



Review

Biochars as media for air pollution control systems: Contaminant removal, applications and future research directions



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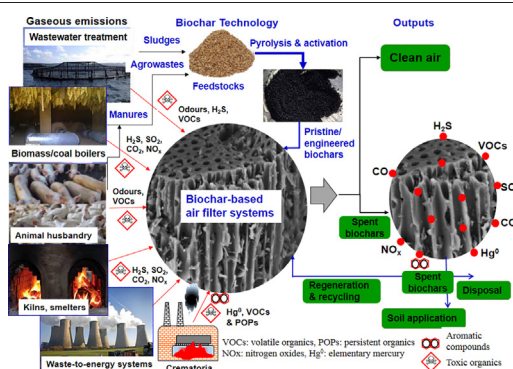
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HIGHLIGHTS

- Properties of biochars critical for removal of gaseous contaminants are presented.
- Gaseous Hg⁰, H₂S, SO₂, CO₂, NO_x, ozone, volatile organics and odours are removed.
- Removal mechanisms (adsorption, precipitation, size exclusion) are summarized.
- Biochar air filters can be used in incinerators, kilns, cremation, and smelters.
- Constraints and future directions of biochar-based air filter systems are highlighted.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochars are low-cost and renewable biomaterials with several applications, including soil amendment, mitigation of greenhouse gas emissions, and removal of both inorganic and organic contaminants in aqueous systems. An increasing body of recent evidence indicates that biochars can also remove gaseous chemical contaminants, such as those occurring in industrial flue gases. However, unlike other applications such as in agroecosystems, soil amendments, and aquatic systems, comprehensive reviews on biochar applications in the field of air pollution control are still lacking. The current paper examined existing evidence to understand the nature of contaminants, particularly the gaseous ones, potential applications, constraints, and future research needs pertaining to biochar applications in air pollution control. The preparation of biochars and their functionalized derivatives, and the properties influencing their capacity to remove gaseous contaminants are summarized. The removal capacity and mechanisms of various organic and inorganic gaseous contaminants by biochars are discussed. Evidence shows that biochars effectively remove metal vapours, particularly elemental mercury (Hg⁰), acidic gases (H₂S, SO₂, CO₂), ozone, nitrogen oxides (NO_x), and organic contaminants including aromatic compounds, volatile organic compounds, and odorous substances. The mechanisms for the removal of gaseous contaminants, including; adsorption, precipitation, and size exclusion were presented. Potential industrial application domains include remediation of gaseous emissions from incinerators, waste-to-energy systems, kilns, biomass and coal-fired boilers/cookers, cremation, smelters, wastewater treatment, and agricultural production systems including livestock husbandry. These industrial applications, coupled with the renewable, low-cost and sustainable nature of biochars, point to opportunities to further develop and scale up the biochar technology in the air pollution control

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industry. However, the biochar-based air filter technology still faces several challenges, largely stemming from constraints and several knowledge gaps, which were highlighted. Hence, further research is required to address these constraints and knowledge gaps before the benefits of the biochar-based air filters are realized.

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Contents

1. Introduction	2
2. Overview of methodology	3
3. Biochar materials	3
3.1. Nature and preparation methods	3
3.2. Properties critical for the removal of gaseous pollutants	4
3.2.1. Aromaticity and polarity	5
3.2.2. Ash, mineral content, cation exchange capacity, and surface charge	6
3.2.3. Textural properties	6
4. Biochar as air filter media	6
4.1. Inorganic pollutants	6
4.1.1. Toxic metals	9
4.1.2. Greenhouse gases	10
4.1.3. H ₂ S and SO ₂	10
4.2. Organic contaminants	11
4.2.1. Volatile organic compounds (VOCs)	11
4.2.2. Emerging contaminants	11
4.3. Mechanisms of contaminant removal	11
5. Thermodynamics, kinetics and isotherm models	12
5.1. Adsorption kinetics	12
5.2. Thermodynamics	13
5.3. Isotherm modelling	13
5.4. Biochar catalysis	14
5.5. Interactions in multi-component gaseous systems	15
6. Potential applications, regeneration and disposal	15
6.1. Opportunities and potential applications	15
6.2. Regeneration of spent biochars	16
6.3. Final disposal for spent biochars	17
7. Future perspectives	17
7.1. Constraints	17
7.2. Future research needs	18
7.2.1. Knowledge gaps	18
7.2.2. A framework for the development of biochar air filters	18
8. Conclusions and outlook	18
CRedit authorship contribution statement	19
Declaration of competing interest	19
Acknowledgements	19
References	19

1. Introduction

Industrial processes, including the combustion of municipal solid waste, biomass, and coal, release complex mixtures of chemical contaminants such as acidic gases (SO₂, HCl, HF), volatile organic compounds (VOCs), nitrogen oxides (NO_x), toxic metals (Hg, Cr, Pb), odorous compounds, dioxins and furans, poly-halogenated aromatic compounds, carbon dioxide, and carbon monoxide (Jo et al., 2011; Xiong et al., 2013; Klasson et al., 2014; Xu et al., 2016a, 2016b; Maurer et al., 2017; Wang et al., 2017a, 2017b; Zhang et al., 2017; Hwang et al., 2018; Lee et al., 2018; Braghiroli et al., 2019; Ma et al., 2019). These chemical contaminants pose significant environmental and human health risks when emitted to atmosphere, hence there is a strong need to reduce their emission. Current systems for the control of toxic flue gas emissions include the use of electrostatic precipitators, fabric filters and activated carbon injection (Yang et al., 2018). However, these methods are not effective in removing some of the toxic metal vapours such as Hg⁰. Besides, the high cost associated with these methods

(electrostatic precipitators, fabric filters and activated carbon injection) constrains their full-scale installations in large-scale commercial applications and/or systems. Recent efforts to develop effective and low-cost alternatives have focused on biochars and its functionalized derivatives (Yang et al., 2018; Bamdad et al., 2018a, 2018b).

Biochars are carbon-rich biomaterials produced via pyrolysis of biomass under high temperature and low/no oxygen (Gwenzi et al., 2017). Biochars are regarded as low-cost, renewable and sustainable biomaterials. This is because they can be produced from readily available biomass and biowaste materials as feedstock through a relatively simple pyrolysis process. Besides pristine biochars, several functionalized, modified, or engineered biochars have been prepared via physical, chemical, and thermal activation processes (Yang et al., 2018). The bulk of earlier studies focused on biochar application as a soil amendment (Wang et al., 2017a, 2017b), immobilization of contaminant removal in soils (Beesley et al., 2011), as an adsorbent for contaminant removal in aqueous systems (Alkurdi et al., 2019), and in the mitigation of greenhouse gases (Tayade et al., 2012).

Recently, biochars have been applied for the removal of gaseous contaminants including those occurring in industrial flue gases such as biomass and coal-fired combustion systems and waste-to-energy systems. An increasing body of experimental literature shows that biochars and their derivatives can remove a wide range of gaseous contaminants. Available studies have focused on the removal of the following gaseous contaminants: (1) acidic gases including CO₂, H₂S and SO₂ (Bhandari et al., 2014; Zhang et al., 2014; Sun et al., 2017; Chatterjee et al., 2018; Braghiroli et al., 2019), (2) metals, specifically elemental mercury (Hg⁰) (Yang et al., 2018; Yang et al., 2018), and (3) volatile organic compounds (VOCs) (Maurer et al., 2017; Zhang et al., 2017), and nitrogen oxides (NO_x) (Jo et al., 2011; Wang et al., 2017a, 2017b; Lee et al., 2018). Some of these studies used pristine biochars prepared from a wide range of feedstocks including agricultural waste such as cottonseeds and lignin, (Klasson et al., 2014; Liu et al., 2018), microalgae (Chen et al., 2018), sewage sludge, and animal waste such as chicken manure (Klasson et al., 2014) under various pyrolysis conditions (Li et al., 2015a, 2015b, 2015c), while others prepared and applied functionalized or engineered biochars using various activation methods (Yang et al., 2018).

Despite the existence of a substantial body of literature, comprehensive reviews on biochar removal of gaseous contaminants, constraints, potential applications and future research needs are still lacking. The bulk of earlier reviews were limited to: (1) overview articles discussing biochar feedstock, production and applications particularly in agroecosystems (Duku et al., 2012; Gwenzi et al., 2015), (2) biochar as an agricultural soil amendment (Oliveira et al., 2017), and (3) removal of contaminants in aqueous systems (Mohan et al., 2014; Gwenzi et al., 2017). The only exception is a recent review focusing on two acidic gases, specifically H₂S and CO₂ (Bamdad et al., 2018a, 2018b). However, that work (Bamdad et al., 2018a, 2018b) excluded several organic and inorganic gaseous contaminants which had been recently reported in be removed in gaseous streams. These include; toxic metals (e.g., Hg⁰), NO_x, VOCs, odorous compounds, aromatic compounds, and carbon dioxide, which are harmful to the environment and human health. Hence, there is a strong need for a research which comprehensively reviews all these gaseous contaminants and their removal by a cost-effective biochar application.

The current study examined the research advances on the use of biochar for the removal of gaseous contaminants. Fig. 1 summarizes the uses of biochar in industrial gaseous emissions, the contaminant removal mechanisms by biochars filters, and the constraints and knowledge gaps. First, preparation of biochars and their functionalized derivatives, and properties determining their capacity to remove gaseous contaminants were summarized. The capacity of biochars to remove a wide spectrum of inorganic and organic gaseous pollutants, and mechanisms involved were discussed. The potential and novel applications of biochars in the removal of flue gas contaminants, and finally, the constraints and hotspots for future research were discussed.

2. Overview of methodology

The procedure for literature retrieval used in the current study is similar to that reported in earlier reviews (Gwenzi et al., 2017). Briefly, literature was retrieved from on-line scholarly databases including ScienceDirect®, Clarivate's Web of Science®, Researchgate®, Scopus®, and Google Scholar®. A Boolean search procedure using 'AND'/'OR' was applied to search for a combination of keywords. The combination of keywords included a term representing a specific groups or names of contaminants, biochar(s), removal, and a corresponding term referring to the gaseous phase. Typical terms for contaminants were: 'volatile organic compound(s)', 'metals', 'mercury', 'lead', 'NO_x', 'N₂O', 'CO₂', 'SO₂', 'H₂S', 'flue gas', 'odorous gases', 'poly-aromatic(s)', 'HCl', 'HF', 'poly-halogenated', 'dioxin(s)', 'furan(s)' and 'biphenyl(s)', among others. To retrieve articles on biochars, the term 'biochar(s)', 'char(s)', 'charred', 'engineered (bio)char(s)', 'activated biochar(s)', 'functionalized

biochar(s)' and 'black carbon' were used. To limit the search to the gaseous phases, the terms, 'gaseous', 'gas', 'air', 'flue gas(es)', 'volatile(s)', 'odor/odor' and 'smell' were used. A search of the reference lists of the relevant articles provided further literature.

The articles were individually checked for relevance to the review topic. Selected articles were reviewed and examined for results related to the review objectives. The current review is based on qualitative analysis. This is because the articles were sparsely distributed over various gaseous contaminants and based on different types of biochars. Hence, given the broad nature of the contaminants and biochars used, a meta-analytic or bibliometric quantitative review was considered not feasible.

3. Biochar materials

Biochar can be used in the pristine or modified forms for particular applications. Feedstock are derived from a wide range of biomaterials such as municipal sewage sludge, agrowaste, industrial by-products, and household biowastes (Li et al., 2015a, 2015b, 2015c; Madzaki and KarimGhani, 2016; Sun et al., 2017; Li et al., 2019). For instance, biochar was synthesized from pig manure, sewage sludge, and wheat straw applied for CO₂ sorption (Xu et al., 2016a, 2016b). Other studies synthesized biochar from marine biomass (Yang et al., 2018), almond shells, chicken manure, cottonseed hulls (Klasson et al., 2014), cigarette butts (Lima et al., 2018), poultry manure (Contescu et al., 2018), rubber wood (Shaaban et al., 2013), and chili seeds (Ocampo-Perez et al., 2019).

While some applications have used pristine biochar, it is usually desirable to produce biochar that performs targeted applications. In most cases, therefore the properties of biochar have been modified to suit the subsequent uses. Processes such as steam activation, heat treatment, acid/alkali activation, and impregnation with a range of other reactive materials such as metal oxides and nanoparticles have been used to tailor biochar for desired applications (Yang et al., 2018; Hwang et al., 2018; Braghiroli et al., 2019).

3.1. Nature and preparation methods

A range of methods can be used for biochar production, and the biochar yield depends on the operation conditions and type of biomass. Biochar production methods include carbonization, gasification, hydrothermal carbonization, pyrolysis, and torrefaction. A detailed treatment of these methods has been presented in previous reviews (Bamdad et al., 2017; Gwenzi et al., 2017; Bedia et al., 2018; Zhang et al., 2019a, 2019b, 2019c).

Biochar synthesis is commonly conducted by slow pyrolysis in a single carbonization step, where the biomass is thermally treated up to 500 to 800 °C under inert conditions, and held at that temperature for a certain time. Subsequently, the biochar is allowed to cool to ambient temperature. Slow pyrolysis produces comparatively high biochar yields, especially with large particle size biomass feedstock of high ash and lignin content (Gwenzi et al., 2017). These parameters increase biochar yield by reducing bio-oil through cracking. In addition, it is a low-cost, simple, and robust process appropriate for the production of biochar at small-scale (Zhang et al., 2019a, 2019b, 2019c). The key variable influencing the porosity of biochar is the pyrolysis temperature (Bedia et al., 2018). A range of reactors including drum rotating kilns, wagon reactor and paddle pyrolysis kiln, the *Kon Tiki* reactor, and the Elsa stove, have been used to produce biochar (Gwenzi et al., 2017; Zhang et al., 2019a, 2019b, 2019c; Maya et al., 2020). Thermal treatment introduces more basic surface functional groups onto biochar which are commonly used in the sorption of hydrocarbons. It thus enhances surface hydrophobicity by eliminating hydrophilic groups (Liu et al., 2016). Research has demonstrated that H₂ can stabilize the biochar surface by deactivating some active sites, resulting in a highly stable basic carbon structure (Ahmed et al., 2016).

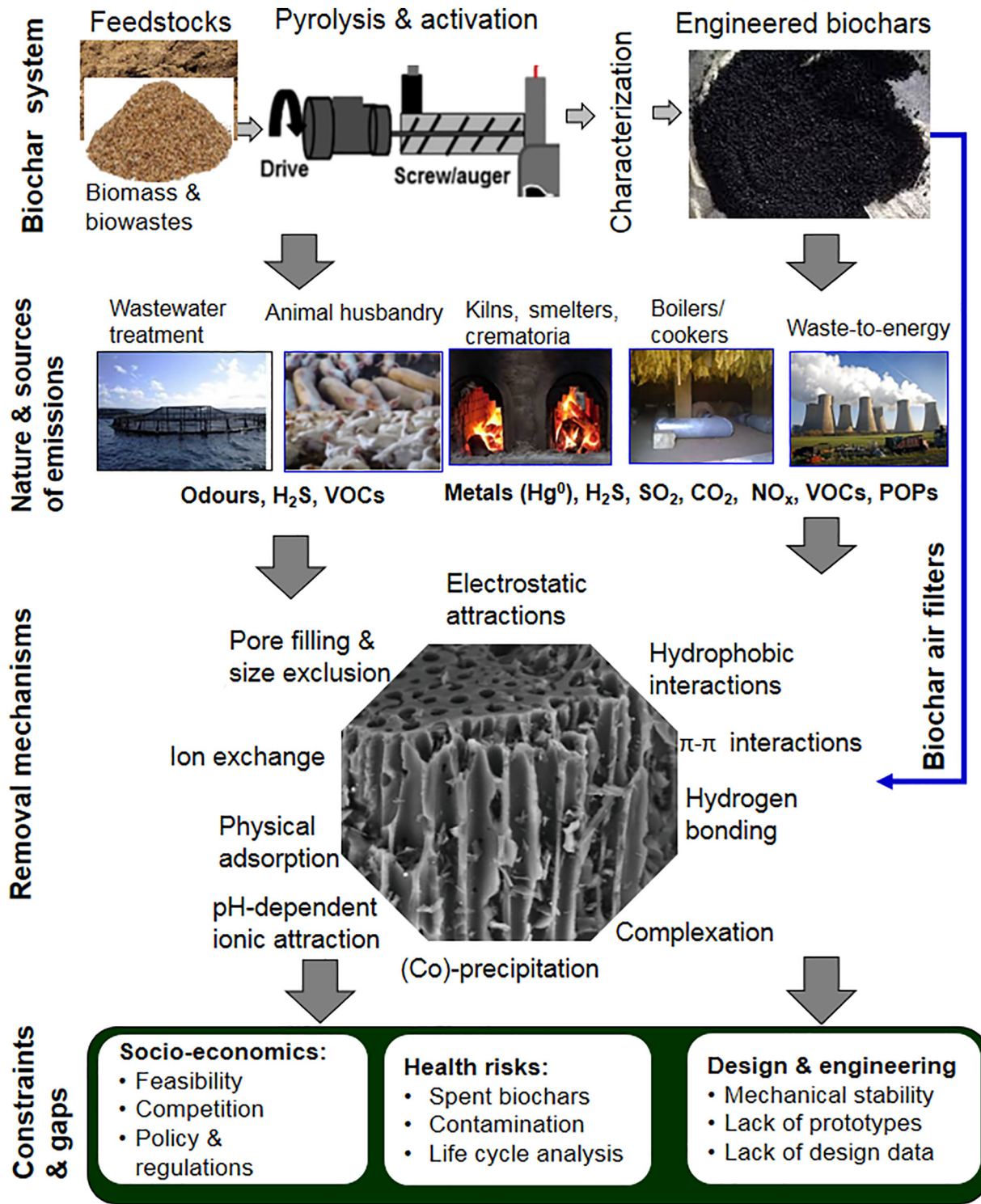


Fig. 1. Summary depiction of biochar technology, industrial gaseous emissions, contaminant removal mechanisms by biochars filters, and constraints and knowledge gaps.

Although pristine biochar can be suitable for various applications, it can be tailored to produce materials with desired properties for specific applications (Vijayaraghavan, 2019). Surface functional groups such as amine, carboxyl, hydroxyl, phosphonate, and phenolic groups provide suitable binding sites for the sorptive removal of different pollutants. However, to enhance the physicochemical properties, and hence the performance of biochar, certain modifications are possible. These modifications can be achieved through chemical activation and physical activation (Bedia et al., 2018; Manyà et al., 2018; Vijayaraghavan, 2019;

Zhang et al., 2019a, 2019b, 2019c). Recently, hydrothermal carbonization and microwave heating have been introduced in addition to the conventional processes. Fig. 2 summarizes the different synthesis routes for biochars from various feedstocks.

3.2. Properties critical for the removal of gaseous pollutants

The physicochemical characteristics of biochar considerably affect the subsequent applications, and therefore deserve a full evaluation

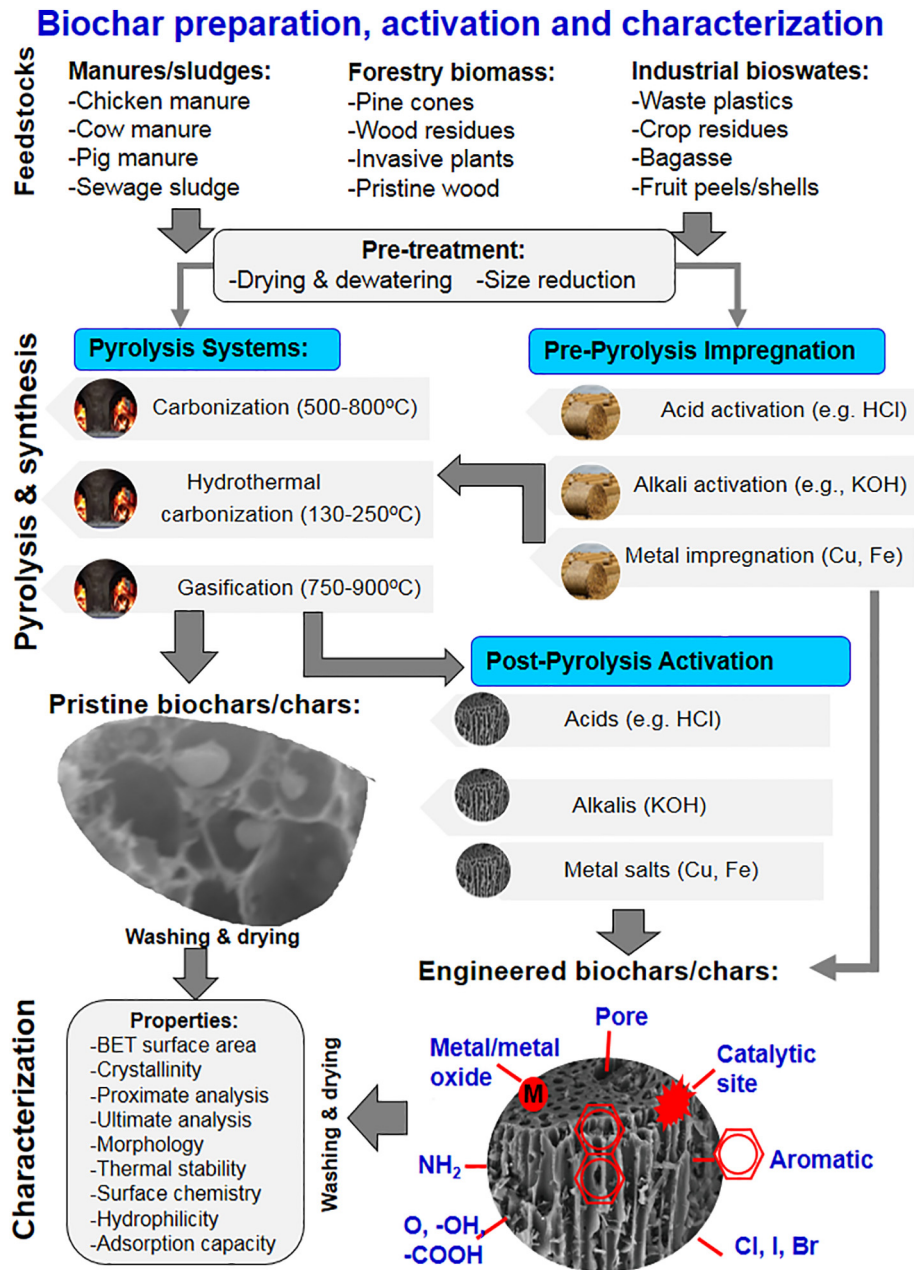


Fig. 2. A schematic of biomass feedstocks, synthesis and characterization biochars.

(Fig. 2). Properties such as surface area, surface charge, pH, porosity, mineral composition, and functional groups determine the application of biochars (Vijayaraghavan, 2019). Oxygenated functional groups are required for the sorption of inorganic or polar organic pollutants to facilitate electrostatic interactions (Bedia et al., 2018).

A number of techniques have been used to evaluate the characteristics of biomass precursors and the resulting biochar (Table 1). For instance, the Fourier Transform Infrared (FTIR) spectroscopy is useful for the identification of surface functional groups (Chia et al., 2012). The peaks denote specific surface functional groups whose wavelengths may shift from the original owing to various modifications. Through impregnation, additional peaks consistent with the compounds used are generated (Ahmed et al., 2016). Most researchers have also used elemental analysis, Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption isotherms, Raman spectroscopy, elemental analysis, X-ray diffraction spectroscopy, high resolution scanning electron microscopy,

and X-ray photoelectron spectroscopy to examine the physicochemical characteristics of biochar and its precursors (Chang et al., 2015; Liu and Huang, 2018; Liu et al., 2018; Yi et al., 2018; Jung et al., 2019). The key properties for the removal of gaseous pollutants include polarity, aromaticity, ash, mineral content, cation exchange capacity, surface charge, and textural properties (Table 2).

3.2.1. Aromaticity and polarity

Polarity and aromaticity indicate the content of organic matter in biochar. Aromaticity, being the ratio of aromatic carbons relative to total carbon content, is represented by the H/C index (Bedia et al., 2018). A low H/C value shows high organic carbon content and high aromatic character. Like other properties, the aromatic character of biochar is influenced by the biomass feedstock and carbonization conditions (Al-Wabel et al., 2013). High pyrolysis temperatures are associated with high aromatic character. The carbon content of biochar

increases with pyrolysis temperature, and aliphatic carbons are integrated into aromatic structures via dehydrogenation (Tong et al., 2019). The H/C and O/C elemental ratios of biomass fall within the ranges of 1.4 to 1.8 and 0.55 to 0.75, respectively, indicating high aliphatic and low aromatic character. The O/C and ((O + N)/C) ratios represent the polarity index (Cha et al., 2016). Pyrolysis decreases the ratios, more notable at high temperatures (Bedia et al., 2018). The modification of the reactive groups during carbonization of biomass influences the subsequent adsorption capacity. In addition to introducing π -electron systems that interact with organic pollutants, the increased aromaticity of biochar enhances the chemical and biological stability of biochar (Premarathna et al., 2019). As a result, highly aromatic biochar is more suitable for high temperature application, for example industrial flue gas treatment.

3.2.2. Ash, mineral content, cation exchange capacity, and surface charge

Ash content is a function of the feedstock composition. High ash content occurs for biochar derived from mineral-rich biomass such as grass, industrial wastes, and municipal biosolids, and lower ash content is typical for biochar produced from woody biomass (Premarathna et al., 2019). Compared to the type of biomass, pyrolysis temperature has less effect on the ash content (Tong et al., 2019). Intrinsic mineral constituents in biochar, for example carbonates, oxides, or phosphates of alkali or alkaline earth metals, affect the characteristics, and can improve the sorption capacity of biochar for acidic gases (Xu et al., 2017). In general, ash content is a key determinant of surface polarity and the distribution of pores.

The sorption of ionic species can involve electrostatic attraction (Tong et al., 2019). Owing to the presence of dissociable reactive groups such as -COOH, -H, and -OH within the biochar matrix, the surface charge on biochar may be inadequate. Cation exchange capacity, zeta potential/isoelectric point, or pH at zero point charge (pH_{zpc}), can be used as an indicator of surface charge (Tong et al., 2019; Xu et al., 2019a, 2019b). Zeta potential and pH_{zpc} can be used to predict the electrostatic interactions between the biochar and pollutant molecules (Tong et al., 2019).

3.2.3. Textural properties

The carbon framework of biochar is usually endowed with slit-like pores or honeycomb geometries. The pore sizes can vary from sub-nanometer to micrometers, with a large proportion of micropores within the pore structure, while mesopores interconnect to the surface (Madzaki and KarimGhani, 2016). The surface area and porous structure of biochar can be modified from the carbonization process of biowastes in accordance with the subsequent activation steps. Chemical and physical activation enhance the surface area and control the porosity of biochar (Jung et al., 2019). For instance, a study modified biochar using a CO_2 - NH_3 mixture at high temperature, and reported a significant increase in surface area (up to approximately $627 \text{ m}^2/\text{g}$), while the ammonia treatment introduced N-carrying moieties onto the biochar surface (Zhang et al., 2014). Steric hindrance occurs when pore apertures are too constricted for pollutants to rapidly diffuse into deeper micropores (Tong et al., 2019). Therefore, pore geometry has to be tailored for removal of specific pollutants.

4. Biochar as air filter media

Compared to aqueous systems, the application of biochar in the sorption of pollutants in the gaseous or vapour phase has been relatively neglected, and comparatively few studies have been reported in the literature. Biochars have the capacity to effectively remove both organic and inorganic contaminants (Table 1). Inorganic contaminants reported in literature include acidic gases and metals specifically mercury, and organic contaminants include aromatics, VOCs, and odorous compounds. (See Tables 3.)

4.1. Inorganic pollutants

Inorganic pollutants are noxious to living organisms especially at elevated concentrations, thereby posing health risks to the public and the environment (Zhang et al., 2013). These pollutants include heavy metals such as Hg, Pb, Cd, Cu, Zn, and Ni (Oliveira et al., 2017; Zhang et al., 2013;) and other non-metals such as NO_3^- , NH_4^+ , NH_3 , and H_2S , which are sometimes found in aquatic systems and industrial flue gases (Inyang and Dickenson, 2015). Mercury has been the focus in this section because of its toxicity, and has been missing in the previous reviews.

Biochar has been used for the removal of toxic metals from industrial flue gas, and the removal efficiency is influenced by biochar and pollutant properties (Oliveira et al., 2017). Fig. 3 summarizes the efficiency of biochar formed from a variety of feedstock at temperatures of 350°C and 800°C in removal of Hg^0 . Generally, biochar formed at low temperature (around 350°C) performed best in Hg^0 removal than that synthesized at high temperatures (around 800°C) (Klasson et al., 2014).

Biochar with specific porous structure, high organic carbon content, and numerous functional groups, interacts with inorganic pollutants in different ways such as precipitation, complexation, ion exchange, electrostatic interaction (chemisorption), and physisorption (Oliveira et al., 2017). Some researchers reported that sorption through ion-exchange is the leading mechanism for the removal of toxic metals (Uchimiya et al., 2011). In contrast, other studies demonstrated that sorption mechanism is the predominant removal mechanism (Lu et al., 2012; Cao et al., 2009). This is because biochars have different functional groups, including: R-COOH, R-OH, and OH. Hence, the removal of toxic metals by biochar occur via: (1) complexation between functional groups on biochar and metal ions, (2) surface interactions such as ion-exchange and co-precipitation of metals with inorganic constituents, and (3) coordination of metal ions with π -electrons on biochar (Klasson et al., 2014).

In addition, many biochars have been reported to have high surface area with a well-distributed pore network including micropores, mesopores, and macropores (Tan et al., 2012). Biochars with high surface area and pore volumes have a high affinity for metals because metallic ions can be physically sorbed onto the biochar surface and retained within the pores (Tan et al., 2012). Many biochars have negatively

Table 1
Techniques used for the characterization of biochars and their precursors.

Property	Measurement technique	Remarks
Thermal stability	Thermogravimetry	Information on decomposition profile.
Texture	BET, N_2 adsorption-desorption isotherms	Generates data on specific surface area and pore volume
Morphology	Electron microscopy	Scanning electron microscopy (SEM), transmission electron microscopy (TEM)
Surface chemistry	Vary from wet chemistry to instrumental according to specific characteristic	Point of zero charge (pH_{zpc}), isoelectric point (pH_{IEP}), Acid functional groups (Bohem titration), FTIR
Hydrophobicity	Sessile drop method	Water contact angle
Adsorption capacity	Iodine number, methylene blue number, molasses number	Generates information on porosity.
Physico-chemistry	Vary according to specific characteristic.	Bulk density, cation exchange capacity, hardness
Proximate analysis	Gravimetric methods	Moisture, volatiles, fixed carbon, ash
Ultimate analysis	Elemental (C, H, N, S) analysis	Aromaticity, hydrophobicity
Crystallinity	X-ray diffraction (XRD)	d-spacing, particle size, crystal deformation.

Table 2
Properties and performance of biochars fabricated from various feedstock.

Feedstock	Pyrolysis conditions	Modification	Properties of biochar	Adsorbate gas	Uptake and conditions	Reference
Black spruce and white birch residues from sawmills	Fast pyrolysis at 454 °C using CarbonFX technology	Activated in presence of: KOH, CO ₂ , and superheated steam.	Basic; surface area (590 m ² /g); volume of ultra- (0.22 cm ³ /g), micro- (0.23 cm ³ /g), mesopores (0.11 cm ³ /g)	SO ₂	Dynamic tests at 20 °C. q_{max} in the range: 20.4–76.9 mg/g.	Braghiroli et al., 2019
Spruce (<i>Picea sp.</i>)	Pyrolysis in a fixed bed reactor. Heating rate 5 to 10 °C/min up to 650 °C	None	ash content (0.9%), uniformly distributed pores,	H ₂ S	Maximum removal of the compost and compost + biochar biofilter were approx. 19 and 33 g/m ³ h, respectively, with >99% removal efficiency at an EBRT of 119 s	Das et al., 2018
Sewage sludge	Pyrolysis at 950 °C, heating rate: 10 °C/min under N ₂ , fixed bed reactor.	Treated with 18% HCl.	Surface area and pore volume increased 100% after acid treatment.	H ₂ S	The biochars efficiently removed H ₂ S until the pores were blocked with S. Removal was mainly by chemisorption.	Bagreev et al., 2001
Camphor tree	pyrolysis at various temperatures (100–500 °C) at 10 °C/min in a muffle furnace	None	Alkaline surface. C=O, COO surface groups.	H ₂ S	$1.2 \leq q_{max} \leq 121.4$ mg/g	Shang et al., 2012
Potato peel waste	Pyrolysis at 500 °C, for 5 min in a fluidized reactor	None	Surface are: 62 m ² /g, alcoholic carboxylic, phenolic, surface groups	H ₂ S	q_{max} : 53 mg/g	Sun et al., 2017
Pine	495–505 °C pyrolysis,	None	ash: 1–25% wt; carbon: 60–75% wt; particle diameter: 175 µm; pH: 7.28 ± 0.07.	NH ₃	q_{max} : 0.84 mg/g	Maurer et al., 2017
Pig manure, sewage sludge, wheat straw	Pyrolysis of ground biomass up to 500 °C in a stainless steel reactor in a Muffle Furnace, under N ₂ at 10 °C/min.	None	Surface area: 10.1–31.6 m ² /g, alkaline.	CO ₂	$18.2 \leq q_{max} \leq 34.4$ mg/g at 25 °C. Increasing sorption temperature and moisture content caused CO ₂ uptake to change from physisorption to chemisorption. Mg, Ca, Fe, K in biochar facilitated chemisorption through mineralogical reactions	Xu et al., 2016a
Medicinal residue waste	Pyrolysis at 600 °C, 20 °C/min, in a fixed bed reactor.	Microwave activation and NH ₄ Cl impregnation	Pore diameter: 6.01–86.97 nm, surface area: 3.5–67.89 m ² /g	Hg ⁰ vapour	82% removal, $\Delta H < 0$, apparent adsorption energy: 43.3 kJ/mol (chemisorption). NO and O ₂ enhanced adsorption, but H ₂ O inhibited adsorption.	Li et al., 2015a
Nespresso coffee grounds	Dry feedstock were pyrolysed for 1 h in a quartz reactor, at 400 °C under N ₂	Ammonoxidation and KOH activation	Surface area: 1684 m ² /g, pore volume: 0.94 m ³ /g, C–N and N–H functional groups.	CO ₂	q_{max} : 2.67 mmol/g at 35 °C. High selectivity ([CO ₂ /N ₂] = 74.2) for CO ₂ -N ₂ separation.	Liu et al., 2018
Cotton stalk	Fast pyrolysis at 600 °C, under N ₂	Treatment with CO ₂ -NH ₃ mixture at high temperature	O–H, C–O, N–COO, C=N, C–N groups, surface area: 627.15 m ² /g.	CO ₂	At low temperature (20 °C) q_{max} proportional to micropore volume; but depends on the N content at high temperature (120 °C)	Zhang et al., 2014
Vine shoots	Pyrolyzed in a packed-bed reactor at 600 °C and 0.1 MPa	Activation with CO ₂ and KOH	Surface area: 538–1671 m ² /g, micropore volume: 0.177–0.587 m ³ /g	CO ₂	Sorption capacity: KOH activated: 2.16–2.42 mmol/g, CO ₂ activate: 1.79–1.89 mmol/g at 0 °C, Pressure: 15 kPa. at different temperatures (0, 25, and 75 °C)	Manyà et al., 2018
Sawdust	Gasification at 850 °C	Monoethanolamine treated	Pristine biochar was acidic, had surface area: 182.04 m ² /g. pH increased after modification. Modified biochar surface area: 0.15 m ² /g	CO ₂	Sorption capacity for pristine biochar: 0.47 kg/kg	Madzaki and KarimGhani, 2016
Miscanthus Straw Pellets (MSP), Oil Seed Rape Straw Pellets (OSR), Rice Husk (RH), Soft Wood Pellets (SWP), Wheat Straw Pellets (WSP) and Sewage Sludge	Pyrolysis at 550 °C under N ₂	None	–	O ₃	Removal: 55 ppbv for up to 24 h	Zhou et al., 2018
Whitewood	Fast pyrolysis	KOH activation.	Total micropore volume: 0.62 cm ³ /g, surface area: 1400 m ² /g	CO ₂	Sorption capacity: 1.8 mol/kg. Experimental conditions: 30 mol% CO ₂ at 25 °C	Shahkarami et al., 2015
Olive stones, almond shells	Pyrolysis in a double-jacket quartz reactor in a furnace, CO ₂ atmosphere, 10 °C/min up to 800 °C for 6 h.	None	Surface area: 1215 m ² /g, pore volume: 0.51 cm ³ /g.	CO ₂	Sorption capacity: 0.6–1.1 mmol/g at 15 kPa and 25–50 °C. Fast kinetics and high selectivity of CO ₂ over N ₂	González et al., 2013
Pinewood	Pyrolysed at 550 to 600 °C in a kiln	Acoustic treatment and amination at room temperature	Surface area: 354 m ² /g,	CO ₂	Sorption capacity: 0.55–2.79 mmol/g. Low-frequency ultrasound exfoliates and breaks down graphitic layers of biochar, and forms new or opens blocked pores.	Chatterjee et al., 2018

Table 3
Summary of organic and inorganic gaseous contaminants removed by biochars.

Contaminant	Biochar type	Remarks and removal efficiency (%)	References
Mercury (Hg ⁰)	Magnetic chlorinated- biochars	Cl-biochars were prepared by co-pyrolysis of biomass and polyvinyl chloride (PVC) waste. The Cl-biochars exhibited relatively poor Hg ⁰ removal performance (η_T (removal efficiency) < 50%). But the η_T values of Fe-Cl/biochars were obviously improved the optimum performance for mercury removal.	Xu et al., 2019b
Mercury	modified activated carbons	Chloride impregnated activated carbon showed a steady removal of 26%. For bromide impregnated carbon, 85% removal was observed for 80 min and thereafter dropped to a steady value of 40% removal. The iodide impregnated carbon showed 100% removal efficiency for entire period of adsorption study.	De et al., 2013
Carbon dioxide	Waste biomass derived biochars	Biochars derived from pig manure, sewage sludge and wheat straw were evaluated and all had high sorption abilities with the highest reaching 18.2–34.4 mg/g at 25 °C.	Xu et al., 2016a, 2016b
Mercury (Hg ⁰)	Medicine residue derived biochars	Medicine residue biochars activated by microwave demonstrated high mercury removal (76%) and those that were activated by microwave and impregnated with ammonium chloride had the highest removal efficiencies (80%)	Li et al., 2015a
Carbon dioxide	Coffee grounds volarized biochars	Results obtained from this study reveal that the adsorbents which are nitrogen doped by melamine from ammoxidation treatments, followed by potassium hydroxide chemical activation, have the highest CO ₂ uptake of 2.67 mmol CO ₂ /g sorbent at 35 °C.	Liu and Huang, 2018
Carbon dioxide	Nitrogen enriched biochar modified by high temperature	The CO ₂ adsorption of modified biochars maximum (99.42 mg/g) was obtained at 800 °C.	Zhang et al., 2014
Mercury	Poultry manure biochars	Washed biochars made from poultry manure at 650 and 800 °C, sorbed over 95% of mercury from flue gas. It was also shown that the majority of mercury sorbed to the biochar at 150 °C was stable and was not thermally desorbed at 450 °C, suggesting the presence of sorbed oxidized mercury species such as HgSO ₄ or HgO.	Klasson et al., 2014
Elementary mercury	Brominated flame retarded plastic	Brominated flame retarded plastic/ Biomass ratio of 1:1 resulted in 40% removal efficiency at 140 °C	Xu et al., 2018
Carbon dioxide	Vine shoots derived biochar	At 25 °C biochars with KOH impregnation exhibited the highest carbon dioxide absorption capacity of 68%. Activated carbon prepared through physical treatment with carbon dioxide and soaking time of 1 h appears as the most promising adsorbent with 83.7% absorption efficiency at 75 °C	Manyà et al., 2018
Carbon dioxide	Saw dust biochar	The study indicated that raw sawdust gasified at 850 °C gave the highest adsorption of 0.47 kg CO ₂ / Kg biochar at a temperature of 30 °C.	Madzaki and KarimGhani, 2016
Gaseous ozone	Biomass derived biochars	The study indicated that biochars showed an excellent performance in removing ozone (55 ppbv) for periods up to 24 h and no volatile by-products were observed during the reaction.	Zhou et al., 2018
Mercury	Tobacco biochars	Tobacco biochars treated with 1 M HCl had 100% absorption efficiency which was a large increase from the 8.2% of untreated tobacco biochars.	Wang et al., 2018
Toluene, NH ₃ , H ₂ S	Switch grass biochar	Among the four catalysts used in the experiment, biochar based catalysts where the most feasible for simultaneous removal of contaminants with a 86% removal efficiency for toluene, 0.008 g NH ₃ / G NH ₃ absorption capacity and 0.008 g H ₂ S / g biochar for H ₂ S.	Bhandari et al., 2014
Cyclohexane, acetone and toluene	Feedstock biochar	The results in the study showed that different feedstock biochars had sorption capacities in the range 5.58 to 91.2 mg/ g.	Zhang et al., 2017
Toluene	Neem biochar	Neem based biochar showed a very high removal efficiency of 65.5 mg/g for toluene	Kumar et al., 2020
Benzene vapour	Coconut shell granular	Hydrophobic modified (polydimethylsiloxane) coated biochars had more absorption capacity (336 ± 15.1 mg/g) than bare activated carbon (165 mg/g)	Liu et al., 2016
SO ₂	Black spruce wood residues biochar	Stream activated biochar had the highest performance on SO ₂ with an absorption capacity of 56.9 mg/g.	Braghiroli et al., 2019
Methyl tert butyl ether	Bagasse biochar	Bagasse biochar showed the highest absorption capacity of 8.26 mg/g and bone biochar had the lowest absorption capacity of 3.51 mg/g. It was believed that bagasse biochar had more ester groups that assisted in absorption.	Pongkua et al., 2018
H ₂ S	Compost + biochar biofilter	The elimination capacity of a compost biofilter was 19 and that of a compost + biochar biofilter was 33 g/m ³ /h with a 99% removal efficiency at an empty bed residence time of 119 s.	Das et al., 2019
Formaldehyde	CuO-MnO _x - modified pinecone biochar	Cu-Mn mixed oxides supported on biochars showed the highest removal efficiency of HCHO and elementary mercury (89% and 83% respectively) at 175 °C.	Yi et al., 2018.
Odorous volatile organic compounds	poultry manure and straw biochar	Biochar significantly reduced the levels of nitrogen volatile compounds, which are the most abundant VOC family, originated from microbial transformation of the N-compounds originally present in manure. The most efficient VOC reduction was observed in oxygenated volatile compounds (ketones, phenols and organic acids),	Sánchez-Monedero et al., 2019
Odorous volatile organic compounds	Plant biomass and oak biochar	Plant-biomass-based biochars had considerably larger sorption capacity for Dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS). Oak biochar pyrolyzed at 500 °C (OK500) showed high sorption capacities for both DMDS and DMTS.	Hwang et al., 2018
NO _x	Water vapour and KOH activated sewage sludge biochars	NO _x removal occurred via selective catalytic reduction in the presence of NH ₃ . Oxygen functional groups on biochar responsible for catalytic activity.	Jo et al., 2011
NO _x	Empty fruit bunch biochar (EFB) activated by KOH (KEFB) and Cu ions (Cu-KEFB)	KOH activated biochar had higher NO _x removal than water vapour activated biochar KEFB had higher NO _x removal than non-activated EFB and activated carbon. Cu impregnation reduced NO _x removal at low temperatures, but enhanced removal at higher temperatures above 150 °C due to the catalytic activity of Cu. Thus, at higher temperatures above 150 °C, Cu-KEFB had higher NO _x removal than KEFB.	Lee et al., 2018

charged surfaces and can sorb positively charged metals through electrostatic attractions. Specific ligands and functional groups on biochars can also interact with various metals to form complexes or precipitates of their solid mineral phases (Klasson et al., 2014).

The sorption behaviours of biochar for different contaminants are well correlated with the properties of contaminants. In addition, the sorption mechanism may also depend on the various properties of biochar, including surface functional groups, specific surface area, porous

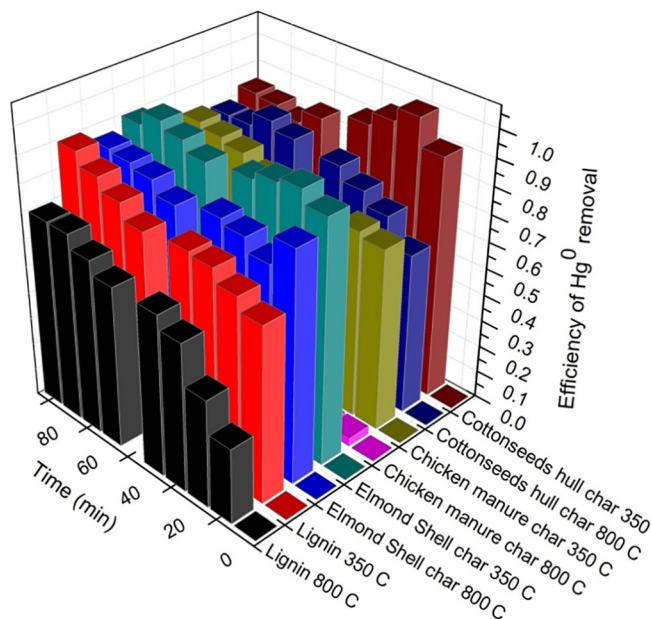


Fig. 3. Efficiency of biochar formed at different temperatures in removal of Hg⁰ (drawn based on data in Klasson et al., 2014).

structure and mineral components (Vijayaraghavan, 2019). The possible adsorption mechanism usually involves combined effects of several kinds of interactions including electrostatic attraction, ion-exchange, physical adsorption, surface complexation and/or precipitation (Oliveira et al., 2017). Various mechanisms are proposed for the interaction of biochar with toxic metals. Abundant surface functional groups (mainly oxygen-containing groups, e.g. -COOH; and -OH) exist on biochar surface, which can have strong interactions such as electrostatic attraction, ion-exchange and surface complexation with heavy metals. These effects can be shown by changes in functional groups and shifts in wavenumber of functional groups on biochar before and after adsorption (Khare and Goyal, 2013).

4.1.1. Toxic metals

Mercury is one of those noxious and volatile metals that is emitted into the environment. Mercury originates from different sources such as coal-fired boilers and mining industries. It is estimated that mercury emitted from coal-fired boilers only into the atmosphere constitutes one-third of the total atmospheric mercury (Lee et al., 2004). Mercury from coal combustion boilers exists as particulate mercury, oxidized (Hg²⁺), and elemental (Hg⁰) mercury (Liu and Wang, 2014). Particulate mercury can be easily removed by electrostatic precipitators and fabric filters, while Hg²⁺ can be efficiently captured by wet flue gas desulfurization systems since it has a high water solubility (Liu and Wang, 2014). Because it is volatile, has low melting point, and poor solubility in water, Hg⁰ is not easily removed using existing air pollution control systems (Oliveira et al., 2017).

Several studies have investigated the removal of Hg⁰ in flue gas by biochars derived from animal wastes (e.g., broiler litter, chicken manure) and agro-processing wastes (e.g., almond shell, cottonseed hull, wheat straw) (Klasson et al., 2014; Liu and Wang, 2014; Lee et al., 2004; Liu et al., 2018). The capacity of biochars to remove metals depends on feedstock type, pyrolysis conditions and operating temperature. Mercury removal from flue gas by biochars derived from various agricultural residues such as wheat straw, cottonseed husk, switch grass, and cow and chicken manures at low and high pyrolysis temperatures (300, 600 and 700 °C) were examined (Klasson et al., 2014). Biochars derived from animal manure were highly effective due to high sulphur content (SH groups and sulphate). Hg²⁺ removal efficiencies

exceeding 90% were achieved via co-precipitation with anions (Cl, O and S) from biochars, resulting in the formation of Hg(OH)₂ or HgCl₂ precipitates (Oliveira et al., 2017).

Aside from using pristine biochar, several researchers modified pristine biochar in order to enhance the efficiency in mercury removal. Liu et al. (2018) modified biochars derived from seaweeds, sargassum and enteromorpha using KCl, KBr, and KI to capture Hg⁰ from simulated flue gas. Biochars modified with KI showed a better Hg⁰ adsorption performance than biochars modified by KCl and KBr. Increasing reaction temperature from 80 °C to 160 °C during the adsorption process significantly increased Hg⁰ removal from 71.7% to 95.7%. The presence of O₂ promoted the Hg⁰ removal, while SO₂ inhibited Hg⁰ removal over enteromorpha biochars, and showed a double impact on Hg⁰ removal over sargassum biochars. Low concentrations of NO and H₂O were beneficial for Hg⁰ removal, whereas high concentrations of NO and H₂O inhibited removal. Chemisorption was the dominant mechanism for Hg⁰ adsorption at 120 °C and 160 °C. The covalent groups (C—I) and the chemisorbed oxygen and/or weakly bonded oxygen species participated in the Hg⁰ removal process and were the dominant chemisorption sites on the surface of KI modified seaweed biochars.

Modified biochar from wheat straw had excellent Hg⁰ removal capacity due to improved pore structure and formation of new active sites which is often governed by pyrolysis temperature and feedstock type (Zhou et al., 2019). Pyrolysis at approximately 800 °C produced biochar with a highly porous structure relative to those produced at 450 to 600 °C. Thus, biochar produced at 800 °C had higher removal of Hg⁰ than those produced at 450 to 600 °C. In another study, four different feedstock (cottonseed hulls, almond shells, chicken manure, and lignin) were pyrolyzed at 350, 500, 650, and 800 °C and evaluated the potential of the formed biochars to remove Hg⁰ from a simulated flue gas (Klasson et al., 2014). The materials that performed the best were washed biochars made from poultry manure at higher temperature i.e., 650 and 800 °C, with a removal capacity exceeding 95%. Shen et al. (2015) supported the findings of Zhou et al. (2019) by comparing the biochar from medicinal residues and activated carbon in mercury removal. Li et al. (2015a, 2015b, 2015c) further investigated the influence of modifying biochars by impregnating seaweed biochars with halides (Cl, Br, and I). Modified biochars showed higher Hg⁰ removal than unmodified ones, and followed the order: KI > KBr > KCl. Having a smaller atomic size than I and Br, Cl has stronger forces of attraction with Hg⁰ than I and Br, hence biochar modified with Cl exhibited lowest efficiency in removal of Hg⁰ (Li et al., 2015a, 2015b, 2015c). The removal of Hg⁰ increased from 32.5 to 89.8% when the concentration of KI increased from 0 to 3%. The increase was due to the creation of more chemisorption sites on the biochar surface which favour Hg⁰ adsorption. Nevertheless, further increasing halide concentration decreased Hg⁰ removal, perhaps due to the decrease of surface area and pore volume of sorbents. Halogen impregnation has been reported to obstruct the physical adsorption but introduce chemisorption sites on the biochar surface which enhance Hg⁰ removal (Tan et al., 2012; Li et al., 2015a, 2015b, 2015c).

Kinetic modelling of Hg⁰ removal from flue gas using sargassum biochars showed that, at a low temperature (80 °C), the pseudo-first order model fitted the data well (Liu et al., 2018). However, at a higher temperature (160 °C), the experimental data were best described by a pseudo-second order model. It was suggested that at low temperature mass transfer was the controlling factor, whereas at high temperature removal was controlled by chemisorption (Liu et al., 2018). The adsorption process can be summarized into several steps: (1) the gaseous Hg⁰ is adsorbed on the sorbent to form adsorbed mercury, and (2) the adsorbed mercury reacts with chemisorbed oxygen and/or weakly bonded oxygen species or functional groups to form HgO. During this process, the chemisorbed oxygen can be supplemented or regenerated by gas phase O₂. In the case of modified biochars, the impregnated iodine ions react with carbon atoms on the surface of biochar to form the C—I groups; the gas phase O₂ introduced into the reactor is

adsorbed on the surface of biochars to form the chemisorbed oxygen and/or weakly bonded oxygen species. The gas phase Hg^0 introduced into the reactor is adsorbed on the surface of biochar to form the adsorbed mercury, and the adsorbed mercury reacts with chemisorbed oxygen and/or weakly bonded oxygen species to form Hg^0 . The adsorbed mercury is oxidized to mercury iodide by the C—I groups on the biochar (Lee et al., 2004; Liu et al., 2018).

In actual combustion systems, there is possible competitive adsorption for chemical adsorption sites between Hg^0 and flue gas components (NO , SO_2 , and H_2O) (Liu et al., 2018; Oliveira et al., 2017). Furthermore, the actual coal-fired flue gas has an extremely complex composition, with components such as other heavy metals, halides, alkaline substances, volatile organic compounds (Liu et al., 2018). Therefore, the mercury removal mechanism is complex and is still poorly understood. Meanwhile, studies on the use of biochar as an adsorbent have been largely limited to laboratory studies of toxic metal removal, and its potential for large-scale industrial application is scarce and requires further study.

4.1.2. Greenhouse gases

The worldwide greenhouse gases emissions into the atmosphere have increased by 35% between the year 1990 and 2010, reaching approximately 50 Gton CO_2 equivalent per yr (IPCC, 2014). The main greenhouse gases are CO_2 , CH_4 , and N_2O , and are emitted into the atmosphere through the combustion of biomass and fossil fuels, farming practices, degradation of soils, and deforestation (Oliveira et al., 2017; Smith, 2016). Mitigation strategies for greenhouse gases include increasing energy efficiency in industry, sequestration of excess CO_2 , wider use of renewable energies such as wind, solar, biofuels, and hydro-energy, and the use of energy storage technologies (Arfin et al., 2015). Among CO_2 sequestration strategies, using biochar has potential to lower greenhouse gas emissions (Tayade et al., 2012; Thomazini et al., 2015; Smith, 2016). Biochar applications to sequester and mitigate greenhouse gases in soils are well documented and several reviews exist (Gwenzi et al., 2015). Hence this aspect is beyond the scope of the current study. Rather, the current review focuses on greenhouse gases mitigation from non-soil sources.

The pyrolysis of biomass converts relatively unstable C to its recalcitrant form in biochar. Hence, in the short-term, the CO_2 assimilated via photosynthesis will no longer be released back into the atmosphere (Lal, 2004). Instead, the recalcitrant carbon, which has a longer residence time than carbon in biomass, will be bound to the biochar, thereby sequestering carbon and reducing CO_2 emissions (Gwenzi et al., 2015). Overall, pyrolysis of biomass to produce biochar diverts carbon from a rapid biogeochemical cycle into the biochar cycle, which is much slower than the former (Gwenzi et al., 2015). In addition, converting waste biomass into biochar reduces potential methane and CO_2 emissions from landfill and waste dumps. It is estimated that storing carbon in biochar can prevent the emission of approximately 0.1 to 0.3 billion tons of CO_2 /yr (Liu et al., 2015).

The sequestration and capture of CO_2 are strategic approaches for the mitigation of CO_2 emission from anthropogenic sources that use fossil fuels (Li et al., 2015a, 2015b, 2015c). It is therefore important to develop CO_2 adsorption materials that are efficient and cost-effective; of which biochar is one such material (Li et al., 2015a, 2015b, 2015c; Bamdad et al., 2017; Liu and Huang, 2018). The physicochemical characteristics of an adsorbent are critical in the adsorption process (Zhang et al., 2014). The high carbon content, large surface area, high alkalinity and mineral content of biochar make it suitable for application in CO_2 capture (Xu et al., 2016a, 2016b; Bamdad et al., 2017).

The structural and compositional variations in biomass precursors and pyrolysis conditions result in changes in structure and properties of biochar. The relationship between pyrolysis conditions and their resulting physicochemical characteristics is important in controlling biochar properties for CO_2 capture. There is naturally CO_2 physisorption via van der Waals forces on the biochar surface, whereas metal oxides

and aminated biochars have chemisorption. Due to the low CO_2 affinity of biochar and the complexity of the subsequent gas separation, surface modification or heteroatom doping of biochar can enhance CO_2 capture. For use in sequestering CO_2 in industrial processes which emit flue gas at high temperature, potential biochar adsorbents should be chemically and thermally stable, and should have high CO_2 sorption capacity and selectivity (Bamdad et al., 2017). To achieve this, the biochar should have a large surface area, high pore volumes, appropriate surface functional groups, high aromaticity, and suitable elemental composition (Jung et al., 2019).

Nitrogen-doped biochar fabricated by ball milling pristine biochar with NH_4OH carried basic nitrogenous groups which enhanced CO_2 uptake by about 32 to 55% relative to pristine biochar (Xu et al., 2019a, 2019b). In another study, biochar synthesized at high temperature had a high CO_2 sorption capacity (73.55 mg/g at 25 °C), which was due to the physisorption of CO_2 (Cha et al., 2016). At sufficiently large biochar surface area, the amounts of N-containing groups were more dominant in CO_2 adsorption (Cha et al., 2016). A similar study demonstrated that the surface area of biochar derived from cotton stalk increased considerably after CO_2 modification, while nitrogenous compounds on the biochar surface were enriched through NH_3 modification (Xiong et al., 2013). Consequently, CO_2 uptake increased significantly. The adsorption of CO_2 was mostly due to physisorption, and q_{max} (99 mg/g) was influenced by the micropore volume of the biochar. Another study optimized the activation conditions (CO_2 purge, residence time) for the synthesis of biochar from olive stones and almond shells to form narrow micropores and maximize the CO_2 uptake (González et al., 2013). Biochar is appropriate for CO_2 capture due to its well-developed porosity and surface area (Bamdad et al., 2017). For instance, KOH modified biochar with a total micropore volume and specific surface area of 0.62 cm^3/g and 1400 m^2/g , respectively, had a high CO_2 uptake (1.8 mol/kg) under optimum temperature of 25 °C (Shahkarami et al., 2015). Minerals inherent in biochar play an important role in CO_2 sorption. A study demonstrated that mineral constituents in biochar facilitated the chemisorption of CO_2 through mineralogical reactions (Xu et al., 2016a, 2016b).

Biochars also effectively remove NO_x in the presence of NH_3 via selective catalytic reduction (Jo et al., 2011; Lee et al., 2018). For example, sewage sludge biochars activated by water vapour (SCW) and KOH (SCK) effectively removed (Jo et al., 2011). NO_x removal was higher for SCK than SCW due to higher oxygen functional groups, surface area and NH_3 adsorption on the former than the latter (Jo et al., 2011). The selective catalytic reduction of NO_x in the presence of NH_3 have been reported in other studies for other biochars, and carbonaceous materials including coke and activated carbons (Teng et al., 2001; Szymański et al., 2004; Lee et al., 2018). In these studies, catalytic reduction was attributed to oxygen functional groups on the carbon surface.

4.1.3. H_2S and SO_2

H_2S is a major component of swine manure and biogas production processes, and it is obnoxious to the environment. As a result, a number of studies have investigated the use of biochar in sequestering H_2S from stored manure. For instance, biochar produced from bamboo, camphor, hardwood chips, pig manure, rice hull, and sludge was effective for H_2S uptake from biogas with a high q_{max} (100–380 mg/g) and removal efficiency exceeding 95% (Oliveira et al., 2017). The adsorption process was a function of biochar moisture (> 80% v/w), pH (> 7.0), surface area, and the presence of COOH and OH reactive groups. Another study used biochar derived from sewage sludge to capture H_2S from moist air (Bagreev et al., 2001). The adsorption capacity was double that of commercial activated carbon, and this increased with increasing pyrolysis temperature. The presence of metal oxides enhanced the sorption capacity of biochar. Yet another study investigated the properties and sorption mechanisms of H_2S on biochar produced from the camphor tree (Shang et al., 2012). All the biochars effectively removed H_2S (1.2–121.4 mg/g), and the removal capacity was governed by the

carbonization temperature, biochar pH, and particle size. The FTIR and pH data showed that hydroxide and carboxylic reactive groups governed H₂S sorption (Shang et al., 2012). Using an aerobic filter packed with compost and biochar, a related study reported a maximum H₂S removal capacity of 19–33 g/m³/h, with over 99% removal at a residence time of 119 s (Das et al., 2018).

A hazardous gas, SO₂, is produced when oxygen in air reacts with sulphur from human activities such as mineral ore smelting. A previous study assessed the potential application of biochar for SO₂ sequestration, and compared the influence of activation on pore formation and functional group evolution for SO₂ sorption (Braghiroli et al., 2019). The results showed that biochar developed porosity and surface functional groups, making it suitable for SO₂ sorption. The correlation between textural characteristics of biochar and SO₂ sorption was not obvious, and the maximum SO₂ sorption capacity did not correspond to biochars with the largest surface area, or pore volume. In fact, steam-activated biochar exhibited the highest SO₂ sorption owing to its optimum surface area (590 m²/g), pore volume (56 cm³/g), basicity, and the low content of acidic oxygen-carrying surface functional groups (Braghiroli et al., 2019).

A study demonstrated that simultaneous sequestration of NH₃, H₂S and toluene from producer gas is achievable with catalysts derived from biochar (Bhandari et al., 2014). The acidic surface of biochar showed the highest removal efficiency for toluene (97.5%) and longest breakthrough time for NH₃ (145 min). In another study, biochar exhibited high removal of ozone (55 ppbv) for up to 24 h, without evolving volatile by-products (Zhou et al., 2018).

In summary, a systematic understanding of how biochar synthesis procedures, biomass precursors, and resulting biochar characteristics are interrelated will assist in designing efficient biochars for the sorption of gases and other pollutants. The properties and sorptive performance of biochar are contingent upon the feedstock, pyrolysis conditions.

4.2. Organic contaminants

4.2.1. Volatile organic compounds (VOCs)

A range of VOCs are toxic even at trace concentrations. Their removal in the environment is therefore compelling. For instance, airborne benzene is harmful even at very low concentrations. Hence, an effective approach is necessary for its sequestration. High breakthrough volume, in this regard, the sorptive performance of biochar derived from biowastes in the sequestration of benzene was evaluated (Khan et al., 2018). The maximum amount of benzene adsorbed at 298 K (q_{max}) was in the range of 0.35 to 144 mg/g, and the 10% high breakthrough volume varied from 0.22 to 492 L/g. In a similar study, polydimethylsiloxane-coated biochar showed a significant increase in the adsorption of benzene relative to uncoated biochar (Liu et al., 2016). Another VOC, methyl *tert*-butyl ether (MTBE), which is a gasoline additive, was removed using biochar produced from agrowaste (Pongkua et al., 2018). Biochar derived from bagasse had the highest q_{max} (8.26 mg/g), whereas biochar from bones had the least (3.51 mg/g). This was attributed to the high ash content of bone biochar, and the surface functional groups which were mostly phosphates and ethers, and cannot bind with MTBE. In contrast, biochar derived from bagasse had lower ash content and the highest carbonyl and ester surface functional groups, which can effectively react with MTBE. Thus, ash content and surface functional groups can be used as a selection criterion for biochars for MTBE sequestration. A related study investigated gas phase sorption of acetone, cyclohexane, and toluene on biochar fabricated from common precursors at 300, 450, and 600 °C (Zhang et al., 2017). All the biochar materials had q_{max} for VOC in the range of 5.58 to 91.2 mg/g. The adsorption capacities were mostly affected by the biochar surface area and the amount of non-carbonized organic matter. Yet another study demonstrated that biochar derived from wood waste can effectively remove trace VOCs in biogas (Papurello et al., 2018). The q_{max} values were 158.8, 140.1,

and 64 mg/g for 2-butanone, toluene and limonene, respectively. Another study used biochars derived from coconut shell, oak, poultry litter, and swine manure pyrolyzed at 350 and 500 °C, and AC to eliminate indolic and phenolic compounds, reduced sulphur compounds, and volatile fatty acids from stored pig manure (Hwang et al., 2018). A range of other volatile organic compounds (VOCs) were adsorbed on biochar derived from bamboo, neem, and sugarcane biomass (Kumar et al., 2019). The porosity and surface area were the key determining factors for adsorption.

4.2.2. Emerging contaminants

Emerging contaminants are chemicals found at low concentrations in the environment as a result of new consumer habits and the emergence of advanced analytical technologies. Owing to their recency in different environmental compartments, emerging contaminants are usually not regulated, posing environmental and human health risks. Emerging contaminants include a variety of compounds, such as endocrine disrupting chemicals, illicit drugs, food additives, fire retardants, persistent organic pollutants, pharmaceutical and personal care products, pesticides, plasticizers, and solvents (Bedia et al., 2018). Emerging contaminants in flue gas may occur during the production of chemicals containing such emerging contaminants, and even in solid waste (Arukwe et al., 2012; Marcoux et al., 2013). Hence combustion of such wastes in water-to-energy, and pyrolysis systems may release flue gas enriched in emerging contaminants. Although emerging contaminants from industrial processes have been detected in atmospheric systems (Hoh and Hites, 2005; Cahill et al., 2007; Stock et al., 2007; Cecinato et al., 2012; Barroso et al., 2019), data on their removal in the gaseous phase using biochars has not been widely reported. However, several studies have demonstrated the capacity of biochars to remove emerging contaminants in aqueous solution (Sun et al., 2011; Jung et al., 2013; Wang et al., 2017a, 2017b; Ahmed et al., 2016; Lonappan et al., 2018; Ocampo-Perez et al., 2019; Silvani et al., 2019; Hassan et al., 2020; Keerthanan et al., 2020; Luo et al., 2020; Tong et al., 2020). It is unclear where the removal mechanisms of emerging contaminants in aqueous systems by biochars are also applicable to the gaseous systems. Hence, there is need for further research on the removal mechanism of emerging contaminants in gaseous systems.

4.3. Mechanisms of contaminant removal

Contaminant removal mechanisms are usually governed by the interactions between pollutant molecules and different biochar aspects. Reviews on the removal mechanisms for gaseous pollutants using biochar are limited. However, parallels can be drawn from the removal of similar pollutants from aqueous systems, and a number of reviews on this exist (e.g., Rajapaksha et al., 2016; Oliveira et al., 2017; Tran et al., 2017; Xu et al., 2017; Dai et al., 2019; Premarathna et al., 2019; Tran et al., 2020). Fig. 4 summarizes the key removal mechanisms of various gaseous contaminants. The sorption of organic molecules is largely through chemisorption and physisorption processes (Rajapaksha et al., 2016). Chemisorption processes include electrophilic interactions, ion-exchange, surface complexation, and physisorption processes comprise of electrostatic interactions through π - π electron donor-acceptor between biochar and aromatic functional groups of organic molecules, hydrogen bonding via oxygenated moieties such as -COOH, -OH, and R-OH groups, hydrophobic interactions, and pore-filling (Rajapaksha et al., 2016; Premarathna et al., 2019). Such mechanisms are dominant in the removal of compounds such as glyphosate (Herath et al., 2016), benzene (Liu et al., 2016; Khan et al., 2018), toluene (Papurello et al., 2018), and polycyclic aromatic hydrocarbons and phenolic compounds (Ahmed et al., 2016; Oliveira et al., 2017), which either have aromatic rings and/or oxygen-carrying groups. Heavy metals such as Hg⁰ are also predominantly removed through complexation via the lone electrons of the oxygen atoms and other heteroatoms such as nitrogen and sulphur that can be deliberately introduced into the biochar matrix

during synthesis (Penido et al., 2019; Xu et al., 2019a, 2019b). Another mechanism involved in the removal of heavy metals is via precipitation (Shen et al., 2015a, 2015b; Wang et al., 2017a, 2017b). The main driving force of hydrophobic interactions is entropy. Although its underlying principle is unclear, these interactions are thought to be non-specific, and emanate from the aggregation of non-polar functional groups (Tong et al., 2019). Furthermore, other mechanisms such as partitioning in non-carbonized fraction owing to the reduction of the polarity of biochar (Zhang et al., 2017; Tong et al., 2019), chemical conversion through reductive processes or electrical conductivity, and mineralization through biodegradation by various microorganisms in the micro-pores and on the biochar surface, have been reported (Oliveira et al., 2017). The distribution of organic pollutants into the non-carbonized fraction usually yields strongly linear isotherms, whereas adsorption onto the carbonized regions is associated with curved isotherms (Tong et al., 2019). However, few studies have investigated the relative contribution of the various mechanisms to the removal of gaseous contaminants by biochars.

From a thermodynamic perspective, attachment through adsorption occurs spontaneously since Gibbs free energy change (ΔG) < 0 . The driving force is the summation of several forces contributing to ΔG , including intra- and inter-molecular interactions originating from electrostatic attractions such as dipole interactions, covalent bonding, and coulombic attractions. A more detailed treatment of thermodynamics is presented in Section 5.2. Examples of dipole interactions are charge-dipole interactions, hydrogen bonding, fluctuating dipoles, and π -interactions (Herath et al., 2016; Tong et al., 2019). Biochar surfaces can carry a net negative or positive charge depending on pH of the solution. When $\text{pH} > \text{pH}_{\text{zpc}}$, the biochar surface is negatively charged, and when $\text{pH} < \text{pH}_{\text{zpc}}$, the surface carries a positive charge. This can enable electrostatic attraction between the biochar surface and the anionic or cationic species of pollutants (Premarathna et al., 2019). The degree of dissociation of organic pollutants is also pH dependent (Tong et al., 2019).

Hydrogen bonding is a form of strong dipole interactions arising from interactions between a hydrogen donor and an acceptor. Usually

the hydrogen donor is chemically bonded to hydrogen acceptors, for instance N, O, or F, and electron-dense π -systems. The hydrogen donor/acceptor moieties on either biochar or organic pollutants can participate in hydrogen bonding. In some instances, adsorption is governed by physical bonding/intermolecular forces such as van der Waals forces and dipole-dipole interactions (Premarathna et al., 2019).

Apart from reaction thermodynamics, kinetic and isotherm modeling provide information of removal mechanisms. Compared to literature on removal of contaminants in aqueous systems (Gedam et al., 2019; Liu et al., 2019a, 2019b; Tong et al., 2019), limited data exist on the thermodynamics, and isotherm and kinetic models for the adsorption of gaseous contaminants on biochars. The available data are also limited to a few gaseous contaminants, specifically CO_2 (Bamdad et al., 2019) and VOCs (Zhang et al., 2019a, 2019b, 2019c). The reasons for the limited data are unclear, but could be attributed to the challenges associated with setting up and conducting such experiments for gaseous systems. Yet such information provides critical insights on the contaminant removal rate, mechanisms and thermodynamic feasibility (Bamdad et al., 2019). The available evidence on kinetic and isotherm models, and thermodynamics are summarized in Section 5.

5. Thermodynamics, kinetics and isotherm models

5.1. Adsorption kinetics

Studies investigating adsorption kinetic in gaseous systems are limited to CO_2 and some VOCs, and H_2S . These studies are based on two techniques; (1) fitting kinetic models (e.g., pseudo-first order, pseudo-second order) to experimental data (Bamdad et al., 2019; Zhang et al., 2019a, 2019b, 2019c; Shen and Zhang, 2019; Zhou et al., 2019), and (2) thermogravimetric analysis (Xu et al., 2019a, 2019b). For CO_2 , the pseudo-first order kinetic models gave a better fit to data than the pseudo-second order at room temperature (273 °C) (Bamdad et al., 2019). This suggests that CO_2 adsorption occurs via physisorption (Bamdad, 2019). In the case of VOCs, the best kinetic model varied among the various VOCs and biochars investigated. On the one hand,

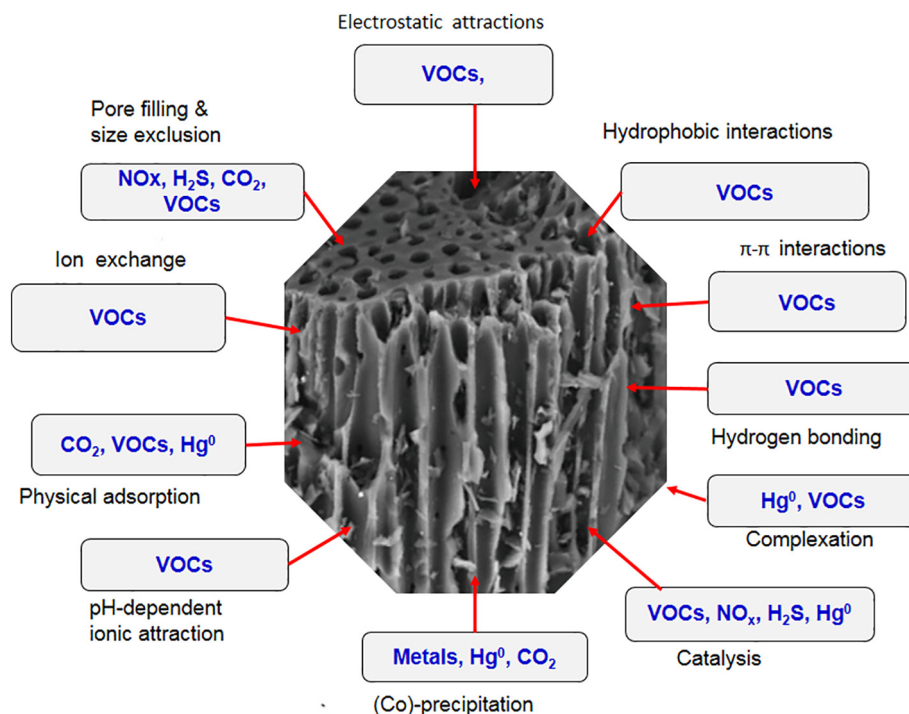


Fig. 4. Summary of contaminant removal mechanisms by biochars.

the first-order kinetic model gave a better fit ($r^2 = 0.946$ – 0.946) than the pseudo-second order model ($r^2 = 0.879$ – 0.887) for VOCs (acetone and cyclohexane) adsorption on H_3PO_4 -activated hickory hydrochar (HHP), which had a large surface area (Fig. 5, Zhang et al., 2019a, 2019b, 2019c). On the other hand, the same study showed that, the pseudo-second order kinetic model gave a better fit ($r^2 = 0.966$ – 0.999) to the experimental data on VOC adsorption on the other biochars than the pseudo-first order model ($r^2 = 0.877$ – 0.986) (Fig. 5, Zhang et al., 2019a, 2019b, 2019c). Thus, VOC removal by HHP occurred via physisorption, while chemisorption was dominant for the other biochars.

The adsorption kinetics of H_2S in a plug flow reactor with a fixed bed packed with biochars derived from camphor (CB), bamboo (BB) and rice husk (RHB) were investigated using the Michaelis–Menten model (Shang et al., 2012). This model has two parameters describing the adsorption process: (1) the maximum removal capacity (V_m , g S/kg dry material/h), and (2) the saturation constant (K_s , $\mu\text{L/L}$). The model showed a good fit to the experimental data as evidenced by high regression coefficients (r^2) close to unity (i.e., BB: $r^2 = 0.9938$; CB: $r^2 = 0.9962$; RHB: $r^2 = 0.9938$). The V_m (g S/kg dry material/h) values were: CB: 0.036 ± 0.01 ; BB: 0.058 ± 0.02 and RHB: 0.070 ± 0.02 , and the corresponding K_s ($\mu\text{L/L}$) values were: CB: 9.90 ± 0.12 ; BB: 28.72 ± 0.11 and RHB: 173.36 ± 0.15 . Accordingly, the maximum H_2S removal capacity of RHB ($49.2 \pm 0.03 \mu\text{L/L}$) was higher than that of BB ($46.5 \pm 0.05 \mu\text{L/L}$) and CB ($43.8 \pm 0.04 \mu\text{L/L}$). The same authors proposed that H_2S removal occurred via a series of processes entailing: (1) the adsorption of H_2S on the biochar surface, (2) the dissolution and subsequent dissociation of adsorbed H_2S in the water film, (3) the surface reaction of the H_2S with adsorbed O_2 , and the subsequent formation of elemental sulphur or sulphur dioxide, and (4) further oxidation of S or SO_2 by O_2 under aqueous conditions to form H_2SO_4 (Shang et al., 2012). A study on the adsorption of acetone and cyclohexane on pristine and activated peanut hull and hickory wood hydrochars showed that the adsorption capacities of different gaseous contaminants (acetone and cyclohexane) is affected by different types of hydrochars (Fig. 5) (Zhang et al., 2019a, 2019b, 2019c).

Studies also show that the adsorption capacity of VOCs depends on the molecular kinetic diameter and polarity of the VOCs (Zhang et al., 2017). Specifically, VOCs with smaller kinetic diameters and higher polarity exhibit higher adsorption capacities than their counterparts with higher kinetic diameters and lower polarity (Zhang et al., 2017). For example, the adsorption capacities of acetone on different biochars (7.06–91.16 mg/g) were higher than that of cyclohexane (5.58–69.33 mg/g) and toluene (12.63–62.91 mg/g). The higher adsorption capacity of acetone was attributed to its high polarity and smaller kinetic diameter relative to that of toluene and cyclohexane (Zhang et al., 2017).

However, the available data on adsorption kinetic only represent a small fraction of typical gaseous contaminants in flue gases. Thus, further work is required to include additional gaseous contaminants such as metals, non- CO_2 acidic and greenhouse gases, and emerging contaminants. In addition, the interactive effects (e.g., synergistic, or inhibitory) of co-occurring inorganic constituents and gases on the adsorption kinetics require further investigation. Depending on the nature of the inorganic constituents, the biochar and the gaseous contaminant under consideration, synergistic, inhibitory and neutral effects may occur.

5.2. Thermodynamics

Thermodynamic studies provide the following critical parameters: (1) change in Gibbs free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS). These thermodynamic parameters provide further insights into the reaction mechanisms, behaviour, and feasibility (Chen and Zhang, 2014; Bamdad et al., 2019). Specifically, ΔG is used to evaluate the spontaneity of the adsorption processes, where negative values of ΔG indicate that the process is energetically feasible (Bamdad

et al., 2019). Negative and positive values of ΔH indicate that the adsorption process is exothermic and endothermic, respectively (Bamdad et al., 2019). The ΔS is a measure of the degree of randomness and affinity of the gaseous contaminant (adsorbate) towards the biochar surface (Chen et al., 2009b). Negative values of ΔS indicate a decrease in randomness in the arrangement of the adsorbate at the fluid/solid interface during adsorption, while positive values reflect an increase in randomness at the interface (Chen et al., 2009; Al-Salehin et al., 2019; Tran et al., 2019).

Barring a few exceptions (Bamdad et al., 2019; Zhang et al., 2019a, 2019b, 2019c), data is even more limited for thermodynamics than kinetics. As for kinetics, the few available studies are limited to CO_2 and VOCs (Bamdad et al., 2019; Zhang et al., 2019a, 2019b, 2019c). For example, Zhang et al. (2019a, 2019b, 2019c) investigated the adsorption of VOCs, specifically acetone on H_3PO_4 -activated peanut hull hydrochar. The differential scanning calorimetry curve for acetone showed that the adsorption processes was accompanied by a distinct exothermic peak (Zhang et al., 2019a, 2019b, 2019c). Hence, VOC adsorption on biochar occurred via a physical exothermic process. This conclusion is consistent with earlier studies showing that the adsorption of VOCs, specifically toluene, acetone and cyclohexane on biochars is an exothermic process (Zhang et al., 2017).

Bamdad et al. (2019) investigated the thermodynamics of CO_2 adsorption on biochar derived from softwood sawdust produced in an auger pyrolysis reactor at 500 °C. Thermodynamic parameters (ΔG , ΔH , ΔS) were determined at four temperature values: 293 K, 313 K, 333 K and 353 K. In the same study, negative ΔG values were observed for all temperatures, indicating that the adsorption process was spontaneous across the investigated temperature ranges. Increasing the temperature from 293 to 353 K reduced the absolute values of ΔG , demonstrating that, adsorption of CO_2 on softwood sawdust biochar was more favourable at lower temperatures than at higher temperature. The values of ΔH were negative for all the four temperatures, indicating that the adsorption was an exothermic process (Plaza et al., 2014). Some studies show that, exothermic physisorption typically releases heat of adsorption values (ΔH) ranging from 0 to 20 kJ/mol compared to 80 to 400 kJ/mol for chemisorption (Gereli et al., 2006). Bamdad et al. (2019) observed ΔH values of -3.49 to -15.39 kJ/mol, suggesting that the adsorption process was dominated by physisorption. Similar findings were observed for CO_2 adsorption on activated carbon derived from eucalyptus wood modified by NH_3 solution via heat treatment (Heidari et al., 2014). The values of ΔS were negative, ranging from -9.16 to -33.7 kJ/mol, indicating a reduction in randomness, and high affinity of CO_2 for the biochar/ CO_2 interface (Chen et al., 2009; Bamdad et al., 2019). However, besides CO_2 and VOCs, the thermodynamic studies investigating the removal of several other flue gas contaminants on biochars remain limited. Hence further studies are required to investigate this aspect, because such information is critical for the design of large-scale flue gas filters using biochar as an adsorbent.

5.3. Isotherm modelling

Isotherm modelling provides insights on the adsorption equilibria, biochar surface properties and the distribution of the adsorbate on the biochar surface (Bamdad et al. 2019). Several isotherm models exist, but the Langmuir and Freundlich isotherms are the most studied. On the one hand, the Langmuir isotherm is commonly used for homogeneous monolayer adsorption, and is premised on the following assumptions: (1) adsorbents have a fixed number of well-defined adsorption sites on which adsorbates undergo adsorption, (2) all adsorption sites have the same energy and probability of adsorbing the adsorbates, and (3) no interactions occur among neighbouring adsorbed molecules of the adsorbate (Langmuir, 1916; Tran et al., 2017). On the other hand, the Freundlich isotherm is commonly applied to describe multi-layer adsorption on heterogeneous surfaces, characterized by variable

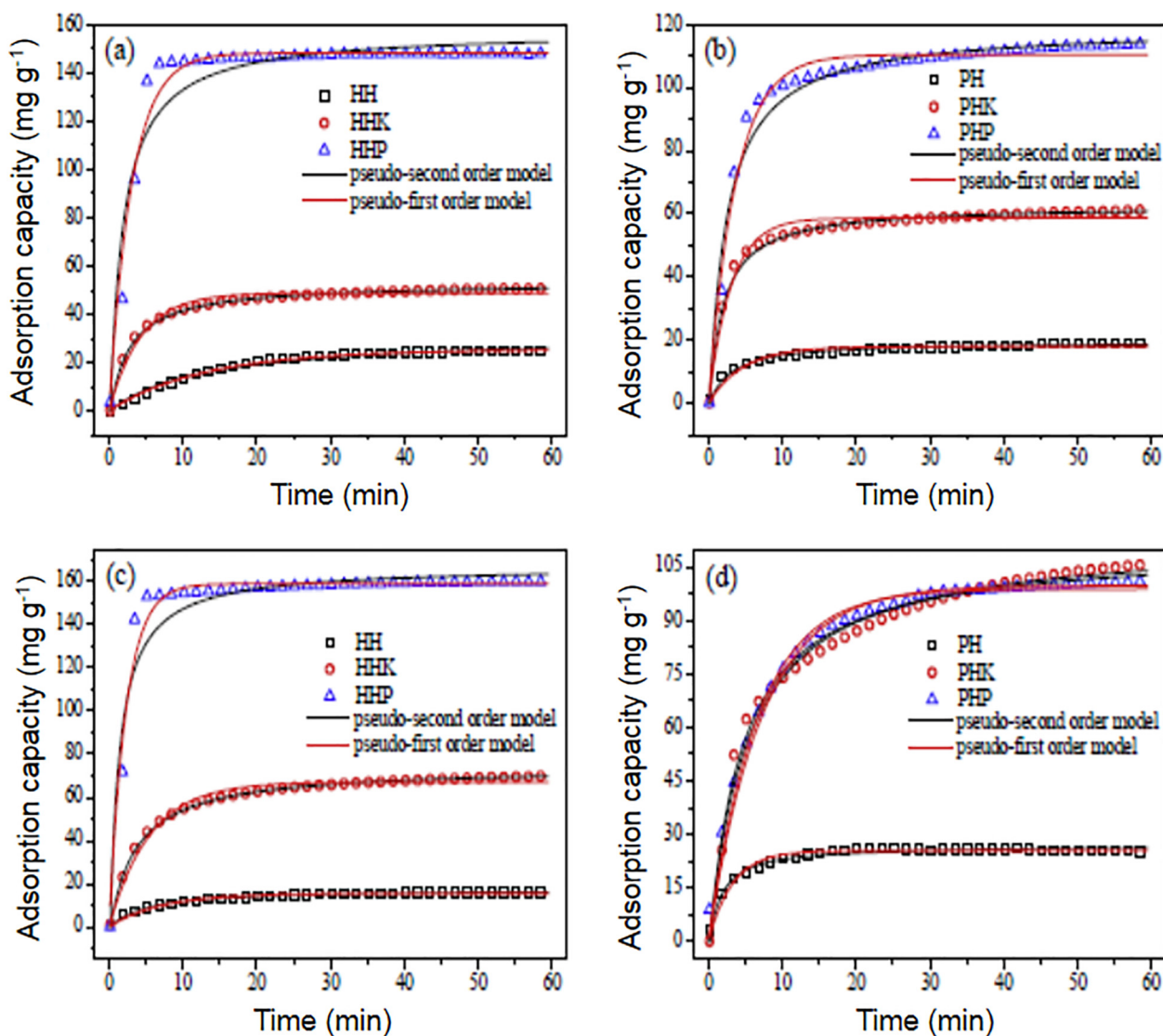


Fig. 5. Adsorption kinetics of acetone (a, b) and cyclohexane (c, d) on pristine and activated peanut hull (pH) and hickory wood hydrochars (HH). HH: pristine hickory hydrochar, pH: pristine peanut hull hydrochar; HHK: KOH-activated hickory hydrochar, PHK: KOH-activated peanut hull hydrochar HHP: H₃PO₄-activated hickory hydrochar, PHP: H₃PO₄-activated peanut hull hydrochar. Zhang et al., 2019c. Reproduced with permission from Elsevier Pvt.

distribution of heat of adsorption as well as the affinity of the adsorbate (Freundlich, 1926; Tran et al., 2017; Bamdad et al., 2019). According to the Freundlich isotherm, the binding strength of the adsorbate to the adsorbent decreases with increase in occupation of the adsorption sites. Hence, adsorption sites with high binding affinities are preferentially occupied by adsorbate molecules relative to those with weaker binding affinities (Khan and Khan, 2015; Tran et al., 2017; Bamdad et al., 2019).

Few studies have investigated isotherm modelling of flue gas on biochars, and these studies are limited to the Langmuir and Freundlich isotherms (Bamdad et al., 2019). Bamdad et al. (2019) investigated isotherm modelling of CO₂ on biochar from softwood sawdust produced at a pyrolysis temperature of 500 °C. The maximum adsorption capacity (q_{max}) of the biochar (2.4 mmol CO₂/g) was approximately 1.4 times that of a commercial Zeolite-13X, which had a q_{max} of 1.7 mmol CO₂/g. The Freundlich isotherm ($r^2 = 0.99$) produced a better prediction of the experimental results than the Langmuir isotherm ($r^2 = 0.86$). This suggests that, the biochar investigated had a highly heterogeneous surface that enabled multilayer adsorption (Tran et al., 2017; Bamdad et al., 2019). The Freundlich isotherm parameters related to adsorption capacity (K_f) and intensity ($1/n$) were 2.5 and 1.47, respectively. Being higher

than 1, the value of $1/n$ suggests a sigmoidal or S shaped adsorption curve. Such an adsorption isotherm is indicative of strong adsorbate-adsorbate interactions, but weak adsorbate-adsorbent interactions (Ryu et al., 1999). However, isotherm modelling studies for several other gaseous contaminants in flue gases are scarce.

5.4. Biochar catalysis

Recently, biochar-based catalysis has received significant research attention (Lee et al., 2017). For example, pristine biochars and their derivatives such as metal/metal oxide-biochar composites act as auto-catalysts, photo-catalysts and even as a carriers of catalysts for various applications (Dehkoda et al., 2010; Kim and Kan, 2016; Lee et al., 2017; Mian and Liu, 2018). For example, oxygen functional groups on biochar surfaces also act as catalysts in the selective catalytic reduction of NO_x in the presence of NH₃ (Jo et al., 2011; Lee et al., 2018). A few reviews presenting an overview of the synthesis and potential applications of biochar catalysts exist (Lee et al., 2017; Mian and Liu, 2018). Thus, besides adsorption, reactive gaseous contaminants in flue gases such as H₂S, SO₂, VOCs and even emerging contaminants may undergo biochar-catalysed reactions. For example, a biochar catalyst prepared

by the sol-gel method using walnut shell biochar, $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$ and NaCO_3 as precursor materials was used for the catalytic hydrolysis of carbon disulphide (CS_2) and carbonyl sulphide (COS) (Song et al., 2017).

Biochar-based catalysts can also be used for the catalytic oxidation of VOCs (Shen, 2015; Shen et al., 2015a, 2015b) and even other organics such as emerging contaminants (Kim and Kan, 2016). Li et al. (2019) showed that pine biochar impregnated with CuO-MnO_x oxides removed 89% of formaldehyde (HCHO) and 83% of Hg^0 at 175 °C. The authors attributed the high removal rates to both adsorption and catalysis. A few studies have investigated biochar catalysis for contaminants including pharmaceuticals in aqueous systems (Kim and Kan, 2016). However, the application of biochar catalysis in remediation of gaseous contaminants typical of those in flue gases is still in its infancy. Adsorption as a remediation technology is often criticized because it only transfers contaminants from the fluid phase (gaseous or aqueous) to the solid phase, and generates spent adsorbents whose disposal pose challenges. Biochar catalysis overcomes these challenges by combining adsorption and subsequent degradation, for example via catalytic oxidation. Thus, biochar catalysis has the potential to transform toxic organics such as VOCs and gaseous emerging contaminants into less toxic or even benign degradation products such as water. In this regard, the development and subsequent applications of biochar catalysts in an emerging area of research in biochar-based air filter systems. On the one hand, metal/metal oxides are well-known catalysts, but their key limitation is a low surface area due to particle aggregation especially at high temperatures (Zhou et al., 2019). Moreover, catalysts require frequent replacement (Zhang et al., 2019a, 2019b, 2019c). On the other hand, pristine biochars have high surface area, but low or limited catalytic activity, hence rely predominantly on adsorption for the removal of contaminants (Gwenzi et al., 2017). Thus, metal/metal oxide-biochar catalysts are particularly promising in environmental remediation, because they combine the capabilities of both biochar and metal/metal oxides, while minimizing the limitations of the individual components.

5.5. Interactions in multi-component gaseous systems

The bulk of studies investigating the removal of gaseous contaminants using biochars focuses on single component systems (e.g., Bamdad et al., 2019; Xu et al., 2019a, 2019b), while a few studies have considered binary adsorbate systems. Yet in reality, gaseous contaminants in flue gas are complex multi-component systems that may entail both organic and inorganic contaminants. These organic and inorganic gaseous contaminants may interact among themselves, and even with inorganic and organic phases on the biochar. For example, biochars enriched in inorganic constituents, specifically CaCO_3 and $\text{Ca}(\text{PO}_3)_2$, increased SO_2 adsorption through the formation of various sulphate minerals (Xu et al., 2019a, 2019b). Xu et al. (2019a, 2019b) demonstrated that, SO_2 sorption via the formation of sulphate minerals accounted for about 45 to 85% of the total SO_2 sorption.

Zhu et al. (2016) investigated the synergistic removal of mercury by ammonium halides modified rice husk biochar (RHC) in the presence of SO_2/NO in flue gas from a coal-fired system. Unlike metal halides and oxides, which have catalytic activity, ammonium halides are neither strong catalysts nor strong oxidants (Zhu et al., 2016). However, the ammonium bromide impregnated biochar showed excellent gaseous mercury removal of 80% in a fixed-bed system (Zhu et al., 2019). The same study showed a synergistic removal of SO_2/NO for both the ammonium halides modified biochar and coal-based activated carbon. The ammonium halide impregnated biochar retained the micropore structure of the RHC, but the physisorption energy decreased significantly (Zhu et al., 2019). The authors attributed the synergistic removal of SO_2/NO to the potential oxidation effect of the O_2 and H_2O in the flue gas, and possibly the catalytic effect of the carbonaceous adsorbent. One study investigated the adsorption of phenol and toluene on rice husk biochar

in a binary mixture of the two gases (Shen and Zhang, 2019). The results showed that, in a binary mixture of the two gases, the adsorption of toluene preceded that of phenol (Shen and Zhang, 2019). (Shen and Zhang, 2019).

Besides synergistic effects, neutral and even inhibitory/competitive effects may also occur in multi-component systems. For example, the NO and SO_2 inhibited the removal of formaldehyde by a CuO-MnO_x -biochar composite (Li et al., 2019). In the same study, NO slightly improved Hg^0 removal, while SO_2 had an inhibitory effect. The strong synergistic effect between a mixture of CuO and MnO_x was critical for the removal of HCHO and Hg^0 via a redox equilibrium processes ($\text{Mn}^{4+} + \text{Cu}^+ \leftrightarrow \text{Mn}^{3+} + \text{Cu}^{2+}$). In some cases, inhibitory effects may also occur via competitive adsorption processes driven by gas pressures (concentrations) and even differences in molecular sizes. Competitive adsorption, driven by concentration differences and molecular sizes may also occur, particularly for aromatic compounds (Shen and Zhang, 2019). Thus, removal of gaseous contaminants in multi-component systems is more complex than often reported in single component systems. However, the available data on interactions among adsorbates, and between adsorbates and solid constituents on biochars are still limited. Thus, the extent to which biochar-catalysed reactions and interactions among flue gases, and inorganic and organic constituents affect the adsorption process of various other gaseous contaminants in flue gases remain poorly understood. Moreover, studies investigating the thermodynamics, kinetics and isotherm modelling of such systems are still limited. Hence, the capacity of existing kinetic and isotherm models to predict adsorption behaviour in multi-component gaseous systems is largely unknown. The interactive effects occurring in multi-component systems, and their thermodynamic, kinetic and isotherm modelling warrant further research.

6. Potential applications, regeneration and disposal

6.1. Opportunities and potential applications

Increasing interest in renewable materials, coupled with global interest to reduce industrial emissions, present immense opportunities for the application of biochar technology in mitigation of gaseous industrial emissions. The potential application domains of biochar are highlighted, including; (1) industrial production processes, (2) livestock production systems, (3) energy generation, (4) solid waste disposal, and (5) wastewater treatment. These application domains points to the existence of opportunities to further develop and scale up the biochar technology.

(1) Waste-to-energy systems

Waste-to-energy systems are an emerging technology for the concurrent disposal of biosolids such as sludges from wastewater and energy generation. However, waste-to-energy systems generate significant quantities of toxic emissions such as HCl , SO_2 , NO_x (Ma et al., 2019), which can be mitigated using biochars as filter materials.

(2) Incinerators

Incineration is the recommended disposal method for hazardous solid wastes including infectious materials from health care systems and the funeral industry, and livestock carcasses with infectious diseases such as foot and mouth diseases. Incineration of these hazardous waste materials releases toxic gaseous pollutants such polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs), SO_2 and NO_x . Hence, scope exists for the application of biochar-based air pollution control systems to reduce gaseous emissions. Meanwhile, future work is required to investigate the potential of biochars to remove PCDDs, PCDFs, and PCBs.

(3) Smelters

Smelters widely used in the mining and mineral processing sectors such as metallurgy may release gaseous emissions including toxic metals, and organic contaminants from the combustion of coal. Environmental regulations require that gaseous emissions from such smelters should not exceed the set maximum guidelines. Hence, biochar-based filters can be developed for the removal of metals and organic contaminants in gaseous emissions.

(4) Industrial kilns

Biomass and coal-fired kilns are widely used in industrial production systems including the production of ceramics, fired bricks and cement. Flue gases from such kilns contain a wide range of toxic contaminants. Evidence summarized in the current review show that, such contaminants can be potentially removed using biochar-based filters.

(5) Cremation

Cremation of human cadavers releases inorganic and organic contaminants including, among others, (1) elementary mercury (Hg^0) from dental amalgams (Takaoka et al., 2010), and (2) highly toxic and persistent organic pollutants such as poly-chlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) (Kuchnicki, 2019). Biochars have the capacity to remove Hg^0 , and possibly persistent organic pollutants, although further research is required on the latter.

(6) Boilers and cookers

Biomass and coal-fired industrial boilers and cookers are still widely used in some countries for industrial and institutional heating and cooking systems including in schools and hospitals. Biochar-based filters can be integrated in such systems to minimize gaseous emissions.

(7) Agricultural production systems

Biomass and coal-fired curing systems are widely used in developing countries for curing crops such as tea, coffee and tobacco, and concerns have been raised about emissions from such systems (Gwenzi et al., 2020). Animal husbandry such as chicken, cattle and pig production systems release odorous VOCs, which are a public health nuisance. A few studies show that biochars have capacity to remove such odorous VOCs (Maurer et al., 2017; Zhang et al., 2017; Hwang et al., 2018).

(8) Wastewater treatment

Wastewater treatment releases odorous organic compounds, while anaerobic digestion produces H_2S and methane. Thus, biochar filters can be used to reduce emissions of such gases from point sources in the wastewater treatment process.

6.2. Regeneration of spent biochars

Besides the adsorption capacity, the large-scale application of biochars also depends on their capacity to be regenerated (Bamdad et al., 2019). Spent biochars can be regenerated for a number of cycles via physical and chemical desorption methods before final disposal. However, to date, studies investigating the regeneration of biochars following sorption of gaseous contaminants are limited to thermal desorption methods (Bamdad et al., 2019; Shen and Zhang, 2019; Xu et al., 2019a, 2019b). A few studies have investigated the regeneration of spent biochars after adsorption of gaseous contaminants. For example, Xu et al. (2019a, 2019b) investigated the regeneration of biochar/Fe oxyhydroxide composite using low temperatures ranging from 50 to 125 °C. Results showed that, the low temperatures effectively

desorbed about 99% of the chemically-sorbed CO_2 by raising the temperature to 50 °C. Hence, the biochar/Fe oxyhydroxide composite had a competitive advantage over other carbon based CO_2 sorbents, which are either not regenerable or require high regeneration temperature. The low desorption temperature for the biochar-Fe oxyhydroxide is indicative of physisorption (Creamer et al., 2014; Xu et al., 2019a, 2019b).

Shen and Zhang (2019) investigated the desorption of VOCs from spent rice husk biochar using thermogravimetric analysis. The thermogravimetric profiles of both the pristine and spent biochars exhibited remarkable mass loss. The maximum mass loss was observed in the spent biochar, indicating the highest desorption of toluene and phenol. The thermogravimetric profiles for spent biochars had two sharp peaks, one at 30 to 100 °C corresponding to the evaporation of water, and another one at 150 to 350 °C ascribed to the evaporation of toluene (Yang et al., 2018; Shen and Zhang, 2019). By contrast, the thermogravimetric profile of the pristine biochar had one peak at 30–100 °C indicating water evaporation. The authors further noted that, the high boiling temperatures of toluene (110.6 °C) and phenol (181.9 °C) made them difficult to volatilize under ambient conditions, justifying the need for thermal regeneration at higher temperatures.

Bamdad et al. (2019) investigated the regeneration of biochar derived from softwood sawdust via thermal desorption of CO_2 at 100 to 500 °C. The same authors observed that the adsorption capacity of the biochar slightly decreased after each regeneration cycle (Fig. 6). Specifically, the adsorption capacity was reduced by just 0.8% after the first three cycles (Fig. 6), while the BET surface area was reduced by just 12% from 0.033 cm^3/g for the pristine biochar to 0.029 cm^3/g for the spent biochar. The 12% reduction in BET surface area accounted for the slight decrease in the adsorption capacity. Overall, these results indicate the high stability of the spent biochar relative to its pristine counterpart. The FTIR spectra for the spent and regenerated biochars showed CO_2 peaks, indicating residual CO_2 even after desorption (Fig. 6 insert). This observation was further supported by desorption tests conducted in 3Flex surface characterization analyser (MicroMetrics) showing CO_2 on the structure the regenerated biochar.

In another study, Bamdad et al. (2019) conducted a series of adsorption-desorption experiment under ambient room temperature using N_2 . The use of ambient temperature was motivated by three reasons: (1) the need to minimize thermal degradation of the biochar, which could compromise its subsequent use as a soil amendment, and (2) to understand the binding energy and CO_2 sequestration capacity of the biochar under ambient conditions, and (3) to avoid changes in biochar structural properties induced by high temperatures in order to understand the impacts of regeneration on subsequent adsorption capacity. In summary, the results showed that; (1) the adsorption capacity is only slightly decreased after the first three cycles, a trend similar to that in Fig. 6 observed at high temperatures of 100–150 °C (Bamdad et al., 2019); and (2) the adsorption capacity has decreased by 4–8% after five cycles, and 20% after ten cycles. As observed in another study by the same author (Bamdad, 2019), FTIR vibrations similar to Fig. 6 (insert), and desorption tests using 3Flex surface characterization analyser (MicroMetrics) showed that some residual CO_2 occurred on the surface of the regenerated biochar, possibly due to chemisorption (Bamdad, 2019). This residual CO_2 , coupled with a slight decline in BET surface area explained the slight decline in adsorption capacity with increasing regeneration cycles.

Taken together, the available evidence (Bamdad, 2019; Bamdad et al., 2019; Shen and Zhang, 2019; Xu et al., 2019a, 2019b) shows that biochars have good regeneration potential using thermal desorption. The thermal regeneration temperatures reported in these studies are lower than the 400 to 500 °C required for commercial activated carbon (Shen and Zhang, 2019). This suggest that, thermal regeneration of biochars is less energy intensive, hence could be relatively cheaper and environmentally friendly than that of activated carbon, but further evidence covering other gaseous contaminants is required. The thermal desorption depends on the nature and properties of the adsorbed gas

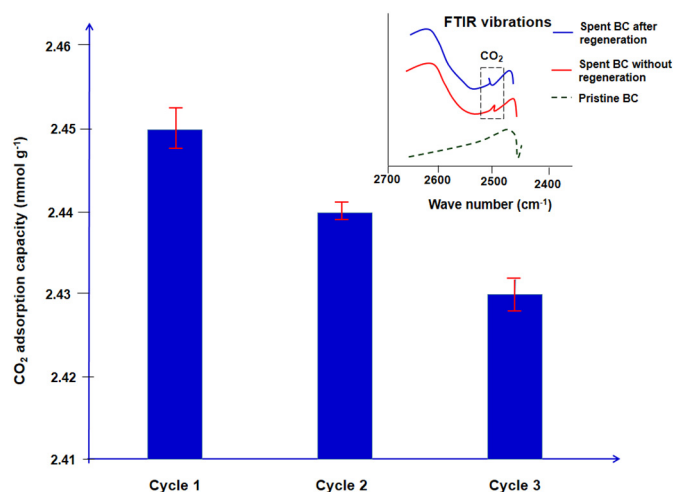


Fig. 6. CO₂ adsorption capacity of softwood biochar produced at 500 °C as a function of three regeneration cycles. **Insert:** FTIR vibrations indicating CO₂ on spent biochars with and without regeneration, but not on pristine biochar. Exaggerated to facilitate visualization. Adapted from data in Bamdad et al., 2019.

(e.g., boiling point) and the biochar (e.g., surface properties), specifically the binding energy between the two. Although high regeneration temperatures accelerate the desorption process, they are costly and could degrade the biochar (Chatterjee et al., 2018; Bamdad et al., 2019). The thermal degradation of the biochar at high temperatures may compromise the subsequent applications of the spent biochars as a soil amendment, energy source and construction materials (Section 6.3). Therefore, in cases where spent biochars are intended for other applications, low regeneration temperatures could be ideal in order to avoid degradation of the biochar. Regeneration of spent biochars potentially releases the previously sorbed gaseous contaminants back into the environment. Thus further research is required to explore the possibility to capture the desorbed gaseous contaminants, and possibly use them to develop novel value-added products. However, the feasibility of capturing and using the previously adsorbed contaminants as industrial raw material remain largely unexplored. Barring thermal regenerations, limited data exists on chemical desorption techniques using inorganic and organic solvents. Hence, this aspect calls for further research.

6.3. Final disposal for spent biochars

Strongly acidic, alkaline, and redox conditions, coupled with high turbulence in industrial air filter systems may cause the mechanical and chemical degradation of the biochars (Shen and Zhang, 2019). Moreover, the adsorption capacity may also decline after several regeneration cycles (Fig. 6). Therefore, after a number of regeneration cycles, spent biochars will ultimately lose mechanical and chemical stability, and contaminant adsorption capacity. The disposal of such spent biochars has received limited attention in the literature. Potential disposal methods include: (1) land application as a soil amendment, (2) briquetting and subsequent combustion as a solid fuel, and (3) use as a filler material in novel construction materials. The application of spent biochars as a soil amendment is motivated by its capacity of biochars to sequester soil carbon, and improve soil quality and crop growth (Gwenzi et al., 2015). However, concerns have been raised about the environmental health risks, behaviour, and fate of contaminants in spent biochars (Gwenzi et al., 2017). For example, soil application of spent biochars may transfer contaminants into the human food chain via plant uptake and subsequent bioaccumulation in edible plant plants (Gwenzi et al., 2017).

Biochars have higher calorific values (16–35 MJ/kg) comparable to, or even higher than, those of wood and most types of coal (Mullen

et al., 2010; Gwenzi et al., 2015; Gwenzi, 2018), hence can be used as an energy source. Due to its loose nature, granular biochars have low energy value per unit volume, and is difficult to handle. The conversion of granular biochars into high-energy solid fuel via briquetting have the potential to overcome these limitations (Abdullah and Wu, 2009; Abdullah et al., 2010; Peters et al., 2015; Gwenzi, 2018). Abdullah and Wu (2009) developed a solid fuel from biochar made from mallee wood pyrolysed at 400 °C, and evaluated its mechanical and energy properties. The volumetric energy density of the biochar solid fuel (19 GJ/m³) was double that of the pristine wood (8 GJ/m³) (Abdullah and Wu, 2009). Some studies also evaluated the particulate and gaseous emission of biochar solid fuels (e.g., Gao and Wu, 2011; Peters et al., 2015). The resulting biochar solid fuel can be used as a stand-alone fuel or in co-combustion systems. However, detailed studies are required to understand the environmental footprints of such biochar fuels relative to conventional fuels such as wood, charcoal and coal.

Recent studies show that, due to their low density and low thermal conductivity, biochars can be used as filler materials in novel construction material with excellent thermal and acoustic insulation properties (Gupta et al., 2018; Wang et al., 2019). For example, biochar has been used in the following applications: (1) as a filler material in high insulation biochar-clay plaster (Schmidt and Wilson, 2014), (2) carbon capturing and sequestering construction material (Gupta et al., 2018), and (3) as a green admixture in sediment-based construction materials (Gupta et al., 2018). However, the long-term engineering and thermal behaviour of such novel biochar-based construction materials require further investigation. The extent to which the use of spent biochars stabilizes the inherent contaminants in such construction material require further investigation. In addition, the behaviour and fate of contaminants in construction and demolition debris containing spent biochars are still poorly understood. These early results suggest that, scope exists to use spent biochars as a soil amendment, solid fuel and as a novel construction material. However, the behaviour, fate, and health risks associated with such applications need further research. To gain a better understanding of the environmental footprints, such studies should be based on life cycle analysis.

7. Future perspectives

7.1. Constraints

Biochars are widely touted as a low-cost, renewable and sustainable biomaterials (Mohan et al., 2014; Gwenzi et al., 2017). Yet surprisingly, its application at industrial scale is still lacking, a scenario pointing to potential constraints. The generic constraints associated with biochar technology in general, and its application in drinking water treatment were discussed in our earlier papers (Gwenzi et al., 2015, 2017). Evidently, the bulk of the constraints stem from several knowledge gaps on biochar technology. With respect to biochar applications in mitigation of gaseous industrial emissions, potential constraints include:

(1) Lack of large-scale applications

Current evidence on the capacity of biochars to remove gaseous contaminants is limited to laboratory studies, while pioneering large-scale applications are still lacking globally perhaps due to lack of knowledge, expertise in biochars industry, and failure to accept its application which require biochar educational campaigns, pilot plants as well as demonstration plants in different regions of the world. Thus, industrialists may remain skeptical about the feasibility of the technology.

(2) Lack of comprehensive socio-economic feasibility studies

Concerns have been raised about the sources of biomass feedstock to support large scale applications (Gwenzi et al., 2015). Sceptics even suggest biochar will lead to land grabs in developing countries, causing

displacement of poor communities, and food and household insecurity. Limited comprehensive evidence exists to demonstrate the socio-economic feasibility of biochars, and the capacity of biowastes to provide adequate feedstock to support large-scale applications.

(3) Competition from established technologies

The development and application of biochar-based air pollution control systems are still in the infancy stage. Despite the advantages highlighted, such technology may face competition from existing technologies such as bio-oil production from biowaste, dominating the market. Such perceived competition may slow research progress and investments in research and development on biochar-based air filters.

(4) Policy and regulatory framework

As an emerging technology, conducive policy and regulatory frameworks promoting the development and application of biochar technology are still lacking. This partly stems from limited knowledge about various aspects of the technology.

(5) Environmental health risks and footprints of biochar systems

Concerns have been raised that poorly designed pyrolysis systems may release highly potent particulates (black carbon) contributing to climatic forcing, and high toxic and persistent dioxins posing human and ecological health risks. Barring a few cases, comprehensive life cycle analysis to determine the environmental footprints in terms of water, carbon, energy and toxic emissions footprints are still lacking for various potential applications including air pollution control.

7.2. Future research needs

7.2.1. Knowledge gaps

Further research is required to address the following aspects pertaining to biochar application in air pollution control systems:

(1) Development of novel engineered biochars

A few laboratory-scale studies have demonstrated the potential to develop and apply novel biochar-based materials including biochar catalysis, and biochar-metal oxide composites. Further studies are required to develop and test tailor-made or engineered biochars for specific applications in the air pollution control systems, including catalytic degradation of persistent organic pollutants and emerging contaminants. Further studies should also include systematic optimization studies using tools such as response surface methodology, which is largely missing in existing literature.

(2) Adsorption versus degradation

Biochar-filters based on adsorption, without subsequent capacity to degrade the contaminants to less toxic or benign by-products face potential criticism. This is because adsorption technologies merely transfer contaminants from one phase (gas) to a solid phase (adsorbed), hence does not provide a long-term solution. Thus, there is need to develop systems with capacity to adsorb, then degrade contaminants especially organics.

(3) Mechano-chemical stability and regeneration capacity of biochar filters

Biochars used in air filters are subjected to turbulent air flows and potential chemical attack from acid gases such as SO₂, H₂S. Limited data exist on the mechanical and chemical stability of biochars when subjected to such stresses and chemical attack. Literature on biochar use as an adsorbent for contaminants in aqueous systems has demonstrated the capacity to regenerate biochars using chemical methods.

However, data demonstrating similar capacity in biochars used as air filter media are still lacking.

(4) Disposal of spent biochars

Biochars, like other designer materials, have a design life beyond which they need to be disposed of. However, data on the best practices for the disposal of spent biochars often laden with toxic contaminants is still lacking. One possibility is to use spent biochars as a soil amendment to improve soil quality and crop yields. However, the long-term behaviour and fate of contaminants, and the risks of human exposure via contaminated food grown on soils amended with spent biochars are still poorly understood.

(5) Life cycle analysis of environmental footprints

Comprehensive life cycle analysis comparing the carbon, water and energy footprints of biochar-based air filters to conventional air filters are required. Such information is critical in demonstrating the low-cost, sustainability and renewable nature of biochar-based air filters.

7.2.2. A framework for the development of biochar air filters

Research on the highlighted knowledge gaps should be addressed within a framework for the development and application of biochar filters for air pollution control (Fig. 7). In summary, the framework for the development of biochar filters entails four key steps: (1) synthesis and characterization of novel engineered biochars, including biochar catalysts and metal/metal oxide biochar composites, (2) development and testing of laboratory-scale prototypes of biochar air filters, including the determination of design and operating conditions, (3) design and subsequent evaluation of pilot scale prototypes of the biochar filters at relevant industrial scale and conditions, and (3) field application, and subsequent monitoring and evaluation of large-scale biochar filters. Fig. 7 summarizes the typical activities to be undertaken under each step. Note that, the development process involves feedback processes among the various steps.

8. Conclusions and outlook

Until now, reviews on the biochar application in the removal of gaseous contaminants in industrial emissions have been lacking. Therefore, the current study examined existing evidence and provides a comprehensive review on various aspects on biochar application in air pollution control. The preparation methods and properties of biochars and their functionalized derivatives were summarized. Evidence shows that a diverse range of biochars and their functionalized derivatives have been developed and used for the removal of a wide range of gaseous contaminants. The studied gaseous contaminants include acidic gases (SO₂, CO₂, H₂S), nitrogen oxides (NO_x), elemental mercury (Hg⁰), volatile and odorous organic compounds, and aromatic compounds, specifically benzene. The various mechanisms accounting for the removal of contaminants, including adsorption, precipitation and size exclusion were discussed. Several potential industrial applications of biochar air filters were highlighted, including use in smelters, livestock production systems, biomass and coal fired energy systems, incinerators, cremation, industrial kilns, and wastewater treatment. Coupled with the renewable, low-cost and sustainable nature of biochars, these industrial application domains point to the existence of immense opportunities to further develop and scale up the biochar technology in the air pollution control industry. However, the biochar air filter technology still faces several challenges largely stemming from knowledge gaps on several aspects. Therefore, further research is required to address these constraints and knowledge gaps before the benefits of the technology are realized.

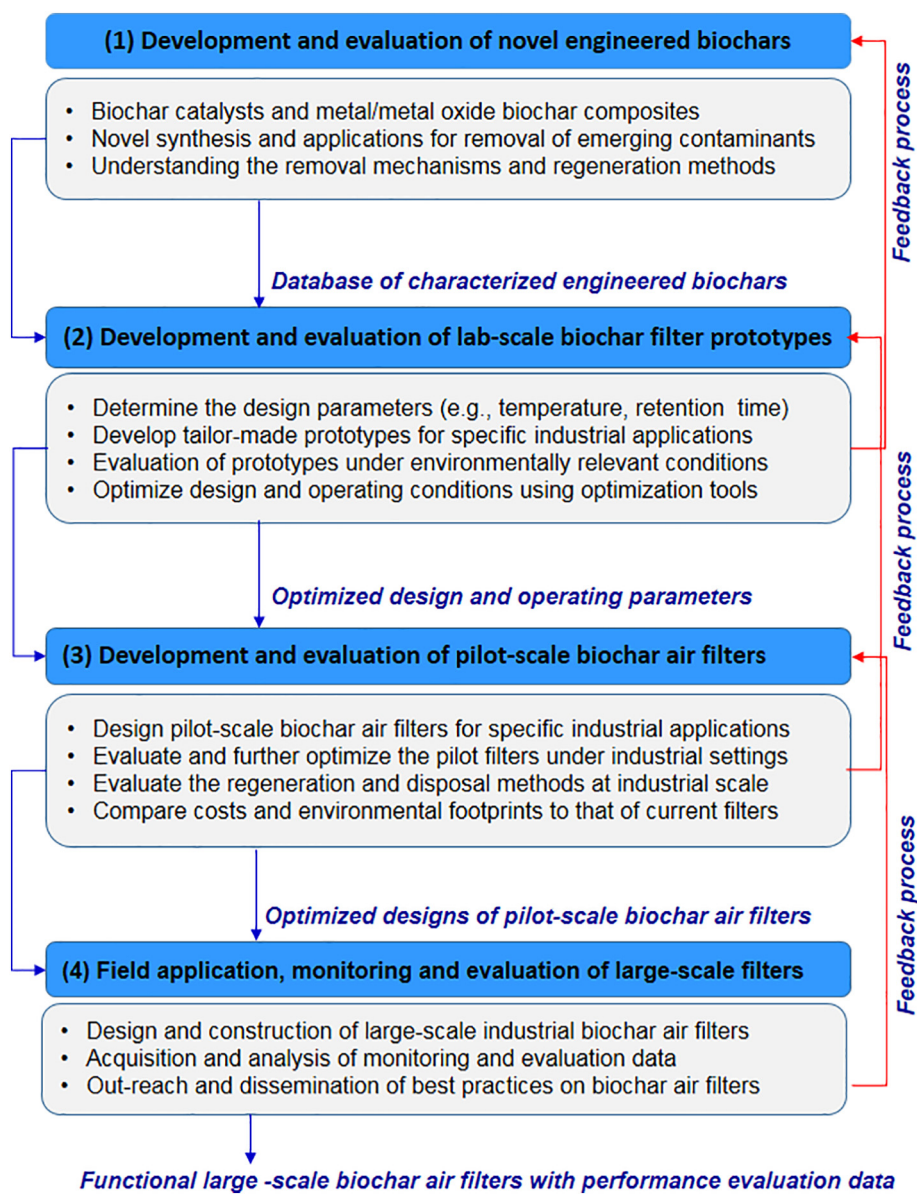


Fig. 7. A conceptual summary of the development of biochar filters for air pollution control.

CRediT authorship contribution statement

Willis Gwenzi: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – review, editing, finalization & revision. **Nhamo Chaukura:** Methodology, Investigation, Formal analysis, Writing – original draft & review. **Terrence Wenga:** Methodology, Investigation, Formal analysis, Writing – original draft & review. **Munyaradzi Mtisi:** Investigation, Formal analysis, Visualization, Writing – original draft.

Declaration of competing interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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