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### Biochar as a novel technology for treatment of onsite domestic wastewater: A critical review

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Globally, about 2.7 billion people depend on onsite sanitation systems (OSS) (e.g., septic tanks) for their sanitation needs. Although onsite sanitation systems help in providing primary treatment for domestic wastewater, they don't effectively remove nutrients, pathogens, and other inorganic contaminants. Previous studies have posited that the use of post treatment systems which incorporate biochar leads to improved contaminant removal efficiency. However, the mechanism through which contaminants are removed and factors potentially affecting the removal are still understudied. To fill this knowledge gaps, this review discusses factors which affect efficiency of biochar in removing contaminants found in onsite domestic wastewater, modifications applied to improve the efficiency of biochar in removing contaminants, mechanisms through which different contaminants are removed and constraints in the use of biochar for onsite wastewater treatment. It was noted that the removal of contaminants involves a combination of mechanisms which include adsorption, filtration, biodegradation, ion exchange, pore entrapment. The combination of these mechanisms is brought about by the synergy between the properties of biochar and microbes trapped in the biofilm on the surface of the biochar. Future areas of research such as the modification of biochar, use of biochar in the removal of antibiotic resistant genes (ARGs), application of wet carbonization methods and resistance of biochar to physical disintegration are also discussed. This study provides useful information that can be applied in the use of biochar for the treatment of wastewater and guide future design of treatment systems for optimized treatment performance.

#### KEYWORDS

biochar, biomass, greywater, organic waste, wastewater treatment, pyrolysis, biofiltration, wastewater reuse



#### 1 Introduction

In many low- and middle-income countries, the sanitation needs of most people are met by on-site sanitation systems (OSS) due to their low capital and maintenance costs (Strande et al., 2014; Manga et al., 2019; Krueger et al., 2020; Manga et al., 2020). Although these systems are costeffective, they are unsustainable due to their inability to properly treat human excreta. Furthermore, the liquid released from these systems into the surrounding soils is a source of environmental pollution and a threat to public health and environmental quality (Manga et al., 2022a; Capone et al., 2022). One such system is the septic tank discharging to a soak away pit, that is currently in use by about 1.7 billion people worldwide and is considered a minimum standard for use in public/congregated places in some developing nations (WHO and UNICEF, 2021). Limitations of these systems have brought about the need to explore subsequent post-treatment or polishing technologies required to achieve the desired effluent disposal or reuse standards. Various ecologically safe and cost-effective technologies such as constructed wetlands (CW) or subsurface wastewater infiltration systems (SWIS), have shown to be promising systems (Mburu et al., 2013). However, these systems are not effective in removing phosphorus from wastewater due to the fact that they make use of sand bed media and do not have sufficient capacity to bind phosphorus for a prolonged period (Brix and Arias, 2005). Different kinds of media such as oyster shell, limestone, calcite, zeolite, and biochar have been applied to improve the contaminant removal efficiency of these soil-based biofiltration systems (Gungor and Unlu, 2005; Gill et al., 2009; Wang et al., 2013; Zhang et al., 2015). Amongst the aforementioned amendment materials, biochar holds great potential to improve the removal of contaminants due to its ability to

adsorb various organic and inorganic compounds, good cation exchange capacity and ability to serve as growth media for biofilm. Though a lot of investigations have been carried out on the use of biochar for centralized wastewater treatment, the use of biochar for the treatment of effluent from onsite containment units is still nascent and there are still some knowledge gaps. Mechanisms through which different contaminants can be removed and factors which affect the ability of biochar to adsorb contaminants found in onsite domestic wastewater are not well documented. The aim of this paper is to critically evaluate the applicability of biochar for the treatment of effluent from onsite containment units especially septic tanks. The review specifically discusses: 1) Factors which affect efficiency of biochar in removing contaminants in onsite domestic wastewater; 2) biochar modifications to improve contaminant removal efficiency; 3) mechanisms of different contaminants removal; and 4) constraints, gaps and areas of future research in the use of biochar for onsite wastewater treatment.

## 2 Composition of domestic onsite wastewater

Domestic on-site wastewater emanates from onsite wastewater treatment systems (OWTS) which are used for the treatment and disposal of household wastewater in places where centralized sewerage systems are not available (Babcock et al., 2014). Some of the most commonly used OWTS are septic systems, cesspools, aerobic treatment units (ATUs), above-ground mounded soil systems, subsurface drip irrigation systems, land application systems such as spray irrigation, and aquatic systems such as wetlands and lagoons. OWTS are multistage

рН	Turbidity (mg/L)	TS (mg/L)	TDS (mg/ L)	TSS (mg/L)	DO (mg/L)	COD (mg/L)	BOD₅ (mg/L)	TN (mg/ L)	NH <sub>4</sub> +- N (mg/L)	NO <sub>3</sub> -N (mg/L)	PO <sub>4</sub> <sup>3—</sup> P (mg/L)	TP (mg/ L)	Reference
6.7	210.0	328.0	96.0	232.0	1.02	305.6	176.0	17.3	12.5	1.8			Oladoja and Ademoroti (2006)
				1,653 ± 1,174			1,160 ± 350	100 ± 56	99 ± 19		39 ± 28		Pishgar et al. (2021)
7.6 ± 0.1					1.3 ± 0.8	690 ± 150	330 ± 103	120 ± 31	110 ± 20	8 ± 5.3		13 ± 6.5	Lusk et al. (2017)
6.4–10.1		252-3,320		22-1,690		139—4,584	112-1,101	16-189	1.6–94	0.2-8.5		0.2-32	Lowe et al. (2009)
	17–394				0.19-21.9	17-394			0.06-112	0.24–26.5	0.02-5.12		Agoro et al. (2018)
		800		240		325	225	35	20			10	Alley (2007)
				653		1,202	505		59			13	Awuah et al. (2014)

TABLE 1 Physicochemical properties of domestic wastewater.

TS, total solids; TSS, total suspended solids; TDS, total dissolved solids; DO, dissolved oxygen; BOD, biological oxygen demand; COD, chemical oxygen demand; TN, total nitrogen; TP, total phosphorus; NH<sub>4</sub><sup>+</sup>-N, ammonium nitrogen; NO<sub>3</sub> -N, nitrate nitrogen; PO<sub>4</sub><sup>3-</sup>P, orthophosphate.

systems which make use of a combination of technology and natural processes to collect and treat wastewater. The treated effluent is released into the environment through a dispersal unit which makes use of a network of soil infiltration trenches (leach field) where the effluent is further treated as it percolates through the vadose zone prior to discharge to local groundwater (Lamichhane, 2007; Manga et al., 2022a).

Domestic on-site wastewater is made up of human faeces, urine, cleansing material, flush water and at times grey water and contains various pollutants which include organic matter (biochemical oxygen demand (BOD) and chemical oxygen demand (COD)), nutrients (i.e., nitrogen and phosphorous) (Table 1), pathogens, heavy metals, pharmaceutical, and personal care products (PPCPs) (Manga et al., 2016; Martikainen et al., 2018; Guruge et al., 2019; Farkas et al., 2020; Semiyaga et al., 2022; Tokwaro et al., 2023). Pathogens found in onsite domestic wastewater include bacterial pathogens (i.e., Escherichia coli, Legionella pneumophila, Leptospira spp, Salmonella spp, Shigella spp, Vibro cholera, and Yersinia enterocoliticia), viral pathogens (e.g., adenovirus, enterovirus, hepatitis A, norovirus, reovirus, rotavirus, and echovirus) and helminths (ascaris, hookworm, whipworm) (Table 2) (Lusk et al., 2017; Manga, 2017; Manga et al., 2023). Heavy metals in domestic wastewater emanate from detergents and body care products (Akpor et al., 2014). The most common heavy metals in domestic wastewater are lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), silver (Ag), zinc (Zn), manganese (Mn), and iron (Fe) (Table 3) (Chino et al., 1991; Manga et al., 2022b). Different kinds of PPCPs have been found in domestic onsite wastewater and they include ibuprofen, caffeine, erythromycin, ciprofloxacin, sulfamethoxazole, ketoprofen, carbamazepine (Table 3) (Miège et al., 2009).

The quantities of each of the aforementioned contaminants in domestic wastewater stream usually varies with factors such as weather conditions, number of users, water use patterns (Oteng-Peprah et al., 2018). Majority of these pollutants are persistent in nature (especially PPCPs) and cannot be easily removed using conventional onsite treatment techniques, such as sand filter and soil infiltration treatment systems. These systems have been proven to be only partially effective in removing different kinds of organic micropollutants found in domestic wastewater including PPCPS. For instance, Gros et al. (2016) noted low to intermediate removal of PPCPs in soil beds that are used for onsite filtration (e.g., 46% removal for ibuprofen, 86% for diclofenac, 44% for metoprolol, and 73% for caffeine), while Blum et al. (2017) reported insignificant (>10%) removal of acetaminophen in soil beds A summary of the concentration and ranges of these pollutants in domestic wastewater, quality of effluent from onsite systems as well as removal efficiencies are presented in Tables 1–3.

Currently, the methods used for removing PPCPs from wastewater include electrochemical method (Barrios et al., 2016), microbial method (Ferreira et al., 2016), membrane process, chemical oxidation process and adsorption method (Acero et al., 2015). Amongst the aforementioned methods, adsorption is widely accepted because of its cost effectiveness, high efficiency, and wide processing range. The most commonly used adsorbents are activated carbon, silica gel, alumina, polyacrylamide, adsorbent resin, and zeolite (Esmaeeli et al., 2017; Qu et al., 2018; Peng et al., 2019; Jiang et al., 2020). Though activated carbon has very large specific surface area and in turn a large adsorption capacity, it is expensive while other adsorbents like silica gel, alumina, adsorbent resin have narrow adsorption surface and polyacrylamide is difficult to produce (Cheng et al., 2021). This necessitates the need for other treatment techniques which are efficient, economical, and environmentally friendly such as the use of biochar. When compared with other adsorbents, biochar presents a potential low-cost and effective adsorbent; the properties of biochar such as its large surface area, porous structure, enriched surface functional groups and mineral components make it possible for it to be used as proper adsorbent for contaminants in domestic wastewater. The specific properties of biochar including large specific surface area, porous structure, enriched surface functional groups and mineral components make it possible to be used as proper adsorbent to remove pollutants from aqueous solutions (Tan et al., 2015).

TABLE	2	Microbial	composition	of	domestic	wastewater
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Pathogenic micro-organism	Concentration in domestic wastewater	Concentration in effluents from onsite wastewater systems	Removal efficiencies (%)	Reference
Bacterial pathogen				
Total coliform	4.4-8.6 log <sub>10</sub> CFU/100 mL	1.15-7.78 log <sub>10</sub> CFU/100 mL	84.15-99.99	Quiñónez-Díaz et al. (2001); Winward et al. (2008); Horn et al. (2014)
Fecal coliform	4.1-7.9 log <sub>10</sub> CFU/100 mL	0.6–9.91 log <sub>10</sub> CFU/100 mL	96.02–99.99	Karim et al. (2004); Garcia et al. (2008); Akunna et al. (2017)
Fecal streptococci	3.1-6.1 log <sub>10</sub> CFU/100 mL	_	99.29–99.93	Reinoso et al. (2008); Abdel-Shafy and El-Khateeb, (2013)
Escherichia coli	5.8–7.8 log <sub>10</sub> CFU/100 mL	0.17–6.7 log <sub>10</sub> CFU/100 mL	73.91–99.99	Boutilier et al. (2010); Akunna et al. (2017); Manga et al. (2022a)
Salmonella	4.7 log <sub>10</sub> CFU/100 mL	_	68.38-99.99	Eregno and Heistad, (2019); Amin et al. (2020)
Shigella	1.0-3.8 log <sub>10</sub> CFU/100 mL	_	96.33-99.72	Zhou et al. (2015); Amin et al. (2020)
Clostridium perfringens	0-6.0 log <sub>10</sub> CFU/100 mL	_	93.69–99.96	García et al. (2013); Morató et al. (2014)
Pseudomonas aeruginosa	3.8-5.0 log <sub>10</sub> CFU/100 mL	_	96.92–99.21	Winward et al. (2008); Morató et al. (2014)
Enterococci	3.3-6.6 log <sub>10</sub> CFU/100 mL	0.3–16.5 log <sub>10</sub> PFU/100 mL	80.05-99.99	Akunna et al. (2017); Humphries et al. (2020)
Viral pathogen				
F-specific bacteriophage	2.8–6.3 log <sub>10</sub> PFU/100 mL	_	36.90-99.99	Karim et al. (2004); Torrens et al. (2009); Perez-Mercado et al., 2019
Rotavirus	2.9–8.1 log <sub>10</sub> copies/mL	_	97.28–99.99	Zhou et al. (2015); Zhang et al., 2016; Humphries et al. (2020)
Norovirus GI and GII	3.1-8.9 log <sub>10</sub> copies/mL	_	73.80-99.99	Kauppinen et al. (2014); Amin et al. (2020); Humphries et al. (2020)
Adenovirus	5.0–7.3 log <sub>10</sub> copies/mL	_	77.83–99.99	Kauppinen et al. (2014); Kaliakatsos et al. (2019)
Enterovirus	7.6–7.8 log <sub>10</sub> copies/mL		98.73-99.99	Kaliakatsos et al. (2019); Humphries et al. (2020)
Protozoa				
Giardia	0.6-4.9 log <sub>10</sub> cysts/L		99.91	Karim et al. (2004); Amin et al. (2020)
Cryptosporidium	0-140 oocysts/L		99.87	Falabi et al. (2002); Reinoso et al. (2008)
Helminths	9.6-244 eggs/L	0.5-16.5 eggs/L	53.70-99.98	Stott et al. (2003); Reinoso et al. (2008); García et al. (2013); Manga et al., 2016; Capone et al., 2022; Manga, 2017

CFU, colony forming unit; PFU, plaque forming unit.

## 3 Biochar and factors influencing contaminant removal by biochar

#### 3.1 Production of biochar

Biochar is a solid residue produced either by pyrolysis or gasification of biomass with former being the widely used technique. Pyrolysis refers to the thermal decomposition of organic materials in an inert atmosphere (oxygen-limited environment). The pyrolysis process can be represented by a generic chemical reaction (Eq. 1).

$$C_{a}H_{b}O_{c}(biomass) \xrightarrow{heat} \sum_{liquid} C_{r}H_{s}O_{t} + \sum_{gas} C_{x}H_{y}O_{z} + H_{2}O + C(char)$$
(1)

Depending on the operating conditions such as as temperature, heating rate, residence time, and pressure, pyrolysis process can be divided into three classes: Slow pyrolysis (carbonization), fast pyrolysis, and flash pyrolysis (Demibras, 2001). Flash pyrolysis is distinguished from fast pyrolysis by relatively higher heating rates, and very low

Contaminant	Concentration (ng/L)	Concentration in effluent (ng/L)	Median removal efficiency (%)	Reference
Erythromycin	53-340	_	_	Miège et al. (2009), Sim et al. (2011), Terzić et al. (2008), Yang et al. (2011)
Ciprofloxacin	413-620	_	_	Terzić et al. (2008); Miège et al. (2009); Sim et al. (2011); Yang et al. (2011)
Sulfamethoxazole	29–1,180	4–2,900	40	Terzić et al. (2008); Kasprzyk-Hordern et al. (2009); Miège et al. (2009); Behera et al. (2011); Sim et al. (2011); Schaider et al. (2017)
Trimetoprim	205–2,192	30-1,500	60	Terzić et al. (2008); Kasprzyk-Hordern et al. (2009); Miège et al. (2009); Behera et al. (2011); Sim et al. (2011); Yang et al. (2011); Schaider et al. (2017)
Diclofenac	131–1,340	10-1,400	82	Terzić et al. (2008); Kasprzyk-Hordern et al. (2009); Miège et al. (2009); Behera et al. (2011); Sim et al. (2011); Yang et al. (2011); Schaider et al. (2017)
Ibuprofen	2,265-69,700	2,900-13,500	53	Miège et al. (2009); Santos et al. (2009); Behera et al. (2011); Schaider et al. (2017)
Ketoprofen	123–1,580	50-1,500	_	Terzić et al. (2008); Kasprzyk-Hordern et al. (2009); Miège et al. (2009); Santos et al. (2009); Behera et al. (2011); Schaider et al. (2017)
Caffeine	2,349-80,000	4,800-93,800	34	Santos et al. (2009); Behera et al. (2011); Yang et al. (2011); Schaider et al. (2017)
Naproxen	335-6,000	30-161	54	Terzić et al. (2008); Kasprzyk-Hordern et al. (2009); Miège et al. (2009); Santos et al. (2009); Behera et al. (2011); Sim et al. (2011); Schaider et al. (2017)
Carbamazepine	64–1,694	5-13,800	6–10	Terzić et al. (2008); Kasprzyk-Hordern et al. (2009); Miège et al. (2009); Behera et al. (2011); Sim et al. (2011); Yang et al. (2011); Schaider et al. (2017)
Atenolol	30-12,913	_	_	Terzić et al. (2008); Kasprzyk-Hordern et al. (2009); Miège et al. (2009); Behera et al. (2011)

TABLE 3 Pharmaceutical and personal care products detected in domestic wastewater, concentrations in effluent of onsite systems, and removal efficiencies by onsite systems.

residence time (0.5–2 s). The choice of pyrolysis process used depends on the most preferred product. If the aim is the production of liquid and/or gaseous products, then fast pyrolysis is recommended but if the aim is more formation of biochar, then slow pyrolysis is to be used. The use of pyrolysis for biochar production from biomass is considered to be an affordable and environmentally friendly process (Ahmad et al., 2012). Biochar production is considered environmentally friendly since it stores carbon in a stable form thereby offsetting the release of greenhouse gases into the atmosphere (Xiang et al., 2020). In producing biochar from pyrolysis, process parameters such as temperature, residence time, heating rate are responsible for determining the yield of the biochar.

## 3.2 Factors for contaminant removal using biochar

#### 3.2.1 Internal factors

The ability of biochar to remove contaminants present in wastewater is governed by some of its intrinsic properties (physicochemical and spectral properties of biochar) such as the feedstock type, specific surface area and porosity. The factors which influence the ability of biochar to remove contaminants can be external (related to pyrolysis conditions, feedstock type and properties of the solution to be treated). The later depends on the preparation process and pyrolysis conditions used the following sections will elaborate more about these factors:

#### 3.2.1.1 Specific surface area and porosity

The specific surface area (SSA) and porosity of biochar are major parameters that influence its ability to adsorb contaminants (Liu et al., 2015). When biomass is being pyrolyzed, some of the volatile components are lost and this leads to the formation of micropores on the surface of the biochar (Bagreev et al., 2001). The pore size is very important for adsorption as biochar with small pore size cannot trap large sorbate, regardless of their charges or polarity (Ahmedna et al., 2004). When biochar is highly porous, it has high potential for filtration and this presents two major advantages when it is used as a biofilter for water/wastewater treatment: 1) Good water-holding capacity in the pores and 2) ability to harbor biofilm in pores without clogging (Li et al., 2016).

Biochar porosity and SSA vary considerably with pyrolysis temperature with high temperature ranges leading to larger pore size and larger surface area which in turn leads to increased

#### TABLE 4 Characteristics of biochar from various feedstock.

Biochar		Ultim	ate analys	is (%)		T	EC	Porosity	Ash	рН	Particle	Surface area	Reference
	С	Н	N	S	0	( C)	(ms/cm)	(%)	content (%)		size (mm)	(m <sup>-</sup> /g)	
Sewage sludge and cotton stalks	40.86	1.52	2.65						48.45	9.08		$21.56 \pm 1.56$	Wang et al. (2021)
Sewage sludge	$24.27\pm0.03$	$0.87\pm0.01$	$2.97\pm0.03$	$0.44 \pm 0.01$	$5.13\pm0.07$				$65.61\pm0.02$				Ali et al. (2022a)
Sewage sludge	16	0.87	2.10	0.60		550			76.6	7.98	13.4	12.0	Zhao et al. (2020)
Sewage sludge	39.57	1.17	5.67	0.38		550	745			9.77	3.95	3.98	Stylianou et al. (2020)
Faecal sludge	21.1	1.55	1.32	0.03	13.69	750	2.70			11.81		3.52	Nicholas et al. (2022)
Faecal sludge	38.8	4.1	1.9	1.2	9.13	250			42.9			4.4	Fakkaew et al. (2018)
Poultry litter	28.46	0.88	1.58	0.48		550	4123			10.43	3.94	14.03	Stylianou et al. (2020)
Poultry litter	7.49	0.43	0.76	0.43		550			87.2	9.95	16	7.09	Zhao et al. (2020)
Poultry litter	44.77	0.91	1.94	0.41	5.8	700	0.981		49.9	9.9		66.7	Cantrell et al. (2012)
Spent coffee grounds (SCG)	87.38	2.36	4.28	0.25		550	2723			9.42	60.39	1.53	Stylianou et al. (2020)
Orange Peels	67	1.47	2.05			700			14.9		1.6	501	Chen et al. (2011)
Fir TW	74.6	1.9	0.1		21	600			2.4		14.5	695.1	Rahman et al. (2021)
Olive stones	51.5	6.3	0.3	0.1	41.9	800			0.61	7.8		278	Petrov et al. (2008)
Olive pulp	56.7	5.5	0.3	0.3	37.4	800			1.34	7.7		295	Petrov et al. (2008)
Rubberwood sawdust	$86.7\pm0.10$	$3.32\pm0.40$	0.49	0.04	$7.89\pm0.05$				$5.79\pm0.02$				Ali et al. (2022b)
Willow Pine-spruce								60-74				170-200	Perez-Mercado et al. (2018)
Corn Cobs	$46.92\pm0.30$	$6.08\pm0.05$	$0.61 \pm 0.02$		44.8 ±0.29				$1.54\pm0.01$	7.86			Intani et al. (2018)
Husks	$44.96\pm0.32$	$6.02\pm0.07$	$0.49\pm0.02$		$45.57\pm0.29$				$2.97\pm0.02$	9.09			
Straw	$47.42 \pm 0.20$	5.98 ± 0.02	0.26±0.02		$41.75 \pm 0.16$				$4.60 \pm 0.06$	9.31			
Corn cobs	82.8	2.08	1.39	0.19	9.28		$2.39\pm0.01$		$5.65 \pm 0.35$	$8.74\pm0.07$		10.38	Pipíška et al. (2022)
Wood chips	79.9	1.59	0.45	0.18	11.72		$0.36 \pm 0.01$		$6.61\pm0.46$	$8.58\pm0.01$		53.68	
Oak Bark	71.25	2.63	0.46	0.02	12.99	450			11.1			1.9	Mohan et al. (2011)

(Continued on following page)

Biochar		Ultin	mate analys	is (%)		С Н °	EC /mc//m)	Porosity	Ash	Hd	Particle	Surface area	Reference
	U	т	z	S	0	)		(02)				(6/ 111)	
Soybean stover	81.98	1.27	1.3		15.45	700			17.18	11.3		420.3	Ahmad et al. (2012)
Peanut shells	83.76	1.75	1.14	0.00	13.34	700			8.91	10.57		448.2	Ahmad et al. (2012)
Rice husk	42.1	2.2	0.5		12.1	500			42.2			34.4	Liu et al. (2012)
Rice straw	45.7	2.13	1.17	0.29		550			42.9	10.3	7.85	4.15	Zhao et al. (2020)
Swine solid	52.9	0.74	2.61	0.85	4.03	700	0.194		52.9	9.5		4.1	Cantrell et al. (2012)
			-				_			-			

adsorption efficiency. The aforementioned trend has been noted in quite a number of studies. Chen et al. (2014) noted that when pyrolysis temperature increased from  $500^{\circ}$ C to  $900^{\circ}$ C, the pore volume of biochar increased from 0.056 to 0.099 cm<sup>3</sup>/g while the surface area increased from 25.4 to  $67.6 \text{ m}^2$ /g. However, in some cases, biochar produced at high temperature has lower surface area and porosity. Chun et al. (2004) observed that the surface area of wheat straw biochar reduced when the pyrolysis temperature decreased from 700°C to  $600^{\circ}$ C. The reduced surface area is due to the fact that at high temperature, the porous structure of biochar may be reduced by graphitization bringing about reduced surface area. Thus, it is necessary to optimize pyrolysis temperature to obtain biochar with the required adsorptive characteristics.

#### 3.2.1.2 Feedstock type

Different kinds of organic materials can be used as feedstock to produce biochar; these organic materials can be plant-based, manure-based, or agricultural/food processing residual-based biomass (Table 4). The composition of the parent material influences the yield, elemental content, and the microstructure of the biochar. Generally, plant-based biochar has high lignin content, which results in high biochar yield. Animal manure and sludge have high inorganic content implying that large quantities of ash will be generated from the feedstock when it is pyrolyzed leading to significant reduction in the surface structure and reaction properties of the biochar (Zielinska et al., 2015).

Feedstock type and pyrolysis temperature influence the quantity of ash in biochar and in turn the use to which the biochar can be put (Ali et al., 2022a). Generally, biochar from sewage sludge and faecal sludge have higher ash contents than biochar from wood and agricultural/food processing residue. The high ash content of biochar from sewage sludge is principally due to the high mineral/inorganic matter content of sludge which is turned into ash after pyrolysis (Zielinska et al., 2015). The high ash content of biochar from sludge implies that it can be applied as soil amendment while biochar from wood and agricultural/food are better suited for the removal of contaminants in wastewater (Perez-Mercado et al., 2018). This implies that if biochar from faecal sludge and sewage sludge are to be utilized for wastewater filtration, they will need to be co-pyrolyzed with other biomass with lower ash content.

Pyrolysis process leads to a change in elemental composition of the raw material, which is usually reflected by an increase in carbon (C) content and a decrease in hydrogen (H), and oxygen (O) contents. This results in an increase in the aromatic properties and a decrease in the polarity of the biochar. Generally, livestock manure and sewage sludge biochar have relatively higher nitrogen (N) and sulfur (S) contents than plant-based biochar which has higher C contents. The higher carbon content of plant-based biochar is due to the fact that they are lignocellulosic materials which have high lignin content that promote carbonization and increase the biochar carbon content (Tomczyk et al., 2020). Also, due to the fact that wood-based biochar maintains its plant cell structure and contains interconnected pores (5-10 µm diameter), it allows for better retention and entrapment of bacteria (Abit et al., 2012). This fact was corroborated by Lau et al. (2017) who noted that

biochar produced from forestry wood waste removed 92%–99% *E. coli* from synthetic storm water.

#### 3.2.2 External conditions

Pyrolysis process parameters such as temperature, heating rate, residence time as well as absorbent dose and solution pH influence the intrinsic properties of biochar and in turn its ability to adsorb contaminants (Gopinath et al., 2021).

#### 3.2.2.1 Temperature

The temperature at which pyrolysis is carried out influences the ability of biochar to remove contaminants as it affects the yield, specific surface area, types, and abundance of the surface functional groups on biochar (Zhou et al., 2019). Various researchers have conducted experiments to determine the effect of temperature on adsorption properties of biochar. Hossain et al. (2011) carried out the pyrolysis of dried sewage sludge under different temperatures, which ranges from 300°C to 700°C at heating rate of 10°C/min under nitrogen gas atmosphere in a horizontal tubular reactor. It was observed that biochar yield decreased from 72.3% to 63.7%, 57.9%, and 52.4% when temperature was increased from 300 to 400, 500 and then 700°C, respectively. This is because, when temperature increases, the decomposition of the organic material occurs at a faster rate and certain parts of the raw biomass are lost (Qurat-ul-Ain et al., 2021). In addition, Konczak et al. (2019) reported that the specific surface area increased from 69.7 to 75.5 and 89.2 m<sup>2</sup>/g, when the pyrolysis temperature increased from 500 to 600°C and 700°C, respectively. This is due to removal of volatile matter leading to the opening of pores and in turn providing additional surface area. Also, pyrolysis temperature influences the percentage of carbon (C), oxygen (O), and hydrogen (H) contents in biochar as increase in temperature leads to an increase in the percentage of carbon but decreases the oxygen and hydrogen content in the mixture (Weber and Quicker, 2018). The considerable changes in H and O contents have been attributed to the cleavage of heterocyclic compounds and nitrile group at elevated temperature (Konczak et al., 2019).

#### 3.2.2.2 Adsorbent dose

The amount of biochar applied has significant influence on the adsorption efficiency and in turn application of the optimum dose for contaminants removal, which is vital for cost-effective application. Increase in adsorption dosage enhances the adsorption efficiency of both organic and inorganic pollutants due to the availability of numerous bonding or sorption sites. Chen et al. (2011) investigated the removal of toxic metals (Cd, Cu, Pb, and Zn) from wastewater using biochar made from hardwood and corn straw. They observed that the adsorption efficiency of toxic metals by biochar improved when biochar concentration increased from 0.5 to 5 g/L. The increase in adsorption efficiency was attributed to increase in the number of active sites and surface area brought about by increase in amount of biochar. This observation is similar to results obtained by Lalhruaitluanga et al. (2010); Tsai and Chen (2013); Lu et al. (2017); Wang et al. (2018) observed similar results when they noted that increasing the biochar amount increased adsorption of organic pollutants. This shows that high concentration of biochar has a positive impact on the adsorption of pollutants and it would be

therefore useful to find the optimum dose, which is a key factor to minimize the biochar production costs in view of its industrial application, (Ambaye et al., 2021). However, the adsorption efficiency can be negatively correlated with adsorbent dose when its optimized dose is exceeded (Saltah et al., 2007). This can be attributed to the unsaturation of sorption sites and also overcrowding of adsorbent molecules, which may lead to overlapping (Merrikhpour and Jalali, 2012).

#### 3.2.2.3 Residence time

Residence time which is the amount of time the water molecules spend within the adsorbent is another important factor to consider during adsorption process. In general, the adsorption process has two-stages; a first stage which is rapid and quantitatively significant and a second stage which is slower. In the first stage, a larger surface of adsorbent is easily available but the pores of the biochar get clogged with time, leading to reduced adsorption and higher residence time in the second stage. Kizito et al. (2015) investigated the effect of contact time on the adsorption of ammonium ion (NH<sub>4</sub><sup>+</sup>) and observed that NH<sub>4</sub><sup>+</sup> adsorption increased rapidly with time in the first 6–8 h and became significantly slower until equilibrium was reached. A similar observation was also made by Saltalı et al. (2007).

#### 3.2.2.4 Solution pH

The solution pH is an essential parameter in the adsorption process and its influence depends on the biochar type and target contaminants. The pH influences both the surface charge and the degree of ionization and speciation of the biochar (Kołodyńska et al., 2012; Regmi et al., 2012). Changes in solution pH bring about changes on the surface functional groups found on biochar; when the solution is acidic, most of the functional groups on biochar are protonated and are present in positively charged form favoring adsorption of anions (Oh et al., 2012; Abdel-Fattah et al., 2014). With an alkaline solution, the surface of biochar is negatively charged, and the cations can easily be captured by biochar surface. The aforementioned trends have been noted in studies of different heavy metals adsorption on various kinds of biochar. Tong et al. (2011) investigated Cu (II) ion adsorption on three different types of biochar and observed that the adsorption of Cu (II) ion was increased when the solution pH was increased from 3.5 to 6.0. In another study by Chen et al. (2011) where biochar made from hardwood and corn straw were used to adsorb metals like copper, zinc, and lead, it was noted that when the pH increased from 2.0 to 5.0, the adsorption capacity of the metallic cations also increased. But at pH above 5.0, there was a decrease in the adsorption capacity due to hydroxide complex formation (Ambaye et al., 2021) Similar results were reported by Lu et al. (2012) who noted enhanced Pb adsorption on sludge derived biochar at increased pH.

#### 3.2.2.5 Heating rate

The heating rate during pyrolysis usually affects the structural and physicochemical properties of the resulting biochar most especially the pore structure (Yaman, 2004). When the heating rate is low and residence time is long and the pyrolysis process will occur slowly leading to full carbonization of the organic matter content. This brings about perforation in the pore wall structure of the biochar and subsequent decrease in the number of micropores in the biochar. When heating rate is high, large amount of volatile matter will escape from the feedstock within a short time leading to formation of a loose, and well-developed pore structure (Pan et al., 2021).

#### 4 Modification of biochar for enhanced contaminant removal

When biochar is produced without any modification, it has surface functional groups (only C - O, C =poor O, and OH groups are present) and possesses small surface area and micro-pores (Xiang et al., 2020). These poor properties hinder wide application of biochar necessitating the need for modification of its properties to improve its function. The functionality of biochar can be improved by physical and chemical methods and through impregnation with nanomaterials. Table 5 shows the characteristics of activated biochar from different sources.

#### 4.1 Physical activation

Water vapour and carbon dioxide  $(CO_2)$  are the most commonly used oxidizing agents for physical activation of biochar (Sajjadi et al., 2018). Biochar is subjected to extremely high temperatures (800°C–1,100°C) and active atmosphere pressure with vapour, CO<sub>2</sub> or a mixture. The process increases the porosity and specific surface area of the biochar. The chemical reactions governing physical modification by steam using CO<sub>2</sub> and H<sub>2</sub>O as reagents, are expressed in Equations (2)–(4) (Bansal et al., 1988).

 $C + H_2O \rightarrow CO + H_2, \ \Delta H = 117 \text{ kJ/mol}$  (2)

$$C + CO_2 \rightarrow 2CO, \ \Delta H = 159 \text{ kJ/mol}$$
 (3)

$$CO + H_2O \leftrightarrow CO_2 + H_2, \ \Delta H = 41 \text{ kJ/mol}$$
 (4)

In the study by Kołtowski et al. (2017), significant changes in physical properties such as specific surface area, micro-pores, and surface chemical characteristics (such as functional groups, polarity, and hydrophobicity) were observed after physical activation. The activation of cotton shell biochar using steam and  $CO_2$  independently and then in combination was investigated by Yang et al. (2010), where results showed that the specific surface area of the activated carbon increased by over 2000 m<sup>2</sup>/g irrespective of the activation agent used.

#### 4.2 Chemical activation of biochar

In chemical activation, biochar is impregnated with either acids (sulfuric acid,  $H_2SO_4$ ; hydrochloric acid, HCl; phosphoric acid,  $H_3PO_4$ ; nitric acid HNO<sub>3</sub>; and carbon dioxide, CO<sub>2</sub>), alkalis (potassium hydroxide, KOH; sodium hydroxide, NaOH and potassium carbonate  $K_2CO_3$ ) or oxidizing agents (hydrogen peroxide,  $H_2O_2$ , and potassium permanganate KMnO<sub>4</sub>). Acidic activation is purposely done to introduce acidic surface functional groups to biochar. Depending on the type and concentration of the acidic agent, SSA and pore structure of biochar can be altered. Peng et al. (2016) reported that 1 M of HCl enhanced the surface area of biochar by more than 50%. Another study by Vithanage et al. (2015) reported a significant increase of more than 2,400% (i.e., 2.3 to  $571 \text{ m}^2/\text{g}$ ) when biochar was activated by 30% H<sub>2</sub>SO<sub>4</sub> and oxalic acids. Feedstock type and method of preparation have a strong effect on the properties of biochar modified by alkali. Similarly, it is reported that the type and proportion of alkali activator have profound effect on the characteristics of biochar (Shen and Zhang, 2019). The activation of biochar by oxidizing agents such as H<sub>2</sub>O<sub>2</sub> and KMnO<sub>4</sub> is reported to enhance oxygen-containing surface function groups. In a study by Wang et al. (2015) where hickory-wood biochar was activated by impregnating it with KMnO<sub>4</sub>, it was observed that there was an increase in the surface area from 101 to 205 m<sup>2</sup>/g. Also, the adsorption capacity towards Pb (II), Cu (II), and Cd(II) was enhanced after the modification. In another study by Xue et al. (2012) where biochar from agricultural residue was modified with H2O2, it was noted that when compared to the control group without modification, the modified one had higher oxygen functional groups particularly the carboxyl group and this lead to enhanced lead adsorption capacity (22.82 mg/g for the modified biochar and 0.88 mg/g for unmodified biochar).

#### 4.3 Impregnation methods

In impregnation, metal salts or oxides, hydroxides and nanoparticles are being applied for biochar surface modification to enhance contaminant removal capacity due to their high abundance, cost-effectiveness, environmental friendliness, and chemical stability (Li et al., 2017). Biochar impregnation can be conducted by 1) soaking or suspending the biomass followed by pyrolysis and 2) pyrolysis of the biochar followed by impregnation (Ahmed et al., 2016). In a study by Chen et al. (2011), biochar was produced at different temperatures and impregnated with magnetite (Fe<sub>2</sub>O<sub>3</sub>) for the removal of phosphorus. It was observed that the modified biochar showed higher phosphorus adsorption (~99% removal) than unmodified biochar. In another study by Li et al. (2017), it was noted that adding ferric chloride (FeCl<sub>3</sub>) to biochar increased the phosphorus adsorption rate from 1 to 16.58 mg/g of biochar. Zhou et al. (2014) observed that when biochar surface was loaded with zerovalent iron (ZVI)-silver (Ag) nanoparticles (NPs) complex, the growth of E. coli was completely hindered. Silver nanoparticles (Ag-NPs) serve as antimicrobial particles due to a range of mechanisms such as disruption of cell wall and cytoplasmic membrane, denaturation of ribosomes, interruption of ATP production, and interference of DNA replication (Yin et al., 2020). Biochar composites impregnated with nanomaterials have also been found to improve the removal of PPCPs. For instance, the adsorption capacities of a group of PPCPs [salicylic acid (683 mg g-1), naproxen (533 mg g-1), and ketoprofen (444 mg g-1)] were 11-45 times higher in iron oxide (Fe2O3)-impregnated biochar when compared with those of unmodified biochar (Baccar et al., 2012; Karunanayake et al., 2017; Ahmed & Hameed, 2018; Anfar et al., 2020). Higher adsorption capacities of caffeine, ibuprofen, and acetylsalicylic acid were observed in biochar impregnated with iron oxide nanoparticle (Liyanage et al., 2020).

#### TABLE 5 General characteristics of activated biochar from different sources.

Activation method	Feedstock	Temp (°C)	Hold time (min)	Yield (%)	S <sub>BET</sub> (m²/g)	V <sub>tot</sub> (cm³/g)	V <sub>micro</sub> (cm³/g)	D <sub>ave</sub> (nm)	Reference
PA (steam: N <sub>2</sub> ), CH	WT	800	78		840		0.22	2.74	Kołtowski et al. (2017)
PA (CO <sub>2</sub> ), CH	WT	800	78		512		0.17	2.16	Kołtowski et al. (2017)
PA (steam), MWH	CS	900	75	42.2	2,079	1.21	0.97		Yang et al. (2010)
PA (CO <sub>2</sub> ), MWH	CS	600	210	37.5	2,288	1.30	1.01		Yang et al. (2010)
PA (CO <sub>2</sub> +steam)	CS	900	75	39.2	2,194	1.30	1.01		Yang et al. (2010)
PA (Steam: N <sub>2</sub> +H <sub>2</sub> O), CH	CS	800	120	76.3		0.39	0.35	0.68	Cagnon et al. (2009)
PA (35% steam, 65% N <sub>2</sub> ), CH	CS	800	120		524.5	0.23	0.21	1–6	Achaw & Afrane (2008)
PA (inter atm), CH	CS	600	60	21.29	378	0.26	0.12		Singh et al. (2008)
PA (steam), CH	CS	1,000	120	45	1,926	1.26	0.93	2.62	Li et al. (2008)
РА (CO <sub>2</sub> ), СН	CS	900	480		1,964	0.98		1.3-2.1	Wei et al. (2007)
PA (N <sub>2</sub> +H <sub>2</sub> O), CH	DS	700	180	22.31	421		0.484		Bouchelta et al. (2008)
PA (Steam), CH	OP	800	120	12.20	1,090	0.860	0.430		Petrov et al. (2008)
	SEOP	800	120	17.80	998	0.820	0.400		
PA (CO <sub>2</sub> )	OS	850	120	65.3	778	0.342	0.406		Román et al. (2008)
PA (Steam)	-		60	82.5	1,074	0.377	0.525		
PA (CO <sub>2</sub> /Steam)	-		60	76.5	1,187	0.384	0.553		
PA (CO <sub>2</sub> )	MCA	800	60		383	0.2028	0.1884	21.21	Aworn et al. (2008)
	CCA	-			770	0.4026	0.3637	20.33	
	BBA	-			467	0.2785	0.2189	23.84	
	SFA	-			518	0.3246	0.2365	25.05	
PA (Steam)	MCC	800	60		718	0.4283	0.3338	23.88	Aworn et al. (2008)
	CCC	-			651	0.3447	0.3139	21.18	
	BBA	-			491	0.3253	0.2231	26.51	
	SFA	-			464	0.4211	0.4256	20.18	
CA (NaOH)	РС	800	120		13,060.3		0.307		Jung et al. (2013)
CA (PTFE)	РМ	700	120		218.1	0.315		57.8	Zhang et al. (2013)
CA (ZnCl <sub>2</sub> ), CH	SBB	700	90		1826	0.966	0.711	2.22	Demiral and Gündüzog (2010)
PA&CA (KOH followed by $CO_2$ ), CH	CS	850	120		1,026	0.58		2.25	Din et al. (2009)
CA (H <sub>2</sub> SO <sub>4</sub> ), CH	CS	600	60	99.35	380	0.36	0.12		Singh et al. (2008)
CA (NH <sub>3</sub> .H <sub>2</sub> 0), CH	CS	850	210		2061	1.01			Wei et al. (2007)
CA (ZnCl <sub>2</sub> ), CH	CS	500	180		1,266	0.73	0.68		Azevedo et al. (2007)
CA (ZnCl <sub>2</sub> ) followed by PA (steam), CH	CS	900	30		2,114	1.31	1.14		Azevedo et al. (2007)
СА (К <sub>2</sub> СО <sub>3</sub> ), СН	ОР	500-1,100	60	15.20	1,610	0.843	0.437		Petrov et al. (2008)
	SEOP	500-1,100	60	16.2	1850	0.819	0.461	-	
CA (H <sub>2</sub> O <sub>2</sub> )	CW	900	120	22.7	1705	1.041	0.764		

(Continued on following page)

Activation method	Feedstock	Temp (°C)	Hold time (min)	Yield (%)	S <sub>BET</sub> (m²/g)	V <sub>tot</sub> (cm³/g)	V <sub>micro</sub> (cm³/g)	D <sub>ave</sub> (nm)	Reference
									<b>López</b> de Letona Sánchez et al. (2006)
CA (CO <sub>2</sub> )	ATP	800	60		840	0.55	0.39		Gañán et al. (2006)
CA (H <sub>3</sub> PO <sub>4</sub> )	Eucalyptus	500	60	26	1,239	1.109	0.9815	8.49	Patnukao and Pavasant (2008)

 TABLE 5 (Continued) General characteristics of activated biochar from different sources.

PA, Physical activation; CA, Chemical activation; MWH, Microwave heating; CH, Conventional heating; CS, Coconut shells; WT, willow tree; V<sub>tob</sub> total pore volume; V<sub>micro</sub>, micropore area; D<sub>avo</sub>, average pore diameter; BET, Brunauer-Emmett-Teller; DS, Date stones; OP, Olive pulp; SEOP, Solvent extracted olive pomace; MCA, Macadamia nutshell char; CCA, Corn cob char; BBA, Bagasse bottom ash; SFA, Sawdust fly ash; PTFE, polytetrafluoroethylene (Teflon); PM, Pig manure.

# 5 Mechanisms of contaminants removal from domestic wastewater using biochar

When biochar is applied as a support media for the treatment of domestic wastewater, several physical, chemical, and biological mechanisms are responsible for pollutant removal. However, the dominant removal mechanism depends on several factors which include the biochar's physicochemical properties, system configuration and operational condition (Quipse et al., 2022). These mechanisms include adsorption, biodegradation, ion exchange, and pore filling/entrapment.

#### 5.1 Adsorption

The mechanism used by biochar for adsorption is dependent on the heterogeneity of the adsorbent surface and the nature of the pollutant (adsorbate). Adsorption to the biochar surface occurs through van der Waals forces and hydrogen bonds with functional groups, filtration, electrostatic interaction, ion exchange, and surface complexation (Li et al., 2019; Cheng et al., 2021). When organic contaminants are to be removed, electrostatic attraction, hydrophobic sorption, hydrogen bond,  $\pi$ - $\pi$  electron-donor acceptor interactions and pores fillings facilitate the adsorption process. For the removal of inorganic pollutants (heavy metals), the adsorption process occurs through electrostatic attraction, ion exchange, complexation, and coprecipitation. In complexation and co-precipitation, the metals present in the domestic wastewater form complexes with oxide minerals or free carboxyl and hydroxyl functional groups available on the biochar surface after which they settle (physical sorption) or form layers (precipitation) on the biochar surface (Li et al., 2014). Pharmaceutical and personal care products which are emerging contaminants are usually adsorbed by biochar mainly by mechanisms of electrostatic attraction, hydrophobic effects, aromatic p-donor and cationic p-acceptor conjugation, hydrogen bonding and pore filling (Zhang et al., 2019; Xiang et al., 2020).

Pore filling is another mechanism through which contaminants are removed from onsite wastewater by adsorption. The pore network of biochar is usually made of micropores <2 nm, mesopores  $\sim$ 2–50 nm, and macropores >50 nm; the micropores and small mesopores (2–20 nm) contribute majorly to the surface area of the biochar and mostly influence its uptake for organic compounds (Pignatello et al., 2006). Pore filling is usually applied for the removal of organic contaminants in domestic wastewater and this is a function of the total micropore and mesopore volume on biochar pore surface (Nguyen et al., 2007; Hao et al., 2013). The pore fling mechanism depends upon nature, type of the biochar, as well as the polarity of the organic contaminant. Kasozi et al. (2010) studied the removal of organic contaminants from wastewater using biochar made from oak, gamma-grass and loblolly pine; it was noted that the biochars' strong affinity for catechol (PPCP) was mainly due to micropore filling.

#### 5.2 Biodegradation

The synergy between the properties of biochar and the metabolism of microbial organisms attached to the surface of biochar play a significant role in its removal of contaminants (Faulwetter et al., 2009). Biochar's distinct physicochemical characteristics such as large surface area and excellent pore structure make it support several microbial communities (Wang et al., 2020; Deng et al., 2021). The pH of biochar and the nature of dissolved oxygen carbon (DOC) are also important parameters for microbial growth on biochar. There is limited evidence in literature documenting the effects of biochar on the composition, activities and diversities of microorganisms during the treatment of household wastewater. Dalahmeh et al. (2014) evaluated the effect of bark, charcoal and sand filters on microbial diversity and potential respiration during the treatment of greywater. It was observed in the study that charcoal filters enhanced the development of diverse microbial communities. For the bacterial community composition, 33%, 25%, 13%, and 11% were reported for classes g-proteobacteria, a-proteobacteria, b-proteobacteria and Clostridia, respectively. There was a negative correlation between potential respiration and depth in both charcoal and bark filters due to fast mineralization of easily biodegradable matter in the topmost layer and subsequent oxygen depletion in the layers underneath. This is an indication that charcoal filters should be prepared to be more shallow in comparison with sand filters in greywater treatment systems; Deng et al. (2021) revealed that the use of biochar as a substrate in constructed wetlands was found to support many functional microbes such as nitrifying and denitrifying bacteria.

This is because biochar has large SSA and several pores making it easier to trap huge amounts of organic matter which supports reproduction and metabolism in microorganisms (Gul et al., 2015; Ji et al., 2020; Jia et al., 2020; Yuan et al., 2020). Other researchers also observed an enhancement of functional microorganisms in relation with organic matter degradation and nitrogen removal due to biochar amendments in constructed wetlands (Guo et al., 2020; Ji et al., 2020; Liang et al., 2020; Deng et al., 2021). The addition of biochar has the potential to increase the proportion of microorganism groups. With this, microbial activity is enhanced and the stress in removing toxic substances is eliminated (Wang et al., 2020). The overall effect of biochar incorporation is that there is regulation of microbial activities which enhances the removal of pollutants.

#### 5.3 Ion exchange

Ion exchange is a reversible reaction which occurs between ions in the liquid phase and ions in the solid phase. During ion exchange, when ions in the liquid phase get adsorbed by the ion exchange solid, the ion exchange solid releases equivalent ions back into the solution to maintain the electrical neutrality of the aqueous solution. (Cheng et al., 2021). Ion exchange is the main mechanism for removing heavy metals from wastewater by biochar and the ion exchange capacity is usually influenced by pyrolysis temperature as temperatures greater than 350°C decreases the ion exchange capacity of biochar. Several studies have noted that higher ion exchange capacity leads to higher adsorption efficiency for metals (El-Shafey, 2010; Trakal et al., 2016). Though ion exchange is the main mechanism for removing metals from onsite domestic wastewater, PPCPs cannot be easily removed by ion exchange. This is due to the fact that they cannot be easily converted into ionic forms. (Cheng et al., 2021).

### 5.4 Synergetic removal of contaminants from onsite domestic wastewater

Synergetic removal of PPCPs, organic matter and nutrients from wastewater using biochar filters involves the combination of adsorption and biodegradation processes. When adsorption and biodegradation processes are used together, biochar filters can be made self-sustaining through bio-regeneration; microbes (naturally present in water or externally introduced to suit target contaminants) can be immobilized on the surface of porous carbon forming biofilms which then metabolize and degrade the adsorbed contaminants in a bio-regeneration process. This bio regeneration process frees up clogged pores of the biochar, rejuvenating its adsorptive capacity thereby increasing its lifespan (Simpson, 2008; Jin et al., 2013). Also, nutrients such as nitrogen which are retained on the surface of biochar filters can help to enhance the biodegradation process. A study conducted by Jefferson et al. (2001) showed increased biological treatment (increased COD removal and oxygen uptake) after micronutrients (Zn) and macronutrients (N, P) were added.

Figure 1 shows the various mechanisms through which contaminants are removed from domestic onsite wastewater by biochar.

# 6 Previous studies on the use of biochar for the treatment of onsite domestic wastewater

Previous studies have successfully incorporated biochar into on-site sanitation facilities for the treatment of domestic wastewater. Mwenge and Seodigeng (2019) carried out experiments in laboratory plastic columns where activated biochar from agricultural wastes sandwhiched between two gravel layers was used as filter for the removal of TSS, NH3-N, NO3-N, and COD in kitchen, floor cleaning, showering and laundry greywater. Two different loadings of biochar-200 and 400 g-were used and it was observed that as the amount of biochar used increased, removal efficiency of contaminants across the wastewater types increased. Also, the initial concentration of pollutants used in the biochar had effect on the removal efficiency as it was noted that kitchen wastewater which had the highest pollutant concentration had the highest removal rate for most of the contaminants. The results of the study showed that the biochar column had efficiency with TSS (95% on kitchen greywater), NH4-N (85% on bathroom greywater), NO3-N (76% on kitchen greywater) and COD (63% on kitchen greywater).

Sidibe (2014) determined the effectiveness of salix leaves biochar filter for the removal of COD, Salmonella spp. And male-specific phages from artificial greywater in a laboratory filtering columns. The hydraulic loading rate was 0.032  $m^3\,m^{\text{-2}}\,day^{\text{-1}}$  and the organic loading rate was 76 mg BOD<sub>5</sub> m<sup>-2</sup> day<sup>-1</sup> (240 g COD m<sup>-2</sup> day<sup>-1</sup>). It was noted that the reduction of COD in 60 cm high biochar filter was 90%, 3 log<sub>10</sub> reduction for Salmonella spp. But there was very low reduction for the virus (2 log<sub>10</sub> reduction for male-specific phages). Very low reduction in MS2 virus concentration has also been noted by Dalahmeh et al. (2016) who carried out an experiment using laboratory scale columns loaded with biochar. Perez-mercado et al. (2019) studied the suitability of hardwood biochar filter for the removal of pathogens (S. cerevisiae, E. coli, Enterococcus spp and bacteriophage (MS2)) in domestic wastewater prior to use for irrigation. It was observed that biochar filter effectively removed S. cerevisiae from greywater. However, its effect on virus removal was found to be insignificant. These poor reductions in virus concentration in the laboratory scale biochar filters suggest that biochar has low capacity for the removal of virus. Lalander et al. (2013) reported that the virus removal by greywater filtration systems depends on the pH of the filter medium as the charge of the viruses changes with pH. The isoelectric point (pH at which a molecule is electrically neutral) of most viruses is in the acidic pH range (Dowd et al., 1998). Hence, for the removal of virus, further measures that can be used to make the pH of biochar acidic should be explored. Also, the use of finer particle biochar media to ensure better straining can be investigated. From a review of the studies, it can be seen that most of the studies were carried out with the use of column filters. More studies need to be carried out using other kinds of filters like the horizontal flow filters instead of the column filters.

Dalahmeh et al. (2016) used pilot scale sand bed biochar filter for the treatment of household grey water and reported the removal efficiency of biochar filter for BOD<sub>5</sub>, TSS, and *E. coli* to be 93%, 85% and  $1\log_{10}$  reduction, respectively. Niwagaba et al. (2014) constructed a 60 cm high gravel biochar filter for greywater treatment and reported high removal efficiency of BOD<sub>5</sub>, TSS and faecal coliforms (FC) which are 96%, 85.2%, and 95%, respectively after



36 h of operation. In contrast to the study of Dalahmeh et al. (2016), it can be seen that the study by Niwagaba et al. (2014) achieved high removal of faecal coliform. These differences can be a direct influence of the properties of the bacteria, the features of the biofilm-supporting materials (sand versus gravel), environmental factors as pH and temperature, the presence of other bacteria, the nutrients (quality and quantity) in the media which together play a role in the removal of faecal coliform (Van Houdt & Michiels, 2010).

Perez-mercado et al. (2018) studied the effect of different biochar filters (pine-spruce, willow and activated biochar) on the removal of COD, total phosphorus and nitrate phosphorus from onsite wastewater before irrigation. All types of biochar and all particle sizes of pine-spruce biochar achieved a high degree of removal of organic material (COD >90%). Willow biochar and activated biochar showed higher removal of total and phosphate phosphorus (>70%) than in pine-spruce biochar. It was noted that the particle size influenced the COD removal efficiency as the larger particle size (2.8 mm) had significantly lower removal efficiency (94%) than the smaller particle sizes (0.7 and 1.4 mm with greater than 99% removal efficiency). The lower removal efficiency of the larger particle size may be attributed to the fact that the larger particle size allows for larger macropores between the particles and it is likely that there is rapid passage through the filter which gives less contact time between the filter and the contaminants in the wastewater and thus less treatment efficiency.

In a study by Kholoma et al. (2016), biochar (about 0.2 m) was placed on top of a sand layer (0.8 m) in a filtration unit which was used for reclaiming domestic wastewater containing 1.9 mg P/L. It was observed that the phosphorus removal efficiency improved by 25.6% in the biochar-amended sand column when compared to the column with only sand. Gupta et al. (2016) mixed oak tree biochar with horizontal flow constructed wetland filter media used for treating synthetic wastewater. The application of biochar brought about increased contaminant removal with removal rates of 91.3% for COD, 58.3% for TN, 58.3% for NH<sub>3</sub>, 92% for NO<sub>3</sub>-N, 79.5% for TP, and 67.7% for PO<sub>4</sub>. In a pilot-scale study by Bolton et al. (2019), the addition of 100% chipped hemp fibre biochar filter after a horizontal flow gravel wetland for the treatment of domestic wastewater brought about better phosphorus (P) removal in the long term (5 months); 97% P removal was noted compared with 87% in the control (Bolton et al., 2019). The aforementioned studies show that using biochar as a filter media can improve the removal efficiency of phosphorus by constructed wetlands (constructed wetlands typically do not have high removal efficiency for phosphorus).

Forbis-Strokes et al. (2018) applied wastewater containing high concentrations of nitrogen to both unsaturated biochar trickling filters and saturated filters for 1 year and observed that the ammonium ion (NH4 <sup>+</sup>) removal rate was higher in unsaturated biochar nitrifying column (0.075-0.100 kg N/m<sup>3</sup>. day) than that of the control gravity column (0.041-0.094 kg N/m<sup>3</sup>. day). In another trickling filter study, when biochar was added to the sand column, the total nitrogen removal efficiency of the system increased from 8% to 42% (Tait et al., 2015). From all the aforementioned studies, it is seen that the addition of biochar to the treatment units improves the quality of the effluent from these systems making it a suitable alternative for the treatment of onsite domestic wastewater. Biochar-amended onsite sanitation systems have also been applied for enhanced PPCP adsorption (Cheng et al., 2021). Williams et al. (2015) noted that when eucalyptus wood and wheat residue biochar were applied to the soil matrix (0.5 t/ha), the removal of selected active pharmaceutical ingredients (propranonol and carbamazepine) increased by threefold. In another case study, various filtration matrices - (a) 100% silica sand, (b) 100% ZVI, (c) biochar-amended sand (50% v/v), and (d) 10% ZVI +40% biochar +50% sand (v/v)- were compared for their PPCP removal performance. It was observed that the column with a combination of ZVI, biochar, and sand showed the highest PPCP removal efficiency (>97% removal of all PPCPs at 10 µg/L of each chemical) within the top 10 cm of the column while the 100% sand control column did not show effective removal for the tested PPCPs ( $0.3 \mu g/L$  in the effluent) (Liu et al., 2019). Table 6 is a summary of studies which have investigated the suitability of biochar for greywater treatment.

#### 7 Management of spent biochar, constraints, gaps and areas of future research in the use of biochar for wastewater treatment

#### 7.1 Management of spent biochar

Since biochar is usually applied for the removal of toxic pollutants, its disposal needs to be carefully considered. The management option depends on the contaminant removed by the biochar and some of the management options include: Use as a soil conditioner, re-use in wastewater treatment, energy source and landfilling. The following sections discusses these mentioned management options:

#### 7.1.1 Spent biochar as a soil conditioner

If biochar is loaded with nutrients such as ammonium, nitrate, and phosphate, without other toxic pollutants, it can be used as slow-release organic fertilizer into surrounding fields and degraded lands to improve soil fertility and consequently improve crop yield and quality (Yao et al., 2011; Zhang et al., 2013). This is a practical solution which can be used to promote organic farming, and even alleviate agricultural non-point pollution runoff leading to multiple agronomic and environmental benefits (Werner et al., 2018; Kizito et al., 2019; Zheng et al., 2019). However, if biochar is used to adsorb toxic pollutants such as heavy metals and organic pollutants, it cannot be applied to the soil and there will be need to investigate its desorption/regeneration.

### 7.1.2 Re-use of spent biochar in wastewater treatment

The desorption/regeneration properties of biochar have been investigated by several studies in order to determine the economic feasibility of reusing it as an adsorbent. Zhang et al. (2013) reported that the adsorbed uranyl ion U(VI) could be effectively desorbed from the spent biochar using 0.05 mol/L HCL in four times of adsorption-desorption cycles. In another study, food waste biochar which was loaded with dye was desorbed using ethanol. The results showed that the biochar could be used repeatedly without much loss in the total adsorption capacity of the dyes (Parshetti et al., 2014). Despite the feasibility of reuse, the wide source of waste biomass for producing biochar may make the recovery process economically unnecessary. Therefore, the assessment of the economic feasibility of desorption/ regeneration process is needed in the future adsorption process.

#### 7.1.3 Spent biochar as energy source

Apart from regeneration, spent biochar can be used for energy conversion, storage devices, capacitors, and catalyst/catalyst support. Studies have shown that metal impregnated biochar can replace carbon nanotubes and might also be used for tar removal or as supercapacitors (Qian and Chen, 2013). Also, spent biochar can be used for energy production by combustion (Kaetzl et al., 2019).

#### 7.1.4 Landfilling of spent biochar

After re-use, spent biochar can be safely disposed into landfills and can be incinerated. However, knowledge on the disposal of spent biochar using these methods is limited. The stability, potential pollution, effect on the carbon sequestration, and economical feasibility of using these methods to deal with the spent biochar remain unclear necessitating the need for further research in this area.

# 7.2 Constraints, gaps and areas of future research in the use of biochar for onsite wastewater treatment

Although biochar presents a cost effective and innovative technique for the treatment of onsite domestic wastewater, it still has some constraints which affect its applicability. Biochar is known to physically disintegrate in aqueous solution (Bangham and Razouk, 1938); the physical breakdown occurs through several mechanisms. High oxygen to carbon (O:C) ratio biochar. Can dissolve readily when it is exposed to rewetting or saturation cycles (Parr et al., 1931). Water and water vapor absorption may put stress on the physical structure of biochar due to exothermic graphite sheet swelling. The aforementioned mechanisms lead to the swelling and expansion of biochar's physical structure which paves way for further fragmentation (Théry-parisot et al., 2010). Moreover, the mechanical strength of biochar reduces with age (Spokas et al., 2014). Consequently, the prolonged exposure of biochar to stress may lead to the formation of fragments during

Reference	Country	Type of wastewater	Scale	Main findings	Practical implications	
Boano et al. (2021)	Italy	Artificial greywater	Lab-scale	20% biochar additive resulted in the highest removal of 50.7% COD.	The study demonstrated the potentia benefits of incorporating biochar into GW treatment in green walls	
				In terms of BOD <sub>5</sub> , and MBAS, the removal efficiency was 96%, and 71.4%, respectively. 3.1log <sub>10</sub> reduction was recorded for <i>E. coli</i>	GW treatment in green walls	
Moges et al. (2015)	Norway	Student dormitory-bathrooms, laundries, hand washing basins, dish washing machines, and kitchens	On-site	The removal of OM, TN, turbidity and odor by biochar was significant	The research demonstrated a unique opportunity to enhance the performance of decentralized greywater treatment system by using appropriate materials to improve effluent quality	
Perez-mercado et al. (2019)	Sweden		On-farm	Biochar filters for on-farm treatment system did not result significant removal of bacterial and viruses. However, the removal of <i>S. cerevisiae</i> from greywater was significant (>1.0 log <sub>10</sub> CFU)	The findings, as well as certain technical and management factors can help build a systematic strategy for designing biochar filters for on-farm treatment of GW for irrigation	
Dalahmeh et al. (2016)	Jordan	Household greywater	Small-scale: household of 7 members	Biochar filter effectively eliminated 93 percent of $BOD_5$ and 85 percent of TSS, but the removal of <i>E. coli</i> by biochar filter medium was not significant	This study demonstrated the suitability of biochar for onsite greywater treatment system for garden irrigation	
Berger (2012)	Sweden	Artificial greywater	Lab-scale	Biochar filter had a COD removal efficiency of 99%	The performance of biochar filters in removing TP from greywater is an	
				Biochar filters remarkably removed 89% and 86% of TP and PO <sub>4</sub> -P, respectively. The study did not report on pathogens	the removal of OM and phosphorus in GW treatment plants	
Mwenge & Seodigeng (2019)	South Africa	Kitchen, floor cleaning, shower and laundry	Lab-scale	Results from the study found 95%, 76% and 63% removal of TSS, $NO_{3}$ -N and COD, respectively, on kitchen GW and NH <sub>4</sub> -N had a removal efficiency of 85% on GW from bathroom, as the highest removal efficiency of the studied contaminants	The results indicated the suitability of biochar to treat greywater for onsite non-potable reuse purposes such as irrigation, flushing of toilets, <i>etc.</i>	
Hussain et al. (2021)	Belgium	Bathroom, kitchen	Pilot scale, full- scale	Findings from the study indicate that the removal rates of total coliforms and ammonium were 99% and 97%, respectively. Also, turbidity (86%), TSS (67%), and BOD <sub>5</sub> (83%) were significantly removed	This study established that Total Value Wall (TVW) is a sustainable treatment technique for the treatment of greywater and reuse purposes such as toilet flushing	
Sidibe (2014)	Sweden	Artificial greywater	Lab scale	Biochar medium filters was found to be effective in the reduction of <i>Salmonella</i> spp. On the average, <i>Salmonella</i> spp. And bacteriophages log <sub>10</sub> reduction were determined to be 2.72 and 1.47, respectively. COD removal was observed to be 90%, on average	Observations made in the work confirms possibility of the use of biochar to enhance the greywater quality for reuse	
Ndung'u (2020)	Kenya	Male and female students' hostel	Lab scale	Results obtained from this study indicated that biochar produced at a temperature of 500°C had a percentage removal of 60.60% for COD, 89.36% for $K^+$ and 65.43% for Na <sup>+</sup>	The study established that biochar derived from banana stalks can be used for GW treatment, which can be reuse for agricultural purposes	
Dalahmeh et al. (2014)	Sweden	Artificial GW	Lab scale	Charcoal filters efficiently removed 97% $BOD_5$ and 98%, 95% and 84% reductions of N, COD and TSS, respectively, were observed	Suitable performance by charcoal indicates that, it can be used for GW treatment to reach irrigation quality	

#### TABLE 6 Summary of the effect of biochar on household wastewater treatment.

wastewater treatment necessitating the need to develop biochar which can withstand physical breakdown in order to maximize the long-term biochar potential for wastewater treatment. Biochar is a promising material for on-site sanitation treatment due to its excellent properties. Nevertheless, research on this technology is still in its infancy. Further research is required to optimize the usage of biochar to minimise the release of harmful substances into the atmosphere. It is also important to identify the optimum biochar dose and the number of times each dose can be used for faecal sludge management to enhance adsorption of pollutants. Even though there are similarities between biochar and modified carbon, the physicochemical properties of biochar are known to be highly heterogeneous, depending on the type of feedstock and pyrolysis operating conditions. Thus, validated standardized protocols for biochar technology and its subsequent adoption in on-site sanitation treatment systems is still lacking (Gwenzi et al., 2017). Advanced pyrolysis techniques with precise reaction condition control, high energy efficiency, and low environmental impact at a reduced cost are required for increased biochar usage.

In addition, biochar production through pyrolysis technology is inefficient and energy intensive making it less attractive option now. Homagain et al. (2016) carried out life cycle and cost assessment (LCCA) for the production of biochar from wood and posited that biochar production by pyrolysis is a costly investment. This is especially true in a situation where biochar has to be activated/modified to improve its functionality; if pyrolysis is to be used for the production of biochar, then the substrate has to be pyrolyzed first before it is activated and this methodology usually requires multiple treatment steps, high electricity and energy inputs, and corrosive chemicals, which makes it a tedious, expensive, and complex method (Zhou et al., 2019). Thus, efforts should be geared towards more techniques which can improve the functionality of biochar such as simultaneous pyrolysis and activation. One notable option is through the use of wet carbonization methods such as the use of hydrothermal carbonization (HTC) which is used for producing hydrochar. HTC has an added advantage of eliminating pre-drying, which is highly energy intensive and a huge financial load in biomass pretreatment when performed under pyrolysis. Additionally, a higher conversion efficiency (40%-70%), and lower operating temperatures make HTC a more suitable technology than pyrolysis (Kambo & Dutta, 2015) on sustainable point of view. Also, the use of hydrothermal carbonization enables the addition of active reagents to the liquid media during carbonization and activation, to form functional biochars in a one-step reaction (Fu et al., 2018).

In developing economies, environmental groups may consider biochar technology to be futuristic and overly ambitious since there is lack of pilot-scale and industrial level adoption. Presently, studies on biochar for onsite sanitation including treatment of faecal sludge and greywater have been investigated using only laboratory-scale. The effects of biochar for onsite sanitation on the environment is not properly understood. The conditions of real environment are more complicated than the conditions created in the laboratory, resulting in high uncertainties in biochar application on the environment. Thus, more *in situ* experiments are required to ascertain the real effect of biochar on the environment before full-scale applications.

Physical and chemical modification which are predominantly used for biochar activation are energy intensive, expensive and are associated with environmental concerns. Thus, the design of lowcost, highly effective biochar-based adsorbent for on-site sanitation and faecal sludge treatment using biological modification needs to be explored. Due to its high surface area and porous structure, biochar can be employed as a scaffolding material for colonizing and growing biofilms. The microorganisms may adhere to the surface of biochar and develop an extracellular biofilm. In this modification system, while biochar adsorbs other contaminants such as heavy metals due to its porous structure, high surface area and different functional groups, the microorganisms will enhance the degradation of organic contaminants. This synergistic removal effect makes biologically modified biochar effective for on-site sanitation treatment systems. Simultaneously, both organic and inorganic pollutants can be removed *via* biodegradation and sorption processes, respectively.

Finally, the use of biochar for wastewater treatment is widely reported in the literature but its effect in mitigating antimicrobial resistance in household wastewater is largely unknown; the effect of biochar in mitigating the migration of antibiotic resistant genes (ARGs) is still unexplored. Emerging microbial pathogens with ARGs have become a major public health problem. These genes are dangerous because they can easily proliferate through horizontal gene transfer (unresistant bacteria obtain the necessary gene element from the mobile genetic element and become resistant) and when released into waterbodies/ environment, they can alter the microbial community structure and in turn affect the quality of water (Feng et al., 2020). Thus, there is urgent need for detailed investigations to ascertain the potential of biochar in mitigating ARGs present in onsite wastewater. There is need to explore how intrinsic properties of biochar can influence its ability to remove ARGs in onsite wastewater. Also, modifications such as the use of transition metals to increase the amount of persistent free radicals (PFRs) present on biochar surface should be investigated.

#### 8 Conclusion

A critical review of biochar production technologies, properties and its application for the treatment of onsite domestic wastewater is presented in this paper. It is observed that the application of biochar to onsite wastewater treatment systems brings about improvement in the treatment efficiency of these systems. The removal of different contaminants by biochar is achieved through the combination of mechanisms which include adsorption, ion exchange, filtration, electrostatic attraction, biodegradation and pore-filling. The synergistic removal of contaminants is brought about by the properties of biochar together with the microbes found in biofilm trapped on biochar surface. There are still other areas where further research is required in the application of biochar for the treatment of onsite domestic wastewater. There is need to research on the validation of standardized protocols for biochar production and scaling up of biochar production from laboratory scale to fullscale. Further research is also needed to enhance biochar properties and its subsequent potential for the removal of AMR/drug resistance and emerging pollutants in domestic wastewater.

#### Author contributions

CM: Conceptualization; methodology; software; formal analysis; investigation; writing-original draft preparation; visualization. PO: Conceptualization; methodology; software; formal analysis; investigation; writing-original draft preparation; visualization. AN: Writing-review and editing. SL: Formal analysis; investigation; writing-review and editing. SS: Formal analysis; investigation; writingreview and editing; visualization. OI: Conceptualization; formal analysis; investigation; writing-review and editing; visualization; supervision. MM: Conceptualization; methodology; software; formal analysis; investigation; resources; writing-original draft preparation; writing-review and editing; visualization; supervision; project administration. All authors read and approved the final manuscript.

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#### Conflict of interest

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