



Review

Biochar as potential sustainable precursors for activated carbon production: Multiple applications in environmental protection and energy storage



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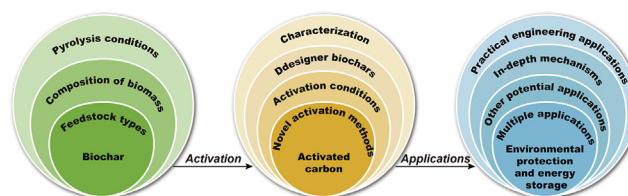
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HIGHLIGHTS

- Biochars are potential sustainable precursors for activated carbon production.
- Physical activation and chemical activation are applied in the production process.
- Production parameters affect the properties of resultant activated carbon.
- Multiple applications in environmental protection and energy storage are reviewed.
- Future perspectives about biochar activation and applications are highlighted.

GRAPHICAL ABSTRACT



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ABSTRACT

There is a growing interest of the scientific community on production of activated carbon using biochar as potential sustainable precursors pyrolyzed from biomass wastes. Physical activation and chemical activation are the main methods applied in the activation process. These methods could have significantly beneficial effects on biochar chemical/physical properties, which make it suitable for multiple applications including water pollution treatment, CO₂ capture, and energy storage. The feedstock with different compositions, pyrolysis conditions and activation parameters of biochar have significant influences on the properties of resultant activated carbon. Compared with traditional activated carbon, activated biochar appears to be a new potential cost-effective and environmentally-friendly carbon materials with great application prospect in many fields. This review not only summarizes information from the current analysis of activated biochar and their multiple applications for further optimization and understanding, but also offers new directions for development of activated biochar.

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1. Introduction

Activated carbon is the carbonaceous material known as its large specific surface area, superior porosity, high physicochemical-stability, and excellent surface reactivity, which is widely employed as functional materials for various applications (Delgado et al., 2012; Sevilla and Mokaya, 2014; Shafeeyan et al., 2010). The commonly used feedstocks for traditional activated carbon production are wood, coal, petroleum residues, peat, lignite and polymers, which are very expensive and non-renewable (Chen et al., 2011). Therefore, many researchers have been focusing on preparing activated carbon using low-cost and sustainable alternative precursors, including agricultural residues (rice husk, corn straw, bagasse etc.) and solid wastes (sludge, food waste, garden waste etc.) (Chen et al., 2011; Yahya et al., 2015). Producing activated carbon from waste and by-products have gained attention since availability of low-cost precursors is necessary for the economic feasibility of large scale activated carbon production.

Recently, much attention has also been focused on the application of these biomass resources for biochar production via various thermochemical processes under oxygen-limited conditions and at relatively low temperatures (<700 °C), including pyrolysis, hydrothermal carbonization, flash carbonization, and gasification (Meyer et al., 2011). Considerable studies have highlighted the benefits of using biochar in terms of carbon sequestration, soil amendment, soil productivity improvement (Manyà, 2012; Sohi, 2012) and pollution control (Ahmad et al., 2014; Mohan et al., 2014; Tan et al., 2015). In addition, the thermochemical treatment of biomass has energy recovery potential, which can generate bio-fuels and syngas accompanied with biochar production (Manyà, 2012). The resultant biochar usually exhibit porous structure, maintained surface functional groups and mineral components due to the removal of the moisture and the volatile matter contents of the biomass by thermal treatment (Liu et al., 2015). These favorable properties lead to high reactivity of biochar, and hence, make it possible to be used as an alternative carbon material.

However, the applications of biochar in different fields are also restricted due to its limited functionalities, inherited from the

feedstock after thermochemical treatment (Tan et al., 2016b). For instance, the un-activated biochar usually shows relatively lower pore properties (especially for micropore volume), which restricts its ability in CO₂ capture and energy storage. In addition, the raw biochar has limited ability to adsorb various contaminants (Nair and Vinu, 2016; Yao et al., 2013), particularly for high concentrations of polluted water. Therefore, there is a growing interest of the scientific community on physical and chemical activation of biochar for expanding its applications in various areas by improving its chemical/physical properties in the past few years (Ahmed et al., 2016b; Rajapaksha et al., 2016; Tan et al., 2016b). Biochar has been used as a renewable and low-cost precursor for activated carbon production. Globally, the mean price for biochar was \$2.65 kg⁻¹, which was highly variable depending on the origin of biochar production sites and ranged from as low as \$0.09 kg⁻¹ (Philippines) to \$8.85 kg⁻¹ (UK) (Ahmed et al., 2016a). Activated biochar appears to be a new potential cost-effective and environmentally-friendly carbon materials with great application prospect in many fields. Compared with traditional activated carbon, the main advantage of activated biochar is that the feedstocks of biochar production are abundant and low-cost, which mainly obtained from agricultural biomass and solid waste (Table S1) (Tan et al., 2015). The performances of activated biochar applied in various fields have also been reported to be equivalent to or even higher than that of commercial activated carbon and other much more expensive materials such as CNTs and graphene (Angin et al., 2013; Dehkhoda et al., 2014; Jung et al., 2015b; Nguyen and Lee, 2016).

According to the above-explained considerations, the production of biochar from low-cost and sustainable biomass appears to be a very attractive alternative precursor for activated carbon production, which integrates carbon sequestration and renewable energy generation into multiple applications including water pollution treatment, CO₂ capture, and energy storage. The purpose of the current review is to review and summarize recent information concerning physical and chemical activation of biochar and their effects on the properties of resultant activated carbon. The influence of these activation methods on the water pollution

Table 1
Recent researches on activation of biochar for water pollution treatment.

Feedstock	Pyrolytic conditions ^a	Type(s) of methods	Technique used	Characteristic/advantages	Contaminants	Effect on removal capacity	References
Broiler litter and broiler cake	700 (1 h)	Physical activation	Steam activation	Significant physic-chemical changes depending on activation conditions and post-treatment strategies	Cu(II)	The copper uptake was significantly affected by activation flow rate and manure type	Lima et al. (2014)
Corn stalks	550 (–)	Physical activation	Activation with CO ₂	Improved the pore structures	Methylene blue	The adsorption increased gradually with the increase of the activation time	Wang et al. (2014)
Giant <i>Miscanthus</i>	500 (1 h)	Physical activation	Steam activation	Higher surface area	Cu(II)	–	Shim et al. (2015)
<i>Sicyos angulatus</i> L.	300, 700 (2 h)	Physical activation	Steam activation	Larger surface area and pore volume	Sulfamethazine	55% increase in sorption capacity	Rajapaksha et al. (2015a)
Cactus fibres	600 (1 h)	Chemical activation	Nitration and reduction	Laminar structures with carboxylic moieties presented on the surface and higher external surface	Cu(II)	Almost an order of magnitude higher than other activated biochars	Hadjittofi et al. (2014)
Cherry stones	400 (15 min)	Chemical activation	Chemical activation with NaOH	Enhanced microporous structure and acidic surface character	Iodine	Increased sorption abilities by factors of 2.9	Pietrzak et al. (2014)
Hickory chips	600 (2 h)	Chemical activation	Chemical activation with NaOH	Surface area, cation-exchange capacity, and thermal stability were significantly improved	Pb ²⁺ , Cd ²⁺ , Cu ²⁺ , Zn ²⁺ , and Ni ²⁺	2.6–5.8 times of pristine biochars	Ding et al. (2016)
Kenaf fibre	1000 (–)	Chemical activation	Washed with HCl	Increased the BET surface area and pores	Methylene blue	High adsorption ability, which lies in the middle between different adsorbents	Mahmoud et al. (2012)
Loblolly pine chip	300 (15 min)	Chemical activation	Chemical activation with NaOH	High surface area and micropore volume	Diclofenac, naproxen, and ibuprofen	–	Jung et al. (2015a)
Municipal solid wastes	500 (0.5 h)	Chemical activation	Chemical activation with KOH	Increased of surface area, porous texture and functional groups	As(V)	More than 1.3 times of pristine biochars	Jin et al. (2014)
Peanut hull	300 (5 h), HTC	Chemical activation	Modified by H ₂ O ₂	Increased the oxygen-containing functional groups, particularly carboxyl groups	Pb(II)	The sorption capacity was more than 20 times of that of untreated biochar	Xue et al. (2012)
Rice straw	350, 500 and 700 (6 h)	Chemical activation	Oxidized with an HNO ₃ /H ₂ SO ₄ mixture	Increased carboxyl functional groups and nitro groups	Al	–	Qian and Chen (2014)
Safflower seed press cake	500 (–)	Chemical activation	Chemical activation with KOH	High surface area and micropore volume	Dyestuff	A low-cost adsorbent compared with the commercial activated carbon	Angin et al. (2013)
Saw dust	500 (–)	Chemical activation	Nitration and reduction	The amino groups were chemically bound to the functional groups on the biochar surface	Cu(II)	The adsorption capacity was five-folds of the pristine biochar	Yang and Jiang (2014)

^a Pyrolytic temperature/°C (residence time).

Table 2
Recent researches on activation of biochar for CO₂ capture and energy storage.

Feedstock	Pyrolytic conditions ^a	Technique used	Characteristic/advantages	Applications	Performance	References
Palm kernel shell	700 (2 h)	CO ₂ activation	Increase in both surface area and micropore volume	CO ₂ capture	Near 1.3 times higher CO ₂ uptake at 4 bars was obtained after activation	Nasri et al. (2014)
Cotton stalk	600 (fast pyrolysis)	Activation by high temperature CO ₂ –ammonia mixture	Significant increase in surface area and N-containing groups are introduced into the biochars	CO ₂ capture	Dependent on the micropore volume and N content	Zhang et al. (2014a)
Almond shells and olive stones	400–650 (–)	Single-step activation with different oxygen concentrations	High micropore volume in the narrow micropore domain (0.3–0.5 nm)	CO ₂ capture	High CO ₂ /N ₂ selectivity	Plaza et al. (2014)
Mesquite	450 (4 h)	One-step KOH activation	High surface area and total pore volume	CO ₂ capture	High performance up to 26.0 mmol/g	Li et al. (2016b)
Chicken manure	450 (1 h)	Chemically treated with HNO ₃ and NH ₃ at high temperature	High surface area with increased amine functional groups	CO ₂ capture	Much higher than that of commercial activated carbon and great selectivity	Nguyen and Lee (2016)
Rice husk	600 (0.5 h)	Hydrofluoric acid pre-deashing of biomass + ammonification treatment	Improved the pore structure and enhanced the introduction of nitrogen-containing functional groups	CO ₂ capture	Near 1.8 times higher at adsorption temperature 120 °C than non-activated biochar	Zhang et al. (2015b)
Distillers dried grains with solubles	–	KOH catalytic activation + HNO ₃ treatment	Improved surface oxygen content and porous structure	Energy storage (supercapacitor)	Much better than general bio-inspired activated carbons, ordered mesoporous carbons and commercial graphene	Jin et al. (2013)
Inner spongy layer of pomelo pericarp	400 (1 h)	KOH activation	High surface area and pore volume	Energy storage (porous matrix to host active substances for cathodes)	Effectively hosts a 56.1 wt% of elemental selenium	Zhang et al. (2015a)
Red cedar wood	750 (1 h)	HNO ₃ activation	Slightly decreases in surface area, while an increase in the coverage of surface oxygen groups	Energy storage (supercapacitor)	7 times increase in the capacitance	Jiang et al. (2013)
Woody biomass	–	Chemical (7 M KOH) and thermal (at 675 and 1000 °C, respectively) activation	Increase in the surface area and porosity	Energy storage (supercapacitor)	Competitive with much more expensive systems such as CNTs and graphene-based electrodes	Dehkhoda et al. (2014)
Spruce whitewood	600 (fast pyrolysis)	Chemical activation with KOH	High content of micropores and mesoporous	Energy storage (supercapacitor)	Very high total capacitance (222–245 F/g)	Dehkhoda et al. (2016)

^a Pyrolytic temperature/°C (residence time).

treatment using activated biochar and the mechanisms of improved adsorption for various contaminants are discussed. In addition, the application of activated biochar for CO₂ capture, and energy storage are also reviewed. Furthermore, knowledge gaps and future research needs that exist in the activation and application of activated carbon produced from biochar are highlighted.

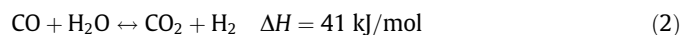
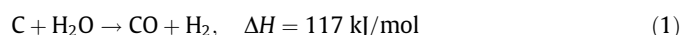
2. Activation of biochar for activated carbon production

2.1. Physical activation

Recently, many researches utilize physical methods for biochar activation, which could optimize surface structure of biochar. Significant physical changes in surface area, pore volume, and pore structures of biochar may be achieved by means of physical activations, which are the important parameters for biochar applications. In addition, physical activation may not only change the porosity of biochar but also affect its surface chemical properties (surface functional groups, hydrophobicity and polarity). Generally, the widely used physical activations to biochar mainly include: steam activation and gas activation (Table 1 and 2).

2.1.1. Steam activation

Steam activation is usually applied for biochar activation after thermal carbonization of biomass. The pyrolysis process can create initial porosity in the biochar, and the further steam activation will then produce the activated biochar with high porosity. The chemical reactions of steam activation can be expressed as follows (Liu et al., 2015):



Three effects exist during the activation process by the reaction between H₂O and carbon (Cagnon et al., 2003; Zhang et al., 2014b): (1) the elimination of volatile materials and decomposition of tar, (2) the development of new micropores, and (3) the further widening of existing pores. Considerable increases in surface area, micropore surface area, and micropore volume were observed by steam activation of various biochars. For instance, biochars from the fast-pyrolysis of different feedstocks were steam activated at atmospheric pressure at 800 °C for 45 min, and the results suggested that BET surface area of activated biochars increased from negligible to 136–793 m² g⁻¹, accompanied with pore development (Lima et al., 2010). Similar results were obtained by Rajapaksha et al. (2015b). In their study, the steam activated biochar produced from tea waste at 700 °C got higher surface area (576.1 m² g⁻¹), pore volume (0.109 cm³ g⁻¹) and pore diameter (1.998 nm) compared to that of non-activated biochar produced at the same condition (surface area = 342.2 m² g⁻¹, pore volume = 0.022 cm³ g⁻¹ and pore diameter = 1.756 nm). Shim et al. (2015) also reported that the surface area of biochar produced from a giant *Miscanthus* nearly doubled after steam activation (surface area was 181 and 322 m² g⁻¹ before and after activation, respectively), possibly because of micropore development. As shown in the SEM images of biochar before and after activation (Fig. S1), an increased density of micropores was observed after activation of the biochar.

The varying steam activation parameters, including activation temperature, activation time, and water vapour flow, have significant effects on the surface area and porosity of activated biochar (Table S2). The surface area and pore volume are reported to increase with rising activation temperature (Rajapaksha et al., 2015a; Zhang et al., 2014). This may be attributed to that low temperatures cannot create enough new pores, while higher

temperatures play a better role in pores structure improvement, which can develop new micropores and widen existing pores (Zhang et al., 2014b). However, high activation temperature may have significant effect on activated biochar yield. While very high temperatures might enhance the porous structure, the yield of biochar can be low and might not be economically favorable. As shown in Table S1, the common activation temperature of activated biochar during the activation process is near 800 °C. Little information was available about the typical yields of activated biochar and gases during the activation process, which need to be addressed in the further researches. The increasing activation times, but to a certain limit, can also improve the surface area and pore structure (Fu et al., 2013). At initial activation stage, the increase of activation times facilitates the development of new pores, resulting in the increase of surface area. However, during the further increasing activation times, the existing pores are mainly widened with little new pore formation, which cause the reductions in surface area and pore volume (Demiral et al., 2011; Zhang et al., 2014b). Lima et al. (2014) studied the steam activation of broiler litter and cake biochar at different water flow rates from 1 to 5 mL, the results suggested that surface area increased with flow rate from 1 to 3 mL min⁻¹, but decreased slightly at 5 mL min⁻¹ due to structural collapse. Chen et al. (2016) also reported that the activated carbon with elevated specific surface area of 1057.8 m² g⁻¹ was obtained at the optimal conditions (activation temperature 850 °C, activation time 80 min, and steam/biochar ratio 1.5). Furthermore, the feedstock types may also influence the activation efficiency, due to different biomass composition (e.g. lignin, cellulose, hemicellulose) and inorganics (ash) in feedstock (Lima et al., 2010, 2014), which need further study to figure out the in-depth influence mechanisms. Lima et al. (2010) studied the physical properties of eight activated biochars by steam activation at same activation condition, and the results suggested that surface area of activated biochars varied from 136 to 793 m² g⁻¹.

Steam activation not only improved the porosity of biochar but also affect its surface chemical properties. As to the oxygen-containing groups (such as carboxylate, -COOH; and hydroxyl, -OH), Zhang et al. (2014b) found that steam activation had no effects on the species of oxygen-containing groups but changed the amounts of these species in activated biochar. Shen et al. (2015) reported that physical activation (microwave and steam) improved both pore structure and oxygenic functional groups of activated biochar. In addition, steam activation may also decrease the hydrophobicity and increase the polarity of the biochar surface (Rajapaksha et al., 2015b).

2.1.2. Gas activation

Similarly, the activation of biochar with gas can also enhance its surface area and pore volume by the reaction between biochar surface and gas, which may create microporous and mesoporous structures (Burhenne and Aicher, 2014). Different gases such as CO₂, N₂, NH₃, air, O₂ or their mixtures are most commonly used in the activation process (Table S3). CO₂ is the most commonly used activation gas. It may react directly with the char according to the Boudouard reaction (C(S) + CO₂ → 2CO) (Cho et al., 2015; Guizani et al., 2014). The Boudouard reaction is thermodynamically favorable at temperatures higher than 710 °C based on the theoretical thermodynamic calculation (i.e., ΔG ≤ 0) (Cho et al., 2015; Kwon et al., 2014). The effects of CO₂ activation temperature (600–900 °C) and time (1 and 2 h) on the physicochemical characteristics of hickory and peanut hull hydrochars were investigated by Fang et al. (2016). The results suggested that the surface area and pore volume of the activated biochar increased with increasing temperature and activation time (Fang et al., 2016). Furthermore, the mixture CO₂ and other gases could both improve the pore structure

and surface characteristics of biochar. Jung and Kim (2014) prepared activated oak biochar by three different methods (N_2/CO_2 without cooling, N_2/CO_2 with cooling and direct CO_2), and their maximum surface area of activated oak biochar was $1126\text{ m}^2\text{ g}^{-1}$ by using the N_2/CO_2 without cooling method, and the surface area obtained by direct CO_2 method was approximately $800\text{ m}^2\text{ g}^{-1}$. The physically activated corn stalks biochar with CO_2 at $850\text{ }^\circ\text{C}$ had specific surface area up to $880\text{ m}^2\text{ g}^{-1}$, and exhibited microporous structure (Wang et al., 2014). Cotton stalk biochar activation by CO_2 /ammonia at $500\text{--}900\text{ }^\circ\text{C}$ suggested that this method combined the advantages of both CO_2 and ammonia activation, which obtained high surface area up to about $627.15\text{ m}^2\text{ g}^{-1}$, accompanied with the introduction of N-containing groups into biochar (Xiong et al., 2013; Zhang et al., 2014a). The chemical reactions of ammonia activation can be expressed as follows (Liu et al., 2015; Xiong et al., 2013; Zhang et al., 2014a):

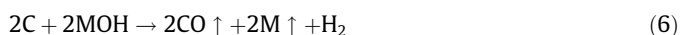


2.2. Chemical activation

2.2.1. Acid, alkali, and oxidation treatment

Acid, alkali, and oxidation treatment were applied to activate biochar, which showed significant improvement in the physico-chemical properties of biochar (Tables 1 and 2). Some acid (HCl , HNO_3 , H_2SO_4 , and H_3PO_4), base (KOH , NaOH , and K_2CO_3) and oxidant (H_2O_2 and KMnO_4) are commonly used in the treatment process. Two positive effects exist in the acid treatment process. Firstly, acid treatment could improve the pore properties of biochar, including the surface area and porosity (increasing the amounts of micropores and mesopores on biochar), which may be attributed to the removal of impurities on the surface of biochar by acid. For instance, the acid treatment using HCl for kenaf fibre biochar could cause an increase in the BET surface area (from 289.497 to $346.57\text{ m}^2\text{ g}^{-1}$) (Mahmoud et al., 2012). The SEM images revealed that the pores within kenaf fibre biochar surface exhibited honeycomb shape gaps with different sizes after treatment (Mahmoud et al., 2012). The chemically activated corn stalks biochar with H_3PO_4 had specific surface area up to $600\text{ m}^2\text{ g}^{-1}$, and exhibited mesoporous structure (Wang et al., 2014). Secondly, acid treatment could also introduce or increase many functional groups (such as amino functional groups, carboxylic functional groups and other oxygen-containing functional groups) onto the surface of biochar. The oxidation treatment by $\text{HNO}_3/\text{H}_2\text{SO}_4$ introduced carboxylic functional groups on biochar surfaces, which could increase binding sites for Al^{3+} (Qian and Chen, 2014). Similarly, the extraordinary adsorption capacity of the HNO_3 -activated biochar for $\text{Cu}(\text{II})$ ions was attributed to the laminar structures and the carboxylic moieties present on its surface (Hadjittofi et al., 2014).

Two main effects of alkali treatment are also existed, including the improvement of pore properties and functional groups of biochar (Azargohar and Dalai, 2006; Jin et al., 2014; Pietrzak et al., 2014). The mechanism of porosity development was investigated by FTIR analysis suggesting conversion of KOH to K_2CO_3 played a major role in tailoring the structure (Dehkhoda et al., 2016). The chemical reactions of alkali treatment by using alkali hydroxides (NaOH and KOH) as activating agents can be expressed as follows (Dehkhoda et al., 2016; Liu et al., 2015):



where M represents the alkaline metal (Na or K). Angin et al. (2013) used potassium hydroxide (KOH) to modify biochar, which provided high surface area ($1277\text{ m}^2\text{ g}^{-1}$) and micropore volume ($0.4952\text{ cm}^3\text{ g}^{-1}$). Similar results were obtained by Dehkhoda et al. (2014) and Trakal et al. (2014) in their studies on KOH -activated biochar. In another work, a biochar activated by another strong base (NaOH), showed increased surface area ($932\text{ m}^2\text{ g}^{-1}$) and strongly microporous structure (micropore volume = $0.42\text{ cm}^3\text{ g}^{-1}$) (Pietrzak et al., 2014). NaOH was applied to activate the biochars pyrolyzed from loblolly pine chip under pure nitrogen or 7% oxygen with 93% nitrogen gas. Both biochars exhibited high surface area (1360 and $1151\text{ m}^2\text{ g}^{-1}$) and micropore volume (0.307 and $0.313\text{ cm}^3\text{ g}^{-1}$) after NaOH modification (Jung et al., 2015a). K_2CO_3 , as weak base, could also be used to modify the biochar for higher porosity according to the studies conducted by Galhetas et al. (2014). O-containing groups can also be introduced into biochar after alkali treatment (Ding et al., 2016). The activation of municipal solid wastes biochar by 2M KOH solution increased the functional groups on the surface of activated biochars (Jin et al., 2014).

As can be seen from Table S4, chemical activation can have significant effects on the pore and surface chemical properties of biochar. However, the properties of activated biochar vary widely between different feedstocks and activation processes. Most activation methods mainly focus on improving one target property of biochar. For a specific treatment process, it can significantly modify one kind of biochar properties (i.e., pore properties or surface functional groups), while it may have little or even effect on other properties simultaneously (Table S4). Xue et al. (2012) examined the effect of H_2O_2 treatment on hydrothermally produced biochar from peanut hull to remove heavy metals in aqueous. The results showed that H_2O_2 modification increased the oxygen-containing functional groups on the biochar surfaces, while H_2O_2 oxidation could not create or change the pore structure of biochar to dramatically enhance its surface area. In another investigation, the authors found that the nitration and reduction treatment of biochar introduced the amino functional groups onto the activated biochar surface, but no significant difference in physical surface structure between the pristine and activated biochars was observed (Yang and Jiang, 2014).

Comparative research was conducted by Iriarte-Velasco et al. (2014) to investigate the changes occurring during the acid/alkali treatment of pork bone char impregnated with different agents: H_3PO_4 , H_2SO_4 , NaOH and K_2CO_3 . The H_2SO_4 treatment resulted in a highly microporous biochar, while the treatment with NaOH and K_2CO_3 could increase more evenly the amounts of micropores and mesopores on biochar. However, the reaction of H_3PO_4 with biochar was extremely aggressive, which may destroy the pore structures on the biochar. Similarly, Li et al. (2014) compared the properties of biochars treated with different acid/alkali (KMnO_4 , HNO_3 and NaOH). They elucidated that HNO_3 was more effective in introducing a large amount of acidic functional groups on the biochar surface than KMnO_4 , while NaOH treatment had the opposite effects, which led to the increase of biochar basicity.

2.2.2. Microwave assisted activation

Thermal treatment of functional group-rich biochar is an important step after chemical activation. Compared to conventional heating, microwave-assisted heating is an attractive technique that offers internal and volumetric heating, which enable it to accelerate the rate of chemical reactions at lower activation temperature, and hence shorten treatment time and reduce energy

Table 3
Adsorption characteristics of various contaminants with activated biochar.

Feedstock	Pyrolytic conditions ^a	Activating agent	BET surface area (m ² g ⁻¹)	Adsorption temperature (°C)	Adsorption pH	Adsorbent dosage (g L ⁻¹)	Contaminants	Q _{max} (mg/g)	Isotherm ^d	Kinetic model ^e	References
<i>Activated biochar</i>											
Municipal solid waste	500 (0.5 h)	KOH	49.1, N ₂ ^b	25 ± 1	–	2	As(V)	30.98 (L) ^c	L	PSO	Jin et al. (2014)
Alamo switchgrass	300 (0.5 h)	KOH	5.01, N ₂	23 ± 1	5	1	Cd(II)	34	–	–	Regmi et al. (2012)
Alamo switchgrass	300 (0.5 h)	KOH	5.01, N ₂	23 ± 1	5	1	Cu(II)	31	–	–	Regmi et al. (2012)
Brewers draff	650 (–)	KOH	11.6, N ₂	–	–	2	Cu(II)	10.257 (L)	L	PSO	Trakal et al. (2014)
Cactus fibres	600 (1 h)	HNO ₃	–	23	6.5	0.67	Cu(II)	224 (L)	L	–	Hadjittofi et al. (2014)
Saw dust	500 (fast pyrolysis)	Amino	2.524, N ₂	20	5	–	Cu(II)	16.13 (L)	L	PSO	Yang and Jiang (2014)
Peanut hull	300 (5 h)	H ₂ O ₂	1.4, N ₂	–	–	2	Pb(II)	22.82 (L)	L	E	Xue et al. (2012)
Loblolly pine chip	300 (15 min)	NaOH	1360, N ₂ ^b	–	7	2	Diclofenac	372 (L) ^f	L	–	Jung et al. (2015a)
Bamboo	550 (–)	KMnO ₄	27.2, N ₂	–	–	75	Furfural	93.55 (L)	L	PSO	Li et al. (2014)
Bamboo	550 (–)	HNO ₃	0.5, N ₂	–	–	75	Furfural	96.34 (L)	L	PSO	Li et al. (2014)
Bamboo	550 (–)	NaOH	0.4, N ₂	–	–	75	Furfural	102.04 (L)	L	PSO	Li et al. (2014)
Rice husk	700 (2 h)	Steam	229.94, N ₂	–	4	0.5	Glyphosate	123.03 (L)	F	PFO	Herath et al. (2016)
Loblolly pine chip	300 (15 min)	NaOH	1360, N ₂	–	7	2	Ibuprofen	311 (L)	L	–	Jung et al. (2015a)
Parthenium hysterophorus	300 (1 h)	NaOH	308, N ₂	20	2	2	Ibuprofen	3.759 (L)	L	PSO	Mondal et al. (2016)
Safflower seeds	500 (–)	KOH	1277, N ₂	25	2	10	Levafix Red	8.128	D–R	PSO	Angin et al. (2013)
Bamboo waste	450 (1 h)	Steam	1210, N ₂	25	–	4	Methylene blue	330 (L)	L	–	Zhang et al. (2014b)
Wood sawdust	800 (fast pyrolysis)	H ₂ SO ₄	5.045, N ₂	30	7	–	Methylene blue	161.29 (L)	L	PSO	Wang et al. (2013)
Loblolly pine chip	300 (15 min)	NaOH	1360, N ₂	–	7	2	Naproxen	290 (L)	L	–	Jung et al. (2015a)
Sicyos angulatus L.	700 (2 h)	Steam	7.1, N ₂	25	7	1	Sulfamethazine	30.015 (L)	T	–	Rajapaksha et al. (2015a)
<i>Conventional activated carbon</i>											
Coconut shell	Mitsubishi Chemical W10-30 ^f	DIASORB	1000, N ₂	20	<6.1	2	Cu(II)	3.584 (L)	L	–	Machida et al. (2005)
Coconut shell	Mitsubishi Chemical W10-30 ^f	DIASORB	1000, N ₂	20	<6.1	2	Pb(II)	10.764 (L)	L	–	Machida et al. (2005)
Coconut shell	BDH (Merck) ^f		1118, N ₂	30 ± 2	5	0.025	Methylene blue	289.1	–	PSO	Wang et al. (2005)
Coal	F100 (Calgon Corp) ^f		957, N ₂	30 ± 2	5	0.025	Methylene blue	218.8	–	PSO	Wang et al. (2005)
Coal	BPL (Calgon Corp) ^f		972, N ₂	30 ± 2	5	0.025	Methylene blue	309.4	–	PSO	Wang et al. (2005)
Coal	Steam activation at 1000 °C for 6 h ^f		857.1, N ₂	–	7	1	Methylene blue	345	L	–	El Qada et al. (2006)

^a Pyrolytic temperature/°C (residence time).

^b Determined from the N₂ adsorption data.

^c Calculated from Langmuir model.

^d Isotherm model: Langmuir (L), Freundlich (F), Temkin (T), and Dubinin–Radushkevich (D–R).

^e Kinetic model: pseudo-first-order (PFO), pseudo-second-order (PSO) and Elovich.

^f Suppliers or production conditions of conventional activated carbon.

consumption considerably (Ahmed, 2016; Alslaibi et al., 2013; Nair and Vinu, 2016). Recently, microwave-assisted activation is shown to be promising over conventional thermal activation of biochar. While microwave activation is just another form of supplying heat during the activation process, the mechanism of pore generation via microwave plasma results in different pore structure and surface area (Ahmed, 2016; Alslaibi et al., 2013; Hoseinzadeh Hesas et al., 2013; Nair and Vinu, 2016). For instance, activated biochar with high surface area and controlled pore size was prepared from *Prosopis juliflora* biomass by a simple process that involved H₂O₂ treatment followed by microwave pyrolysis (Nair and Vinu, 2016). Nanostructured biochar with narrow and deep pores of 357 m² g⁻¹ specific surface area was produced at optimized conditions (H₂O₂ impregnation time of 24 h and microwave power of 600 W). In further research, more relevant investigations regarding the application of microwave-assisted method for biochar activation are needed.

3. Application for water pollution treatment

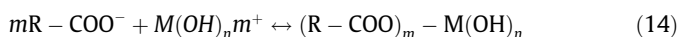
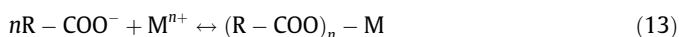
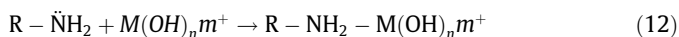
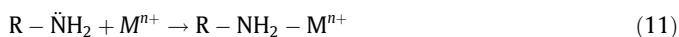
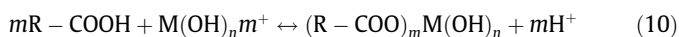
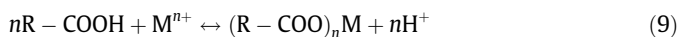
As discussed above, physical and chemical activation could have significantly beneficial effects on biochar chemical/physical properties, including increasing biochar surface areas, improving pore structures, adding surface functional groups, and changing the hydrophobicity of biochar surface. These changes could result in the enhancement of adsorption ability of biochar for various contaminants (Table 1). As shown in the Tables 1 and S4, in most cases, physical and chemical activation usually have significant improvement on the surface areas and pore structures of biochar at different extent (Jung and Kim, 2014; Lima et al., 2010; Pietrzak et al., 2014; Rajapaksha et al., 2015b). All of the activation methods may exert great positive influences on the surface functional groups of biochar (Ding et al., 2016; Shen et al., 2015; Wang et al., 2013). As for the hydrophobicity, it is reported that steam activation and acid/alkali treatment may decrease the hydrophobicity of biochar (Li et al., 2014; Rajapaksha et al., 2015b). These different functions of activation methods on the specific properties of biochar result in the different adsorption ability of activated biochar for various contaminants.

The activation of biochar and the mechanisms of improved adsorption for various contaminants are shown in Fig. S2. The modification of physical properties (surface areas and pore structures) may enhance contaminants removal, as it can create microporous and mesoporous structures and increase surface area of biochar (Jung and Kim, 2014; Lima et al., 2010; Pietrzak et al., 2014; Rajapaksha et al., 2015b). These changes in physical properties may provide more available contact sites between biochar and contaminants, as well as form easily accessible pores structure to contaminants (Fig. S2a). Modification of surface chemical properties of biochar can also have great effects on the contaminants removal. The increase of surface functional groups of biochar (like carboxyl, hydroxyl and amino groups) may provide more bonding sites for heavy metals and promote the driving force of metals adsorption onto biochar including electrostatic attraction, ion-exchange, and surface complexation (Fig. S2b) (Hadjitofi et al., 2014; Song et al., 2014; Wang et al., 2015; Yang and Jiang, 2014). Similarly, increased amount of surface functional groups on biochar may create more active sites for organic contaminants bonding and strengthen the reactions between biochar and organic contaminants such as electrostatic attraction and hydrogen bond (Fig. S2c) (Rajapaksha et al., 2015a; Wang et al., 2013). Especially, some modification methods can increase the hydrophobicity of biochar, which may enhance the hydrophobic interactions between organic contaminants and the hydrophobic biochar surface (Fig. S2c) (Jung et al., 2015a; Sun et al., 2015).

3.1. Removal of heavy metals

The presence of heavy metals in water bodies is becoming a serious environmental and public health problem, thus many studies have been focused on the application of activated biochar for metals removal from aqueous solutions. Adsorption characteristics of activated biochar exposed to various heavy metals are presented in Table 3. Utilization of activated biochar for adsorption of heavy metals from aqueous solutions was the subject of study for several researchers, including As(V) (Jin et al., 2014), Cd(II) (Regmi et al., 2012), Cu(II) (Hadjitofi et al., 2014; Regmi et al., 2012; Yang and Jiang, 2014; Zuo et al., 2016), Hg(II) (Tan et al., 2016a), and Pb(II) (Xue et al., 2012). Of which, Cu(II) is the most commonly studied metals (Table 3). The maximum adsorption quantity of Cu(II) by various activated biochar range from 10 to 224 mg g⁻¹ based on Langmuir adsorption isotherm. The cactus fibres biochar activated by nitric acid oxidation had the highest adsorption ability (Hadjitofi et al., 2014). In general, the diversity of adsorption ability mainly varies with the raw materials, activation methods, and the target heavy metals.

As well known, adsorption mechanisms of metals on biochar mainly include electrostatic attraction, ion-exchange, physical adsorption, surface complexation and/or precipitation (Tan et al., 2015; Yang and Jiang, 2014). Accordingly, the technology for modifying biochar majorly focus on increasing oxygen-containing functional groups, surface area and pore volume of biochar to enhance its adsorption capacity to metals. Numerous studies indicated that activated biochar have higher sorption efficiency than pristine biochar and even commercially available powdered activated carbon (PAC) in removal of heavy metals, and one of the important factors was the increased surface functional groups like carboxyl (–COOH), hydroxyl (–OH) and amino groups (–NH₂) (Hadjitofi et al., 2014; Song et al., 2014; Wang et al., 2015; Yang and Jiang, 2014), which could combine with metals through cation exchange (Eqs. (9) and (10)), strong complexation (Eqs. (11) and (12)) or electrostatic attraction (Eqs. (13) and (14)) as indicated in the following equations (Hadjitofi et al., 2014; Song et al., 2014; Wang et al., 2015; Yang and Jiang, 2014):



where R and M represent the activated biochar matrix and metal ions, respectively. M(OH)_n^{m+} represents different species of metal in aqueous solutions. For instance, Xue et al. (2012) applied the peanut hull biochar activated by H₂O₂ to remove Pb²⁺ from aqueous. They found that the removal capacity (22.82 mg g⁻¹) of activated char for Pb²⁺ was more than 20 times of that of raw biochar (0.88 mg g⁻¹). And the enhanced Pb²⁺ removal by the H₂O₂-activated biochar could be mainly attributed to the increase of oxygen-containing functional groups, particularly carboxyl groups on the activated biochar surfaces. In another study, saw dust biochar activated by nitration and reduction was prepared to removal Cu(II) from synthetic wastewater, which exhibited five fold high adsorption capacity than the pristine biochar, and the Cu(II) combined with the amino groups through strong complexation served as the main bonding force (Yang and Jiang, 2014). However, some

Table 4
Summary and comparison of the CO₂ capture of the activated biochar.

Feedstock	Activating agent	BET surface area (m ² g ⁻¹)	Adsorption temperature (°C)	Pressure (bar)	CO ₂ uptake (mmol/g)	References
<i>Activated biochar</i>						
Palm kernel shell	CO ₂	167.08	30	4	7.32	Nasri et al. (2014)
Cotton stalk	CO ₂	610	20	–	2.26 (C) ^a	Zhang et al. (2014a)
Cotton stalk	CO ₂ + ammonia	297	120	–	0.89 (C)	Zhang et al. (2014a)
Mesquite	KOH	3167	25	30	26.0	Li et al. (2016b)
Chicken manure	HNO ₃ + NH ₃	301.5	20	1	10.15	Nguyen and Lee (2016)
Rice husk	N ₂ + NH ₃	451.02	30	–	77.9	Zhang et al. (2015b)
Horse manure	CO ₂	749	0	0.1	1.36	Hao et al. (2013)
Grass cuttings	CO ₂	841	0	0.1	1.45	Hao et al. (2013)
Beer waste	CO ₂	622	0	0.1	1.31	Hao et al. (2013)
Biosludge	CO ₂	489	0	0.1	0.84	Hao et al. (2013)
Beer waste	H ₃ PO ₄	1073	0	0.1	0.80	Hao et al. (2013)
<i>Conventional activated carbon</i>						
Polyacrylonitrile	KOH	780.17	25	–	3.1	Shen et al. (2011)
Polyacrylonitrile	–	3172	30	41	11.6	Drage et al. (2009)
Phenolic resin	KOH	2400	0	1	8.9	Wickramaratne and Jaroniec (2013)

^a Calculated amount.

Table 5
Summary and comparison of the electric double layer total capacitances of the activated biochar electrodes.

Feedstock	Activating agent	BET surface area (m ² g ⁻¹)	Electrolyte	Specific capacitance (F g ⁻¹)	References
<i>Conventional activated carbon</i>					
Red cedar wood	HNO ₃	317	H ₂ SO ₄	115 ± 5	Jiang et al. (2013)
Distillers dried grains with solubles	KOH + HNO ₃	3310	KOH	260	Jin et al. (2013)
Fibres from oil palm empty fruit bunches	KOH + CO ₂	1704	H ₂ SO ₄	150	Farma et al. (2013)
Corn cob residues	Steam	1210	KOH	314	Qu et al. (2015)
Woody biomass	KOH	990	NaCl + NaOH	122–167	Dehkhoda et al. (2014)
Spruce whitewood	KOH	488–2670	NaCl + NaOH	182–245	Dehkhoda et al. (2016)
<i>Conventional activated carbon</i>					
Polyaniline base	K ₂ CO ₃	917	KOH	210	Xiang et al. (2011)
Lignite	ZnCl ₂	1024	KOH	207.5	Li et al. (2016a)
Polyacrylonitrile	H ₃ PO ₄	709	KOH	156	Zhi et al. (2014)

studies reported that the effect of activation on the surface area was not the determinant factor for better heavy metals adsorption. For instance, after steam activation, the surface area of *giant Miscanthus* biochar reached 322 m² g⁻¹, higher than raw biochar (181 m² g⁻¹), while the Cu(II) sorption capacities of raw biochar and activated biochar are not significantly different ($p > 0.05$) (Shim et al., 2015). Similarly, Lou et al. (2016) reported that steam activation doubled the surface area of the biochar produced at 550 °C, however, it did not increase biochar's ability for sorption of Cu(II), which indicated that surface area was not the determinant factor for better Cu(II) sorption.

3.2. Removal of organic contaminants

3.2.1. Dyes removal

The improved physicochemical properties of activated biochar showed significant advantages for organic dye removal. Many studies reported that activated biochar were used for dyes removal including methylene blue (Mahmoud et al., 2012; Wang et al., 2013) and levafix red (Angin et al., 2013), remazol brilliant blue (Nair and Vinu, 2016), of which, the majority are methylene blue (Table 3). For the biochar produced from sawdust, H₂SO₄ treatment can significantly improve its removal ability for methylene blue (Wang et al., 2013). The improvement in functional group composition and pore structure would favor the adsorption (Wang et al., 2013). Mahmoud et al. (2012) reported that the formation of more negatively charged surface by HCl treatment and the presence of mesopores by the removal of impurities are both favorable for methylene blue adsorption by HCl-activated biochar.

3.2.2. Pharmaceuticals removal

Most pharmaceutical substances are ubiquitous in the aquatic environment, mainly derived from the municipal wastewater effluents, aquaculture, livestock breeding, land application of manure and slurry from livestock, and pharmaceutical manufacturing (Boxall et al., 2012; Daughton and Ternes, 1999). The existence and spread of these compounds could potentially lead to long-term adverse consequences on ecosystems, including acute and chronic toxicity and propagation of antibiotic resistance in microbes (Boxall et al., 2012; Petrie et al., 2015). A series of studies demonstrated that activated biochar could be available for pharmaceuticals removal, such as acetaminophen (Galhetas et al., 2014), caffeine (Galhetas et al., 2014), atrazine (Tan et al., 2016a), diclofenac (Jung et al., 2015a), glyphosate (Herath et al., 2016), naproxen (Jung et al., 2015a), ibuprofen (Jung et al., 2015a; Mondal et al., 2016), and sulfamethazine (Rajapaksha et al., 2015a,b) (Table 3).

The mechanisms of activated biochar for pharmaceuticals removal mainly include hydrophobic interactions, π - π electron donor-acceptor interactions, electrostatic interactions and hydrogen bond. Rajapaksha et al. (2015a) investigated the effects of steam-activated biochars synthesized from *Sicyos angulatus* L. on the sorption of sulfamethazine in aqueous solution. The steam-activated biochar showed the highest sorption capacity (37.7 mg g⁻¹) at pH 3, with a 55% increase in sorption capacity compared to that of non-activated biochar. Electrostatic interactions contributed to the major force for sulfamethazine sorption, accompanied with other mechanisms such as hydrophobic, hydrogen bond, and π - π interactions. Jung et al. (2015a) applied

NaOH-activated loblolly pine chip biochar to adsorb three drugs (diclofenac, naproxen, and ibuprofen), and the results suggested that hydrophobic interactions were the dominant adsorption mechanisms in pharmaceutical adsorption.

3.2.3. Miscellaneous pollutants removal

Apart from the common contaminants including dyes and pharmaceuticals, activated biochars were also applied to remove other miscellaneous pollutants from water. Li et al. (2014) compared the furfural removal efficiency of several activated bamboo biochar by oxidation treatment using HNO₃ and KMnO₄, base treatment using NaOH, and heat treatment. The heat-treated biochar exhibited the highest capacity for furfural adsorption, with a removal efficiency of 100% at 10 g L⁻¹ furfural, and the maximum removal capacity was 253.16 mg g⁻¹. However, the chemical treatments inhibit the adsorption of furfural, due to their effects on increasing hydrophilicity of biochars. The mechanism of enhanced adsorption is that heat treatment increased surface area, basicity, micropore volume and decreased hydrophilicity of biochar. Jung et al. (2015b) used chemical activation to improve the physicochemical properties of biochar and applied for the removal of natural organic matter (NOM) with different humic acids (HA) and tannic acids (TA) combinations. Removal of NOM by activated biochar was significantly higher than that of commercial powdered activated carbon. The higher adsorption affinity of TA ($K_F = 32.4 \text{ (mg/g)/(mg/L)}^{1/n}$) than HA ($K_F = 1.39 \text{ (mg/g)/(mg/L)}^{1/n}$) onto activated biochar produced in the laboratory was also observed. Further assessment of the activated biochar role in an adsorption–coagulation hybrid system as nuclei for coagulation in the presence of aluminum sulfate (alum) showed a synergistic effect in a HA-dominated NOM solution.

4. Application for CO₂ capture

The reduction of anthropogenic CO₂ release into the atmosphere has been recognized as the crucial matter due to its huge contribution to global climate change (Nasri et al., 2014; Toro-Molina et al., 2012). Adsorption is considered as a promising method for CO₂ separation and the surface physical and chemical properties of adsorbent play a critical role during the adsorption process (Zhang et al., 2014a). Biochar produced from biomass waste followed by activation usually showed high surface area, micropore volume and appropriate surface properties, which can be used as potential CO₂ adsorbents. The adsorption behavior of activated biochars and their correlation with physical porosity and surface chemistry have been investigated by several studies (Tables 2 and 4).

4.1. Effect of physical properties

In general, for gas-phase adsorption applications, the main requirement of the adsorbent is to possess a high micropore volume (Plaza et al., 2014). The surface area and pore structure of carbon materials are important parameters for CO₂ capture. Therefore, activation processes are needed for biochar to achieve desired physical porosity. Biochar based porous carbons as adsorbents for CO₂ capture was produced by carbonization of the palm kernel shell at 700 °C followed by CO₂ activation. The results indicated that activation of the biochar increased both surface area and micropore volume (89.5% of the total pore volume was within the micropore range), which implied that it was suitable for CO₂ capture. Higher CO₂ uptake of 7.32 mmol/g was obtained for palm kernel activated carbon at 30 °C and pressures up to 4 bars (Nasri et al., 2014). Biochars obtained by activation of almond shells and olive stones with different oxygen concentrations: 3%, 5% and 21% (balance N₂) at temperatures between 400 and 650 °C were

applied for the adsorption of CO₂ (Plaza et al., 2014). The obtained biochars had a relatively high micropore volume in the narrow range of 0.3–0.5 nm and exhibited high CO₂/N₂ selectivity, which showed potential to be used as CO₂ adsorbents. Different biochar types were produced by one-step KOH activation and applied as CO₂ sorbents with high surface area (Li et al., 2016b). The results suggested that the different activated biochar samples exhibited the differences in CO₂ uptake performances at 30 bar almost overlaps with the differences in BET surface area and total pore volume, which confirmed the relation between the physical properties and CO₂ adsorption values at high pressure (Li et al., 2016b).

4.2. Effect of chemical properties

The CO₂ adsorption properties of activated biochar depend to a large extent not only on the surface area and pore structure, but also the chemical property (Shafeeyan et al., 2010; Zhang et al., 2016). It has been shown that introduction of nitrogen functional groups into the biochar surface can increase the capacity of resultant activated carbon to adsorb CO₂ (Nguyen and Lee, 2016; Zhang et al., 2014a, 2015b, 2016). Cotton stalk biochar was activated by high temperature CO₂–ammonia mixture to combine the advantages of both CO₂ activation and ammonia treatment (Zhang et al., 2014a). The activated chars had high surface area and abundant N-containing groups, which was benefit to CO₂ adsorption. The CO₂ adsorption capacity of biochar is proportional to the micropore volume at lower temperature (20 °C); however, it is dependent on the N content of biochar for CO₂ adsorption at higher temperature (120 °C) (Zhang et al., 2014a). In order to further enhance CO₂ adsorption capacity of nitrogen-enriched biochar, the biomass was pre-deashed by HF (hydrofluoric acid) and used to produce nitrogen-enriched biochar using high temperature ammonia treatment (Zhang et al., 2015b). The deashing treatment improved both the pore structure and the introduction of nitrogen-containing functional groups of nitrogen-enriched biochar, resulting in the larger CO₂ adsorption capacity. The mechanisms of CO₂ capture in nitrogen enriched biochar were also studied (Zhang et al., 2016). The results showed that the hydroxyl, primary amide, amines, azo compound N = N, secondary amide groups and aliphatic C–N/C–O are effective active sites to adsorb CO₂ (Fig. S3). In another study, HNO₃/NH₃ treatment also successfully introduced amine groups onto the biochar surfaces, which generated new active sites for the CO₂ adsorption (Nguyen and Lee, 2016).

As can be seen, activated carbon produced from biochar by physical and chemical activation showed high capacities to adsorb CO₂ (Table 4). In addition, high selectivity was also observed (Nguyen and Lee, 2016; Plaza et al., 2014). Both physical (surface area and pore structure) and chemical properties (functional groups) of activated biochar are the important parameters for the CO₂ adsorption performance (Fig. S3). Activated biochar appear to be a sustainable and low-cost substitution of commercial materials for the capture of CO₂ from flue gas and air. In the future large-scale application in soil, activated biochar may earn a win-win solution for both soil improvement and carbon capture. This can be achieved as it can play a role in soil amendment/remediation, as well as act as an adsorbent for CO₂ adsorption from soil and atmosphere simultaneously.

5. Application for energy storage

In addition to these applications mentioned above, biochar-based activated carbons have also been used in energy storage fields. For example, activated biochar have been employed as electrode materials for supercapacitors or as porous matrix to host active substances for cathodes (Tables 2 and 5).

5.1. Application as electrode materials for supercapacitors

To achieve high capacitance, biochar requires proper activation. The porous network is responsible for the performance of the supercapacitors. In most cases, a microporous and mesoporous structure are necessary to obtain improved performance (Taberna and Gaspard, 2013). The improvement of surface area and microporous structure after activation could significantly contribute to the promoted capacitance performance (Dehkhoda et al., 2016; Farma et al., 2013; Gupta et al., 2015). Significant enhancement of the capacitance (near 2.8 times higher than untreated biochar) was achieved by oxygen plasma activation. This enhancement of the charge storage capacity is attributed to the creation of a broad distribution in pore size and a larger surface area (Gupta et al., 2015). A KOH-activated biochar was applied for Electric Double Layer adsorption of NaCl/NaOH to be employed in water treatment (capacitive deionization) or energy storage (supercapacitor) processes (Dehkhoda et al., 2016). Activated biochar electrodes with majorly microporous structure showed very high total capacitance (222–245 F/g) mainly due to their high content of micropores. Increase of mesoporous structure resulted in slight lower capacitances of 182–240 F/g with significantly reduced electrode resistance and improved capacitive behavior (Dehkhoda et al., 2016). Apart from the pore properties, the modified chemical properties of activated biochar also played important role in supercapacitors application (Elmouwahidi et al., 2012; Jiang et al., 2013). For instance, it was reported that simple activation of biochar in diluted HNO₃ at room temperature could lead to 7 times increase in the capacitance (Jiang et al., 2013). The HNO₃-activation slightly decreased the BET surface area of the biochar, and the substantial capacitance improvement was mainly attributed to the increase in the coverage of surface oxygen groups.

The performances of activated biochar applied in supercapacitors have also been reported to be equivalent to or even higher than that of other synthesized carbon materials (e.g. commercial activated carbon, graphene, carbon nanotubes) (Table S5). As a low-cost, environmental-friendly material, biochar has the potential to replace these materials for use in future supercapacitors. Koutcheiko and Vorontsov (2013) produced biochar-derived activated carbon by physical activation and applied as an electrode material for supercapacitor manufacturing and to measure the electrochemical characteristics of fabricated single and stack coin supercapacitors. The obtained activated carbon under optimal activation conditions had a high BET surface area up to 1500 m² g⁻¹ and iodine number up to 1200 mg/g, which was a promising material used for supercapacitor electrode fabrication. Fabricated single coin cells demonstrated stable, reliable performance and their electrochemical characteristics (3 F, <1 Ω ESR) compared favorably with commercially-available devices of similar form and size factors (Koutcheiko and Vorontsov, 2013). The chemical (7 M KOH) and thermal (at 675 and 1000 °C, respectively) activated biochars were applied as renewable and low-cost carbon-based electrode materials for electric double layer (EDL) applications (Dehkhoda et al., 2014). The total capacitances of the activated biochar electrodes measured by cyclic voltammetry analysis was up to about 50 times higher than that of Vulcan electrodes prepared by the same technique, and also competitive with much more expensive systems such as CNTs and graphene-based electrodes. Jin et al. (2013) also reported that the capacitive performances of the KOH activated biochar were much better than general bio-inspired activated carbons, ordered mesoporous carbons and commercial graphene.

5.2. Application as porous matrix to host active substances for cathodes

Activated biochar can also applied as matrices to host active substances for cathodes of lithium-sulfur (Li-S) and lithium-

selenium (Li-Se) batteries. Biochar produced from inner spongy layers of pomelo pericarp was KOH activated and served as cathode materials for Li-Se batteries (Zhang et al., 2015a). The obtained biochar had high BET surface area of 1539.4 m² g⁻¹ and a micropore volume of 0.612 cm³ g⁻¹, and enriched surface functional groups, which facilitated the effective encapsulation of elemental selenium (effectively hosted a 56.1 wt% of elemental selenium). The Se loaded activated biochar delivered a high reversible capacity of 597.4 or 466.8 mA h/g in the 2nd or 300th cycle. In another study, bamboo biochar was activated via a KOH/annealing process and used to encapsulate sulfur to prepare a microporous bamboo carbon-sulfur nanocomposite for use as the cathode for Li-S batteries (Gu et al., 2015). The resulted nanocomposite with 50 wt% sulfur content delivered a high initial capacity of 1295 mA h/g at a low discharge rate of 160 mA/g and high capacity retention of 550 mA h/g after 150 cycles at a high discharge rate of 800 mA/g with excellent coulombic efficiency (≥95%) (Gu et al., 2015).

The abundance, applicable physical/chemical properties (abundant oxygenated functional groups and high surface area), and ease of processability of activated biochar make it suitable to be employed as low-cost and environmentally-friendly material for energy storage (Liu et al., 2015; Sevilla and Mokaya, 2014). These appropriate properties are significantly affected by its biomass feedstock, pyrolysis conditions and activation conditions, therefore, the proper adoption of these parameters is important to the capacitance performance and the amount of energy stored in the biochar supercapacitor. In addition, the reusability and stability of carbon matrix under a wide range of potentials is of great significance in promoting cycle application of the electrode materials, which needs to be concerned in the future production and application of activated biochar in energy storage. Furthermore, the activated biochar may also be used as hydrogen storage materials, which remains a potential candidate in the search for porous materials application in hydrogen storage.

6. Future perspectives

Thus it can be seen that, activated biochar appears to be a new potential cost-effective and environmentally-friendly carbon material with great application prospect in many fields. Despite recent researches on production and application of activated biochar in multiple areas are increasing, a number of research gaps still exist (Fig. 1). To close these knowledge gaps, the following recommendations are suggested:

- (i) The feedstock with different compositions, production conditions and activation parameters of biochar may significantly affect the properties of resultant activated biochar. Future studies are needed to choose feedstock with appropriate compositions, and optimize production conditions and activation parameters to produce biochar with proper and designed properties for specific applications.
- (ii) Apart from the activation methods existed, there are other potential methods which are suitable for biochar activation. The researches for more appropriate and novel treatments for activation, and improving the existing methods are needed. In addition, the incorporation of different primary activation methods for biochar activation could provide a good possibility to enhance activation efficiency by combining the advantages of different methods.
- (iii) It's possible to design and produce activated biochar with its own set of characteristics by that can make it suitable for target applications. Biochars can be engineered from strategic selection of design parameters to create "designer biochars" to match specific applications (Fig. 1b). After set-

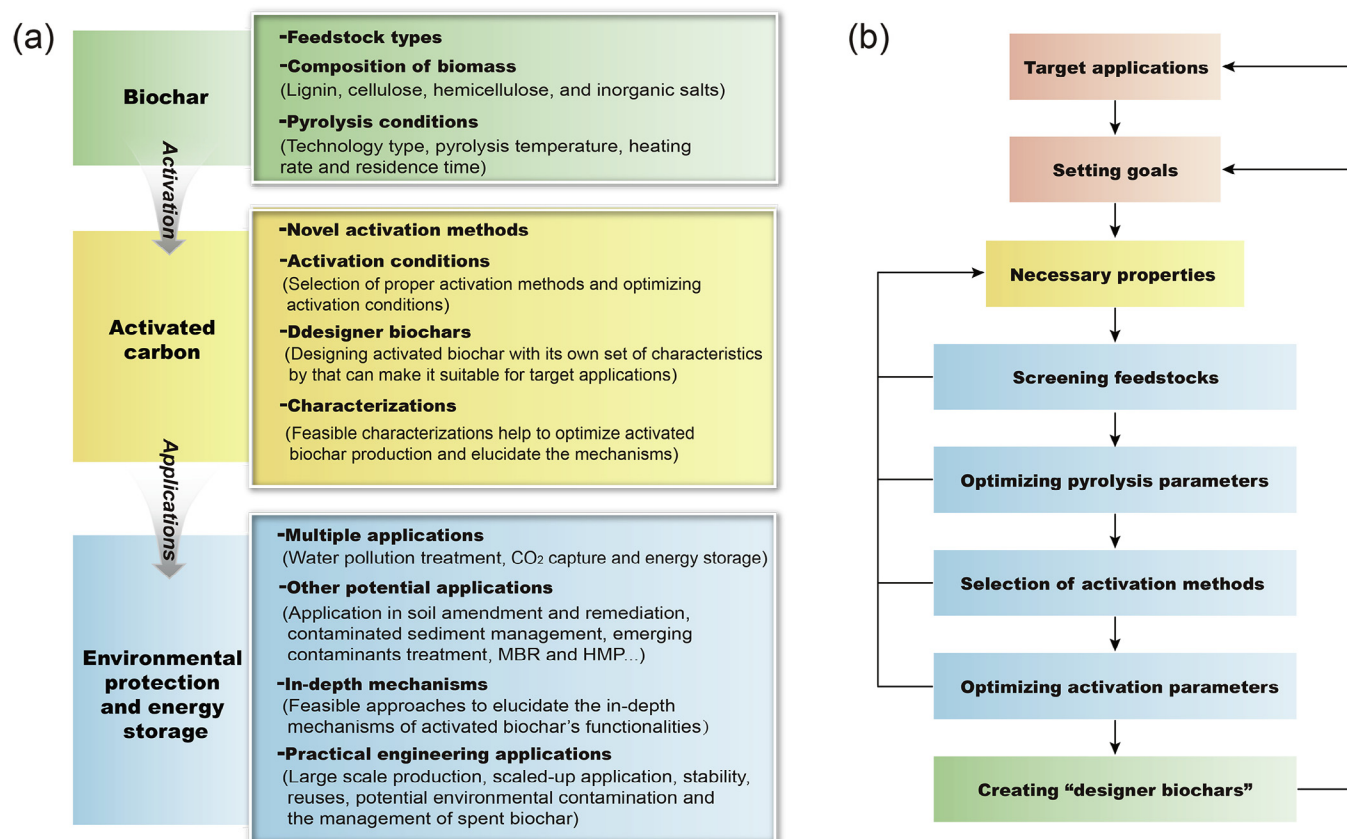


Fig. 1. (a) Schematic illustration of the future perspectives for biochar as potential sustainable precursors for activated carbon production and multiple applications; (b) schematic illustration of creating "designer biochars".

- ting goals of target applications, the necessary properties of "designer biochars" including physical porosity and surface chemistry can be achieved by screening feedstocks (composition of various feedstocks types), optimizing pyrolysis parameters (technology type, pyrolysis temperature, heating rate and residence time), selection of activation methods (physical activation, chemical activation or combined method), and optimizing activation parameters (activating agent, activation temperature, and activation time).
- (iv) Most application of activated biochar are concentrated on its application for water pollution treatment, while the application for CO₂ capture and energy storage are relatively lacked, which need to be strengthened. Furthermore, many potential applications of activated biochar exist which should be investigated in the future. For instance, it may be used as a new potential in-situ amendments for contaminated soil and sediment management. The proper physical/chemical properties allow activated biochar to be applied as a catalyst support. In addition, it can also be applied in other wastewater treatment processes, such as its application in membrane bioreactor (MBR) and Hybrid Membrane Process (HMP).
 - (v) Much attention has been paid on using activated biochar for tackling common pollutants. Recently, there is an increasing concern over the issue of emerging contaminants (Ecs) in environment, and more investigations about Ecs removal by activated biochar are needed.
 - (vi) Future studies should take feasible approaches to analyze the characterizations of activated biochar and to elucidate more precisely the in-depth mechanisms of activated bio-

char's functionalities in multiple applications, which may help to develop more effective methods for activated biochar production and optimize their efficiency in actual applications.

- (vii) For the future practical engineering application of activated biochar, we should get insight into the problems regarding its large scale production, scaled-up application, stability, reuses and the management of spent biochar. Very little information is available about these aspects, which need further investigations.
- (viii) During the activation and application process, undesired pollutants may release into the environment, such as acid/alkali (H₂SO₄, HNO₃, KOH, etc.) and undesired gases (SO₂, NO₂, etc.). Therefore, special concerns should be paid to improve the stability of activated biochar, as well as evaluate and minimize the potential environmental contamination.

7. Conclusions

This review presents a summary of biochar activation and the multiple applications of resultant activated carbon. The different functions of activation methods on the specific properties of biochar result in the different adsorption ability of activated biochar for various contaminants. The abundance, applicable physical/chemical properties, and ease of processability of activated biochar make it suitable to be employed as cost-effective and environmentally-friendly material for CO₂ capture and energy storage. The proper adoption of production parameters is important to the further applications. Further exploration about biochar activation and applications are needed to close the existing knowledge gaps.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2016.12.083>.

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