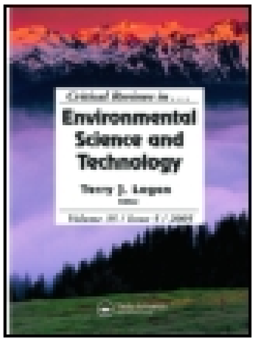

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Recent advances in engineered biochar productions and applications

Bing Wang [a,b], Bin Gao[b], and June Fang[b]

[a]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China; [b]Department of Agricultural and Biological Engineering, University of Florida, Gainesville, Florida, USA

ABSTRACT
Biochar is mainly used as a soil amendment and for carbon sequestration; while other applications such as environmental remediation may be equally important. Recently, different engineering methods have been developed and used to expand biochar's applications. A systematic literature review on the linkages between the production methods and applications of engineered biochar, therefore, is in critical need. In this work, the production and application prospects of engineered biochar are reviewed comprehensively based on the current literature. The application values and effect of engineered biochar in energy, environment, and agriculture are also expounded. Different from previous ones, this review is more focused on the unique properties and functions of various types of engineered biochars to explain their potential application, particularly environmental application. It not only summarizes recent advances in engineered biochar technology but also offers insights on new directions for development and research of engineered biochar in the future.

KEYWORDS
Biochar; modification; environmental applications

1. Introduction

Biochar is a porous carbonaceous solid material with a high degree of aromatization and strong antidecomposition ability that is produced by the decomposition of biomass from plant or animal waste under limited oxygen conditions (Lehmann, Gaunt, and Rondon, 2006; Lehmann and Joseph, 2009). It is a carbon-rich organic continuum. Biochar has a large specific surface area, is porous, and contains hydroxyl, carboxyl, carbonyl and other functional groups. It can be used to remove or reduce organic and inorganic contaminants in water, such as toxic heavy metals, dyes, and antibiotics (Ahmad et al., 2014; Inyang et al., 2016; Rajapaksha et al., 2014; Tan et al., 2015). As a new type of adsorbent, biochar has been

CONTACT Bin Gao bg55@ufl.edu Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, USA.

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applied to improve the sustainability of the environment, agriculture, and energy (Laird, 2008; Lehmann and Joseph, 2009).

Biochar is produced from a wide range of raw materials, and it has a porous structure and negative surface functional groups. Usually, pristine biochar has lower adsorption capacity than activated biochar to contaminants in aqueous solutions, particularly highly concentrated wastewater. Besides, because of its low density and small particle size, pristine biochar is not easy to separate from water, which largely limits its application (Tan et al., 2016). To maximize the adsorption capacity of biochar and its application in different areas, different engineering methods have been developed and used in water treatment and soil remediation, as well as energy storage. The creation of activated or modified styles of biochar is called biochar engineering (Ok, Chang, Gao, and Chung, 2015). Engineered biochar is the derivative of pristine biochar that is modified by physical, chemical and biological methods to improve its physical, chemical and biological properties (e.g., specific surface area, porosity, cation exchange capacity, surface functional group, pH etc.) and its adsorption capacity compared to pristine biochar (Mohamed, Ellis, Kim, Bi, and Emam, 2016; Rajapaksha et al. 2016; Yao et al., 2013b). While biomass-derived activated carbon can be counted as one type of engineered biochar, the definition of engineered biochar is much broader. Most of the biochar engineering methods are more convenient or less expensive than the typical carbon activation processes.

Previous literature has reviewed common modification methods for the production of engineered biochar (Rajapaksha et al., 2016). Based on the previous studies, this work included the recent advance of novel engineered methods for biochar modification, including ball milling, microwave modification, biological modification, etc. In terms of applications, while the focus of this work was on the environmental application, it also complemented the use of agriculture and energy storage and saving for environmental sustainability. In the end, it also pointed out the future direction of engineered biochar, such as carrying out risk assessments before engineered biochar is used for environmental application, as its fate in environmental systems such as soil and water issues to be concerned about. The overarching objective of this review is to summarize the latest methods of modification of different biochars, the adsorption mechanisms for different organic and inorganic pollutants, and the potential for application in different areas. It is anticipated that this work would set up a bridge to connect laboratory tests and practical applications to promote the research and development of biochar technology.

2. Engineered biochar production

The properties of engineered biochar are largely affected by the pyrolysis process, feedstocks, and modification methods (Sun et al., 2014; Wang et al., 2015f). A variety of feedstocks from forestry and agricultural residues have been used to produce engineered biochar. However, very little is known about the effect of production conditions on engineered biochar (Mayer et al., 2014). Understanding the

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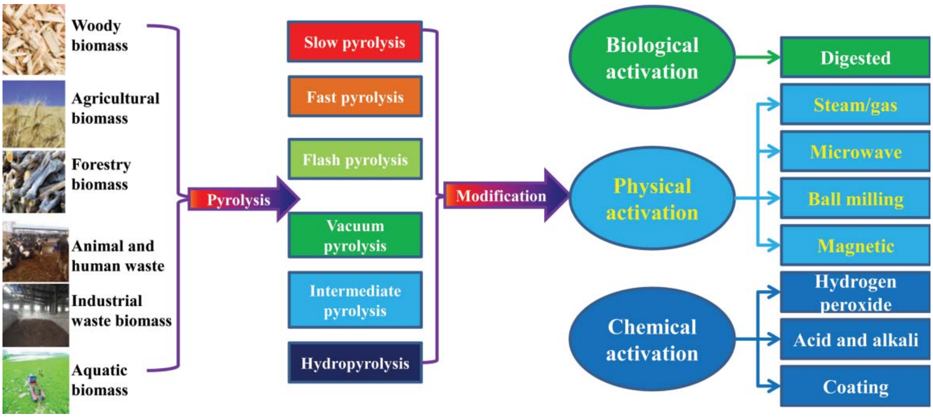

Figure 1. Typical engineered biochar production methods.

influence of production conditions on the characteristics and long-term stability of biochar obtained from pyrolysis is critical for the development of specifically engineered biochar (Crombie and Mašek, 2015). The adsorption properties of the modified biochars are largely determined by the pore structure characteristics, surface functional groups, and specific surface area. Therefore, according to different application requirements, the research and development of different engineered biochar that can improve its environmental application have become the main focus of the present research. Properties of feedstocks, preparation methods, and processes parameters can change the performance of modified biochar adsorbents (Tripathi, Sahu, and Ganesan, 2016). Therefore, the pore structure of the carbonaceous adsorbent can be controlled to a certain extent by selecting specific feedstocks or modifying the raw material through either biological, chemical or physical modification or a chemical–physical combination method (Figure 1).

2.1 Biological modification

Biological modification of biochar is to produce engineered biochar from biologically pretreated biomass feedstocks through anaerobic digestion or bacterial conversion (Inyang, Gao, Pullammanappallil, Ding, and Zimmerman, 2010, 2011; Yao, Gao, Wu, Zhang, and Yang, 2015, 2017). Anaerobic digestion and bacterial conversion technologies are the most effective ways to realize resource utilization of biomass waste (Appels et al., 2011; Inyang et al., 2010; Yao et al., 2015). Biomass anaerobic digestion is the use of anaerobic bacteria in the conversion of organic matter to biogas and digestate. Bacteria such as engineered strains of *Escherichia coli* have also been used to produce biofuel and bioproduct from cellulosic biomass. Economic value is generated from these processes (Holm-Nielsen, Al Seadi, and Oleskowicz-Popiel, 2009; Yao et al., 2015). Biochar produced from the pyrolysis of anaerobically digested residue has been proposed as a beneficial product that could be obtained from digestion residuals (Inyang et al., 2011, 2012; Monlau, Sambusiti, Antoniou, Barakat, and Zabaniotou, 2015; Streubel, Collins, Tarara, and Cochran, 2012; Yao et al., 2011a, 2015, 2017). Previous studies have suggested that anaerobic digestion could be used as a new post modification method to create high-efficiency carbon-based sorbents for heavy metals and cationic methylene blue dye (Inyang et al., 2011, 2012; Sun, Wan, and Luo, 2013b) (Table 1). After anaerobic digestion and pyrolysis, the digested biochar showed higher pH, surface area, CEC, anion exchange capacity (AEC), and hydrophobicity as well as a more negative surface charge than pristine biochar because the digestion process can alter the redox potential and pH values of the feedstock biomass (Inyang et al., 2010). The improvement of CEC and AEC suggests the possibility of using biologically activated biochar as ion exchangers that may sequester both positively and negatively charged ions from water. After anaerobic digestion, the zeta potential of all the samples was negative, indicating strongly negatively charged surfaces and functional groups that might facilitate the deposition of cations onto these sorbents. The previous study has found that anaerobic digestion enhances the heavy metals and phosphate adsorption ability of biochar produced from digested sugar beet tailings, bagasse, and dairy waste residue relative to undigested ones (Inyang et al., 2011, 2012; Yao et al., 2011, 2011a, b). Therefore, this method has been used to modify biochar for use in environmental remediation.

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2.2 Physical modification

Generally, the widely used physical modification methods for biochar include steam/gas activation, magnetic modification, microwave modification, and ball milling. Physical modification improves pore structure, introduces oxygenic functional groups, and offers advantages over chemical modification since physical modification agents are clean and easy to control (Qian, Kumar, Zhang, Bellmer, and Huhnke, 2015). The physical modification increases the adsorption capacity of modified biochar to heavy metal elements, nutrient elements, and organic pollutants by increasing the specific surface area and creating more micropores and mesopores on biochar. The advantages of physical modification include no added impurities and low cost. The basic characteristics of modified biochars produced from different physical modification treatments and their applications are listed in Table 2.

2.2.1 Steam/gas activation

To enhance the adsorption capacity of biochar, steam/gas activation turned out to be effective. A technical steam activation of biochar was found to accelerate its positive effects on nutrient retention and uptake by plants relative to nonactivated biochar (Borchard et al., 2012). Steam activation exhibited almost double the positive effects of biochars in all instances, thus being an interesting option for future biochar applications. Steam/gas activation is usually used for making activated carbon, which is normally made by carbonization and modification using steam or CO_2 (Ahmadpour and Do, 1996; Fang, Gao, Zimmerman, Ro, and Chen, 2016). During carbonization, steam/gases open and develop the porosity of the carbonized

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Table 1. Basic characteristics of engineered biochars produced from biological modification.

Feedstocks	Treatments	Pyrolysis temperature (°C)	C (wt.%)	O (wt.%)	N (wt.%)	H (wt.%)	pH	Surface area ($m^2 g^{-1}$)	Sorption capacity ($mg g^{-1}$)	Sorbates	References
Dairy waste	Anaerobic digestion	600	65.42		3.63	0.68	10.0	555.2	248	Pb(II)	(Inyang et al., 2012)
Whole sugar beet	Anaerobic digestion	600	20.15		0.43	1.07	9.0	128.5	197	Pb(II)	(Inyang et al., 2012)
Sugar beet tailings	Pristine	600	50.78	36.70		2.08	1.83	351	—	Phosphate	(Yao et al., 2011a)
Sugar beet tailings	Digested	600	30.81	39.87		1.38	2.74	449	—	Phosphate	(Yao et al., 2011a)
Food waste and Chinese silver grass	Anaerobic digestion	400	—	—	—	—	—	7.60	9.50	Methylene blue	(Sun et al., 2013b)
Sugarcane bagasse	Anaerobic digestion	600	—	—	—	—	10.9	17.7	653.9	Pb(II)	(Inyang et al., 2011)
Sugarcane bagasse	Pristine	600	—	—	—	—	7.7	14.1	31.3	Pb(II)	(Inyang et al., 2011)

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Table 2. Basic characteristics of engineered biochars produced from different physical and magnetic treatments.

Feedstocks	Treatments	Pyrolysis temperature (°C)	C (wt.%)	O (wt.%)	N (wt.%)	H (wt.%)	pH	Surface area ($m^2\ g^{-1}$)	Sorption capacity ($mg\ g^{-1}$)	Sorbates	References
Medicinal residue	Microwave	400–700	—	—	—	—	—	67.9	0.0305	Hg0	(Shen et al., 2015)
Orange peel	Magnetic modification	250	35.1	—	1.12	3.59	—	41.2	0.512	Phosphate	(Chen et al., 2011)
Orange peel	Magnetic modification	400	29.4	—	0.511	2.25	—	23.4	0.219	Phosphate	(Chen et al., 2011)
Orange peel	Pristine	400	65.7	—	1.80	3.46	—	28.1	0.00686	Phosphate	(Chen et al., 2011)
Orange peel	Magnetic modification	700	0.424	—	0.22	0.175	—	19.4	1.24	Phosphate	(Chen et al., 2011)
Orange peel	Pristine	700	67.0	—	2.05	1.47	—	501	0.477	Phosphate	(Chen et al., 2011)
Cotton Wood	$FeCl_3$-treated	600	—	—	—	—	—	—	3.147	As(V)	(Zhang et al., 2013a)
Pine wood	Hematite-treated	600	51.7	43.1	0.2	1.4	—	193.1	0.429	As(V)	(Wang et al., 2015e)
Pine wood	Pristine	600	85.7	11.4	0.3	2.1	—	209.6	0.265	As(V)	(Wang et al., 2015e)
Pine bark	$CoFe_2O_4$ treated	950	—	—	—	—	—	—	14.960	Cd(II)	(Reddy and Lee, 2014)
Pine bark	$CoFe_2O_4$ treated	950	—	—	—	—	—	—	25.294	Pb(II)	(Reddy and Lee, 2014)
Rice husk	Fe and Ca modified	300	—	—	—	—	—	—	1.000	As(V)	(Agrafioti, Kalderis, and Diamadopoulos, 2014)
Rice husk	Fe and Ca modified	300	—	—	—	—	—	—	0.0585	Cr(VI)	(Agrafioti et al., 2014)
Oak wood	Fe^{3+}/Fe^{2+} treated	400, 450	69.025	—	0.32	2.772	7.2	6.1	10.13	Pb(II)	(Mohan, Kumar, Sarswat, Alexandre-Franco, and Pittman, 2014a)
Oak wood	Fe^{3+}/Fe^{2+} treated	400, 450	69.025	—	0.32	2.772	7.2	6.1	2.87	Cd(II)	(Mohan et al., 2014a)
Oak bark	Fe^{3+}/Fe^{2+} treated	400, 450	56.145	—	0.453	2.191	8.0	8.8	30.2	Pb(II)	(Mohan et al., 2014a)
Oak bark	Fe^{3+}/Fe^{2+} treated	400, 450	56.145	—	0.453	2.191	8.0	8.8	7.4	Cd(II)	(Mohan et al., 2014a)
Empty fruit bunch	$FeCl_3$ impregnated	—	10.26	4.43	—	—	—	890	265	Methylene blue	(Mubarak, Kundu, Sahu, Abdullah, and Jayakumar, 2014)
Ultrafine tea powder	Ball milled+ $ZrOCl_2{\cdot}8H_2O$	—	48.68	41.80	—	—	—	46.27	12.43	Fluoride	(Cai et al., 2016)
Ultrafine tea powder	Ball milled	—	78.28	21.72	—	—	—	3.57	10.12	Fluoride	(Cai et al., 2016)
Corn stover	Magnetic	600	63.47	15.07	1.30	1.76	—	3.61	4.11	Fluoride	(Mohan, Kumar, and Srivastava, 2014b)
Corn stover	Pristine	600	69.78	18.52	1.76	3.36	—	—	6.42	Fluoride	(Mohan et al., 2014b)
Switchgrass	Ball milled	600	45.14	12.96	0.44	1.86	—	46	38.2	Estrone	(Peterson, Appell, Jackson, and Boateng, 2013)
Switchgrass	Ball milled	600	45.14	12.96	0.44	1.86	—	46	31.7	β- estradiol	(Peterson et al., 2013)
Switchgrass	Ball milled	600	45.14	12.96	0.44	1.86	—	46	33.9	Zearalenone	(Peterson et al., 2013)

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Corn stover	Ball milled	600	45.14	12.96	0.44	1.86	—	74	12.8	Estrone	(Peterson et al., 2013)
Corn stover	Ball milled	600	45.14	12.96	0.44	1.86	—	74	17.9	β- estradiol	(Peterson et al., 2013)
Corn stover	Ball milled	600	45.14	12.96	0.44	1.86	—	74	18.3	Zearalenone	(Peterson et al., 2013)
Miscanthus sacchariflorus	Steam activation	500	82.1	11.0	0.31	2.67	—	322	13.8	Cu(II)	(Shim et al., 2015)
Miscanthus sacchariflorus	Pristine	500	80.9	12.2	0.29	2.80	—	181	15.4	Cu(II)	(Shim et al., 2015)
Burcucumber plants	Steam activated	700	50.55	44.88	2.54	1.66	11.72	7.1	32.192	Sulfamethazine	(Rajapaksha et al., 2015)
Burcucumber plants	Pristine	700	69.41	24.45	4.61	1.31	12.32	2.31	18.776	Sulfamethazine	(Rajapaksha et al., 2015)
Burcucumber plants	Steam activated	300	68.10	21.43	5.10	5.11	11.14	1.22	14.681	Sulfamethazine	(Rajapaksha et al., 2015)
Burcucumber plants	Pristine		65.98	23.09	5.08	5.55	10.86	0.85	15.656	Sulfamethazine	(Rajapaksha et al., 2015)
Tea waste	Steam activation	300	71.47	18.16	5.48	4.75	8.64	1.46	1.88	Sulfamethazine	(Rajapaksha et al., 2014)
Tea waste	Pristine	300	68.53	21.91	5.48	3.96	6.74	0.90	2.79	Sulfamethazine	(Rajapaksha et al., 2014)
Tea waste	Steam activation	700	82.37	11.57	3.89	2.06	10.48	576.09	33.81	Sulfamethazine	(Rajapaksha et al., 2014)
Tea waste	Pristine	700	79.91	13.54	4.28	2.17	9.97	421.31	30.06	Sulfamethazine	(Rajapaksha et al., 2014)
Cotton stalk	CO_2–ammonia	600	—	—	3.91	—	—	297	39.37	CO_2	(Zhang et al., 2014c)
Cotton stalk	CO_2	600	—	—	—	—	—	351.49	20	CO_2	(Xiong et al., 2013)
Cotton stalk	NH_3	600	—	—	—	—	—	251.91	99	CO_2	(Xiong et al., 2013)
Pecan shell	KOH steam	800	72.1	2.5	0.23	0.55	7.2	—	125	Cu(II)	(Ippolito et al., 2012b)
Paper mill sludge	ZVI-magnetic biochar composites	700	—	—	—	—	—	101.23	—	Pentachlorophenol	(Devi and Saroha, 2014)
Eichhornia crassipes	Chitosan modification	600	71.24	23.02	3.2	—	—	90.78	120	Cr(VI)	(Zhang et al., 2015)
Kans grass	Fe_3O_4 fabricated	500	54.39	27.37	—	—	—	31.45	2.004	As(III)	(Baig et al., 2014)
Kans grass	Fe_3O_4 fabricated	500	54.39	27.37	—	—	—	31.45	3.132	As(V)	(Baig et al., 2014)

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material at temperatures ranging from 700 to 1100°C (Dias, Alvim-Ferraz, Almeida, Rivera-Utrilla, and Sánchez-Polo, 2007). This makes the carbonized material have developed porosity, large surface area, variable characteristics of surface chemistry, and a high degree of surface reactivity (Dias et al., 2007). Now the technology has been adopted for making engineered biochar (Azargohar and Dalai, 2008). The steam/gas activation method involves pyrolyzing biochar at a certain temperature with water vapor, carbon dioxide, air, etc. Many studies have shown the surface area and porosity largely improved after modification (Chang, Chang, and Tsai, 2000; Mangun, Benak, Economy, and Foster, 2001). Usually, the surface area of biochar correlates with its degree of pyrolysis, while the development of the porosity and internal surface area is dependent on the modification operating conditions (Azargohar and Dalai, 2008). Steam activated biochar nearly doubled the surface area while decreasing the polarity by degrading the carboxyl and phenol functional groups (Shim, Yoo, Ryu, Park, and Jung, 2015). Modification processes and operating conditions largely affect the characteristics of biochar (Azargohar and Dalai, 2008), including the internal surface area and large yield. Steam-activated biochars at 700°C had a larger surface area and pore volume compared to their nonactivated counterparts (Rajapaksha et al., 2015). Surface areas increased with modification from negligible to 136–793 $m^2\ g^{-1}$ of material, with concomitant pore development (Lima, Boateng, and Klasson, 2010).

The steam/gas activated biochars have been applied for the removal of many contaminants, such as heavy metals (Ippolito et al., 2012b; Shim et al., 2015), antibiotics (Mondal, Aikat, and Halder, 2016; Rajapaksha et al., 2015) and greenhouse gases (Fungo et al., 2014). Steam activation showed a pronounced effect on biochar properties that played significant roles in determining sulfamethazine sorption capacities. The maximum sulfamethazine sorption capacity of 33.81 mg g^{-1} was observed at the lowest pH value for tea waste biochars after steam activation (Rajapaksha et al., 2014). The metals adsorption capacity of modified biochar was influenced by the modification strategy, increasing for longer modification times and higher water flow rates, in the presence of a single metal solution (Lima and Marshall, 2005). Lima and Marshall showed that the greatest Cu(II) sorption (93%) was obtained when the biochar was activated under a specific steam flow rate (Lima and Marshall, 2005). Steam-activated biochar showed good performance for Hg removal in the field test (De, Azargohar, Dalai, and Shewchuk, 2013). Meanwhile, CO_2–ammonia treatment combines the advantages of both CO_2 modification and ammonification. The presence of CO_2 in CO_2–ammonia treatment can promote ammonification (Zhang et al., 2014c). The surface area of biochar was increased significantly by CO_2 modification, while N-containing compounds on the char surface were enriched obviously by NH_3 modification. As an effective modified method, steam/gas activation can be used in industrial production of engineered biochars; however, this method may also have some drawbacks due to biochar's strong heterogeneity, such as difficulty to control the reaction temperature, nonuniform activation, and local overheating (Foo and Hameed, 2011).

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2.2.2 Microwave modification

Microwaves have been used in various technological and scientific fields to heat dielectric materials. Microwave pyrolysis is based on the research of traditional pyrolysis to take advantages of the development of microwave heating technology. Microwaves are high-frequency electromagnetic waves at frequencies ranging from 300 MHz to 300 GHz, which can penetrate biomass and send energy rapidly to the functional groups of the reactants. Microwave pyrolysis is a relatively new pyrolysis technique which provides many advantages over conventional processes, as it is often more controllable as well as energy and cost efficient (Mašek et al., 2013; Morgan et al., 2017). It can overcome the disadvantages of conventional pyrolysis methods such as slow pyrolysis and the necessity of shredding feedstock into smaller sizes (Zhao et al., 2010). Because microwave modification is rapid and efficient and allows for a uniform internal temperature distribution, it is more efficient than conventional pyrolysis. Thus, microwave modification could produce biochar with more functional groups and higher surface area than those produced through conventional pyrolysis (Wan et al., 2009). It was reported that the highest biochar yield was >60 wt% and the maximum BET surface area was about 450–800 m^2 g^{-1} for biochar from microwave-assisted pyrolysis. Various types of biomass have been used to produce biochar which is heated in a microwave field in a chemically inert atmosphere. Microwave pyrolysis can produce efficient biochar at low temperature (300°C) and increase soil water holding capacity (WHC) and CEC (Mohamed et al., 2016). Physical properties and stability of produced biochar from microwave systems and slow pyrolysis have been analyzed and compared by Mašek et al (Mašek et al., 2013), who found that microwave pyrolysis can occur even at temperatures of around 200°C, while in the case of conventional pyrolysis, a higher temperature and residence time was required to obtain similar results. Thus, microwave pyrolysis biochar shows a better stability than the conventional pyrolysis one. Microwave pyrolysis was also innovatively explored in pretreatment and graft reaction to modify the low-cost and recyclable jute in order to enhance heavy metal removal (Du, Zheng, Wang, Hao, and Wang, 2016). Microwave modified biochar has been used to absorb mercury (Shen et al., 2015). The previous study has been suggested that microwave modification enhanced the Hg^0-removal capacity of the sorbents, whereas chemisorption of Hg^0 was the main reaction (Li et al., 2015a). Microwave-induced pyrolysis is possible if the raw material is mixed with an effective receptor of microwave energy such as carbon or certain metal oxides (Menéndez, Inguanzo, and Pis 2002, Menéndez, Domıénguez, Inguanzo, and Pis, 2004). Recently, some studies added target chemicals to activated biochar during the process of microwave pyrolysis and achieved good results (Menéndez et al., 2004). Therefore, a future development trend will be adding other pharmaceutical reagents for modification during the microwave pyrolysis process (Li et al., 2015b; Mohamed et al., 2016).

2.2.3 Ball milling

Ball milling is a powerful none equilibrium processing method to refines the grain size of solids, which can provide a common and simple way to modify carbon materials

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for improved properties (Lyu et al., 2017). Ball milling can grind samples including biochar into a powder, which decreases the particle size and increases the specific surface area, thus increasing the potential adsorption sites for organic and inorganic ions (Cai et al., 2016; Lyu et al., 2018a, 2018b). Ball milling is conducted through either physical or chemical means, with each method modifying biochar in different ways. Physical ball milling is used to modify the particle size and surface area, while chemical ball milling is used to modify the functional groups (i.e., through chemical reactions during the milling) in addition to the modification of surface area and micropores. Since the ball milled biochar can reach nanoparticle sizes, it has been reported that the ball milled biochar performed as well as carbon nanotubes and even better than other common adsorbents, such as activated carbon, in term of removing organic and inorganic contaminants (Shan et al., 2016).The surface area of biochar from corn-stover feedstock was increased by a factor of 60 to 194 m^2 g^{-1} by optimizing milling conditions in a planetary ball mill (Peterson, Jackson, Kim, and Palmquist, 2012). There are also some reports showing that the functional groups greatly improved after ball milling (Kónya et al., 2002). Lyu et al. found that ball milled biochar showed much better methylene blue and Ni removal efficiency compared to pristine biochar (Lyu et al., 2018a, 2018b). The disadvantage of this method is that the ball milled biochar disperses very well in water and can be transported very easily, which restricts its role in water and soil remediation. Previous studies have shown that transport of biochar increased with decreasing particle size (Wang, Zhang, Hao, and Zhou, 2013a; Zhang et al., 2010), and a significant fraction of biochar particles were found to have moved to lower soil layers in the saturated sandy soil, especially for the biochar particles in nanometer scales (Wang et al., 2013a). Particles of biochar in soil, being relatively light materials compared to other soil solids, are likely to be prone to preferential erosion and off-site transport in surface runoff. The consequences of the movement of biochar colloids are the off-site migration of pesticides and other contaminants along the soil profile, which leads to a potential risk to groundwater (Chen et al., 2017; Kookana, 2010). Therefore, the next work is to learn how to make biochar stable after it is used to adsorb contaminants.

2.2.4 Magnetic modification

Biochar has been widely applied in pollution control, water purification, and other fields. However, because of its low density and small particle size, it is not easy to separate from water, which largely limits its application. An effective way to solve the problem is by combining the biochar with a magnetic medium and enabling it to realize solid-liquid separation (Chen, Chen, and Lv, 2011; Hu, Ding, Zimmerman, Wang, and Gao, 2015; Reddy and Lee, 2014; Trakal et al., 2016; Zhang et al., 2013a). Magnetic biochar composite material not only has the excellent adsorption properties of carbon materials but also the magnetic material under the action of external magnetic field controlling its movement, giving it an easy to separate characteristic. Magnetic biochar has a wide application prospect in adsorption, purification, and environmental remediation. In general, magnetic

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media associated with biochar are usually iron or iron oxides such as Fe(0), gamma-Fe_2O_3, Fe_3O_4, $CoFe_2O_4$, and so on (Baig, Zhu, Muhammad, Sheng, and Xu, 2014; Chen et al., 2011; Reddy and Lee, 2014; Zhang et al., 2013a; Zhou et al., 2014a, 2014b). Cation exchange is an important metal sorption mechanism for magnetic biochars. The CEC value of magnetically modified biochar significantly increased due to the presence of Fe oxides in biochars (Trakal et al., 2016). Fe oxides in the structure of biochars caused stronger metal binding (Zhou et al., 2014a). Magnetization technology mainly improved sorption of biochars with well-developed structure. The importance of biochar structure to the magnetic modification has also been demonstrated in other studies and the magnetic biochar showed strong sorption ability to aqueous metal ions such as Cd (II) (Trakal et al., 2016). Some studies were also conducted by combining chemical modification with microwave pyrolysis. The modified bamboo biochar has been used as a starting material to prepare Co-Fe binary oxide loaded adsorbent (Co-Fe-MBC) through its impregnation in $Co(NO_3)_2$, $FeCl_3$, and HNO_3 solutions simultaneously, followed by microwave pyrolysis. The low-cost composite was characterized and used as an adsorbent for Cr (VI) removal from water. It was found that a cobalt and iron binary oxide ($CoFe_2O_4$) was uniformly formed on the biochar through redox reactions (Wang et al., 2013b). Chen et al. prepared three novel magnetic biochars at different temperatures by chemical coprecipitation of Fe^{3+}/Fe^{2+} on orange peel powder and found that magnetic biochars show much higher sorption capacity for organic contaminants and phosphate as compared to the corresponding nonmagnetic biochars (Chen et al., 2011). A magnetic biochar also has been synthesized by pyrolyzing a mixture of naturally-occurring hematite mineral and pinewood biomass and showed greater ability to remove aqueous As (Wang et al., 2015e). Strong sorption of phenanthrene to the activated carbon or biochar surfaces was maintained following magnetite impregnation (Han et al., 2015c). Phenol sorption was diminished by magnetite impregnation, probably due to enhanced carbon oxidation. A high surface area biochar nearly reached the strong organic pollutant sorption capacity of activated carbon (Han et al., 2015c). The advantage of this method is that the magnetically modified biochar can be easily separated from the water after adsorption because of its magnetism (Chen et al., 2011; Li et al., 2016b; Zhang et al., 2013a). Recent studies have demonstrated that magnetic modification of biochar may decrease its surface area and pore volume and thus affect its sorption ability (Yang et al., 2016). It is thus necessary to optimize the synthesis for the best performance of the composites (Yang et al., 2016).

2.3 Chemical modification

Chemical modification is a method in which chemicals are added to the feedstock and then heated in an inert gas medium while being carbonized and activated. It could also be conducted by using oxidants (acids or bases) to oxidize biochar, which

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makes the biochar have more functional groups and micropores as well as a higher surface area and CEC. Compared to physical modification, the chemical modification has been significantly promoted. Chemical modification can alter the surface chemistry of biochar, thereby leading to an enhanced sorption capacity after modification (Ding, Hu, Wan, Wang, and Gao, 2016; Usman et al. 2016). Modification of the biomass by treatment with different chemicals enhanced heavy metals uptake and provided further evidence regarding the role of functional groups (Bai and Abraham, 2002; Inyang et al., 2012; Loukidou, Matis, Zouboulis, and Liakopoulou-Kyriakidou, 2003). After modification, the negatively charged carboxyl groups in the biochars increased binding with positively charged metals (Marshall, Wartelle, Boler, and Toles, 1999, 2000; Wang et al., 2015b). Many chemicals have been used to modify biochar for different purposes, such as $KMnO_4$, HNO_3, HCl, H_3PO_4, H_2SO_4, KOH, and NaOH (Rajapaksha et al., 2016). The results show that the alkali treated biochar possesses larger surface area than those of raw and acid treated biochars. Hg^0 removal by chemical modification was 2–3 times of that by microwave pyrolysis (Li et al., 2015b). It is reported that biochar modified by methanol or alkali could improve tetracycline adsorption capacities and reduce the inherent organic compound content in the biochar (Jing, Wang, Liu, Wang, and Jiang, 2014). The adsorption of tetracycline is attributed mainly to π–π interactions and hydrogen bonding (Liu et al., 2012). Biochar has been modified to be a highly efficient and selective absorbent for copper ions Cu(II) by nitration and reduction. The amino-modified biochar exhibited excellent adsorption performance for Cu because the amino groups were chemically bound to the functional groups on the biochar surface. The Cu(II) combined with the amino groups through strong complexation (Ma et al., 2014; Yang and Jiang 2014). The basic characteristics of engineered biochars produced from different chemical treatments and their applications were listed in Table 3.

2.3.1 Hydrogen peroxide modification

Hydrogen peroxide is a strong oxidant that can be used to modify carbon materials including biochar. Recently, H_2O_2 modified biochars began to gain attention because it is cost-effective and environmentally friendly. The previous study has found that H_2O_2 treatment of hydrochar could increase oxygen-containing functional groups on its surface and thus enhance its ability to remove ammonium and heavy metals from water (Huff and Lee, 2016; Xue et al., 2012). After being oxidized by hydrogen peroxide, the adsorption capacity of ammonium by oxidized maple wood biochar largely improved after pH adjustment (Wang, Lehmann, Hanley, Hestrin, and Enders, 2015a, 2016). Fang et al found that H_2O_2 can be effectively activated by biochar, which produces hydroxyl radical (·OH) to degrade 2-chlorobiphenyl (Fang et al., 2014b). Xue et al. found that the modified hydrochar showed enhanced lead sorption ability with a sorption capacity of 22.82 mg g^{-1}, which was comparable to that of commercial activated carbon and was more than 20 times that of untreated hydrochar (Xue et al., 2012). The advantage of this method is the low cost compared to other oxidants and the avoidance of introducing any other interfering elements,

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Table 3. Basic characteristics of engineered biochars produced from different chemical treatments and their applications.

Feedstocks	Treatments	Pyrolysis temperature (°C)	C (wt.%)	O (wt.%)	N (wt.%)	H (wt.%)	pH	Surface area ($m^2 g^{-1}$)	Adsorption capacity ($mg g^{-1}$)	Applications	References
Bagasse	Zinc nitrate-pretreated	450	—	—	—	—	—	21.28	102.66	Cr(VI)	(Gan et al., 2015)
Corn stalks	Fe_3O_4-coated	400	10.69	—	0.15	1.532	—	—	278.55	Crystal violet	(Sun et al., 2015c)
Cotton Wood	$AlCl_3$-pretreated	600	—	—	—	—	—	—	17.410	As(V)	(Zhang and Gao, 2013)
Pine cone	$Zn(NO_3)_2$ loaded	500	71.2	20.4	0.5	3.03	—	11.54	0.007	As(III)	(Van Vinh, Zafar, Behera, and Park, 2015)
Pine cone	Pristine	500	67.88	22.07	0.55	3.89	—	6.60	0.0057	As(III)	(Van Vinh et al., 2015)
Hickory chips	Fe-impregnated	600	68.8	16.75	1.83	2.03	—	16.0	2.16	As(V)	(Hu et al., 2015)
Pine wood	Manganese oxide-modified	600	78.95	14.58	0.26	1.86	—	463.1	0.594	As(V)	(Wang et al., 2015d)
Pine wood	Birnessite-modified	600	61.54	27.65	0.25	1.85	—	67.4	0.91	As(V)	(Wang et al., 2015d)
Pine wood	Pristine	600	85.68	11.19	0.33	2.13	—	209.6	0.20	As(V)	(Wang et al., 2015d)
Rice husks	Iron oxide amended	550	—	—	—	—	—	77.3	1.15	As(V)	(Cope et al., 2014)
Rice husks	Iron oxide amended	950	—	—	—	—	—	220	1.46	As(V)	(Cope et al., 2014)
Sugar beet tailings	$MgCl_2$-pretreated	600	—	—	—	—	—	253.4	835	Phosphate	(Zhang et al., 2012b)
Peanut shell	$MgCl_2$-pretreated	600	—	—	—	—	—	346.5	95	Nitrate	(Zhang et al., 2012b)
Wheat straw	$FeCl_3{\cdot}6H_2O$	450	47.2	18.4	1.1	2.4	—	9.5	2.47	Nitrate	(Li et al., 2016a)
Wheat straw	$FeCl_3{\cdot}6H_2O$	450	47.2	18.4	1.1	2.4	—	9.5	16.58	Phosphate	(Li et al., 2016a)
Tomato leaves	Mg enriched	600	—	—	—	—	—	—	116.6	Phosphate	(Yao et al., 2013a)
Sugarcane	MgO decorated magnetic	550	26.23	—	1.52	2.37	—	27.22	121.25	Phosphate	(Li et al., 2016b)
Cotton Wood	Mg/Al-LDH deposited	600	—	—	—	—	—	—	410	Phosphate	(Zhang, Gao, Yao, and Inyang, 2013b)
Corn	$MgCl_2$-pretreate	300	46.89	—	0.67	5.42	—	382.114	232	Phosphate	(Fang, Zhang, Li, Jiang, and Wang, 2014a)
Corn	Pristine	300	48.82		0.70	5.642		388.193	200	Phosphate	(Fang et al., 2014a)
Corn	$MgCl_2$-pretreate	450	62.33	—	0.72	3.470	—	421.492	233	Phosphate	(Fang et al., 2014a)
Corn	Pristine	450	65.96		0.76	3.670		425.477	201	Phosphate	(Fang et al., 2014a)
Corn	$MgCl_2$-pretreate	600	65.06	—	0.67	2.430	—	490.294	239	Phosphate	(Fang et al., 2014a)
Corn	Pristine	600	70.64		0.73	2.544		494.929	225	Phosphate	(Fang et al., 2014a)
Corncob	Ca/Mg-treated	300	43.29	—	0.62	5.00	—	377.98	294.22	Phosphate	(Fang et al., 2015)
Corncob	Ca/Mg-treated	450	57.27	—	0.66	3.19	—	418.72	315.33	Phosphate	(Fang et al., 2015)
Corncob	Ca/Mg-treated	600	60.97	—	0.63	2.19	—	487.49	326.63	Phosphate	(Fang et al., 2015)

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Table 3. (*Continued*)

Feedstocks	Treatments	Pyrolysis temperature (°C)	C (wt.%)	O (wt.%)	N (wt.%)	H (wt.%)	pH	Surface area ($m^2\ g^{-1}$)	Adsorption capacity ($mg\ g^{-1}$)	Applications	References
Cotton Wood	$AlCl_3$-pretreated	600	—	—	—	—	—	—	135.036	Phosphate	(Zhang and Gao, 2013)
Medicinal residue	NH_4Cl-impregnated	600	—	—	—	—	—	3.5	0.4446	Hg0	(Shen et al., 2015)
Medicinal residue	HCl-impregnated	600	—	—	—	—	—	3.0	0.371	Hg0	(Shen et al., 2015)
Medicinal residue	Pristine	600						2.4	0.0305	Hg0	Shen et al., 2015)
Wheat straw	Graphene pretreated	600	—	—	—	—	7.1	17.3	0.853	Hg(II)	(Tang, Lv, Gong, and Huang, 2015)
Bamboo	H_2O_2	—	—	—	—	—	—	114.44	1.47	Hg0	(Tan, Qiu, Zeng, Liu, and Xiang, 2011)
Rice-husk	H_2SO_4	450-500	43.6	12.2	0.5	2.2	—	46.8	58.82	Tetracycline	(Liu et al., 2012)
Rice-husk	KOH	450-500	76.4	16.9	0.9	3.3	—	117.8	23.26	Tetracycline	(Liu et al., 2012)
Rice-husk	Pristine	450-500	42.1	12.1	0.5	2.2	—	34.4	16.95	Tetracycline	(Liu et al., 2012)
Rice husk	Methanol	450-500	71.26	23.35	0.81	3.64	—	65.97	18.53	Tetracycline	(Jing et al., 2014)
Rice husk	Pristine	450-500	70.61	24.10	0.85	3.48	—	51.86	10.25	Tetracycline	(Jing et al., 2014)
Saw dust char	Amino-modified	500	62.5	—	4.62	4.24	—	2.5241	17.01	Cu(II)	(Yang and Jiang, 2014)
Corn straws	$KMnO_4$ modification	600	73.0	10.9	0.72	0.33	10.8	3.18	160.3	Cu(II)	(Song et al., 2014)
Corn straws	Pristine	600	85.3	5.16	0.80	1.75	10.0	61.0	19.6	Cu(II)	(Song et al., 2014)
Peanut hull	H_2O_2 modification	300	48.3	43.8	0.79	5.8	4.4	114.4	7.00	Cu(II)	(Xue et al., 2012)
Hickory wood	$KMnO_4$-treated	600	66.10	—	0.03	1.49	—	205	34.205	Cu(II)	(Wang et al., 2015b)
Hickory wood	Pristine	600	81.81	—	0.73	2.17	—	101	12.297	Cu(II)	(Wang et al., 2015b)
Switchgrass	KOH	300	—	—	—	—	—	5.01	31	Cu(II)	(Regmi et al., 2012)
Bamboo	Montmorillonite-implanted	600	83.27	12.41	0.25	2.26	—	408.1	—	Methylene blue	(Yao et al., 2014)
Bagasse	Montmorillonite-implanted	600	75.31	18.87	0.75	2.25	—	407.0	11.26	Methylene blue	(Yao et al., 2014)
Hickory chips	Montmorillonite-implanted	600	80.93	15.14	0.28	2.21	—	376.1	—	Methylene blue	(Yao et al., 2014)
Bamboo	Kaolinite-implanted	600	81.02	15.58	0.25	2.15	—	239.8	—	Methylene blue	(Yao et al., 2014)
Bagasse	Kaolinite-implanted	600	70.20	24.44	0.74	2.44	—	328.6	—	Methylene blue	(Yao et al., 2014)
Hickory chips	Kaolinite-implanted	600	78.08	18.12	0.33	2.11	—	224.5	—	Methylene blue	(Yao et al., 2014)
Cotton wood	Graphene-coated biochar	600	—	—	—	—	—	—	174	Methylene blue	(Zhang et al., 2012a)
Hickory	MWCNT-coated	600	80.3	17.4	0.2	2.1	7.5	352	2.4	Methylene blue	(Inyang et al., 2014)
Hickory	Pristine	600	81.8	15.3	0.7	2.2	7.3	289	1.28	Methylene blue	(Inyang et al., 2014)

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Bagasse	MWCNT-coated	600	85.7	11.9	0.7	1.7	7.3	390	5.50	Methylene blue	(Inyang et al., 2014)
Bagasse	Pristine	600	76.4	19.9	0.8	2.9	6.9	9	2.20	Methylene blue	(Inyang et al., 2014)
Coconut husk	KOH	700	—	—	—	—	—	1940	434.78	Methylene blue	(Tan et al., 2008)
Cotton Wood	$AlCl_3$-pretreated	600	—	—	—	—	—	—	85.036	Methylene blue	(Zhang and Gao, 2013)
Safflower seed	$ZnCl_2$	900	76.29	18.97	2.48	2.26		801.5	128.21	Methylene blue	(Angın et al., 2013)
Rice husk	zero-valent iron supported	500	—	—	—	—	—	142.8	709.1	Methyl orange	(Han et al., 2015a)
Lotus stalks	Zinc borate-pretreated	300	47.49	52.35	—	—	—	41	61.7	Ni (II)	(Liu et al., 2014)
Lotus stalks	Zinc borate-pretreated	350	52.09	47.86	—	—	—	18	40.8	Ni (II)	(Liu et al., 2014)
Lotus stalks	Zinc borate-pretreated	400	57.63	41.98	—	—	—	26	40.0	Ni (II)	(Liu et al., 2014)
Peanut hull	H_2O_2 modification	300	48.3	43.8	0.79	5.8	4.4	114.4	6.47	Ni(II)	(Xue et al., 2012)
Wheat straw	Graphene pretreated	600	—	—	—	—	7.1	17.3	25.3	Phenanthrene	(Tang et al., 2015)
Paper mill sludge	Ni–ZVI magnetic	700	—	—	—	—	—	167.86	50	Pentachlorophenol	(Devi and Saroha, 2015)
Hickory	CNTs-modified	600	77.69	20.05	0.19	2.07	6.74	359	31.05	Sulfapyridine	(Inyang et al., 2015)
Bagasse	CNTs-modified	600	84.30	13.09	0.63	1.98	6.72	336	122.63	Sulfapyridine	(Inyang et al., 2015)
Bamboo	Chitosan-modified	600	71.60	21.54	2.64	4.22	8.2	166.9	14.3	Pb(II)	(Zhou et al., 2013)
Rice hull	ZnS nanocrystals (NCs) on magnetic biochar	400	—	—	—	—	—	—	367.65	Pb(II)	(Yan, Kong, Qu, Li, and Shen, 2014)
Hickory	CNTs-modified	600	77.69	20.05	0.19	2.07	6.74	359	28.3	Pb(II)	(Inyang et al., 2015)
Bagasse	CNTs-modified	600	84.30	13.09	0.63	1.98	6.72	336	14.7	Pb(II)	(Inyang et al., 2015)
Peanut hull	H_2O_2 modification	300	48.3	43.8	0.79	5.8	4.4	114.4	22.82	Pb(II)	(Xue et al., 2012)
Peanut hull	Pristine	300	56.3	36.6	0.89	5.6	6.2	96.9	0.88	Pb(II)	(Xue et al., 2012)
Hickory wood	$KMnO_4$-treated	600	66.10	—	0.03	1.49	—	205	153.109	Pb(II),	(Wang et al., 2015b)
Hickory wood	Pristine	600	81.81	—	0.73	2.17	—	101	71.43	Pb(II),	(Wang et al., 2015b)
Pine wood	MnO-modified	600	78.95	14.58	0.26	1.86	—	463.1	4.91	Pb(II)	(Wang et al., 2015d)
Pine wood	Birnessite-modified	600	61.54	27.65	0.25	1.85	—	67.4	47.05	Pb(II)	(Wang et al., 2015d)
Pine wood	Pristine	600	85.68	11.19	0.33	2.13	—	209.6	2.35	Pb(II)	(Wang et al., 2015d)
Pine wood	MnO-loaded	700	—	—	—	—	—	361	91.98	Pb(II)	(Wang et al., 2015c)
Sawdust	KOH	300	51.48	38.47	0.07	6.49	8.13	0.6887	40.78	Cd(II)	(Sun et al., 2015a)
Wheat straw	KOH	300	48.87	39.46	0.23	6.55	9.34	0.4204	38.75	Cd(II)	(Sun et al., 2015a)
Corn stalk	KOH	300	50.33	39.14	0.25	6.48	8.19	1.8367	30.40	Cd(II)	(Sun et al., 2015a)
Switchgrass	KOH	300	—	—	—	—	—	5.01	34	Cd(II)	(Regmi et al., 2012)
Peanut hull	H_2O_2 modification	300	48.3	43.8	0.79	5.8	4.4	114.4	12.38	Cd (II)	(Xue et al., 2012)
Hickory wood	KMnO4-treated	600	66.10	—	0.03	1.49	—	205	28.104	Cd(II)	(Wang et al., 2015b)
Hickory wood	Pristine	600	81.81	—	0.73	2.17	—	101	4.748	Cd(II)	(Wang et al., 2015b)

especially when the modified biochar is used in drinking water purification and soil amendment.

2.3.2 Acid and alkali modification

Appropriate selection of biochar oxidant could produce recalcitrant biochar rich in carboxyl functional groups for a long-term heavy metal stabilization strategy in contaminated water and soils (Uchimiya, Bannon, and Wartelle, 2012). Acid modification showed an extensive increase in the BET surface area of burcucumber plants biochar, which may be due to the increase of micropores. Sulfuric-activated biochar indicated the highest BET surface area, which was more than 250 times that of pristine burcucumber plants pyrolyzed at 700°C. Acid-activated biochar showed an obvious enhancement in the sorption of sulfamethazine, especially when activated by 30% sulfuric acid (Vithanage et al., 2015). Nitric acid oxidation can significantly increase the content of acidic groups on the surface of activated carbon, improve the surface hydrophilicity of biochar, reduce the pH value, and cause the structural collapse of biochar and the decrease of specific surface area, which can significantly affect the biochar adsorption performance of metal ions. Activated biochar produced from *O. ficus indica* cactus fibres were used to adsorb Cu(II) ions from aqueous solutions, and it was found that the material presents relatively very high capacity and chemical affinity for Cu(II) ions even at low pH, which is attributed to the laminar structures and the carboxylic moieties present on the surface, respectively. The effect of physicochemical parameters (e.g. pH, ionic strength, temperature) indicates the formation of outer-sphere and inner-sphere complexes at near-neutral and acidic pH, respectively (Hadjittofi, Prodromou, and Pashalidis, 2014).

NaOH treatment can increase the percentage of surface graphitic carbon and other oxygen-containing groups of carbonaceous materials (Fan et al., 2010). After slow pyrolysis and then further modified with NaOH modification, hickory wood biochar's surface area, cation-exchange capacity, and thermal stability were significantly improved (Ding et al., 2016). The adsorption affinities of different humic acids and tannic acids combinations in natural organic matter (NOM) solutions were evaluated with activated biochar produced in the laboratory impregnated with a NaOH solution, and it was found that there was a higher adsorption affinity of tannic acid for activated biochar (Jung et al., 2015). By selecting the appropriate modification conditions, it can produce microporous activated carbons with a micropore volume up to 1.45 cm^3g^{-1} and a BET surface area of 3290 m^2g^{-1} (Lozano-Castelló, Lillo-Ródenas, Cazorla-Amorós, and Linares-Solano, 2001). In addition, it shows that chemical modification with NaOH can be successfully used to develop activated carbons with high surface area and micropore volumes (i.e., up to 2700 m^2g^{-1} and 1 cm^3g^{-1}) (Lillo-Ródenas, Lozano-Castelló, Cazorla-Amorós, and Linares-Solano, 2001). NaOH modified biochar exhibited an enhanced sorption capacity for Cd(II) because of surface electrostatic attraction, surface complexation, and/or surface precipitation (Li et al., 2017). It was also found that NaOH treatment of bamboo biochar increased the percentage of surface graphitic carbon and other oxygen-containing functional groups. The increased chloramphenicol

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adsorption on NaOH modified biochar was ascribed to the enhanced π–π interaction between the adsorbent and adsorbate (Fan et al., 2010). The porous structure of biochar was tailored by a modified chemical modification method using KOH (Dehkhoda, Ellis, and Gyenge, 2016a). The KOH-activated biochar has a predominantly microporous, mesoporous, or a combined (micro/meso) porous structure (Dehkhoda, Gyenge, and Ellis, 2016b). KOH-activated municipal solid wastes biochars were more favorable for As(V) adsorption (Jin et al., 2014a). Sun et al. also found that KOH modification of hydrochars might have increased the aromatic and oxygen-containing functional groups, resulting in about a 2–3 times increase of cadmium sorption capacity (30.40–40.78 mg g^{-1}) compared to that of unmodified hydrochars (13.92–14.52 mg g^{-1}) (Sun, Tang, Gong, and Zhang, 2015a). Biochar from peanut shell was a good precursor for the preparation of porous biochar through KOH modification. The BET surface area of obtained porous biochar was calculated as 640.57 m^2g^{-1} with 0.76 cm^3g^{-1} of total volume (Han et al., 2015b). Another novel approach was developed to prepare an engineered biochar from $KMnO_4$ treated hickory wood through slow pyrolysis (600°C). Characterization experiments with various tools showed that the engineered biochar surface was covered with MnO_x ultrafine particles. In comparison to the pristine biochar, the engineered biochar had more surface oxygen-containing functional groups and much larger surface area (Li et al., 2017; Wang et al., 2015b). Biochar oxidized by H_2SO_4/HNO_3 has more carboxyl groups and demonstrated higher immobilization of Pb, Cu, and Zn (Uchimiya et al., 2012). Fan et al. compared the chloramphenicol adsorption capacity from acidic treatment and basic treatment and found that H_2SO_4 treatment led to minimal variation in surface functional groups, and NaOH treatment increased the percentage of surface graphitic carbon and other oxygen-containing groups. The increased adsorption of chloramphenicol on NaOH modified biochar was mainly ascribed to the enhancement of the π–π interaction between the adsorbent and adsorbate (Fan et al., 2010). In addition to the removal of heavy metals and antibiotics, KOH modified biochar is also used to adsorb methylene blue. The surface area of the prepared coconut husk-based activated carbon was relatively high with large pore volume and was found to be mesoporous. Dyes and heavy metals were found to adsorb strongly on the surface of the activated carbon (Jin et al., 2014a; Sun et al., 2015a; Tan, Ahmad, and Hameed, 2008). In general, alkali-treated biochar possesses larger surface area than those of raw and acid treated biochars (Ding et al., 2016). Therefore, chemically modified biochar has great potential and performance in the removal of organic and inorganic pollutants from water.

2.3.3 Coating/impregnation through chemical modification

The coating/ impregnation method is achieved by expanding the surface area of the biochar surface, increasing the surface functional groups, cation exchange capacity, and porosity by coating or impregnating different metal oxides or functional nanoparticles to biochar in different ways at different pyrolysis periods. There are three synthesis methods which are applied to produce nano-metal oxide/hydroxide-biochar composites, including supporting with functional

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nanoparticles, pretreating biomass using metal salt, and mixing metal oxide nanoparticles after pyrolysis (Tan et al., 2016).

Nanoparticles have a large specific surface area and many functional groups can provide high-affinity adsorption sites to adsorb various pollutants. However, the shortcomings of nanomaterials limit the application of nanomaterials, such as poor solubility and ease of gathering. The coating of functional nanoparticles onto biochar surface can synthesize a composite material capable of removing various contaminants by combining the advantages of biochar matrix and functional nanoparticles. These functional nanoparticles could make a great improvement in surface functional groups, surface area, porosity, and thermal stability of biochar, which contribute to better performance of contaminants removal (Inyang, Gao, Zimmerman, Zhou, and Cao, 2015; Liu, Gao, Fang, Wang, and Cao, 2016b; Wang, Gao, Li, Creamer, and He, 2017a; Zhang, Gao, Yao, Xue, and Inyang, 2012a, 2012c). Compared to the pristine biochar, the biochar derived from sweetgum biomass pretreated with carbon nanotubes (CNTs) and graphene oxide (GO) through slow pyrolysis showed improved specific surface area and enhanced sorption ability to aqueous Pb(II) and Cd(II) (Liu et al., 2016b). The enhanced adsorption of methylene blue on the graphene-coated biochar is mainly controlled by the strong π–π interactions between aromatic molecules and the graphene sheets on biochar surface (Zhang et al., 2012a). Inyang et al. found that in hybridized CNT–biochar nanocomposites, the addition of CNTs significantly enhanced the physiochemical properties of the biochars and their methylene blue (MB) sorption ability, and the electrostatic attraction was the dominant mechanism for the sorption of MB onto the biochar (Inyang, Gao, Zimmerman, Zhang, and Chen, 2014). Batch sorption experiments showed that the chitosan-modified biochars enhanced removal of heavy metals from solution compared to the unmodified biochars (Song, Yang, Wang, Xu, and Cao, 2016; Zhou et al., 2013).

Another method is pretreating biomass using chemical reagents, bio-accumulation in biomass, or clay before pyrolysis. The metal elements enriched in the biomass can be turned into nano-metal oxide/hydroxide after thermal treatment. Metal salts/clays are usually chosen as the chemical reagents for the pretreatment of biomass. The metal ions may attach onto the surface or get into the interior of biomass after it is dipped into the metal salts solution. After pyrolysis, the metal ions will transform into nano-metal oxide or metal hydroxide, and the biomass impregnated with metal ions will become biochar based nanocomposites (Yao, Gao, Chen, and Yang, 2013a, 2013b). Particularly, magnetic biochar based adsorbents can be fabricated by the pyrolysis of iron ion treated biomass (Zhang et al., 2013a). $AlCl_3$ (Zhang and Gao, 2013), $CaCl_2$ (Fang et al., 2015, Liu et al., 2016a), $MgCl_2$ (Fang et al., 2015; Zhang, Gao, Yao, Xue, and Inyang, 2012b), $FeCl_3$ (Li et al., 2017; Zhang et al., 2013a), $KMnO_4$ (Li et al., 2017; Wang et al., 2015b), $MnCl_2$ (Wang et al., 2015d), and $ZnCl_2$ (Gan et al., 2015) are the commonly applied metal salts for the pretreatment of biomass, which result in the formation of Al_2O_3, AlOOH, CaO, MgO, MnO_x, FeO_x, and ZnO nanoparticles on biochar surface. For instance, highly porous MgO-biochar nanocomposites could be synthesized by slow pyrolysis of $MgCl_2$-pretreated biomass (Zhang et al., 2012b). The results indicated that the MgO nano-flakes dispersed uniformly on the biochar surface, and the MgO-biochar nanocomposite showed excellent removal efficiencies for phosphate and nitrate. The MgO coating decorated magnetic biochar could be separated easily by a magnet, and the capacity was around 121.25 mg g^{-1} for biochar with Mg content around 20% (Li et al., 2016b). Biochar/AlOOH nanocomposite could be fabricated via thermal pyrolysis of $AlCl_3$ pretreated biomass (Zhang and Gao, 2013). The nanosized polycrystalline AlOOH flakes grown on biochar surfaces dramatically increased the reactive area and sites to attract heavy metals, organic, and inorganic contaminants from water. Pine wood feedstock pyrolyzed in the presence of $MnCl_2{\cdot}4H_2O$ and impregnated with birnessite via precipitation following pyrolysis sorbed more As and Pb than the unmodified biochar (Wang et al., 2015d). MnO_x loaded biochar exhibited the highest adsorption capacity for Cd(II) due to an increase in micropore sizes and the number of oxygen-containing functional groups as well as significantly improved pore structure and specific surface areas, compared to the unmodified biochar. Cation exchange and cation-p bonding are the main mechanisms responsible for the higher adsorption capacities of BC-MnO_x (Li et al., 2017). It was also reported that zinc–biochar nanocomposites produced from $ZnCl_2$-pretreated biochar had much higher BET specific surface area and total pore volume than those of the pristine biochar (Angın, Altintig, and Köse, 2013), which exhibited 1.2–2.0 times higher removal efficiency for Cr(VI) (Gan et al., 2015). Three biomass feedstocks were pretreated with montmorillonite or kaolinite suspensions and then pyrolyzed at 600°C for 1 h in an N_2 environment. The experimental data indicated that the presence of clay particles on carbon surfaces had dramatically increased (about 5 times) the biochars' adsorption ability to methylene blue (Yao et al., 2014).

Biochar-based composites with metal oxide nanoparticles attached to the biochar matrix can also be synthesized after the pyrolysis of biomass. Evaporative method (Cope, Webster, and Sabatini, 2014), heat treatment (Song et al. 2014), conventional wet impregnation method (Wang, Sheng, and Qiu, 2015c), and direct hydrolysis (Hu et al., 2015) are the commonly used methods for the treatment of biochar in the presence of metal salts. For instance, biochar could be amended with iron oxides by $Fe(NO_3)_3{\cdot}9H_2O$ via an evaporative method (Cope et al., 2014), which showed approximately a 2.5 orders of magnitude higher surface area. The heat treatment of the mixture of biochar and $KMnO_4$ could synthesize a novel composite composed of porous biochar and MnO_x. The formation of surface and inner-sphere complexes with MnO_x and oxygen-containing function groups were the key factors for increasing the removal capacity of Cu(II) on the MnO_x-loaded biochar (Song et al., 2014). Hydrous-manganese-oxide-loaded biochar was prepared by a conventional wet impregnation method, where the amorphous hydrous manganese oxide loaded onto biochar contributed

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to the higher sorption ability for Pb(II) (Wang et al., 2015c). For iron (Fe)-impregnated biochar, prepared through direct hydrolysis of iron salt onto hickory biochar, the results suggested that iron hydroxide particles on the biochar surface served as the main sites for As sorption (Hu et al., 2015). The effects of coating the biochars with Fe(III) on adsorption of As(III) and As(V) were also studied, and it was found that biochar coated with Fe(III)could be used for removal of both As(III) and As(V) (Samsuri, Sadegh-Zadeh, and Seh-Bardan, 2013). Sun et al. found that the coating of biochar with magnetic Fe_3O_4 nanoparticles not only significantly enhanced the adsorption capacity but also substantially increased the magnetism, thus enabling the recollection of the biochar by a magnet (Sun et al., 2015c). By impregnating magnesium hydroxide onto pyrolytic biochar, Zhang et al. found that salt coexisting in solution slightly increased directly frozen yellow adsorption capacity (Zhang, Mao, Jiao, Shang, and Han, 2014d), Ruan et al. found fast Cr(VI) adsorption with a Cr(VI) removal efficiency of 95% within 1 min and high Cr(VI) adsorption capacity with a maximum Cr (VI) removal up to 81.7 mg g^{-1}. The remarkable improvement of Cr(VI) adsorption on Bt/Bc/α-Fe_2O_3 was attributed to the good dispersion of α-Fe_2O_3 nanoparticles by the biochar network in comparison with other similar adsorbents (Ruan et al., 2015). The removal of Pb(II), Cr(VI), and MB by the biochar-supported ZVI was mainly controlled by both the reduction and surface adsorption mechanisms (Zhou et al., 2014a). Removal of anionic contaminants (As(V) and P) was likely controlled by electrostatic attraction with the iron particles on the zero valent iron biochar composites surfaces. An additional benefit is that the contaminant-laden zero valent iron biochar composites could easily be removed from aqueous solution by magnetic attraction (Zhou et al., 2014a).

In summary, biochar coated nanomaterials can serve as a good adsorbent, but its stability and the existing potential environmental risk cannot be ignored. Future studies should focus more on this aspect.

3. Engineered biochar applications and sustainability

An increasing interest in the beneficial application of biochar has opened up multidisciplinary areas for science and engineering, particularly with respect to environmental science and engineering. Biochar is produced from different feedstocks and then used to treat wastewater and polluted soil. It plays a key role in improving environmental sustainability because of the widespread applications in the atmosphere, water, and soil systems (Figure 2). Biochar has been evidenced to act as an efficient sorbent of various contaminants, both organic and inorganic, because of its huge surface area and special structure (Qian et al., 2015, Xie et al. 2015). Up to now, the production and modification methods, chemical and physical characteristics, and adsorption mechanisms have been extensively studied. The ultimate purpose is to apply differently modified biochars into environmental, agricultural, and energy

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sustainability. As a low-cost and efficient amendment, biochar could be used in different areas. The multiple areas that engineered biochar applications could potentially be used in include carbon sequestration, soil fertility improvement, water/soil pollution remediation, energy storage and agricultural by-product/waste recycling (Ahmad et al., 2014, Tan et al., 2017).

3.1 Environmental remediation

Engineered biochar can potentially be used to reduce the bioavailability and leachability of heavy metals and organic pollutants in soil and water systems through adsorption and other physicochemical interactions due to its special properties (Figure 3). Biochar is typically an alkaline material which can increase soil pH and contribute to the stabilization of heavy metals. Application of engineered biochar for remediation of contaminated water bodies and soils may provide a new solution to the soil and water pollution problems (Zhang et al., 2013c). Engineered biochar has been widely used for soil/water conditioning, remediation, carbon sequestration, and water remediation.

3.1.1 Water treatment

A number of studies have demonstrated that biochar can be used as a low-cost adsorbent for wastewater treatment, particularly with respect to treating heavy metals in wastewater (Ahmad et al., 2014, Inyang et al., 2016). Biochar application to water and wastewater has been reviewed previously (Mohan, Sarswat, Ok, and Pittman Jr,

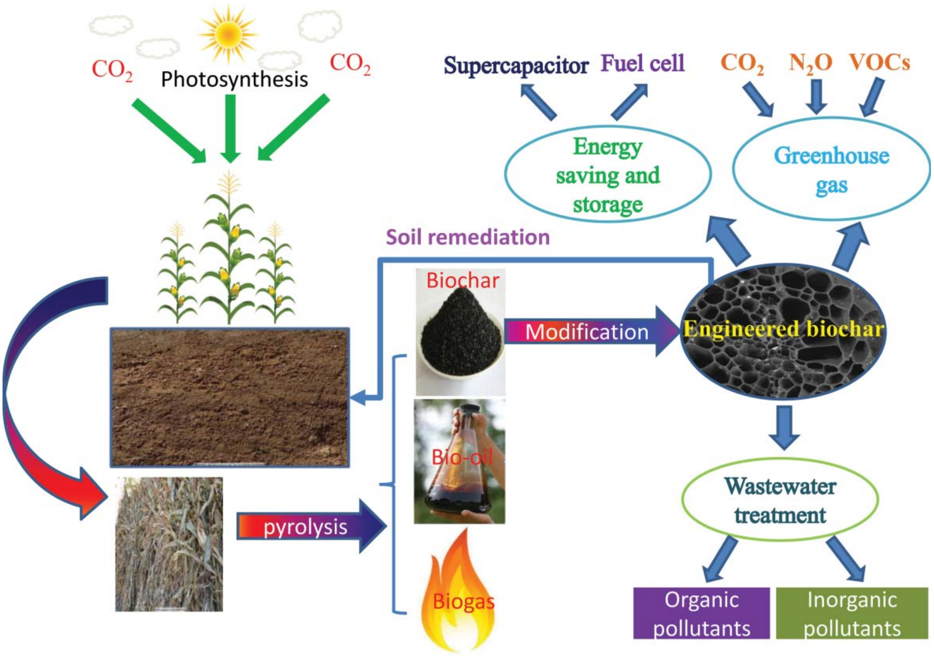

Figure 2. Engineered biochar for environmental sustainability.

2014c). Biochar has exhibited a great potential to adsorb water contaminants due to its low cost and high efficiency. However, raw biochar has limited ability to adsorb contaminants from aqueous solutions, particularly for high concentrations of polluted water. In addition, powdered biochar is difficult to separate from the aqueous solution due to its small particle sizes and low density. In order to overcome these unfavorable factors mentioned above, plenty of investigations have also been carried out to produce engineered biochars with novel structures and surface properties. In recent years, people have turned more and more attention to modified biochar. The modified biochar has been studied by various modification methods because it has more functional groups and larger specific surface area (Zhang et al., 2012a). Engineered biochars with novel structures and surface properties have been produced because of its great improvement in functional groups, pore properties, surface active sites, catalytic degradation ability, and ease of separation (Tan et al., 2016).

With respect to heavy metals removal, a variety of engineered biochars have been developed to adsorb different heavy metals by chemical and physical methods, including magnetic biochars, ball milled biochars, steam activated biochars and biochar-based nano-composites. These engineered biochars have been used to adsorb different heavy metal ions in wastewater such as As(III), As(V), Cd(II), Cr (VI), Cu(II), Hg(II) and Pb(II). The main adsorption mechanism is the formation

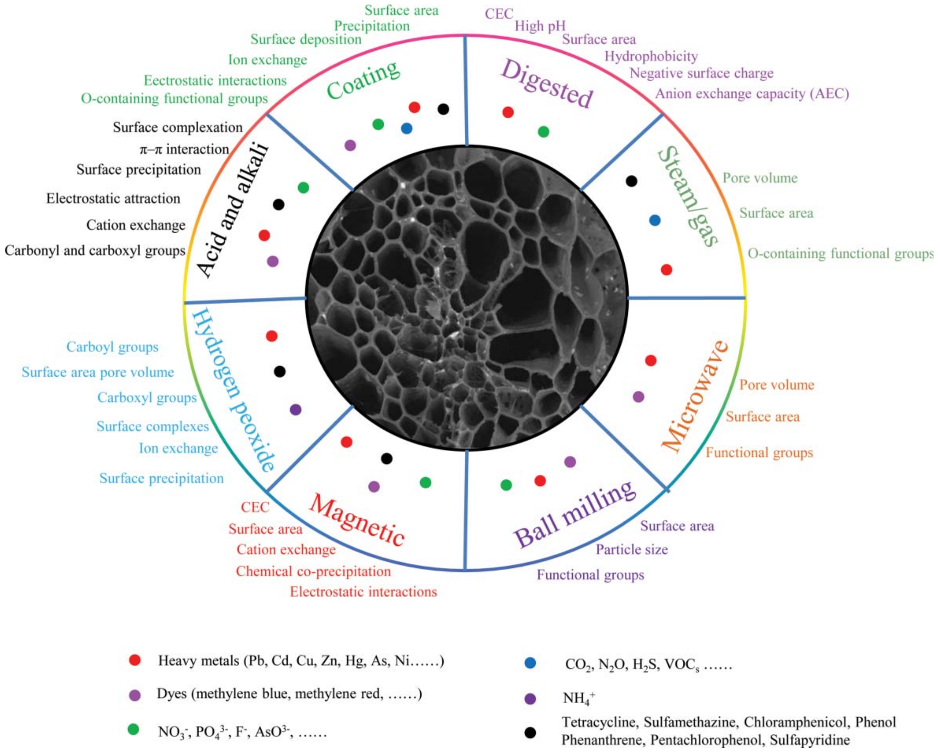

Figure 3. Summary of the effects of different modification methods on physicochemical properties of engineered biochars.

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of surface complexation, ion exchange, and surface precipitation with functional groups on the surface of modified biochar.

Regarding the removal of dyes, the concerned organic contaminants include crystal violet, methylene blue, phenanthrene, phenol, sulfapyridine, tetracycline, naphthalene (NAPH) and p-nitrotoluene (p-NT) (Liu et al., 2012). In addition to the adsorption of heavy metals and organic pollutants, other inorganic pollutants have also been reported, such as nitrate and phosphate (Li et al., 2016a, Wan, Wang, Li, and Gao, 2017, Xue et al., 2016, Yao et al., 2013a, Yao et al., 2013b, Zhang and Gao, 2013, Zhang et al., 2012b). The adsorption ability of these inorganic contaminants varied from 2.47 to 835 mg g^{-1} depending on the various nanomaterials, biochar substrates, and target contaminants (Li et al., 2016a, Wan et al., 2017, Xue et al., 2016, Yao et al., 2013a, Yao et al., 2013b, Zhang and Gao, 2013, Zhang et al., 2012b).

3.1.2 Soil remediation

Soil pollution has led to many food safety incidents. Therefore, the search for a safe and reliable soil remediation agent for contaminated soil is necessary. Previous studies have indicated that biochar could reduce the mobility of some organic and inorganic pollutants in soil. Biochar with many oxygen-containing functional groups, large surface areas, and cation exchange capacities have the effect of retaining, stabilizing, and inactivating heavy metal elements and reducing the bioavailability and phytotoxicity of heavy metals in the soil (Beesley et al., 2011, Park et al. 2011, Paz-Ferreiro, Lu, Fu, Méndez, and Gascó, 2014, Uchimiya et al., 2010b, Uchimiya, Chang, and Klasson, 2011a, Uchimiya, Klasson, Wartelle, and Lima, 2010a, Zhang et al., 2013c). Highly alkaline pH and water-soluble carbon can undesirably immobilize some elements (Beesley et al., 2011). Rees et al. found that effects of biochar on soil heavy metal mobility are controlled by intraparticle diffusion and soil pH increase (Rees, Simonnot, and Morel, 2014).

Biochar has a strong adsorption capacity for organic and inorganic pollutants following modification. Currently, most of the literature on the application of biochar to soil heavy metal remediation is about pristine biochar, and there are relatively few reports on engineered biochar. Some experiments have been carried out in the lab; however, large-scale observation and application are still rare. Further investigations on the stability, cost, collection, and regeneration of engineered biochar as well as evaluations of its potential environmental risks are still needed.

3.1.3 Gases adsorption and emission reduction

Climate change is a major challenge facing the world today. Atmospheric CO_2, CH_4, and N_2O are the most important greenhouse gases, and the contribution rate to the greenhouse effect is nearly 80%. Since it is estimated that 5% to 20% CO_2, 15% ~ 30% CH_4, 80% ~ 90% N_2O in the atmosphere are emitted from soil. Farmland soil is an important source of greenhouse gases (Robertson, Paul, and Harwood, 2000).

A large number of studies have shown that biochar can inhibit the emission of N_2O, CH_4, and CO_2 in agricultural soils (Liu et al., 2011), so it has a certain carbon

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sink effect. It also has the potential to reduce greenhouse gases emissions by reducing soil organic carbon (SOC) decomposition (Lehmann, 2007). It is also well recognized that adsorption of ammonia (NH_3) onto biochar can occur (Taghizadeh-Toosi, Clough, Sherlock, and Condron, 2012). Changing the surface polarity of biochar can change the amount of CO_2 adsorbed. The surface modification of biochar will bring about the change of acid functional groups on the surface of activated carbon, which will inevitably lead to a change in the polarity of the surface of biochar and affect the characteristic adsorption energy of CO_2 on the surface of biochar. Steam activation also enhances the porosity of the biochar, which increases soil aeration and in turn affects the production of N_2O and CH_4 (Fungo et al., 2014). After being impregnated with aluminum hydroxide, magnesium hydroxide, and iron oxide, the porosity and specific surface area of biochar composites are improved, which improves their adsorption capacity for greenhouse gases (Creamer, Gao, and Wang, 2016). By impregnating *Eucalyptus camaldulensis* wood with H_3PO_4, $ZnCl_2$, and KOH, the CO_2 adsorption capacity of the activated carbon prepared with KOH was up to 4.10 mmol/g at 1 bar and 303 K, having an increase of about 63% in comparison with the commercial activated carbon (Heidari, Younesi, Rashidi, and Ghoreyshi, 2014). Carbons obtained under lower oxygen partial pressures and higher temperatures present narrow microporosity, which is essential for the adsorption of CO_2 at low partial pressures (Plaza, González, Pis, Rubiera, and Pevida, 2014). Besides greenhouse gases, biochar from different feedstocks has also been modified by the combination of physical and chemical modification as an alternative method of removing Hg^0 from flue gas (Shen et al., 2015), H_2S gas adsorption (Shang, Shen, Liu, Chen, and Xu, 2013, Xu, Cao, Zhao, and Sun, 2014), and VOCs (Zhang, Gao, Creamer, Cao, and Li, 2017b, 2017c).

3.2 Agricultural sustainability

3.2.1 Reduce contaminant bioavailability

Soil contamination with heavy metals and organic pollutants has increasingly become a serious global environmental issue in recent years (Alloway, 2013). Considerable efforts have been made to remediate contaminated soils. Biochar has a large surface area, which allows it to have a high capacity for adsorbing heavy metals and organic pollutants. Biochar can potentially be used to reduce the bioavailability and leachability of heavy metals and organic pollutants in soils through adsorption and other physicochemical reactions. The toxicity and effectiveness of soil heavy metals are affected by many factors, such as soil pH, soil oxidation and reduction potential, soil organic matter, rhizosphere environment, and so on. Biochar is typically an alkaline material which can increase soil pH and contribute to the stabilization of heavy metals. Application of biochar for remediation of contaminated soils may provide a new solution to the soil pollution problem (Zhang et al., 2013c). Biochar has recently been used to remediate soil with both heavy metal and organic pollutants (Ahmad et al., 2014, Beesley et al., 2011, Tang, Zhu, Kookana, and Katayama, 2013, Zhang

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et al., 2013c). The mechanism is electrostatic interaction and precipitation in the case of heavy metals, and surface adsorption, partition, and sequestration in the case of organic contaminants (Tang et al., 2013).

The feedstocks and carbonization conditions of biochar affect its physical and chemical properties, thus affecting its ability to adsorb heavy metals (Uchimiya, Wartelle, Klasson, Fortier, and Lima, 2011b). Biochar application was effective in metal immobilization, thereby reducing the bioavailability and phytotoxicity of heavy metals (Park, Choppala, Bolan, Chung, and Chuasavathi, 2011). Oxygen-containing carboxyl, hydroxyl, and phenolic surface functional groups of soil organic and mineral components play central roles in binding metal ions, and biochar amendment can provide means of increasing these surface ligands in soil (Uchimiya et al., 2011a).

3.2.2 Reduce nutrient loss

Biochar input into soil could directly or indirectly affect the migration and transformation of nutrients in the soil. Reducing soil nutrient leaching has become the goal for agroecosystem researchers. Biochar, produced by pyrolysis of biomass, may help attain these goals (Ippolito, Laird, and Busscher, 2012a, Yao et al. 2012). The application of biochar to the soil not only can increase carbon uptake, soil quality, crop yield, reduce soil toxicity and harmful heavy metal activity, but also play an important role in improving soil nutrients use efficiency and reducing their loss.

As mentioned above, pristine biochar has limited adsorption capacity compared to activated biochar. Therefore, it is necessary to improve and maximize adsorption capacity of biochar and its application potential through different modification methods.

Steam activation of biochar could accelerate its positive effects on nutrient retention and uptake by plants relative to nonactivated biochar. Steam activation almost doubled the positive effects of biochars in all instances, thus making it an interesting option for future biochar applications (Borchard et al., 2012). Modification increases the sorption capacity of biochar for nitrate and phosphate, which indicates that activated biochars could be used as adsorbents for reducing nutrient-leaching in soils (Zhang, Voroney, and Price, 2017a). Borchard et al. showed that steam activation of biochar increased retention of NO_3^--N by up to 55% compared to nonactivated biochar (Borchard et al., 2012). Mg and Al modified biochars have high adsorption capacity on P adsorption. After adsorption, the loaded biochar could be used as a slow-release fertilizer. Up to now, some engineered biochars have been produced to be applied in agricultural fields (Li et al., 2016b, Yao et al., 2013a).

3.2.3 Improve soil properties

Biochar is produced from the pyrolysis of carbon-rich plant- and animal-residues under low oxygen and high-temperature conditions, and it has been increasingly used for its positive role in soil compartmentalization through activities such as carbon sequestration and improving soil quality. Biochar may significantly affect nutrient retention and play a key role in a wide range

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of biogeochemical processes in soils, especially for nutrient cycling (Liang et al., 2006, Singh, Singh, and Cowie, 2010). Several studies have found that biochar addition to soil improves its water holding capacity (Abel et al., 2013, Beck, Johnson, and Spolek, 2011). The water holding capacity of biochar is attributed to the high porosity, surface functional groups, total pore volume, porosity structure, and specific surface area (Carrier, Hardie, Uras, Görgens, and Knoetze, 2012, Mohamed et al., 2016). These properties of biochar are increased further by different modification methods (Peterson et al., 2012, Shan et al., 2016). Van et al. found that biochars from slow pyrolysis of paper-mill waste significantly increased pH, CEC, exchangeable Ca, and total C in a ferrosol and significantly increased N uptake in wheat grown in fertilizer amended ferrosol (Van Zwieten et al., 2010).

Yao et al. explored the potential application of an engineered biochar prepared from Mg-enriched tomato tissues to reclaim and reuse phosphate (P) from aqueous solution cycled back directly to soils as an effective slow-release P fertilizer (Yao et al., 2013a). Vithanage et al. found that acid modification showed an extensive increase in the BET surface area of Burcucumber biochar, which increased sulfamethazine adsorption and hence can be used as a potential amendment for soils contaminated with sulfamethazine (Vithanage et al., 2015).

3.2.4 Reduce the risks of pesticides, herbicide, and atrazine

Biochar is also considered a unique adsorbent due to its high specific surface area and highly carbonaceous nature. Therefore, soil amendments with small amounts of biochar could result in higher adsorption and consequently decrease the bioavailability of contaminants in microbial communities, plants, earthworms, and other organisms in the soil (Safaei Khorram et al., 2016). Owing to its properties, its amendment to contaminated soils has been considered for the immobilization of organic and inorganic contaminants. The application of biochar in the soil can, however, also have an undesired effect, e.g., by decreasing the efficacy of pesticides; slowing the degradation of organic contaminants; and introducing contaminants such as PAH, PCB, and dioxins (Evangelou, Fellet, Ji, and Schulin, 2015). Biochar has demonstrable effects on the fate and effects of pesticides and has been shown to affect the degradation and bioavailability of pesticides for living organisms (Safaei Khorram et al., 2016). Biochar produced from agricultural crop residues has proven effective in sorbing organic contaminants (Cao, Ma, Gao, and Harris, 2009). Previous studies have evaluated the ability of an unmodified biochar to sorb two triazine pesticides – atrazine and simazine, and thereby explored the potential environmental value of biochar on mitigating pesticide pollution in agricultural production and removing contaminants from wastewater (Zheng, Guo, Chow, Bennett, and Rajagopalan, 2010). Soils rich in Fe and Al oxides (Ferrosol) that were freshly amended with paper mill sludge and poultry litter biochar showed a two to five-fold increase in sorption of herbicides as compared to that in the unamended soil (Martin, Kookana, Van Zwieten, and Krull, 2012). $\pi-\pi$ electron donor—acceptor forces play a role in triazine adsorption (Xiao and Pignatello, 2015).

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Pyrolysis at 400°C seems optimal for producing biochar that is an effective herbicide sorbent (Sun, Keiluweit, Kleber, Pan, and Xing, 2011). The effect of chemical treatment using phosphoric acid on biochars is higher than in charcoal (Taha, Amer, Elmarsafy, and Elkady, 2014). Trigo et al. found that the higher surface area and porosity in aged biochar increased sorption of indaziflam and fluoroethyldiaminotriazine, but interestingly decreased sorption of terbuthylazine and herbicides MCPA (Trigo, Spokas, Cox, and Koskinen, 2014). The decreased surface polarity and increased bulk polarity of biochars after deashing treatment indicated that abundant minerals of biochars benefit external exposure of polar groups associated organic matter. Organic carbon (OC)-normalized distribution coefficients of phenanthrene by biochars generally increased after deashing, likely due to enhancement of favorable and hydrophobic sorption sites caused by mineral removal (Sun et al., 2013a). The activated carbon from N-300 biochar presented the faster initial sorption rate and the higher equilibrium concentration for phenanthrene adsorption, but the activated N-700 biochar exhibited stronger binding with the sorbate (Park et al., 2013). Two wood-derived biochars produced at 400°C and 600°C were treated with alumina and montmorillonite to investigate their interaction with biochars and the influence on herbicide sorption. Both minerals exhibited a pore-expanding effect that was likely relative to the removal of authigenic organic matter away from the biochars' surface. Alumina brought more remarkable pore expansion by doubling the surface area of the BC400 biochar and the mesopore area of the BC600 biochar. Consequently, more adsorption sites were accessible for herbicide molecules, which resulted in higher sorption of herbicides (acetochlor and metribuzin) to the mineral-treated biochars than to the untreated biochars (Li et al., 2015c). Activated biochar was produced from almond shells and used in the field to remove dibromochloropropane from a municipal water well. Results show that activated biochar removed 100 % of the dibromochloropropane for approximately 3 months and continued to remove it to below treatment standards for an additional 3 months (Klasson, Ledbetter, Uchimiya, and Lima, 2013).

3.3 Energy storage

At present, human demand for energy has surged, and energy shortage has become the main threat to energy supply security. Currently, energy storage materials and devices mainly use graphitized carbon (Jin et al., 2014c) and carbon nanotubes because they have good capacity, cycle life, and rate characteristics. Activated carbons from agricultural byproducts are much cheaper than carbon nanotubes and graphene. The use of agricultural waste biomass as a precursor for the production of activated carbons has been on the increase lately because it is cheap, readily available, and also viewed as a veritable way of combating waste disposal problems in the agricultural industries. Biomass activated carbons could viably be used as electrodes in supercapacitors. Under optimum process conditions, activated carbons with specific capacitance as high as 374 F g^{-1} and high-rate long-cycle stability at 4 A g^{-1} have been produced (Abioye and Ani, 2015).

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However, with the development of high-power portable devices and new energy vehicles, the market for energy storage materials and devices has put forward higher requirements, such as high reversible capacity, high current discharge capacity, and fast charge and discharge capacity. The actual capacity of graphitized carbon materials does not meet these requirements, so researchers have turned their attention to other materials such as gravel, nanotubes, graphene, and biochar. However, gravel, nanotubes, graphene, have relatively high costs compared to biochar, and most of the raw materials rely on fossil resources, resulting in greater environmental pollution and unsustainability. As a result, research and development of biochar energy storage materials and devices have become urgent.

Biochar shows good properties of developed pore structure, large specific surface area, good electrical conductivity, high-temperature resistance, and corrosion resistance. It has excellent application prospects in energy storage materials and devices. Biochar is mainly used as an energy storage material because of the following advantages: 1) the structure is stable and the cycle performance is good; 2) the high specific surface area and the developed pore structure improve the electrode capacitance; 3) good electrical conductivity means it can achieve fast charge and discharge rates; and 4) it is cheap and environmentally friendly. Compared to fossil energy storage materials, it has an obvious price and environmental advantages. Usually, the biochar used for storage is the engineered ones (e.g., activated carbon), and the means of engineering it include physical and chemical activation methods that have been mentioned above.

3.3.1 Supercapacitor

Capacitance is the ability to accommodate electric fields. One of the energy storage devices now undergoing rapid development is a supercapacitor, also known as an electric double layer capacitor (EDLCs), which uses the material in the electrode and electrolyte interface of the electrostatic double layer to store energy through the rapid and reversible redox reaction between the electrode interface (Beidaghi and Gogotsi, 2014).

The electrode is the core of the capacitor, which plays a decisive role in the electrochemical performance of the capacitor. Carbon electrode capacitors with charcoal have a high specific surface area in the carbon material surface, which helps form an electrostatic double layer to complete energy storage. Thus, by increasing the electrode surface area, one can significantly improve the capacitance of the capacitor.

It has been reported that biochar has the potential to produce supercapacitors in the future (Cha et al., 2016, Gupta, Dubey, Kharel, Gu, and Fan, 2015, Zhao et al., 2016). In order to get high capacitance, biochar needs to be properly modified. Some conventional approaches have been used to activate biochar, such as mixing biochar with a strong base and baking it at a high temperature. However, these methods have some drawbacks because they are time-consuming and require very high temperatures (requiring temperatures >900°C). Another way to properly dispose of a heavy metal-containing biochar is converting heavy metals loaded biochars into supercapacitors (Wang et al., 2017b).

A recent trend in carbon supercapacitor electrodes has been the use of biomass waste materials to produce activated carbons (Kalyani and Anitha, 2013a, Zhang, Jiang, Holm, and Chen, 2014a). Supercapacitors with carbon electrodes derived from biomass such as seaweed biopolymers (Raymundo-Piñero, Leroux, and Béguin, 2006), waste coffee beans (Rufford, Hulicova-Jurcakova, Zhu, and Lu, 2008), cotton stalk (Chen et al., 2013), banana fibers (Subramanian et al., 2007), corn stover (Jin, Wang, Shen, and Gu, 2014d), and sugarcane bagasse (Rufford, Hulicova-Jurcakova, Khosla, Zhu, and Lu, 2010, Wahid, Puthusseri, Phase, and Ogale, 2014) have been reported. The choice of the carbon precursor and modification conditions determine the electrochemical characteristics of double-layer capacitance, including specific surface area, pore-size distribution, electrical conductivity, and the presence of electrochemically active surface functional groups, and thus affect its performance (Koutcheiko and Vorontsov, 2013).

KOH-modification of cherry stones at 800–900°C can obtain carbons with large specific surface areas (1100–1300 m^2 g^{-1}), average pore sizes around 0.9–1.3 nm (which makes them accessible to electrolyte ions), and conductivities between 1 and 2 S cm^{-1}. These features lead to capacitances at a low current density as high as 230 F g^{-1} in 2 M H_2SO_4 aqueous electrolyte and 120 F g^{-1} in the aprotic medium 1 M $(C_2H_5)_4NBF_4$/acetonitrile (Olivares-Marín et al., 2009). The $ZnCl_2$ modification of bagasse is studied using thermogravimetric analysis and the carbon pore structures are characterized using N_2 and CO_2 adsorption. In two-electrode, sandwich-type supercapacitor cells containing 1 M H_2SO_4 the sugar cane bagasse carbons exhibit specific energy up to 10 Wh kg^{-1} and specific capacitance close to 300 F g^{-1} (Rufford et al., 2010). Materials with the highest level of nitrogen enrichment reveal excellent capacitance characteristics if employed as both the negative and positive electrode in an acidic capacitor (307 and 293 F g^{-1}, respectively) or the negative electrode in an alkaline capacitor (368 F g^{-1}) (Jurewicz and Babeł, 2010). Biochar material not only has a large specific surface area but also has very stable chemical properties. When biochar is used as a supercapacitor electrode material, not only it creates supercapacitors with high capacitance and charge and discharge stability, but it also reduces the production costs involved with supercapacitors. Table 4 lists the different biochars used as a supercapacitor electrode. All the engineered biochar samples have relatively high surface area and large specific capacitance. These excellent characteristics of biochar have made biochar electrode supercapacitors a hot topic for today's research.

3.3.2 Fuel cell

Electrodes play a fundamental role in facilitating exoelectrogenic biofilm growth and electrochemical reactions and are essential in improving the functionality and efficiency of fuel cells. Ideal electrode materials should have high surface area, high conductivity, low cost, stability, and biocompatibility. Many carbonaceous materials have been reported as promising cathode catalysts for fuel cell applications due to their high chemical stability, good electric conductivity, and enhanced mass transport capability. Biochar has a large specific surface area, good porosity,

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and conductivity; these features make it have the potential for high-power charge and discharge and high reversible capacity. Biochar from waste reduced the energy and carbon footprint associated with electrode manufacturing (Ganesh and Jambeck, 2013, Huggins, Wang, Kearns, Jenkins, and Ren, 2014). Biochar cathodes can be found application in fuel cell systems (Hong, Xiaomin, and Zhengrong, 2013, Huggins et al., 2014, Jiang et al. 2013, Yu, Zhao, and Li, 2014, Yuan et al. 2014, Yuan, Yuan, Wang, Tang, and Zhou, 2013). Table 5 lists specific power density when different biochar is used as a cathode. By impregnating the biochars produced via pyrolysis with potassium hydroxide, followed by heat treatment in an inert atmosphere, the total biofuel yield increased up to 25% while producing high surface area (>1900 m^2 g^{-1}) activated carbon biochar for use in electrochemical cells. Coin cell electrodes fabricated with these sustainable activated carbons provide almost 100% coulombic efficiency over 4000 charge-discharge cycles with a specific capacitance of 45 F g^{-1} at a scan rate of 1 mV s^{-1} using a Li-salt electrolyte (Goldfarb, Dou, Salari, and Grinstaff, 2017). After impregnation of elemental sulfur into the micropores of activated carbon fibers, these electrodes demonstrate good electrochemical performance at high current density attributed to the uniform dispersion of sulfur inside the carbon fiber (Elazari, Salitra, Garsuch, Panchenko, and Aurbach, 2011).

4. Perspectives

The latest progress on engineered biochar is reviewed in this study with respect to its modification methods and its environmental, agricultural, and energy storage applications in different areas. Some considerations concerning the mechanism of adsorption have been touched on. Meanwhile, the applications of engineered biochar in sustainable environment, agriculture, and energy development fields have been systematically reviewed. These emerging applications will lay a good foundation for the engineering applications of engineered biochar in the future.

At present, although a great deal of research has been done on modified biochars, most of the work is concentrated in the laboratory and field theoretical stage. There are relatively few reports on the large-scale application of engineered biochar and its performance. Industrial scale production of engineered biochar, as well as the specific application process, is still in its infancy and requires more engineering support. The cost of modification is the key to the promotion and application of engineered biochar.

In terms of modified methods, chemical modification may have more advantages over physical modification because of more specific surface area, better development of porous structure, and more oxygen-containing surface functional groups. Strong oxidant, acids, and alkalis are often used as the chemical modifiers for engineered biochars, which may impose secondary pollution risks to the environment. Environmentally friendly organic acids such as citric, tartaric, acetic, and peracetic acids have been successfully applied as the modification agents for engineered biochars (Sun, Chen, Wan, and Yu,

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Table 4. Engineered biochars as super capacitor electrodes.

Biochar	Modification method	Specific surface area ($m^2\ g^{-1}$)	Specific capacitance ($F\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Electrolyte	Ref.
Rubber wood sawdust	CO_2	683.63	33.74	0.374	1 M H_2SO_4	(Taer et al., 2010)
Coconut shell		3000	368			(Jurewicz and Babeł, 2010)
Yellow pine	Plasma	654	171.4	0.936	6M KOH	(Gupta et al., 2015)
Chemical modification biochar	NaOH	1144	99.5	0.550	6M KOH	(Gupta et al., 2015)
Red cedar wood	HNO_3	317	115	0.10	0.5 M H_2SO_4	(Jiang et al., 2013)
Rice husk	KOH	1886	210	0.79	3M KCl	(Guo et al., 2003)
Woody biochar	KOH	990	167	0.90	0.1M NaCl in 0.1M NaOH	(Dehkhoda, Ellis, and Gyenge, 2014)
Fibers of oil palm fruit bunches	KOH	1704	150	0.88	1M H_2SO_4	(Farma et al., 2013)
Argan seed shells	KOH	2062	355	1.22	1M H_2SO_4	(Elmouwahidi, Zapata-Benabithe, Carrasco-Marín, and Moreno-Castilla, 2012)
Fire wood	Steam	1131	140	0.868	0.5 M H_2SO_4	(Wu, Tseng, Hu, and Wang, 2004)
Pistachio shell	KOH	1096	120	0.608	0.5 M H_2SO_4	(Wu, Tseng, Hu, and Wang, 2005)
Fire wood	KOH	1064	180	0.607	0.5 M H_2SO_4	(Wu et al., 2005)
Hierarchical carbon	HNO_3	3310	260	1.85	6M KOH	(Jin, Wang, Gu, and Polin, 2013)
Bamboo	KOH	1251.67	260	0.609	30 wt.% H_2SO_4	(Kim et al., 2006)
Banana fibers	$ZnCl_2$	1097	296	—	1 M Na_2SO_4	(Subramanian et al., 2007)
Banana fibers	KOH	686	264	—	1 M Na_2SO_4	(Subramanian et al., 2007)
Corn grains	KOH	3199	257	1.645	6 M KOH	(Balathanigaimani et al., 2008)
Waste coffee beans	$ZnCl_2$	1019	368	0.48	1 M H_2SO_4	(Rufford et al., 2008)
Sugar cane bagasse	$ZnCl_2$	1788	300	1.74	1 M H_2SO_4	(Rufford et al., 2010)
Cassava peel waste	KOH	1352	153	0.579	0.5 M H_2SO_4	(Ismanto, Wang, Soetaredjo, and Ismadji, 2010)
Sunflower seed shell	KOH	2509	311	1.34	30 wt.% KOH	(Li et al., 2011)
Tea dust	H_3BO_4	934	89		3M KOH	(Kalyani and Anitha, 2013b)
Cherry stones	KOH	1300	230	0.67	2M H_2SO_4	(Olivares-Marín et al., 2009)
Sugar cane bagasse	$ZnCl_2$	1788	300	1.74	1 M H_2SO_4	(Rufford et al., 2010)
Nickel oxide loaded into AC	$Ni(NO_3)_2$	1232.4	194.01		6M KOH	(Yuan, Jiang, Aramata, and Gao, 2005)

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Table 4. (*Continued*)

Biochar	Modification method	Specific surface area ($m^2\ g^{-1}$)	Specific capacitance ($F\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Electrolyte	Ref.
Spruce whitewood	KOH	1807	245	0.73	0.1M NaCl in 0.1M NaOH	(Dehkhoda et al., 2016b)
Corn stover	KOH	1671.4	245.9	0.831	6M KOH	(Jin et al., 2014d)
Rice husk	NaOH	2696	147	1.496	6 M KOH	(Teo et al., 2016)
Dried Grain	KOH	2684	325	1.65	6 M KOH	(Hong et al., 2013)
Distillers dried grains	KOH	2959	150	1.52	1M $TEABF_4$-AN	(Jin, Wang, Gu, Anderson, and Muthukumarappan, 2014b)
Hemp-derived activated carbons	KOH	2801	167	1.7096	1MLiPF6 in EC:DMC	(Sun, Lipka, Swartz, Williams, and Yang, 2016)
Wood biochar	CO_2	923	260	0.32	2M H_2SO_4	(Cuña et al., 2014)
Sewage sludge	Microwave	31.5	110	0.009	0.5 M KOH	(Wang et al., 2017b)
Dairy manure	Microwave	29.8	123	0.013	0.5 M KOH	(Wang et al., 2017b)
Waste coffee	$ZnCl_2$	1019	368	0.48	1M H_2SO_4	(Rufford et al., 2008)
Cotton stalk	H_3PO_4	1481	114	1.21	1M Et4NBF4	(Chen et al., 2013)
Banana fiber	$ZnCl_2$	1097	74	—	1 M Na_2SO_4	(Subramanian et al., 2007)

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Table 5. Specific power density when different biochar is used as a cathode.

Biochar	Surface area (m^2 g^{-1})	Temperature (°C)	Power density (mW m^{-2})	Gravimetric capacity (mAh g^{-1})	Ref
Bananas	172.3	900	528.2	—	(Yuan, Deng, Qi, Kobayashi, and Tang, 2014)
Wood-based biomass	42.4	1000	187.9	—	(Huggins, Pietron, Wang, Ren, and Biffinger, 2015)
Almond shell biochar	30.35	750	0.0127	—	(Elleuch, Boussetta, Yu, Halouani, and Li, 2013)
Compressed milling residue	469.9	1000	532	—	(Huggins et al., 2014)
Forestry residue	428.6	1000	457	—	(Huggins et al., 2014)
Sewage sludge biochar	—	900	500	—	(Yuan et al., 2013)
Activated carbons	—	800	1410	—	(Zhang et al., 2014b)
Corn cob biochar	—	750	0.0185	—	(Yu et al., 2014)
Pinecone hull	380	450	—	357	(Zhang, Zhang, Li, and Chen, 2007)
Rice husk		700	—	2507	(Fey et al., 2010)
Coconut shells	682.0	900	—	1714	(Hwang, Jeong, Shin, Nahm, and Stephan, 2008)
Banana fibers	1285	800	—	3123	(Stephan et al., 2006)
Peanut shells	2098.9	500	—	4765	(Fey, Lee, Lin, and Kumar, 2003)

2015b, Zhu, Fan, and Zhang, 2008). The development and application of low cost and green chemical reagents for biochar modification thus require more relevant research in the future.

Currently, many studies have focused on the characterization of biochar nanoparticles composite materials and the removal of contaminants in water. The recovery and reuse of modified biochar and its impact on the environment and human health will be the focus of future research. The effect of engineered biochar to the environmental systems such as soil ecosystem and water environment is unclear.

It has been demonstrated that soil amended with biochar, designed specifically for use as a soil conditioner, results in changes to the microbial populations that reside therein. These changes have been reflected in studies measuring variations in microbial activity, biomass, and community structure (Ducey, Ippolito, Cantrell, Novak, and Lentz, 2013). The effects of engineered biochar on soil biota have received much less attention than its effects on soil chemical properties (Lehmann et al., 2011). Experiments suggest that biomass-derived black carbon (biochar) affects microbial populations and soil biogeochemistry (Warnock, Lehmann, Kuyper, and Rillig, 2007). Engineered biochar composites contain clay minerals, nanomaterials, and graphene, which may have a certain toxic effect on the ecosystems including soil microorganisms. Although several studies have pointed out that biochar can distribute and stabilize colloidal and nanosized particles on its surface within the pore networks (Hu et al., 2015, Inyang et al., 2014, Wang et al., 2017a), the long-term stability of those colloids and nanoparticles have not been investigated. The risk management and uncertainty thus need to be further evaluated before the large-scale application of engineered biochars, especially engineered biochar composites (Downie, Munroe, Cowie, Van Zwieten, and Lau, 2012).

The potential risks of biochar to the environment and the ecosystems should be of sufficient attention. It has been suggested that large-scale land application of biochar for carbon sequestration without proper planning and management may have negative impacts on ecosystem health (Wang and Cao, 2011). Furthermore, because of the low density and micro-size of biochar, it may be carried along with the adsorbed organic or inorganic pollutants into surface water and groundwater systems through surface runoff and soil profiles, thus potentially risking the entire environmental ecosystem. Therefore, it is necessary to further study the collection, recovery, and regeneration of spent engineered biochar under various conditions.

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ORCID

Bing Wang http://orcid.org/0000-0003-3769-0191

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