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Characteristics and Applications of Biochars Derived from Wastewater Solids

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Abstract

Pyrolysis is a thermochemical decomposition process that can be used to generate pyrolysis gas (py-gas), bio-oil, and biochar as well as energy from biomass. Biomass from agricultural waste and other plant-based materials has been the predominant pyrolysis research focus. Water resource recovery facilities also produce biomass, referred to as wastewater solids, that could be a viable pyrolysis feedstock. Water resource recovery facilities are central collection and production sites for wastewater solids. While the utilization of biochar from a variety of biomass types has been extensively studied, the utilization of wastewater biochars has not been reviewed in detail. This review compares the characteristics of wastewater biochars to more conventional biochars and reviews specific applications

of wastewater biochar. Wastewater biochar is a potential candidate to sorb nutrients or organic contaminants from contaminated wastewater streams. While biochar has been used as a beneficial soil amendment for agricultural applications, specific research on wastewater biochar is lacking and represents a critical knowledge gap. Based on the studies reviewed, if biochar is applied to land it will contain less organic micropollutant mass than conventional wastewater solids, and polycyclic aromatic hydrocarbons are not likely to be a concern if pyrolysis is conducted above 700 °C. Wastewater biochar is likely to serve as a better catalyst to convert bio-oil to py-gas than other conventional biochars because of the inherently higher metal (e.g., Ca and Fe) content. The use of wastewater biochar alone as a fuel is also discussed. Finally, an integrated wastewater treatment process that produces and uses wastewater biochar for a variety of food, energy, and water (FEW) applications is proposed.

Keywords

Pyrolysis; Sludge; Biosolids; Adsorbent; Soil amendment; Catalyst

1. Introduction

Typical water resource recovery facilities (WRRFs), formerly referred to as wastewater treatment plants, treat wastewater from homes and industries, producing treated water and residual wastewater solids that are rich in organic content. These facilities are currently energy intensive operations, but a new paradigm has emerged viewing WRRFs as community assets that could recover energy and generate value-added products from wastewater.[1,2] Influent wastewater is rich in carbon, nutrients, and heat, all of which are potentially valuable resources.[3] The nutrients can be recovered as a fertilizer product, e.g. struvite, and used for agricultural purposes.[4] The organics have inherent energy content that can be recovered on-site. The wastewater solids, in particular, represent a potentially valuable energy source.

The United States Environmental Protection Agency (USEPA) estimates that approximately eight million dry tons of wastewater solids are produced each year in the United States alone.[5] Wastewater solids are either land applied as a soil conditioner and nutrient source, landfilled, or incinerated. WRRFs do not capture the inherent energy content from the organic matter of wastewater solids that are used as a soil conditioner or landfilled. Additionally, wastewater solids contain micropollutants, *i.e.,* the organic chemicals derived from consumer products that are released to sewers after use, including antimicrobials, pharmaceuticals, personal care products, hormones, and more.[6] Due to the presence of micropollutants, the long-term environmental and public health impacts of land applying wastewater solids have caused concerns to be raised in recent years.[7] For these reasons, alternative wastewater solids handling methods are being considered to recover energy while generating valuable products.[8]

Pyrolysis is the process whereby biomass, such as wastewater solids, is heated between approximately 400 and 900 °C in the absence of oxygen.[9,10] Pyrolysis produces solid, liquid, and gas products. The solid product, biochar, is similar to charcoal. The liquid can consists of multiple phases including non-aqueous phases often referred to as bio-oil, and an aqueous phase that is sometimes called aqueous pyrolysis liquid. The gas product, referred to as py-gas, consists of H_2, CH_4, CO, CO_2 along with lower concentrations of hydrocarbons including C_2H_6, C_2H_4, and C_3H_8.[11,12] Py-gas is a relatively clean-burning fuel that can be used on-site at WRRFs for energy recovery. The bio-oil also has a high energy content, but contains water, organic acids and oxygenated organics that make it corrosive for combustion; therefore, bio-oil typically requires processing before use. The biochar, as reviewed in this paper, has a wide array of potential applications as a sorbent, soil amendment, energy source, or catalyst.[13,14,15,16] It

may be most valuable for WRRF operators to optimize pyrolysis parameters to increase py-gas yield and decrease liquid yields because they require further processing. Slow pyrolysis (defined as pyrolysis with a heating rate less than 100 °C/min) yields more biochar and py-gas than fast pyrolysis (defined as pyrolysis with a heating rate greater than 300 °C/min), and fast pyrolysis typically yields more liquid products.[17,18] Therefore, the focus of this review is on biochars derived from slow pyrolysis of wastewater solids.

Wastewater solids are an emerging biomass source of interest for pyrolysis, in part, because they are centrally produced in urban locations. Therefore, one of the most energy intensive components for biochar generation, *i.e.,* biomass collection in a central location, has already been completed. From this logistical standpoint wastewater solids represent a potentially practical and easily accessible biomass stream to produce biochar via pyrolysis. Biochar derived from wastewater solids, referred to hereafter as wastewater biochar, however, has not been studied to the same extent as other biochars, nor has wastewater biochar been comprehensively reviewed. It is important to understand how wastewater biochars differ relative to other commonly studied biochars. The goal of this review is therefore to describe the characteristics of wastewater biochars relative to other biochars, current and future biochar uses, and research needs. The specific objectives of this review paper are to: i) determine how basic properties of wastewater biochar properties differ from other biochars ii) identify the appropriate uses of wastewater biochar for sorption, iii) establish the benefit of wastewater biochar as a soil amendment, iv) determine toxic hazards related to land applying wastewater biochar v) establish the role of wastewater biochar as a catalyst and vi) determine the feasibility of energy recovery from wastewater biochar.

2. Basic properties of wastewater biochars compared to other biochars

Wastewater biochars have a lower concentration of carbon (C) than other biomass-derived biochars (Table 1). This is not surprising considering that wastewater solids are comprised of organic and inorganic solids whereas biochars derived from other biomass streams such as switchgrass are composed primarily of organic matter. Wastewater biochars, on the other hand, typically have higher concentrations of nitrogen (N), phosphorus (P), and potassium (K), i.e., essential nutrients for plant growth. The relatively high abundance of N, P, and K in wastewater biochars indicate that a beneficial use would be as a soil amendment for agriculture (discussed in Section 4), whereas other biochars that have higher carbon contents might be more appropriately used as an adsorbent (discussed in Section 3). Wastewater biochars also have a higher abundance of micronutrients as well as potential toxicants, including metals (Table 1), so it is important to investigate if these metals are a leaching concern when applied to soils (discussed in Section 5.1) or potentially beneficial for using biochar as a catalyst to convert bio-oil to py-gas (discussed in Section 6).

Table 1. Elemental composition of wastewater biochar relative to other biochars (values are from wastewater solids biochars without any secondary activation processes).

Element	Unit	Wastewater Biochar			Rice Straw	Sawdust	Fescue Grass/Straw	Poultry Litter
		Pyrolysis Temperature Range °C						
		300–500	550–650	700–900	400–700	450–600	400–700	400–700
Ultimate Analysis								
C	%	18.92–47	8.15–30.8	6.5–33	42.1–91.2	50–97.3	77.3–94.2	41.3–87.2
H	%	0.67–2.8	0.38–1.2	0.19–0.70	1.26–4.26	1.0–3.7	1.53–4.70	1.2–1.98
N	%	2.13–6.4	0.37–3.76	0.3–2.98	0.5–1.66	0.1–0.73	0.70–1.24	0.43–5.18
Nutrient Composition								
Major								
P	%	5.6	2.4–5.2	4.86-5.06	0.22–0.26	0.1	0.24	0.03–0.60
K	%	0.24	1.4–1.8	0.31	24.6	0.01–0.03	1.2	0.30–9.15
S	%	4.47–5	2.16–5	6.17	0.06	0.01–0.7		3.1–3.5
Mg	%	0.35–0.43	0.04–0.46	0.54	–	0.01–0.04		0.94–2.4
Na	%	–	8.7	–	–	0.02–0.04		14.8–22.2
Ca	%	3.47–4.17	1.32–4.62	5.35	–	0.27–0.65	0.51	0–6.3
Fe	%	7.8–8.85	10.15	11	–	0.07–0.18	–	0.13–0.19
Minor								
Zn	mg/kg	1250–2980	845–3900	2175	197	8.8–31.7	–	–
As	mg/kg	2	5.9–9	BD	–	< 10	–	–
Cd	mg/kg	1.8–9.7	1.5–9.8	3.22	–	< 10	–	–
Co	mg/kg	–	2.0–69	–	–	< 10	–	–
Cr	mg/kg	80–112.5	54–230	83	–	< 10	–	5.0–6.86
Cu	mg/kg	222–2600	163–2700	1500	47	< 10	–	–
Hg	mg/kg	0.2	–	–	–	–	–	–
Ni	mg/kg	35–182.5	23.7–740	195	–	< 10	–	–
Pb	mg/kg	5–239	19.9–410	132	4.8	< 10	–	–
References		[14,19–26]	[20,21,24–32]	[12,20,21,26,28,33]	[26,34–36]	[26,34,37,38]	[26,39,40]	[26,41,42]

Wastewater biochars typically have higher H to C ratios than other biochars, concomitant with their lower C content (Table 2). For energy purposes, a higher H/C ratio is preferred compared to a higher O to C ratio because a higher H/C ratio results in a fuel that is more reduced and releases more heat energy per unit mass. However, the total C content also affects the energy content and wastewater biochars typically have lower volatile and fixed C content (Table 2). The prospect~~ive~~ of using wastewater biochar as a fuel is discussed in Section 7. Both surface area and pore volume ranges for wastewater biochars are within ranges similar to those of other biochars; these parameters are important when considering the use of biochar as an adsorbent (discussed in Section 3).

Table 2. Proximate and micro-structural analysis of wastewater biochar relative to other biochars (values are from wastewater biochars without any secondary activation processes).

Biochar Material	Pyrolysis Temperature °C	H/C	O/C	Ash (%)	Volatile C (%)	Fixed C (%)	pH	Total Surface Area (m^2/g)	Pore Volume (cm^3/g)	Refs
Wastewater biochars	300–500	0.72–0.87	0.13–0.16	35–72.0	18.4–24.1	4.64–12.9	4.7–9.5	4–35.66	0.0326–0.0738	[12,14,21–23,25,28]
	550–650	0.22–0.50	0.05–0.17	60.3–84.0	11.0–16.7	1.9–25.4	7.22–9	5.5–37.18	0.0144–0.0681	[21,24,25,28,29,31,32]
	700–900	0.16–0.35	0.01–0.18	62.3–82.0	4.6–5.7	23.9–28.4	11.7–12	9.22–107	0.0321–0.0894	[20,21,24,28,33]
Rice Straw	400–700	0.44	0.08–0.22	36.2–54.6	5.88–24.7	35.4–39.5	10	34.4–36.7	0.028	[26,34–36]
Sawdust	450–600	0.03–0.6	0.005–0.17	1.1–20.0	13.6–40.1	57.2–82.6	5.9–12.1	172		[26,33,34,37,38]
Fescue Grass/ Straw	400–700	0.20–0.73	0.03–0.16	15.4–19.3	9.1–26.8	56.9–71.6	–	8.7–139	0.001–0.226	[26,38–40]
Poultry litter	400–700	0.03	0.02–0.16	46.2–53.2	18.3–20.8	29,2–35.5	9.2–10.3	51–94	0.018	[26,40,43]

3. Wastewater biochar as an adsorbent for pollutant removal from wastewater

3.1. Nutrients removal

Biochar derived from a wide range of feedstocks, including wastewater solids, can adsorb nutrients in the form of ammonium and phosphate. Table 3 summarizes research regarding biochars produced from different feedstocks and at different temperatures and washing/preconditioning protocols to adsorb ammonium or phosphate. Among the biochars reviewed, wastewater biochar had intermediate to high ammonium adsorption capacity and high phosphate adsorption capacity.

Table 3. Nutrient adsorption capacity of biochars.

Author	Feedstock	Pyrolysis Temperature °C	Biochar Washing	Biochar Surface Area m^2/g	Cation Exchange Capacity cmol/kg	Nutrient Type	Nutrient Concentration	NH_4 Max Adsorption Capacity mg-N/g	PO_4 Max Adsorption Capacity mg-P/g
[44]	Peanut Shell	300	N/A	N/A	N/A	NH_4	50 mg-N/L	16.5	N/A
		450						16	
		600						15.7	
	Corn Cobs	300						17.4	
		450						17	
		600						16.5	
	Cotton Stalks	300						17.5	
		450						16.5	
		600						16.6	
[45]	**Wastewater solids**	**450**	**Base**	**19**	**N/A**	**NH_4**	**0.66–660 mg-N/L**	**5.3**	**N/A**
[46]	Wheat Straw	500	N/A	N/A	N/A	NH_4	39 mg-N/L	0.63	N/A
			Acid					0.27	
			DI water					0.33	
	Corn Straw		N/A					2.12	
			Acid					0.45	
			DI water					0.92	
	Peanut Shell		N/A					0.73	
			Acid					0.43	
			DI water					0.54	
[47]	$MgCl_2$ pretreated	300	N/A	382	N/A	PO_4	84–2600 mg-P/L	N/A	155
	Corn Cobs	450		421					160
		600		490					162
[48]	Wood	600	N/A	274	N/A	NH_4	520–1400 mg-N/L	54.86	N/A
	Rice Husk			11				47.14	
[49]	Poultry Litter	400	N/A	2.4	N/A	NH_4	2 mg-N/L	0.3	N/A
		500		5.0				0.22	
	Hardwood	400		15.4				0.07	
		500		26.6				0.07	
[50]	Oak Wood	400	N/A	N/A	105.8	PO_4 or NH_4	125 mg-P/L or	129.4	5.5
		600			65.2		778 mg-N/L	123.5	3.6
	Oak Wood	400			60.0			100.9	0
	Commercial	600			76.6			114.4	15.1
	Greenhouse	400			109.5			118.2	18.7
	Waste	600			146.2			99.3	9.1
	Wastewater solids	**400**			**51.0**			**105.8**	**7.8**
		600			**52.6**			**136.2**	**30.0**
	Treated	400			65.7			137.3	11.9
	Municipal Waste	600			67.9			128.3	14.3
[51]	Cacao Shell	300–350	N/A	18.6	37	PO_4 or NH_4	0.1–50 mg-P/L or	1	0
			Millipore Water	94.2	44		0.1–50 mg-N/L	1.3	
	Corn Cob		N/A	36.4	34			1.6	
			Millipore Water	98	18			1.4	

Surface area, surface chemistry, and functional groups are factors that affect interactions between adsorbents and adsorbates. As pyrolysis temperature increases, in general, the biochar surface area increases,[47,49] but the surface area increase does not necessarily confer higher ammonium or phosphate adsorption capacities.[49,51] Cation exchange capacity, which results from the negatively charged biochar surface, is correlated with ammonium ion adsorption because ammonium is a cation.[50,51,52,53] In general, the phosphate adsorption capacities are not as high as ammonium adsorption capacities on biochar because biochar surfaces are negatively charged, and phosphate ions are likely repulsed. In some cases, phosphorus was even released from biochar upon addition to water.[50,51,53] The binding of phosphate to biochar surfaces can depend on formation of ligand bonds or precipitates onto biochar with biochar surface functional groups, *e.g.,* cations such as Ca, Mg, Al and Fe.[47,54] Indeed, when corn cob was modified with the addition of $MgCl_2$, the derived biochar had higher phosphate adsorption capacity than other types of biochar (Table 3).[47] Normally, wastewater solids contains high metal contents (e.g., Ca, Mg, Fe, etc.) relative to other carbon feedstocks;([20] Table 1) that can provide binding sites for negatively charged phosphate ions.

Nutrient adsorption capacities can vary by orders of magnitude, not only between different types of feedstocks, but also among biochars derived from the same type of biomass under different conditions (Table 3). Also noteworthy is that washing biochars with de-ionized water, acid or base did not necessarily increase nutrient adsorption.[46,51] Therefore, the intrinsic properties of a feedstock and the nature of the pyrolysis system might play more essential roles in facilitating ionic bonds between biochar and nutrient ions than washing steps.

In addition to wastewater biochar sorbing nutrients, wastewater biochars are also nutrient-rich and could be good agricultural soil conditioners (discussed in Section 4). After pyrolysis of wastewater solids, N content in biochar was between 1.5% and 3.5% and P content was between 2% and 12.8% by weight.[20,55] Absorbing external ammonium and phosphate could augment the nutrient content of wastewater biochar to use as a fertilizer. Pyrolysis may be promising for WRRFs that must capture N and P from the effluent while recovering energy. However, the unstable and non-homogeneous properties of wastewater solids and heavy metals such as Zn, Cu, Ni, Cr, and Hg[56] could be obstacles for applying nutrient-enhanced wastewater biochar on lands.[57] The risks of heavy metals in wastewater biochars are evaluated in Section 5.1.

3.2. Heavy metals removal

Various types of biochars can sorb heavy metals from water streams, including Pb, Cu, Cr, Cd, and Zn.[58,59,60] While many of the previous studies have focused on wood-derived biochars, wastewater biochar has the potential for on-site remediation applications that target metals removal from wastewater streams. Recent studies conducted with wastewater biochar have demonstrated the ability to remove a wide range of heavy metals from aqueous solutions.[29,61,62,63,64,65]

Heavy metal sorption mechanisms to wastewater biochar have been previously described by[29] and include surface complexation with active carboxyl and hydroxyl functional groups, co-precipitation and inner-sphere complexation of metals with mineral oxides and organic matter, and electrostatic outer-sphere complexation due to metal exchange with available K and Na in the biochar structure.[29] Ion exchange mechanisms may also play important roles in sorption of heavy metal ions.[29,65] In addition, Kong et al. (2011) reported up to 87% removal of Hg from aqueous solutions using biochar produced from soybean stalks, which was attributed to ion exchange and precipitation and reduction reactions.[66]

Batch tests using wastewater biochar as a sorbent have shown that the biochar can effectively bind to positively charged heavy metal ions in solution due to the cation exchange capacity of the negatively charged biochar surface.[22,61,67,68] Agrafioti et al. reported that biochar removed approximately 70% of Cr(III) compared to 30% for As (V) from aqueous solutions. They hypothesized that the higher removal of Cr(III) cations was mainly due to electrostatic interactions with the biochar negative surface charge.[22] Wastewater biochar can also sorb Pb(II) and Cr (VI) from aqueous solutions, and removal is attributed to the large surface area and the presence of organic functional groups on the biochar surface.[65] These studies concluded that Pb sorption to biochar was primarily irreversible, and the metal ions would be very difficult to desorb from the biochar structure.[29,65]

Functional groups such as carboxyl, alcoholic, or phenolic hydroxyl groups have been proposed as key moieties contributing to the interactions between heavy metals and sorbents such as wastewater biochar[9,61,65,29] investigated the use of wastewater biochar for Pb sorption from acidic solutions (e.g. mine drainage), and determined that Pb adsorption was primarily due to interactions with organic

functional groups such as hydroxyl and carboxyl groups. The study also reported another mechanism of Pb removal through ion exchange involving the coprecipitation of Ca^{2+} and Mg^{2+} ions during the Pb^{2+} sorption process.[29] A recent study reported wastewater solids biochar adsorption of Cd^{2+} to be higher than that of activated carbon, and proposed the sorption mechanisms of surface precipitation and ion exchange.[61]

Other reports on Cd sorption by biochars derived from different raw materials include observed maximum adsorption capacities of 26.32 mg/g for biochar derived from corn straw,[69] 6.22 mg/g for biochar derived from household biowaste,[70] and approximately 25 mg/g for straw biochar.[71] Similarly, Mohan et al. (2007) reported Pb(II) and Cd(II) removal efficiencies via oak bark biochar comparable to that of Calgon F-400 activated carbon (0.5157 mg/m^2 for Pb(II) and 0.213 mg/m^2 Cd(II)).[72] Other studies have noted Cu(II) and Zn(II) sorption from aqueous solutions with biochar derived from hardwood (12.52 and 11.0 mg/g) and corn straw (6.79 and 4.54 mg/g).[73] Overall, wastewater solids-derived sorbents compare well with biochars from other feedstocks as researchers have demonstrated heavy metal adsorption capacities of 175.4, 64.1, 30.7, and 15.4 mg/g for Hg(II), Pb(II), Cu(II), and Cr(III), respectively.[64]

3.3. Organic contaminants removal via adsorption with biochar

Pyrolysis parameters such as temperature, residence time, heating rate, and feedstock particle size affect the qualities of the produced biochar and thus biochar interactions with organic contaminants.[22] Though most research involving biochar has been related to the effects of using it as a soil amendment, it may also be beneficial as a sorbent for organic contaminants since it has a high carbon content, large surface area, and microporous structure.[43,74,75] Biochar produced at low temperatures is suitable for agricultural uses, while higher temperatures can improve its porosity and thus enhance its effectiveness in adsorbing contaminants. Based on X-ray diffraction and nuclear magnetic resonance results, it has been suggested that biochars contain an abundance of amorphous aliphatic carbon, which might contribute to its high sorption capacity for hydrophobic organic compounds such as polycyclic aromatic and other petroleum hydrocarbons.[76,77] For example, previous studies have demonstrated adsorption capacities of 31.7 mg/g for trichloroethylene (TCE) using soybean stover biochar,[78] 29.7 mg/g P-nitrotoluene via orange peel biochar,[60] and approximately 20 mg/g phenol using biochar derived from HCl-treated poultry litter.[79]

Wastewater biochar amendments have been shown to sorb endocrine disrupting compounds (EDCs), pharmaceuticals, and pesticides such as atrazine,[33,74,80] though the number of research reports involving this type of biochar as an adsorbent is relatively low compared to biochars from other biomass types. Recent research conducted with wastewater biochar has demonstrated its ability to sorb the antimicrobial compound triclosan with adsorption capacities up to 872 µg/g, compared to over 3500 µg/g for Calgon Filtrasorb® 400 granular activated carbon observed in the same study.[13] Yao et al. investigated the sorption of fluoroquinolone antibiotics (e.g. Gatifloxacin) using wastewater biochar and reported adsorption capacities of up to 19.80 mg/g in batch-scale experiments. The adsorption of organic compounds in this study was attributed to the relatively large surface area that exceeded 110 m^2/g and the high volatile fraction of the specific biochar employed.[81] Comparatively, fluoroquinolone antibiotics similar to Gatifloxacin (e.g., enrofloxacin and ofloxacin) were effectively sorbed to bamboo biochar with maximum adsorption capacities up to 46 mg/g.[82]

Similar to other biochars, wastewater biochars can be altered chemically and physically to increase sorption. Yu and Zhong assessed various methods of physical and chemical activation of wastewater solids targeting COD and color removal from wastewater with dynamic adsorption tests and rapid small-scale column experiments.[83] The results indicated up to 79.1% removal of COD and color removal of 87.5%, with COD adsorption capacities up to 47.8 mg/g.[83] Similarly, other studies have reported aqueous phase sorption of organic compounds including indigo carmine, crystal violet, phenol, and 4-chlorophenol with biochars made from wastewater solids.[84,85]

Several studies have proposed that organic contaminant sorption is enhanced by non-electrostatic interactions with π-electrons between adsorbates containing aromatic rings and the adsorbent surface.[13,84] Other likely factors contributing to the sorption of organic compounds to wastewater biochar include the hydrophobicity, high surface area, and functional group interactions with the biochar structure.[9,13,68] Overall, wastewater biochar is a plausible sorbent for organic contaminant removal from wastewater.[81,86,87]

4. Wastewater biochar as a soil amendment

Wastewater biochars have been investigated as soil amendments to improve growth of a variety of plants, including fruiting plants, grasses[14] and rice as well as garlic[88] and lettuce.[89] Wastewater biochars have been shown to increase the growth rate of peppers[90] and tomatoes.[30] A number of grasses have also been shown to benefit from wastewater biochar soil application, including bentgrass,[91] Kentucky bluegrass[14] and ryegrass.[92]

It is important to consider the type of pyrolysis feed material since it greatly affects the biochar composition and, thus, the biochar influence on plant growth. For example, animal manure and corn stover biochars in soil increased corn growth up to 43% and 30%, respectively, whereas food waste biochar decreased corn growth up to 92% in relation to controls; wastewater biochar was not studied.[93] Information on the influence of biochar derived from feed material other than wastewater solids on plant growth is not within the scope of this review, but can be found in the review by Biederman and Harpole.[94]

It is challenging that some reports regarding biochar influence on plant growth do not clearly describe the pyrolysis feed material employed. Even when wastewater solids biochars are studied, some authors do not describe the type of wastewater solids used, whether primary wastewater solids (the wastewater solids generated from the first sedimentation step at a WRRF), waste activated wastewater solids (the wastewater solids from the secondary treatment process that employs aerobic biological oxidation of chemical oxygen demand) or different types of digested wastewater solids (aerobic, anaerobic, digester feed types). In the future, more careful descriptions of pyrolysis feed materials would be beneficial to discern the influence of biochar characteristics on plant growth.

4.1. Uses of biochar for plant growth

Biochar from materials other than wastewater solids has been shown to be beneficial as a soil amendment for green roofs, commercial potting soil mixes and commercial agriculture. More research is warranted to determine if wastewater biochar can also achieve these benefits. Beck et al.[92] found that green roof soils containing 7 wt% biochar from nut shells and automobile tires demonstrated increased water retention and decreased nutrient and turbidity leaching; this was described as beneficial, helping to maintain plant growth and improving stormwater runoff quality. Biochar has also been added to

commercial potting soil mixes, and reduced nutrient leaching from greenhouse containers,[95] replaced peat moss in potting soil for pepper plant germination,[90] and aided carbon sequestration scenarios.[96] Regarding commercial agriculture, Verheijen at al.[97] reviewed literature on biochar and crop productivity, describing an average net increase in crop production of 10% when biochar was applied to soils. However, careful attention is required to define exact biochar, plant and soil types since a wide range of biochar application affects were observed (from 28–39% increase in crop productivity with biochar addition). The greatest positive outcomes were observed for acidic and neutral pH soils, and in soils with coarse or medium textures that do not hold moisture well. It was suggested that two main mechanisms for crop productivity increase are improved water holding and nutrient availability due to biochar.[97]

Reported benefits of wastewater biochar soil amendment on plants and plant growth also include reduced plant uptake of soil heavy metals.[25] Adding various biochars to soil may also shift rhizosphere microbial and fungal communities to more favorable compositions for plant growth or contribute chemicals to the soil-plant system that increase plant growth.[98,99] More research is required to elucidate relationships among biochar types, microbial community changes with biochar addition, and mechanisms of altered plant growth under various conditions.

Benefits other than plant growth increases include reduced nutrient leaching rates from soil for improved stormwater runoff quality,[91,95] reduced soil greenhouse gas emissions,[27] and decreased cancer risk from consuming crops planted with wastewater biochar.[100] Khan et al.[27] reported that adding wastewater biochar to rice paddy soil can significantly reduce emissions of the greenhouse gasses methane and nitrous oxide over 12 weeks, ostensibly by encouraging the growth of methane and nitrous oxide oxidizing microorganisms. The authors caution that the actual benefits will depend on site-specific conditions and the source of wastewater solids employed to produce biochar and indicate that long-term effects were unknown.

Under some conditions, adding wastewater biochar to paddy soil may yield rice containing lower concentrations of carcinogens, thus reducing cancer risk from rice consumption.[100] For example, wastewater biochar was applied to soil impacted by mining to suppress the phytoavailability of potentially toxic soil chemicals and, thus, the concentrations in the rice. Results and exposure analysis indicated that wastewater biochar addition decreased the daily intake of arsenic, cadmium, dimethylarsinic acid and other chemicals of concern by 22–86%. It was estimated that the lifetime cancer risk associated with consumption of rice grown in mining impacted soil could be reduced by 66%. Overall, wastewater biochars offer benefits as a soil conditioner, but they have been studied to a much lesser extent than other biochars with respect to their impacts on plants and soil. More research is warranted on the specific impacts of wastewater biochars on plant growth and soil communities.

5. Toxicity of wastewater biochar

5.1. Toxicity evaluation of heavy metals

Some biochars contain heavy metals and organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) so they may pose negative impacts to the ecological environment. Therefore, the bioaccumulation and mobility of these potential pollutants is of great concern during land application of biochar.

Previous research indicated that wastewater biochars likely have heavy metals below concentrations of concern, but they should be tested to ensure that levels are safe. In general, the heavy metal contents of wastewater biochars do not preclude them from being land applied (Table 4). There are no legislative standards available for biochar; therefore, wastewater solids land application regulations are used as a reference to understand the levels of heavy metals in wastewater biochar. USEPA and European Union heavy metal standards for wastewater solids land application are also listed in Table 4. The content of heavy metals was greatly influenced by the source biomass for biochar. For the non-wastewater-solids carbonaceous waste derived biochars, Zn had the highest concentration and other heavy metal concentrations were below 100 mg/kg. In contrast, some wastewater biochar has high concentrations of Zn, Cu, Pb and Ni. Except for some specific wastewater biochar samples (e.g., Hossain's biochar from Sydney, Australia, Van Wesenbeeck's biochar from Hawaii, USA, and Lu's biochar from Guangzhou, China) that could pose a risk to the environment, all of the other heavy metal concentrations in the wastewater biochars meet both US EPA and European Union standards for land application.

Table 4. Heavy metal content of biochars.

Author	Feedstock	Pyrolysis Temperature (°C)	Metal Concentration in Original Biochar (mg/kg) [] shows metal extraction concentration from original biochar (mg/kg)								Extraction Method
			As	Cd	Cr	Cu	Pb	Ni	Se	Zn	
Hossain et al. [20,30]	Sewage sludge	550	8.8 [0.02]	4.7 [0.04]	230 [< 0.05]	2100 [6.2]	160 [< 0.01]	740 [1.2]	7 [< 0.05]	3300 [22]	Phytoextraction by cherry tomato
Liu et al. [101]	Sewage sludge	450	N/A	4.12 [0.06]	92.2 [0.49]	124.8 [1.92]	67.5 [0.54]	N/A	N/A	749 [11.3]	Phytoextraction by Chinese cabbage
Agrafioti et al. [22]	Sewage sludge	300	N/A [BDL]	N/A [BDL]	N/A [0.11]	N/A [0.17]	N/A [0.74]	N/A [0.14]	N/A	N/A	US EPA TCLP
Devi and Saroha [102]	Paper mill sludge	300–700	N/A	0.91–1.83 [0.11–0.25]^	12.93–13.56 [1.8–2.72]^	95.74–146.97 [1.97–4]^	20.99–30.46 [0.2–0.8]^	14.94–25.41 [0.54–1.81]^	N/A	220.57–332.79 [1.42–7.98]^	US EPA TCLP ^ unit is mg/L
Hossain et al.	Sewage sludge	300–700	< 3 [N/A]	2.62–3.22 [BDL-0.2]	83–112.5 [N/A]	1125–1500 [0.1–17.25]	115–140 [N/A]	165–292.5 [N/A]	< 6.6 [N/A]	1675–2175 [0.11–142.5]	DTPA extraction
Lu et al. [67]	Sewage sludge	300–500	N/A	3.3–9.82 [BDL]	N/A	401–1267.3 [1.69–23]	189.5–506.4 [BDL-10.38]	N/A	N/A	849.3–2304.8 [1.3–92.6]	DTPA extraction
Luo et al. [103]	Sewage sludge	300–700	N/A	0.69–1.38 [0.45–10.5]^	211–247 [8–11]^	172–202 [45.5–365]^	61–74.2 [27.5–115]^	51–55.2 [20.5–46.5]^	N/A	804–986 [280–970]^	DTPA extraction ^ unit is μg/L
Mendez et al. [25]	Sewage sludge	500	N/A	1.79 [2]^	N/A	222 [12]^	196 [1.3]^	35 [29]^	N/A	1250 [34]^	Water extraction ^ unit is μg/L
Song et al. [88]	Sewage sludge	400–550	9.4–14.8 [0.5–3.2]	3.2–3.6 [BDL-0.07]	58–66 [BDL-0.2]	329–402 [BDL-0.7]	83–98.3 [0.2–1.8]	61.5–77.1 [BDL-0.3]	N/A	1478–1784 [1.1–7.9]	Diluted sulphuric acid & nitric acid
Khan et al. [27]	Sewage sludge	550	9.25 [0.04]	3.69 [0.26]	74.1 [1.24]	222 [6.5]	27 [2.13]	34.5 [2.26]	N/A	1102 [127]	EDTA extraction
Van Wesenbeeck et al. [104]	Sewage sludge	700	7.66–16.7	2–9.1	67.6–281	712–1000	28.4–60	65–635	9.7–19.1	1964.4–2940	N/A
Yuan et al. [109]	Sewage sludge	300–700	N/A	1.06–1.29	124–218	83.5–108	68.9–88.1	51.3–68.2	37.3–45.3	525–690	N/A
Farrell et al. [105]	Sewage sludge		10.7 [< 0.05]* [0.2–0.25]**	3.4 [BDL]* [0.01–0.1]**	56.4 [BDL]* [< 0.15]**	811.6 [BDL]* [< 9]**	62.8 [BDL]* [≈2.1]**	39.5 [BDL]* [≈0.3]**	5.8 [BDL]* [< 0.01]**	1514.4 [BDL]* [10–45]**	Weak extractant (water, CaCl2, and NH4NO3), marked by * Strong extractant (EDTA, acetic acid), marked by **
	Poultry litter	550	4 [0.2–0.4]* [0.7–0.85]**	0.1 [BDL]* [≈0.025]**	12.4 [BDL]* [< 0.1]**	81.9 [BDL]* [< 8.2]**	2 [BDL]* [≈0.2]**	7.2 [BDL]* [BDL]**	0.3 [≈0.015]* [≈0.02]**	445.3 [BDL]* [25–110]**	
	Wheat straw		2.8 [≈0.2]* [≈0.6]**	0.1 [BDL]* [≈0.025]**	32.5 [BDL]* [0.02–0.2]**	54.8 [BDL]* [< 8]**	1.6 [BDL]* [≈0.3]**	17.5 [BDL]* [≈0.3]**	0.2 [≈0.03]* [≈0.03]**	311.9 [BDL]* [20–80]**	
Luo et al. [103]	Corn stalk	300–700	N/A	< 0.014 [0.15–0.75]^	15.6–21.4 [6–11.5]^	40.2–55.3 [75.5–170]^	3.04–3.24 [5–9.5]^	8.57–9.57 [13.5–32.5]^	N/A	98.4–133 [51–115]^	DTPA extraction ^ unit is μg/L
Oleszczuk et al. [106]	Miscanthus	650	N/A	0.87	18	2.22	22.3	9.95	N/A	102	N/A
	Coconut shell		N/A	0.1	1.3	3.81	23.7	BDL	N/A	30.2	
	Wicker		N/A	0.2	BDL	BDL	20.6	BDL	N/A	97.9	
	Wheat straw		N/A	0.04	BDL	BDL	21.6	BDL	N/A	32.9	
Cantrell et al. [41]	Dairy manure	350–700	0.78–1.05	BDL– 0.18	N/A	99–163	0.46–0.89	16.1–25.3	N/A	361–423	N/A
US EPA Standard for Land Application [107]			41	39	1200	1500	300	420	36	2800	N/A
European Communities Standard for Land Application [108]			N/A	20–40	N/A	1000–1750	750–1200	300–400	N/A	2500–4000	N/A

The heavy metal leaching concentration is another parameter of interest to consider for understanding the hazards of land applying biochar. Agrafioti et al., found that wastewater biochar had significantly lower heavy metal leaching compared to that from non-pyrolyzed wastewater solids.[22] The pH buffering capability of biochar derived from intrinsic biochar alkalinity during leaching tests likely reduced heavy metals leaching.[109] Farrell et al., also stated that pyrolyzed organic matter was more difficult to mineralize, and subsequently the release of contaminants bound in the macromolecular structure would be slower.[105] No guideline or standard is available for the leachability evaluation of biochar such as TCLP (Toxicity Characteristic Leaching Procedure), EDTA (Ethylenediaminetetraacetic Acid) or DTPA

(Diethylene Triamine Pentaacetic Acid), but Agrafioti et al. and Luo et al. both found that biochar largely reduced the leaching of most metals compared to the corresponding feedstock.[22,103] Lu et al. also confirmed that the soluble and extractable fractions of heavy metals in the wastewater biochars were greatly decreased when compared to the original wastewater solids feedstock.[67] For example, the extraction rates of Pb, Zn, and Cu were 16%, 82%, and 43%, respectively, in one of the wastewater solids samples, and the extraction rates decreased to 1%, 2%, and 2%, respectively for the corresponding biochars. Additionally, Devi et al. stated that higher pyrolysis temperature resulted in lower TCLP leaching concentration of heavy metals.[102] Hossain et al. also found that pyrolysis conducted at 700 °C yielded lower DTPA available heavy metals than pyrolysis conducted at temperatures below 700 °C.[20] Thus, if leaching is a concern for a particular wastewater biochar it is advised to conduct pyrolysis at higher temperatures.

Bioaccumulation of heavy metals in plants exposed to biochar is a potential mechanism of interest. Hossain et al. investigated the effect of wastewater biochar on cherry tomato growth in terms of soil quality, plant nutrients and the metal bioavailability in plants.[30] They found that, though the heavy metals were taken up by the produced fruits, the bioaccumulation of the trace metals in the fruits was insignificant. All of the metal concentrations in the fruits were below the Australian maximum permitted concentrations for food products. Meanwhile, the addition of biochar significantly improved the chemical properties of the soil (e.g. increased electrical conductivity, pH, total nitrogen, extractable phosphorus and cation exchange capacity), plant height, and crop yield with larger number of fruits per plant. The results of Mendez et al. work[62] agreed with Hossain et al.[30] that the wastewater biochar decreased the plant-available Cu, Ni, Zn and Pb and the risk of leaching of Cu, Ni, Zn and Cd. Also, Liu et al. confirmed that the addition of wastewater biochar did not greatly change the contents of heavy metals in plants. They found that biochar soil addition correlated with higher growth and yield of Chinese cabbage without inhibiting the germination.[101] Furthermore, Khan et al. found that, besides the reduction of bioaccumulation of As, Cr, Cu, Ni, and Pb in rice plants with wastewater biochar amendment, the addition of biochar significantly mitigated greenhouse gas emissions by reducing N_2O emissions and converting soil from a CH_4 source to a sink.[27]

Overall, heavy metals in most wastewater biochars do not pose threats to the environment when biochar is used as a soil conditioner. Moreover, biochars in general reduce the leachability of metals compared to wastewater solids. However, the interactions between metals, soils, and plants varies with metal species in biochar, physico-chemical properties of soil, and plant species. Thus, the toxicity analysis of each specific biochar, scaled-up field studies, and long-term monitoring effects are highly recommended for future research.

5.2. Toxicity evaluation of organic contaminants

The major organic contaminants present in biochar are PAHs. However, if the pyrolysis process temperature is high enough, then the biochar will have very low PAH content, and will be below the USEPA PAH limit for wastewater solids land application, which is 6 mg/kg.[110] PAH content in soil amendments is regulated by the U.S. EPA and the European Union. In particular, naphthalene, a possible carcinogenic compound to humans, is often the most abundant PAH in biochar.[111] Experimental evidence suggests that, above a slow pyrolysis temperature of 700 °C, the total PAH sum will decrease substantially in most types of biochar.[112] Wastewater biochars made at temperatures over 700°C had consistently demonstrated the lowest PAH contents, less than 1.15mg/kg, relative to other biochars

(Table 5). However, in the case of fast pyrolysis or gasification, the PAH content is not substantially decreased and exceeds most values of regulated PAH content.[113]

Table 5. PAH content in biochars.

Refs	Biochar	Pyrolysis Temperature (°C)	PAH Sum Content (mg/kg)
[114]	Sewage Sludge	200	1.64
[114]	Corn Stalk	200	0.76
[114]	Corn Stalk	300	5.32
[114]	Sewage Sludge	300	2.26
[112]	Maize	300	5.66
[112]	Redwood	300	4.54
[112]	Bamboo	300	2.47
[115]	Straw	400	5.20
[115]	Spruce	400	30.70
[115]	Poplar	400	4.30
[114]	Sewage Sludge	400	2.99
[114]	Corn Stalk	400	3.58
[115]	Straw	460	10.70
[115]	Spruce	460	5.80
[115]	Poplar	460	17.90
[28]	Sewage Sludge	500	0.77
[28]	Sewage Sludge	500	0.67
[28]	Sewage Sludge	500	0.56
[28]	Sewage Sludge	500	0.61
[114]	Sewage Sludge	500	70.39
[114]	Corn Stalk	500	3.29
[115]	Straw	525	33.70
[115]	Spruce	525	1.80
[115]	Poplar	525	2.00
[114]	Sewage Sludge	600	1.24
[114]	Corn Stalk	600	0.57
[28]	Sewage Sludge	600	0.98
[28]	Sewage Sludge	600	0.62
[28]	Sewage Sludge	600	0.57
[28]	Sewage Sludge	600	0.67
[112]	Maize	600	1.47
[112]	Rice Straw	600	1.15
[112]	Bamboo	600	1.06
[112]	Redwood	600	0.08
[114]	Sewage Sludge	700	0.18
[114]	Corn Stalk	700	0.36
[28]	Sewage Sludge	700	1.02
[28]	Sewage Sludge	700	0.49
[28]	Sewage Sludge	700	0.81
[28]	Sewage Sludge	700	1.12

Beyond PAHs, other organic contaminants, *i.e.* micropollutants, are present in wastewater solids.[6] Pyrolysis of wastewater solids was shown to remove the micropollutants triclosan, triclocarban, and nonlyphenol to below detection limits in biochar (below 0.25 mg/kg) at 500 °C.[116] Therefore, pyrolysis of wastewater solids followed by application of the biochar could minimize the discharge of micropollutants to the environment via land application relative to applying non-pyrolyzed wastewater solids. Total estrogenicity, i.e. the total estrogenic hormonal response of a sample, was also greatly reduced from wastewater solids during slow pyrolysis.[117] Pyrolysis temperatures greater than 400 °C removed more than 95% of the estrogenicity.[117] Pyrolysis volatilizes and possibly transforms these micropollutants. While micropollutants are present in wastewater solids, they would be present in much lower concentrations or absent from wastewater biochars.

6. Wastewater biochar as a catalyst for thermochemical conversions

Biochar is an effective catalyst for tar cracking, i.e., converting bio-oil constituents into py-gas. Gasification is a process that converts fossil fuel or renewable carbonaceous feedstock into energetic product gas. Tars are the condensable organic fraction of the gasification byproducts and are largely high molecular weight (i.e. larger than benzene) aromatic hydrocarbons.[118] Tars are difficult to destroy and handle, leading to clogging problems in the gasification process. Mani et. al. and Zhang et al. studied the catalytic decomposition of tar model compounds (i.e. toluene and naphthalene) using pine bark biochar and rice straw biochar, respectively; they found that biochar was a good catalyst for tar cracking.[119,120] El-Rub et al. compared the catalytic effect on tar model compound (i.e. phenol and naphthalene) reduction using biomass chars and other catalysts such as olivine and dolomite; they found that biomass chars yielded the highest naphthalene removal rate.[121] The catalytic effect of wastewater biochar for the destruction of tars or model components is unknown and its catalytic potential needs further study.

Biochar can also be used as a catalyst to upgrade pyrolysis vapor (i.e., converting the high molecular weight hydrocarbons in bio-oil to light hydrocarbons in py-gas). Pyrolysis vapor includes non-aqueous bio-oil and aqueous pyrolysis liquid and incondensable py-gas. Similar to the tars formed during the gasification process, bio-oil is predominantly comprised of primary tars with some secondary tars. Primary tars are oxygenated compounds (e.g. furfural and methoxyphenol) derived from the decomposition of cellulose, hemicellulose or lignin in carbonaceous materials. Secondary tars are phenolic and olefinic compounds generated from the decomposition of primary tar.[122] Since biochar has proven to be an effective catalyst for tar destruction, different types of biochar such as wood derived charcoal and corn stover derived biochar were investigated for catalytic upgrading of pyrolysis vapor from different feedstocks (e.g. pinewood, fir sawdust).[123,124,125] The results from Gilbert et al were in agreement with the work by Sun et al. that revealed pinewood biochar catalytically upgraded the pyrolysis vapor from pinewood.[123,124] Ren et al. found that corn stover biochar enhanced the py-gas yield and decreased the heavy hydrocarbons in bio-oil during the microwave-assisted pyrolysis of biomass.[125] Additionally, our previous work demonstrated that wastewater biochar also serves as a good catalyst for increasing py-gas yield and decreasing bio-oil yield because of the high metal content (i.e., Ca, Fe, etc.) in wastewater biochar.[126,127] The catalytic effect of these biochars is summarized in Fig. 1. Biochar as a catalyst can reduce the bio-oil yield by approximately 10–20%, and the mass fraction of py-gas is increased. Li et al. noted that one of the critical interactions is between radicals (especially H radicals) and the char.[128] Free radicals are formed in the carbon matrix during the pyrolysis of organic

matter.[129,130] The porous biochar structure and certain inherent metals such as Ca and Fe can facilitate radical reactions to breakdown tar into smaller molecules.[128,131,132,133]

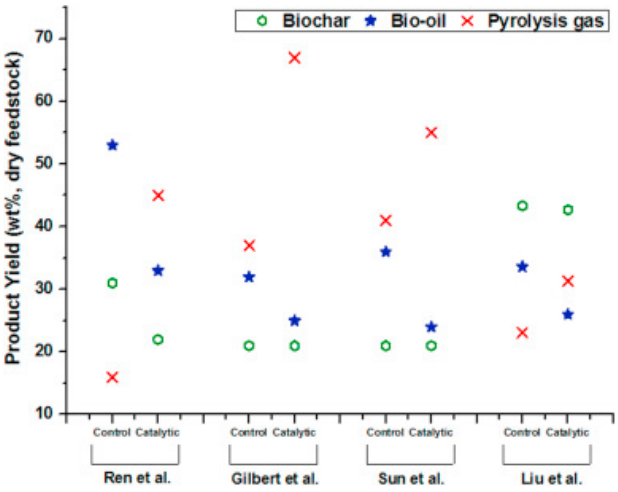

Fig. 1. **The catalytic effect of different biochars on upgrading pyrolysis vapor**. (Ren et al.: Feedstock is Douglas fir sawdust and biochar catalyst is corn stover biochar. Catalyst to feedstock mass ratio is 0.5. The pyrolysis and catalysis temperatures are 480 °C in a microwave oven pyrolyzer with 700 W power and 10 min duration; Gilbert et al.: Feedstock is pinewood and biochar catalyst is pinewood biochar. Catalyst to feedstock mass ratio is 1. The pyrolysis temperature is 500 °C and the catalysis temperature is 700 °C; Sun et al.: Feedstock is pinewood and biochar catalyst is pinewood biochar. Catalyst to feedstock mass ratio is 0.6. The pyrolysis and catalysis temperatures are 700 °C; Liu et al.: Feedstock is wastewater solids and biochar catalyst is wastewater solids biochar. Catalyst to feedstock mass ratio is 0.5. The pyrolysis and catalysis temperatures are 700 °C.).

7. Energy recovery from wastewater biochar

As a reduced carbonaceous material, wastewater biochar can be used for energy generation or fuels production. Combustion of wastewater biochar,[134,135] or co-combustion with a fuel like coal,[135,136,137] can supply process heat or contribute to powering a steam cycle.[137] Gasification or co-gasification of wastewater biochar with steam and a limited amount of oxygen can be used to produce syngas,[138,139,140,141] a mixture of H_2 and CO, that can be combusted for energy generation or used in the production of fuels. Compared to char produced from coal and biomass sources, wastewater biochar has a high content of ash (typically 30–80 wt%), sulfur, and heavy metals and has a reduced heating value.[142]

7.1. Wastewater biochar heating values

Higher heating values (HHV) of wastewater biochars generally decrease as pyrolysis temperature increases, due to the loss of energy-rich organic material and the increasing fraction of ash in the remaining solid. Typical HHV for primary wastewater solids of 16.7 MJ/kg have been reported, whereas digested wastewater solids has a typical HHV of 11.9 MJ/kg on a dry basis.[143,144] HHV of wastewater biochar are lower than the HHVs of the parent wastewater solids, as seen in Table 6, and wastewater biochar produced from primary wastewater solids has a higher HHV compared to wastewater biochar produced from digested wastewater solids.[145,146] For instance, Otero et al. found that, as the pyrolysis temperature increased, the heating value (dry basis) of wastewater biochar decreased due to the

continual loss of volatiles.[135] Inguanzo et al. also measured a decrease in HHV as pyrolysis temperature and heating rate increased.[24] Trinh et al. found that the HHV of wastewater biochar decreased from 8.8 MJ/kg to 5.1 MJ/kg as the pyrolysis temperature increased from 457 °C to 625 °C, with an increase in ash content from 71.3 wt% to 82.3 wt%.[147] Alvarez et al. found that wastewater biochar produced at 450 °C had a HHV of 5.9 MJ/kg, while wastewater biochar produced at 500 °C and 600 °C had a HHV of 5.3 MJ/kg.[148] The ash content increased with pyrolysis temperature from 68.1% to 74.3%.[148] McNamara et al. (2016) found that the heating value of wastewater biochar declined sharply (> 50%) with pyrolysis temperature between 300 °C and 500 °C, and declined more slowly between 500 °C and 800 °C.[149] Kim et al. (2008) found that the heating value of wastewater biochar decreased with increasing pyrolysis temperature between 250 °C and 500 °C.[145] It can be concluded that as pyrolysis temperature increases, the heating value of wastewater biochar decreases due to the release of energy-rich organic matter and the increasing fraction of ash. While not as industrially relevant, it is noted that on a dry, *ash-free* basis, the heating value of wastewater biochar does not decrease with pyrolysis temperature and can even be higher than that of its parent wastewater solids.[135,141]

Table 6. Wastewater Biochar Heating Value.

Author	Wastewater solids /Sludge Feedstock	Sludge Heating Value (HHV unless otherwise indicated)	Pyrolysis Temperature °C	Heating Rate °C/min or Reactor Type	Hold time min	Biochar Ash wt%	Wastewater Biochar Heating Value (HHV unless otherwise indicated)
Inguanzo et al. [12]	Dried, anaerobic digested	16.56	450	60		58.0	11.53
		16.56	650	60		62.2	11.06
		16.56	850	60		66.3	11.96
Otero [135]	Anaerobic digested	16.77	625	Furnace		63.1	10.46
		16.77	900	Furnace		71.8	9.84
	Aerobic digested	16.56	450	Furnace		57.5	11.03
		16.56	780	Furnace		78.4	8.31
	Aerobic digested	13.34	450	Furnace		69.5	6.76
		13.34	780	Furnace		89.9	3.80
Kim et al. [145]	Dried, Dewatered Primary	23	250–500	Batch Reactor	20		17–21
	Dried, Dewatered Thickened Waste Activated	19	250–500	Batch Reactor	20		13–20
	Dried, Dewatered, Digested	17	250–500	Batch Reactor	20		10–16
Pokorna et al. [146]	Dried, Dewatered Thickened Waste Activated	16.5	500	Fluidized Bed-type		57.9	9.9
	Dried, Dewatered, Digested	8.6	500	Fluidized Bed-type		75.1	5.2
	OLDA	15.0	500	Fluidized Bed-type		58.1	10.6
Trinh et al. [147]	Dried, non-digested	10.9	457	12000–60000	20	71.3	8.8
		10.9	625	12000–60000	20	82.3	5.1
Alvarez et al. [148]	Digested	11.1	450	Spouted Bed	2	68.1	5.9
		11.1	600	Spouted Bed	2	74.3	5.3
Gil-Lalaguna et al. [138]	Digested	11.8 (LHV, lower heating values)	530	Fluidized Bed	8	74.2	5.0 (LHV)
McNamara et al. [149]	Anaerobically digested primary sludge blended with Waste Activated Sludge	15	402	37	40		9.1

7.2. Combustion of wastewater biochar

Despite its relatively low heating value, combustion of wastewater biochar for energy recovery has been investigated. In general, wastewater biochar produced at higher pyrolysis temperatures will begin to oxidize at higher temperatures. For example, Inguanzo et al. studied air oxidation of wastewater biochar produced from anaerobic wastewater solids at pyrolysis temperatures of 450 °C, 650 °C and 850 °C using thermogravimetric analysis (TGA).[150] At higher pyrolysis temperatures, oxidation began at higher temperatures, which the authors attribute to a decrease in reactivity associated with increased char densification, similar to the phenomenon of thermal annealing, a process in which the molecular order increases and carbon reactivity decreases with increasing temperature.[151] Otero et al. used TGA to study

wastewater biochar oxidation in air and similarly found that wastewater biochar produced at higher pyrolysis temperatures underwent oxidation at higher temperatures.[135] This may be due to the fact that the biochar produced during pyrolysis still contained some readily-oxidized volatile matter, the fraction of which decreased with increasing pyrolysis temperature,[135] and could also be explained by char densification.

Wastewater biochar combustion kinetics have been examined by several researchers. For air oxidation of wastewater biochar formed during in-situ combustion of stabilized wastewater solids, Font et al. found an activation energy of 144.1 kJ/mol and a reaction order with respect to oxygen of 0.55.[152] It was also found that the oxidation rate did not depend on the extent of conversion. Nowicki et al. studied oxidation of wastewater biochar from pyrolysis of digested wastewater solids at 1000 °C, in a TGA, using 10% O_2 and oxidation temperatures between 450 °C and 550 °C.[153] A shrinking core model for the evolution of reaction rate with conversion was found to be appropriate for wastewater biochar oxidation.[153] The reaction order with respect to oxygen partial pressure was 0.88 and the activation energy was found to be 114 kJ/mol.[153] Kijo-Kleczkowska et al. inferred from combustion experiments on 5–10 mm wastewater solids particles at 800–900 °C that char combustion occurs in Zone II, in which both kinetics and diffusion within the porous char limit the overall rate of the process.[154] Urych et al. studied combustion of wastewater biochar in air at temperatures of 700 °C to 900 °C.[155] For wastewater biochar pyrolyzed at 900 °C, the oxidation rate increased from 0.16 to 0.21 min^{-1} as the oxidation temperature increased from 700–900 °C, with an activation energy (determined from nonlinear fitting to the Arrhenius form) that decreased from 17 to 12 kJ/mol. It is likely that char oxidation experiments at this temperature occurred in the diffusion-limited regime, leading to uncharacteristically low activation energies. More research is needed for a definitive comparison of the oxidation kinetics of wastewater biochar to chars from other fuels.

7.3. Gasification of wastewater biochar

Gasification of wastewater biochar is accomplished by reacting the carbonaceous solid with steam (H_2O) and/or carbon dioxide (CO_2) to produce syngas, a mixture of H_2 and CO which can subsequently be used for energy recovery or chemical production. Scott et al. compared the CO_2 gasification rates of wastewater biochar produced from pyrolysis of undigested wastewater solids at 900 °C to chars produced from car tires and from coal, using a fluidized bed.[156] An adsorption-desorption model was employed to determine the activation energies and pre-exponential factors for gasification. On both a per unit surface area and per unit mass basis, the wastewater biochar was the most reactive, by one to two orders of magnitude, which the authors attribute to its high ash content (74% ash).[156] Vamvuka et al. studied CO_2 gasification of wastewater biochar from undigested wastewater solids pyrolyzed at 950 °C.[157] The gasification reaction was fit to a power law rate expression (with respect to CO_2 partial pressure) with an activation energy of 180 kJ/mol and was found to be two times slower for wastewater biochar than for municipal solid waste and paper waste, a difference attributed by the authors primarily to differences in surface area.[157] Acid washing of the wastewater biochar lowered its reactivity by removing catalytically active mineral matter. While more research is needed, it appears that wastewater biochar gasification may be faster than coal char gasification, but slower than gasification of municipal solid waste and paper waste chars, with the differences being attributed to ash content and surface area.

The kinetics of wastewater biochar gasification have been examined by several researchers and, unlike combustion, some general agreement in kinetic parameters have emerged. Inguanzo et al. studied CO_2 gasification of wastewater biochar produced from anaerobic wastewater solids at pyrolysis temperatures of 450 °C, 650 °C and 850 °C using TGA.[150] At higher pyrolysis temperatures, there was a marked decrease in the time required for gasification of the char. However, similar to oxidation, gasification began at higher temperatures for wastewater biochar produced at higher pyrolysis temperatures, although the effect was not as pronounced as during oxidation. Nowicki et al. studied gasification of wastewater biochar from pyrolysis of digested wastewater solids at 1000 °C, in a TGA, using CO_2 and H_2O as reactants at temperatures between 750 °C and 950 °C.[153] A power–law reaction rate form was assumed. The reaction order with respect to steam was 0.30, and the order with respect to carbon dioxide was 0.39. The activation energy for H_2O was 193 kJ/mol, while for CO_2 the value was found to be slightly higher (227 kJ/mol).[153] The pre-exponential factor for wastewater biochar gasification with steam was roughly six times larger than for gasification with carbon dioxide.[153] Nowicki and Markowski later compared the gasification of raw and stabilized wastewater solids.[140] The wastewater biochar obtained from pyrolysis of the stabilized wastewater solids had a higher reactivity, which the authors attribute to its higher ash content (85.6%) compared to the wastewater biochar obtained from the raw wastewater solids (69.1% ash). In both studies, the variation of reaction rate with conversion was best fit by a shrinking core model for CO_2 and a volumetric model for steam.[140,153] which may indicate that steam fully penetrates the char particle's pore structure, while CO_2 may have more limitations in smaller pores, similar to coal chars.[158] Nilsson et al. studied gasification of wastewater biochar in CO_2, H_2O[159] and mixtures thereof,[160] in a fluidized bed. The char was produced in nitrogen at the same temperature as the subsequent gasification tests. It was found that cooling the char before gasification, which is typical in kinetic experiments, lowers its reactivity by more than 50%.[159] For 1.2 mm particles, diffusion limitations were found to be negligible in the range of 800–900 °C. For the reactions with CO_2 and H_2O individually, a power law expression in reactant partial pressure was found to be valid, with a reaction order of 0.33 for steam and 0.41 for CO_2,[159] similar to the results of Nowicki et al.[153] The activation energy was similar for both reactants (171 kJ/mol for H_2O and 163.5 kJ/mol for CO_2), although the pre-exponential factor was larger by a factor of six for the char-steam reaction,[159] similar to the findings of Nowicki et al.[153] For gasification of wastewater biochar in a mixture of CO_2 and H_2O, the authors found that the total gasification rate could be reproduced by the sum of the individual gasification rates,[160] a result that does not always hold for other types of char, where competition of reactants for active sites is a factor.[161] It appears that gasification of wastewater biochar with CO_2 has an activation slightly higher than the activation energy for gasification with H_2O, while the pre-exponential factor is roughly six times higher for steam gasification. The reaction order for steam gasification is roughly 0.3, while the reaction order for CO_2 gasification is roughly 0.4.

The gasification behavior of wastewater biochar has been compared to other biochars. Sattar et al. studied pelletized wastewater biochar gasification in a tubular reactor between 650 °C and 850 °C and measured the syngas composition and carbon conversion as a function of particle size, temperature and steam flow rate.[139] The steam gasification reaction rate of wastewater biochar was found to be similar to biomass chars typically proposed for gasification, such as miscanthus. However, the authors note that wastewater biochar may not be suitable for standalone gasification due to its low carbon content. At a temperature of 850 °C and with a steam flow rate of 172 g/min/kg wastewater biochar, the syngas produced from wastewater biochar gasification contained approximately 57% H_2, 15% CO and 3% CH_4, by volume.[139] The authors found a minimal impact of biochar particle size on carbon conversion and

syngas composition, which is not surprising given that the low temperatures and slow nature of gasification likely results in a kinetically-controlled reaction regime.[139]

Given its low carbon content, it is questionable whether gasification of wastewater biochar is practical. Gil-Lalaguna and coworkers studied air-steam gasification of wastewater biochar in a fluidized bed and compared the results to gasification of digested, dried sewage wastewater solids.[138,162] Wastewater biochar gasification resulted in a lower carbon conversion compared to wastewater solids gasification, due to the fact that the carbon present in wastewater solids is mostly released as volatiles (during gasification), whereas the carbon content of the char is mostly in the solid state.[138] When taken on a dry, ash-free basis, however, gasification of wastewater biochar produces more syngas than gasification of wastewater solids, and produces a similar amount of gas as lignocellulosic biochars undergoing gasification.[138] Specifically, the yield of H_2 contained in the syngas was approximately the same for wastewater biochar and wastewater solids, while the CO yield was 79% higher for wastewater biochar than wastewater solids.[138] The lower heating value of gas produced from wastewater biochar was 4.09–5.96 MJ/m^3, which was very similar to that of the gas produced from wastewater solids gasification.[138] As expected, increasing the temperature, reactant flow rate and oxygen-to-steam ratio during gasification increased the carbon conversion.[138] Gil-Lalaguna et al. (2014) also evaluated the energy requirements for direct gasification of dried wastewater solids and compared it to a two-stage process consisting of dried wastewater solids pyrolysis and subsequent wastewater biochar gasification.[162] In both processes, the energy requirements of the initial drying step were also considered. Because the industrially-relevant metrics for both processes would be on a per-kg- wastewater solids basis, rather than a dry ash-free basis, the authors determined that the one-step wastewater solids gasification process is exothermic (recall, air as well as steam is supplied to the reactor) while the separate pyrolysis and wastewater biochar gasification process is endothermic.[162] While the authors assumed the pyrolysis liquid is not utilized and its calorific value is lost, if the pyrolysis liquid were utilized, the two-part pyrolysis + air-steam gasification process would also be energetically favorable.[162] In conclusion, wastewater biochar gasification is difficult in general, due to its high ash and low carbon content, but the inherent gasification properties of the carbon contained within wastewater biochar are similar to chars from other sources.

8. Conclusions and future outlook

8.1. Conclusions related to the objectives of the review

Wastewater biochar is chemically different from other biochars and has many potential value-added applications, as noted in the objectives of this review.

Objective 1. Determine how basic properties of wastewater biochar properties differ from other biochars. In general wastewater biochar has a lower C content than other biochars stemming from biomass primarily because wastewater is composed of both organic and inorganic solids. Wastewater biochar also typically has a higher H to C ratio, as well as higher metal content.

Objective 2. Identify the appropriate uses of wastewater biochar for sorption. As an adsorbent, wastewater biochar has intermediate to high ammonium adsorption capacity. Some biochars adsorb phosphate, but other biochars can actually leach phosphate. Therefore, wastewater biochar could be used to recover nutrients from wastewater. It can also remove a wide range of heavy metals from various wastewater streams via cation exchange of the negatively charged biochar surface. Moreover,

wastewater biochar can effectively sorb organic contaminants such as endocrine disrupting compounds, pharmaceuticals, antimicrobial compounds and antibiotics, and could be used as a polishing treatment step to remove micropollutants from wastewater discharge.

Objective 3. Establish the benefit of wastewater biochar as a soil amendment. As a soil amendment, wastewater biochar can improve growth of a variety of plants such as fruiting plants, grasses, rice and lettuce. Still, the research on wastewater biochar as a soil amendment is scarce and more research should be conducted to further validate the benefits of it as a soil amendment.

Objective 4. Determine toxic hazards related to land applying wastewater biochar. Toxic pollutants in most wastewater biochars do not pose threats to the environment during land application. The heavy metal concentrations of most wastewater biochar products can meet both US EPA and European Union standards. PAH contents of wastewater biochar that is made above 700 °C consistently are below the maximum limits set by the US EPA. Moreover, other emerging contaminants such as triclosan and estrogens are not present either.

Objective 5. Establish the role of wastewater biochar as a catalyst. For applications in energy recovery technologies, wastewater biochar can be used as a catalyst for upgrading pyrolysis vapor to increase py-gas yield for enhanced energy recovery.

Objective 6. Determine the feasibility of energy recovery from wastewater biochar. Combustion and gasification of wastewater biochar is difficult because its high ash and low carbon content results in reduced heating values compared to other chars. On a dry-ash free basis, however, wastewater biochars are quite reactive, due to their high content of catalytically active minerals. Co-gasification or co-combustion with fuels like coal or biomass may therefore present the most practical route for energy recovery from wastewater biochar.

8.2. Future outlook

Based on the above benefits, a biochar enhanced solids treatment (BEST) process is proposed here (Fig. 2) to help transit conventional pollutant treatment plants to WRRFs. The future WRRF framework focuses on many emerging nexuses such as FEW (Food, Energy, Water) and NEW (Nutrients, Energy, Water). A common goal of these nexuses is to improve resource and energy recovery while simultaneously mitigating impacts of pollutants inherent to wastewater.

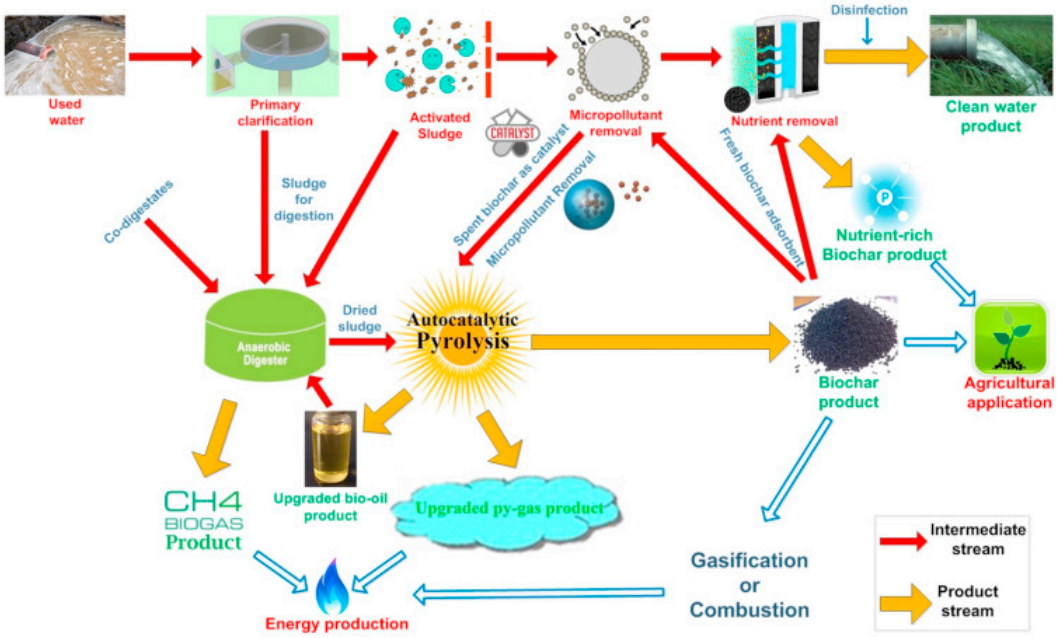

Fig. 2. **The Biochar Enhanced Solids Treatment (BEST) process.** Solids from primary sedimentation and secondary treatment are sent to an anaerobic digester. The digested wastewater solids are dried and processed via autocatalytic pyrolysis, a process that employs wastewater biochar as a catalyst. The py-gas from pyrolysis and biogas from digestion are recovered for energy production. The aqueous condensate from pyrolysis is co-digested in the anaerobic digester. The biochar is either added to soil for agricultural benefits, used as an adsorbent to remove micropollutants from effluent, used as a catalyst, or used as a fuel for co-gasification or co-combustion. The biochar that has adsorbed micropollutants is returned to the pyrolyzer to remove micropollutants.

In the BEST process, fresh wastewater biochar can be used as a fuel or as an adsorbent. For sorption, the activated sorbent is used to remove micropollutants from secondary-treated wastewater. The micropollutant-laden biochar is further used as a catalyst to upgrade pyrolysis vapor. The biochar assisted catalysis can greatly enhance the energetic gas production for improved on-site energy recovery. Meanwhile, micropollutants can be removed from biochar catalyst after reheating to high catalytic temperature. This regenerated clean biochar catalyst is further used as a sorbent to capture nutrients. The nutrient-laden biochar is finally land applied as a soil amendment. The BEST process can reduce both adverse ecological and environmental impacts such as possible aquatic life population decline caused by micropollutants and eutrophication to help promote a healthier community. The improved energy recovery from wastewater solids can supply more renewable energy to the local residents. Furthermore, the final land application of biochar is a sustainable approach for regional agricultural and horticultural development.

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