021). For example, functional corn straw biochar was prepared through two-step activation to remove CO_2 and NH_3 . Although the removal

process mainly occurred in micropores with a pore size less than 7 nm, the contribution of nitrogen and oxygen-containing functional groups to the removal process was higher than that of pore structure (Feng et al. 2021a). In another study, biochar was alternately exposed to CO_2 and NH_3 for 1 h, and then used to remove NH_3 . After three consecutive exposures to CO_2 and NH_3 environment, the NH_3 removal capacity of wood chip biochar (40.57 mg/g) was 1.5 times higher than that of only one exposure. The adsorbed CO_2 by maple wood chip biochar produced carboxyl and ketone groups, which increased the adsorption affinity of biochar for NH_3 (Krounbi et al. 2020). This is because NH_3 is alkaline. Most adsorbents lack surface acidity and can only remove NH_3 through hydrogen bond, electrostatic attraction, or Lewis's base interaction, which leads to a weak removal capacity of adsorbents for NH_3 (Nijem et al. 2015; Ramlogan et al. 2020; Han et al. 2021). Thus, increasing the content of acidic functional groups on adsorbents can improve the adsorption affinity for NH_3 (Lee et al. 2017; Moribe et al. 2019; Han et al. 2021). However, it is also necessary to control the content of large volume groups, which can block the pores of the adsorbent and lead to the decline of NH_3 removal capacity (Jasuja et al. 2015).

In short, increasing the numbers of acidic functional groups on biochar can promote the removal of NH_3 , and the content of nitrogen and oxygen-containing functional groups plays a key role in the removal process (Fig. 4). Higher micropore rate can promote the pore filling effect of NH_3 . At present, the research on NH_3 mainly focuses on the study of ammonium in aqueous phase. Other materials such as zeolite and MOFs are usually used to remove NH_3 or reduce the release of NH_3 in soil or compost (Jasuja et al. 2015; Vikrant et al. 2017; Ahmad et al. 2021; Tratzi et al. 2022). There are few studies on the removal of NH_3 by biochar. Thus, the removal of NH_3 by biochar deserves further study.

4.7 Characteristics and mechanisms of air pollutant removal

Although the properties of air pollutants are quite different, as well as the removal performance of biochar for them, there are still some commonalities in air pollutant removal (Fig. 4). For example, physical adsorption and pore-filling are the basic removal mechanisms for air pollutants, which are mainly due to the electrostatic attraction and van der Waals force brought by large SSA. In addition, a good pore structure, especially a micropore, is the main active site for the removal of air pollutants on biochar. Therefore, it is necessary to find suitable feedstocks and preparation or modification methods to improve the SSA and micropore rate of biochar, which is particularly important for the simultaneous removal of a variety of air pollutants. SFG contributes to the

chemical removal of air pollutants on biochar, so the corresponding SFG can be loaded according to the acidity and alkalinity of air pollutants. For instance, basic functional groups are conducive to the removal of acid gases such as SO_2 , H_2S , and CO_2 (Sun et al. 2016; Hu et al. 2020; Qin et al. 2020), so the biochar can be loaded with $-\text{NH}_2$. On the contrary, acid functional groups are conducive to the removal of alkaline gases such as NH_3 (Han et al. 2021), thus, the $-\text{SO}_3\text{H}$, $-\text{COOH}$, and $-\text{OH}$ are good choices. Catalysis mainly occurs in the removal of H_2S and Hg^0 , which is mainly due to the modification of metals, in which H_2S can be converted into sulfuric acid and sulfate, and Hg^0 can be converted into Hg^{2+} (Yang et al. 2017b; Choudhury and Lansing 2020). Therefore, the use of metal salts or metal oxides as modifiers can increase the numbers of catalytic active sites on the surface of biochar. π - π interaction is an important removal mechanism for VOCs on biochar, especially the removal of benzene VOCs (Sun et al. 2020; Zhang et al. 2020d; Feng et al. 2021b). In addition, the partitioning of VOCs by noncarbonized substances in biochar was also reported (Zhang et al. 2017c). However, few studies have investigated the contribution of different mechanisms to the removal of air pollutants by biochar, this is worthy of further exploration.

5 Factors influencing the removal of air pollutants

5.1 Preparation parameters of biochar

The capacity of biochar for removing air pollutants is closely related to its physicochemical properties, such as SSA, pore structure, SFG, and mineral composition (Fig. 5). These properties, in turn, are related to feedstocks, preparation, and modification conditions.

5.1.1 Feedstock type and pyrolysis conditions

Feedstocks can affect the removal performance and mechanisms of pollutants by affecting the physicochemical properties of biochar. The commonly used feedstocks mainly include plants, animals, and sludge (Song et al. 2022). Previous studies have shown that biochar derived from plant often has larger SSA and better pore structure than other feedstocks, which is mainly due to the volatilization of lignin and cellulose contained in plants (Dissanayake et al. 2020b). The porosity of biochar prepared from sludge is usually the lowest, which is due to its high ash content blocking the pores (Zielińska et al. 2015). In addition, the pore size distribution of biochar prepared from different types of feedstocks is also different. For example, plant and sludge biochars have more micropores and mesopores, while animal-derived biochar is

mainly mesoporous (Song et al. 2022). Different lignin and cellulose contents in plants also affect the pore structure of biochar made from them. It is reported that the pore size of biochar prepared from feedstocks rich in lignin is often large, while that of biochar prepared from feedstocks with high cellulose content is often the opposite (Li et al. 2017b). Other studies have shown that the SSA of biochar prepared from cellulose-rich feedstocks at high temperatures is much higher than that prepared from lignin-rich ones (Meng et al. 2020).

The source and content of SFG on biochar depend on the pyrolysis temperature and feedstock type. With the increase of pyrolysis temperature, the content of SFG on biochar usually decreases (Creamer and Gao 2016; Xu et al. 2018c). This is due to the decomposition of some SFG caused by high temperatures. In terms of feedstock types, cellulose in plants can be transformed into oxygen-containing functional groups such as carboxyl or ester during pyrolysis (Poo et al. 2018). Therefore, at the same pyrolysis temperature, there are more kinds of SFG on biochar from plants (Song et al. 2022), while animal feedstocks usually contain a higher content of nitrogen, which brings more nitrogen-containing functional groups to the prepared biochar (Leng et al. 2020; Wan et al. 2020). Thus, the corresponding feedstocks should be selected according to the needs of pollutant removal.

As mentioned above, pyrolysis is the most commonly used method for preparing biochar. The pyrolysis temperature, heating rate, and residence time selected for the production of biochar have a significant impact on the physical, chemical, morphological, and other characteristics of the product, including pH, surface charge, elemental composition, ash content, volatile and fixed carbon content, SSA, thermal stability, pore structure, and SFG (Yuan et al. 2013; Chen et al. 2014; Kanjanarong et al. 2017; Singh et al. 2019). An increase in carbonization temperature increases the alkaline substances, basic functional groups, ash, fixed carbon, pH, biochar stability, SSA, and microporosity of biochar. At the same time, biochar yield, acidic and organic functional groups, H/C and O/C molar ratios, and volatile substances decrease (Al-Wabel et al. 2013; Yuan et al. 2013; Ahmed et al. 2016; Cha et al. 2016; Johari et al. 2016; Lian and Xing 2017).

The heating rate may also affect the properties and composition of biochar (Tripathi et al. 2016). A low heating rate (1–10 °C/min) is favorable to pore formation by increasing the SSA, microporosity, and TPV of biochar (Angin 2013; Chen et al. 2016; Creamer and Gao 2016; Tripathi et al. 2016). A high heating rate (10–50 °C/min) tends to produce macropores, it can even lead to pore thinning and breakage as well as to inter- and intra-particle accumulation of volatiles (Angin 2013; Chen et al. 2016; Creamer and Gao 2016). In addition, a very high heating rate (> 100 °C/min) can lead

to the crushing of biomass, reducing biochar yield (Tripathi et al. 2016). All in all, a low heating rate is preferable.

In terms of residence time, an extended one would favor feedstock reaction (Tripathi et al. 2016), and increase the SSA, TPV, and total organic carbon content of biochar (Yavari et al. 2017; Zhao et al. 2018). However, the yield of biochar prepared at low temperatures may decrease with the extension of residence time. As the residence time increased from 1 to 5 min, the yield of *Saccharina japonica* biochar prepared at 380 °C decreased from 87 to 59% (Kim et al. 2012). Generally, the influence of residence time on the pyrolysis process is inseparable from that of biomass quality, pyrolysis temperature, heating rate, and other parameters (Rangabhashiyam and Balasubramanian 2019).

5.1.2 Activation conditions

The removal capacity of biochar is affected by activator type and quantity, as well as by activation temperature and time. It is therefore important to use appropriate activation temperature and time in preparing biochar to optimize its removal capacity (Zhang et al. 2019d; Ding and Liu 2020). Low temperature and short activation time may lead to incomplete activation, while too high a temperature or long activation time may change the structure of biochar, cause SFG decomposition, or decrease biochar yield (Song et al. 2017a; Zhang et al. 2019d). Using palm oil sludge biochar activated with CO₂, Ibrahimi et al. (2019) observed that its capacity for removing SO₂ increased continuously with a rise in activation temperature from 300 to 600 °C, and then declined as the activation temperature was further increased. Similarly, the removal capacity of SO₂ increased when the activation time increased from 30 to 60 min but then declined after 90 min. Thus, the various activation parameters need to be adjusted to conditions.

5.1.3 Other influencing factors

Although N₂ is the carrier gas of choice for pyrolysis, CO₂ has been used for this purpose. Indeed, biochar pyrolyzed under CO₂ has a larger SSA, TPV, and microporosity than its counterpart prepared using N₂ (Fan et al. 2018; Liu et al. 2018a; Kim et al. 2019). Kim et al. (2019) found that the SSA and TPV of oak biochar, pyrolyzed under CO₂ were twice as large as the values measured for the sample under N₂. However, CO₂ promoted the VOCs release from biomass during pyrolysis. Thus, the use of CO₂ as carrier gas needs further research.

5.2 Characteristics of biochar

SSA, pore structure, SFG, and mineral composition are important factors influencing the capacity of biochar for

removing air pollutants. The first two parameters play a part in the physical and chemical removal of air pollutants, while SFG and mineral constituents promote chemical conversions.

5.2.1 SSA

Figure 6a shows the relationship between the SSA of biochar and the removal capacity for several air pollutants. It can be found that SSA has a great impact on the removal of air pollutants by biochar. The larger the SSA, the greater the numbers of active sites capable of removing air pollutants (Zhang et al. 2017b). It was reported that, the capacity of rice hull biochar for removing H₂S rose from 2.09 to 382.70 mg/g with an increase in SSA from 4.35 to 115.49 m²/g (Shang et al. 2016a). Similar results were reported for CO₂ removal (Zhang et al. 2015b; Gargiulo et al. 2018).

We should mention, however, that the positive correlation of SSA with removal capacity does not always hold. Shang et al. (2016a), for example, measured an H₂S removal capacity of 54.60 mg/g for camphor biochar with an SSA of 22.6 m²/g, while the SSA was 17.1 m²/g, the corresponding value was 109.3 mg/g. A similar relationship between removal capacity and biochar SSA was found in the removal of Hg⁰ (Xu et al. 2018c). These findings indicate that the removal of air pollutants by biochar is affected by factors other than SSA.

5.2.2 TPV and pore structure

TPV and pore structure also influence the capacity of biochar for taking up air pollutants. The larger the TPV, the greater the numbers of active adsorbing sites (Johari et al. 2016; Dissanayake et al. 2020b). Although some macromolecular VOCs may be adsorbed in the mesopores of biochar, mesopores and macropores mainly function as diffusion channels while micropores provide the active sites for physical adsorption and chemical conversions (Zhang et al. 2017b; Wang et al. 2018c; Saha and Kienbaum 2019; Feng et al. 2021a). Figure 6b shows a good correlation of the removal capacity for CO₂ ($R^2 = 0.8920$) and Hg⁰ ($R^2 = 0.5369$) with micropore volume for various biochars. Braghiroli et al. (2019) suggested that the chemical oxidation of SO₂ occurs in pores of less than 0.7 nm in diameter. On the other hand, CO₂ is largely adsorbed in pores of less than 0.5 nm in diameter at low pressure, while at a pressure of 1 bar, adsorption is largely confined to pores that are smaller than 0.8 nm (Chiang and Juang 2017). Other research found that micropores ($d < 0.7$ nm) mainly provided active sites for the removal of CO₂ and NH₃ by biochar (Feng et al. 2021a). Different air pollutants have different molecular particle sizes, so it is necessary to match the adsorbent with corresponding pore size. Given

the importance of pore structure for biochar to remove air pollutants, feedstocks rich in lignin could be selected before preparation because biochar prepared from that is generally considered to have a better pore structure (Li et al. 2014).

5.2.3 SFG

The function of SFG is to promote the removal of air pollutants (mainly chemical removal), and make the adsorbed gas molecules stable in biochar, so it has attracted a lot of attention (Fig. 5). The SFGs of biochar comprise oxygen-, nitrogen-, sulfur-, and halogen-containing functional groups (Zhang et al. 2017b; Igalavithana et al. 2020). The oxygen-containing functional groups include carboxyl, lactone, phenol, hydroxyl, carbonyl, ketone, pyrone, and chromene (Saha and Kienbaum 2019; Sajjadi et al. 2019; Dissanayake et al. 2020b). Ketone, pyrone, and chromene functional groups contribute to the surface basicity of biochar, promoting the removal of acidic air pollutants, while acidic functional groups such as carboxyl, hydroxyl, and carbonyl promote the removal of CO₂ and phenol by enhancing hydrogen bonding between CO₂ and adsorbent, and strengthening the electrostatic interaction between phenol and adsorbent (Chiang and Juang 2017; Saha and Kienbaum 2019; Dissanayake et al. 2020b; Feng et al. 2021b). Acidic functional groups can also promote the hydrophilic VOCs removal, the absence of them would facilitate the removal of hydrophobic VOCs (Li et al. 2011; Zhang et al. 2017b). On the other hand, oxygen-containing groups promote the oxidation of adsorbed SO₂, H₂S, and Hg⁰ (Xu et al. 2016a; Fang et al. 2017; Song et al. 2017a; Yi et al. 2018). Nitrogen-containing groups are usually introduced by treating biochar with such agents as nitric acid, ammonia, urea, and amine (Chiang and Juang 2017; Dissanayake et al. 2020b; Feng et al. 2021a, b), common nitrogen-containing functional groups are pyridinic-N, pyrrolic-N, pyridinic-N-oxide, amine-N, etc. (Leng et al. 2020). Besides enhancing the physical adsorption of SO₂, H₂S, phenol, and CO₂ through van der Waals, electrostatic, and dipole interactions (Sun et al. 2016; Sethupathi et al. 2017; Bamdad et al. 2018a; Qu et al. 2018; Zhang et al. 2019d; Feng et al. 2021b), nitrogen-containing functional groups enhance chemical adsorption through hydrogen bonding, acid–base neutralization, and covalent bonding (Chiang and Juang 2017; Shao et al. 2018; Ayiania et al. 2019; Zhang et al. 2019d; Dissanayake et al. 2020b). It was reported that, because of the acid–base effect, nitrogen-containing functional groups can promote the removal of CO₂ more than oxygen-containing ones. Similarly, the existence of electrostatic repulsion and weak hydrogen bond interaction led to the greater effect of nitrogen-containing functional groups on NH₃ removal (Feng et al. 2021a).

Modification of biochar with halogen compounds leads to the formation of surface carbon–halogen bonds promoting

the oxidation of adsorbed Hg⁰ to Hg²⁺ (Xu et al. 2018c; Luo et al. 2019). Similarly, the basic C–S group on the surface of biochar can enhance acid–base interaction between biochar and CO₂ (Igalavithana et al. 2020), as well as the chemical conversion of Hg⁰ (Zhang et al. 2019b).

5.2.4 Mineral constituents

Metal elements in feedstocks can be added to, or incorporated into biochar during the modification process (Wang and Wang 2019). Common metal elements are Na, Mg, K, Ca, P, Fe, and Al, while differences in type and content are related to the feedstocks (Skerman et al. 2017; Xu et al. 2017). By increasing the alkalinity of biochar, alkali metals can facilitate the removal of acidic air pollutants (Xu et al. 2017; Lahijani et al. 2018), and stabilize the adsorbed air pollutants by forming various metal salts. For example, mineral components can react with adsorbed SO₂ and H₂S to generate various sulfites and sulfates (Xu et al. 2014, 2016b; Hervy et al. 2018; Papurello et al. 2020), or react with adsorbed CO₂ to form various carbonates and bicarbonates (Xu et al. 2016c; Al-Wabel et al. 2019). Xu et al. (2016b) found that the chemical conversion of SO₂, promoted by the inherent mineral components of biochar from cow manure, sludge, and rice husk, accounted for 44–86% of the total amount of adsorbed SO₂. The addition and incorporation of mineral elements and salts would stabilize the structure of biochar, an important feature in using biochar for soil remediation. By the same token, care should be taken in using biochar derived from feedstocks that contain heavy metals.

5.3 Removal conditions

5.3.1 Reaction temperature

The reaction temperature is an important factor affecting the removal of air pollutants by biochar. Low reaction temperatures tend to favor physical adsorption (Xu et al. 2016c), while high temperatures are conducive to chemical adsorption (Zhao et al. 2019). Excessively high temperatures, however, may destroy the pore structure and active sites of biochar (Zhao et al. 2019). They may also intensify the thermal motion of gas molecules, reducing their adhesion to the biochar surface. As a result, chemical adsorption is inhibited and adsorption capacity decreases (Yang et al. 2016; Xu et al. 2018c; Ding and Liu 2020). For example, Chatterjee et al. (2018) reported that the removal capacity of pine biochar for CO₂ increased from 58.08 mg/g at 25 °C to 89.76 mg/g at 70 °C, and then decreased to 48.4 mg/g at 90 °C. The increase of removal capacity in the initial stage was related to the high activation energy required for

chemical reactions, and the subsequent decrease was due to the decrease in physical adsorption. The reaction temperature for optimal removal varies with the type of air pollutants. The parameter is relatively high for H₂S (Han et al. 2020), SO₂ (Iberahim et al. 2019; Zhang et al. 2020c), and Hg⁰ (Li et al. 2017a; Yi et al. 2018), but low for VOCs (Zhang et al. 2020d), CO₂ (Chatterjee et al. 2018; Wu et al. 2018), and NH₃ (Ramlogan et al. 2020).

The optimal reaction temperature for the removal of air pollutants by biochar is not only affected by the removal mechanisms, but also by the properties of gas molecules (e.g., molecular diameter). This is mainly reflected in the research on VOCs. It was reported that the removal capacity of biochar for acetone decreased as the temperature increased (Zhang et al. 2017c, 2020d), while for cyclohexane, it increased firstly and then decreased. It was attributed to the difference in molecular diameter between the two gases. Increasing the temperature was conducive to the diffusion of the larger-diameter gas molecules in the pores of the biochar, thereby promoting the increase in the removal capacity of cyclohexane (Zhang et al. 2020d).

5.3.2 Relative humidity

Relative humidity also influences the removal of air pollutants by biochar. Here again, its effect varies with air pollutant type. For SO₂, H₂S, NH₃, and CO₂, low relative humidity is conducive to the removal. In that instance, SO₂ and H₂S can react with O₂ and H₂O to form sulfite and sulfuric acid (Xu et al. 2014, 2016b), while CO₂ can transform into bicarbonate and carbonate (Xu et al. 2016c). The presence of water molecules can dissociate the acidic groups on the surface of the adsorbent and protonate NH₃, thus promoting the removal of NH₃ (Khabzina and Farrusseng 2018). At high relative humidity, H₂O and air pollutants compete for adsorption sites (Iberahim et al. 2019). A water film may also form on the surface of biochar impeding pollutant diffusion, and inhibiting the removal (Sun et al. 2018). For example, Iberahim et al. (2019) measured SO₂ removal capacity of 16, 37, 29, and 23 mg/g by palm oil sludge biochar at a relative humidity of 0, 15, 30, and 60%, respectively. Similar findings have been reported for SO₂ (Xu et al. 2016b; Zhang et al. 2020c), H₂S (Sun et al. 2018; Han et al. 2020), NH₃ (Seredych et al. 2016), and CO₂ (Xu et al. 2016c).

However, relative humidity has a negative impact on Hg⁰ removal by biochar, which may be because Hg⁰ cannot react with H₂O under normal conditions. At low relative humidity, Hg⁰ and water compete for adsorption sites, while at high relative humidity the removal of Hg⁰ is blocked by a water film (Xie et al. 2015; Xu et al. 2018a; Zhou et al. 2019). It was reported that, when the water content increased from 0 to 8%, the capacity for removing Hg⁰ by rice straw biochar decreased from 93 to 60% (Xu et al. 2018a). However,

other studies reported that, because of the generation of OH radicals, low concentrations of H₂O (1%) could oxidize Hg⁰ to HgO (Niu et al. 2017; Yang et al. 2017b). Therefore, the removal mechanisms of Hg⁰ under low relative humidity are worthy of further study.

5.3.3 Coexisting gases

The influence of O₂, SO₂, and NO on the removal of air pollutants by biochar is expressed through oxidation and competition. An example of the latter case is the inhibition of SO₂ removal by O₂. Zhang et al. (2020c) observed that the removal capacity of corncob biochar for SO₂ decreased from 185 to 145 mg/g when the O₂ content increased from 0 to 14%. This finding might be due to the oxidation of SFG by O₂, resulting in a decrease in SFG content. On the other hand, O₂ promotes the removal of Hg⁰ by biochar (Yang et al. 2018d). Xu et al. (2018a) found that when the O₂ concentration increased from 0 to 15%, the efficiency of biochar in removing Hg⁰ increased from 46 to 95%. Several studies have shown that O₂ can promote the oxidation of Hg⁰ to HgO by supplementing the surface and lattice oxygen of biochar (Zhao et al. 2016; Zhou et al. 2017; Yang et al. 2018a; Yi et al. 2018).

In the case of H₂S, the effect of O₂ content can promote the removal at low concentrations but inhibit the removal at high concentrations. For the simultaneous removal of H₂S, COS, and CS₂ by tobacco stem biochar, when the O₂ content was 0%, 0.5%, and 5%, respectively, Sun et al. (2018) measured a sulfur removal capacity of 231, 239, and 133 mgS/g, respectively. Similarly, Han et al. (2020) suggested that an appropriate O₂ content be selected for the oxidation of H₂S, and the hydrolysis of COS and CS₂. A high O₂ content would accelerate H₂S oxidation, increase the production of sulfate and other substances, deactivate the added catalyst components, and decrease the removal performance (Sun et al. 2018). Likewise, Hervy et al. (2018) found that O₂ favored the formation of acidic sulfur-rich substances, and hence reduced the capacity of food waste/coagulation–flocculation sludge biochar for removing H₂S. These observations are not consistent with the finding by Iberahim et al. (2019) that the formation of sulfuric acid from H₂S on the surface of biochar would promote the removal of air pollutants. Ding and Liu (2020) also found that the removal of CO₂ by seaweed biochar was not affected by O₂. This might be because the non-polar O₂ is very stable at room temperature, and does not compete with CO₂ for adsorption sites (Zhao et al. 2014).

Zhang et al. (2020c) investigated the effect of NO on the removal of SO₂ by corncob biochar. A removal capacity of 162 mg/g was measured without NO. The values were 216 and 182 mg/g when the NO concentration was 500 and 1000 ppm, respectively. It would appear that at low

concentrations NO reacted with SO₂, while at high concentrations NO competed with SO₂ for adsorption sites. Similarly, others found that low concentrations NO promoted Hg⁰ removal through the conversion of Hg⁰ to HgO or mercury nitrate (Li et al. 2015; Yang et al. 2018d). On the other hand, Ding and Liu (2020) found that NO does not affect the removal of CO₂ by seaweed biochar, it may be because NO did not compete with CO₂ for adsorption sites (Zhao et al. 2014).

The removal of CO₂ and Hg⁰ by biochar is also affected by SO₂. Li et al. (2015) reported that a low concentration of SO₂ (100 ppm) significantly improved the removal of Hg⁰ by medicinal residue waste biochar, while high concentrations (700 and 1000 ppm) had an inhibitory effect. At low concentrations, SO₂ is oxidized to SO₃, and further converted to H₂SO₄, which then reacted with Hg⁰ and HgO to form mercury sulfate (Li et al. 2015; Shan et al. 2019). At high concentrations, SO₂ consumes oxygen (Yang et al. 2018d) and competes with Hg⁰ for adsorption sites (Liu et al. 2012; Zhou et al. 2017). SO₂ also forms sulfate on the surface of biochar, blocking the pores, covering the active sites, and reducing the SSA of biochar (He et al. 2016; Zhou et al. 2016; Zhang et al. 2020b). SO₂ can also inhibit the removal of CO₂ by biochar. When the concentration of SO₂ increased from 0 to 1500 ppm, the CO₂ removal capacity of *Sargassum* biochar decreased from 1.05 to 1.01 mmol/g, respectively, which was due to the competition between SO₂ and CO₂ for adsorption sites (Ding and Liu 2020).

Some studies explored the interference between other different gases. On the removal of H₂S and CO₂ by biochar, when H₂S and CO₂ coexisted, the removal capacity of biochar for H₂S and CO₂ was lower than that for H₂S and CO₂ alone. It was because the removal mechanisms of H₂S and CO₂ on biochar were similar, which could result in competitive adsorption (Sethupathi et al. 2017). Bhandari et al. (2014) explored the removal effect of NH₃, H₂S, and toluene by switchgrass biochar through a fixed bed experiment. The results showed that under separate removal, the breakthrough time of NH₃, H₂S, and toluene was 100, 70, and 80 min, respectively. While NH₃ and H₂S existed simultaneously, the removal rate of toluene by biochar increased to 86.7%, which indicated that the presence of NH₃ and H₂S could promote the removal of toluene. Qin et al. (2020) used sludge modified biochar to remove syngas containing VOCs, H₂S, and NH₃. The removal rate of VOCs, H₂S, and NH₃ was between 95 and 100%. Unfortunately, most researchers did not study the mutual interference in the removal of different gases by biochar. Since these gases may exist simultaneously in industrial production, it is worth further research to clarify the actual removal capacity of biochar under a variety of mixed gases.

In brief, coexisting gases are more reflected in the combined effects of oxidation and competition at different

concentrations. Oxidation is the main reaction at low concentrations, while competitive adsorption occurs at high concentrations. The non-effect may be found in the removal of gases with different properties. However, the research on the gases that may coexist in industrial production (NH₃, HCl, NO_x, CO, VOCs, Hg⁰, and H₂S) is relatively less, which is worthy of further research.

6 Biochar regeneration

The regeneration or recycling of biochar after usage would save on production costs and open the way for the recovery of adsorbed air pollutants and the reuse of biochar. Heat treatment is the most commonly used method of recovering biochar containing adsorbed air pollutants (Table 1). For example, VOCs (toluene, ethanol, cyclohexane, chloroform, and acetone), physically adsorbed to hickory wood biochar, could be completely desorbed by heating at 60–115 °C with a removal efficiency of 80–90% being recorded after five cycles of adsorption–desorption (Xiang et al. 2020). Similarly, the wood residue biochar with adsorbed SO₂ needed to be heated at 600 °C for 1 h for its regeneration. After four thermal regeneration cycles, the removal capacity fell to 78% as compared to the pristine biochar. However, a slight increase in SSA and micropore volume was observed (Braghiroli et al. 2019). Amine-modified wood chip biochar was also regenerated at ambient temperature to remove CO₂. The CO₂ removal capacity decreased by 8 and 20% after 5 and 10 times of desorption, respectively, which indicated that the modified biochar had a better regeneration performance (Bamdad et al. 2018a).

At present, there are few studies on regeneration, especially those involving chemical adsorption. It is speculated that this may be related to the large decrease in efficiency after regeneration, and the difficulty of recovering and reusing the matters generated in the chemical adsorption process. Although increasing the temperature within a certain temperature range is conducive to desorption, this approach can destroy the active sites and SFG on the surface of the biochar (Pi et al. 2017). Current practice is to combine low-temperature regeneration with high-temperature regeneration. Shan et al. (2019) firstly heated magnetic cotton straw biochar at 400 °C for 1 h under N₂ atmosphere, and then regenerated it at 250 °C for 0.5 h under air atmosphere, to desorb Hg⁰ and supplement oxygen, respectively. After five cycles, the removal efficiency of Hg⁰ dropped to 78%, which showed a good regeneration performance. Iberahim et al. (2019) used heat treatment (200 and 400 °C) and water treatment (30 and 70 °C) to regenerate palm oil sludge biochar adsorbed with SO₂, and found that after three cycles, heat treatment at 400 °C has the best regeneration efficiency (46.3%).

Based on the existing research, it is speculated that the regeneration may be related to the removal mechanisms and the properties of air pollutants. Physically adsorbed air pollutants are usually easier to desorb than chemically adsorbed species, which means that the desorption of physically adsorbed gas requires lower temperature and shorter time, as well as higher removal efficiency after regeneration, while chemically adsorbed ones are just the opposite. The reasons for those differences may be related to the properties of the gas (e.g., boiling point) and the binding energy between biochar and the gas (Zhang et al. 2020d; Gwenzi et al. 2021). Since the heat treatment of spent biochar is costly in terms of energy consumption, alternative cost-effective methods of regeneration need to be explored (Wang et al. 2020b).

At present, the regeneration process of biochar is usually carried out in a closed N₂ environment (Braghiroli et al. 2019; Shan et al. 2019), which can prevent desorbed air pollutants from returning to the atmosphere. However, there is no similar research on how to deal with the desorbed air pollutants. To realize the closed-loop treatment of air pollutants, relevant research should be further supplemented.

7 Conclusions and future perspectives

Due to its low cost and potential removal capacity, the removal of air pollutants by biochar has received extensive attention in recent years. The present review systematically summarizes the preparation and modification methods, as well as the removal performance and mechanisms, influencing factors, and regeneration of biochar for six common air pollutants. The removal performance and mechanisms of (modified) biochar for air pollutants can be affected by many factors, such as feedstocks, preparation, and modification methods, properties of air pollutants, and removal conditions. Various mechanisms are involved during the removal process, including physical adsorption, pore filling, catalysis, and oxidation together with π - π interaction and partitioning of VOCs.

Biochar has a wide application prospect in the removal of air pollutants from industrial activities. Nevertheless, there are still some issues that need to be further studied. The following points merit further assessment and examination.

1. Improving the removal capacity of biochar for specific air pollutants. The preparation and operation parameters of (modified) biochar should be further optimized based on specific requirements to achieve the best removal efficiency of air pollutants. There is also scope for exploring the dominant removal mechanisms and influencing factors, and combining adsorption with other approaches and methods, such as nanotechnology and zero-valent iron reduction technology.
2. Reducing the cost of preparing and modifying biochar. Feedstocks and modifiers should be selected based on their availability, price, and requirement for fast processing. The temperature and time in the process of preparation, modification, and regeneration should be optimized to reduce energy consumption, and methods of collecting the generated bio-oil and syngas need to be developed.
3. Regeneration and disposal of biochar. The actual application environment of biochar (single component or multi-component) determines its final disposal method. It is relatively easy to separate (desorb) sole pollutant and allow the spent biochar to be reused. On the other hand, it is problematic to regenerate biochar containing two or more air pollutants (or other pollutants, such as heavy metals, antibiotics, and other difficult-to-degrade pollutants), which limits the recovery and reuse of biochar. Efforts should be made to develop adsorbents with selective removal capacity for air pollutants, because this is beneficial to the recovery of useful components and reuse of biochar. For feedstocks containing heavy metals or toxic and hazardous substances, technologies for removing or passivating at the preparation stage should be further studied. For air pollutants that are difficult to recycle, more technologies should be studied to combine with biochar to eliminate pollutants, such as microbial degradation and photocatalytic oxidation technology. There is also a case for developing new methods of regenerating biochar to save on cost, energy, and ensure regeneration performance and stability of biochar. Regarding the disposal of waste biochar, there is a current study on using waste biochar that adsorbs H₂S to supplement the sulfur fertilizer of the soil (Kanjjanarong et al. 2017; Zhang et al. 2017a). Because of the risk of gas release during application, the final disposal of waste biochar used to remove air pollutants needs further research.

Table 1 General parameters of using thermal regeneration method to treat saturated biochar

Feedstocks	Modification conditions	Adsorbent	Regeneration temperature (°C)	Regeneration time (min)	Adsorption temperature (°C)	Regeneration cycles/Efficiency	References
Rice husk	HF	CO ₂	200	60	120	3/90%	Zhang et al. (2015a)
Rice husk	HCl+HF	CO ₂	200	60	30	3/> 90%	Zhang et al. (2015b)
Cottonwood	FeCl ₃	CO ₂	120	180	25	1/90%	Creamer et al. (2016)
Sawdust softwood	Aminopropyl triethoxysilane	CO ₂	25	–	20	10/80%	Bamdad et al. (2018a)
Pine wood	Tetraethylene-pentamine	CO ₂	180	60	70	15/56%	Chatterjee et al. (2018)
Walnut shell	Magnesium nitrate	CO ₂	120	15	110	10/> 95%	Lahijani et al. (2018)
Coffee grounds	KOH+ Melamine	CO ₂	75	30	35	10/94%	Liu and Huang (2018)
<i>Sargassum</i>	KOH	CO ₂	200	–	25	10/87%	Ding and Liu (2020)
Wood chips	KOH+ CO ₂	CO ₂	150	90	30	10/99%	Dissanayake et al. (2020a)
Food and wood waste	KOH	CO ₂	25	90	25	10/99%	Igalavithana et al. (2020)
Hickory chips	Ball-milling + FeCl ₃ ·6H ₂ O	CO ₂	125	40	25	1/> 95%	Xu et al. (2020)
Rambutan peel	Magnesium nitrate	CO ₂	110	14	30	25/> 95%	Zubbri et al. (2020)
Sugarcane bagasse	–	Acetone	150	–	20	5/~ 90%	Zhang et al. (2017c)
Hickory wood	H ₃ PO ₄	Acetone/ cyclohexane	150	–	20	5/93.8%/92.2%	Zhang et al. (2019c)
Hickory wood	Ball-milling	Ethanol/toluene	150	–	20	5/91.4%/90.5%	Xiang et al. (2020)
Hickory wood chips/peanut shell	CO ₂	Acetone/ cyclohexane	150	–	40	5/90%/83.3%	Zhang et al. (2020d)
Corn stalk	Ball-milling/H ₂ O ₂ / NH ₄ OH	Benzene/M-xylene/O-xylene/P-xylene	200	5	25	5/87.8–96%	Zhang et al. (2021)
Wheat straw	Cerium nitrate + manganese nitrate	Hg ⁰	250	30	150	10/83.9%	Yang et al. (2017b)
Rice straw	Cerium nitrate + copper nitrate	Hg ⁰	260	30	150	10/79%	Xu et al. (2018a)
Cotton straw	Ferric nitrate + manganese nitrate	Hg ⁰	400	60	120	5/78.1%	Shan et al. (2019)
White birch	Steam	SO ₂	600	60	20	6/88.4%	Braghiroli et al. (2019)
Palm oil sludge	CO ₂	SO ₂	400	40	100	3/46.3%	Iberahim et al. (2019)
Coagulation/flocculation sludge	Steam	H ₂ S	750	90	25	1/100%	Hervy et al. (2018)
<i>Sargassum</i>	–	H ₂ S	200	60	25	2/60%	Han et al. (2020)
Wood materials	–	NH ₃	25	1440	25	1/60.6%	Ramlogan et al. (2020)

“–” means “no record”

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Declarations

Conflict of interest The authors have no conflicts of interest nor competing interests to declare.

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