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Review article

Can biochar be an effective and reliable biostimulating agent for the remediation of hydrocarbon-contaminated soils?

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ABSTRACT

Petroleum hydrocarbons represent one of the most common soil contaminants, whose presence poses a significant risk to soil biota and human health; for example, in Europe, hydrocarbon contamination accounts for more than 30% of contaminated sites. The use of biochar as a proposed alternative to the conventional remediation of soil contaminated with petroleum hydrocarbons has gained credence in recent times because of its cost-effectiveness and environmentally friendly nature. Biochar is a carbonaceous material produced by heating biomass in an oxygen-limited environment at high temperature. This review provides an overview of the application of biochar to remediate petroleum hydrocarbon-contaminated soils, with emphasis on the possibility of biochar functioning as a biostimulation agent. The properties of biochar were also examined. Furthermore, the mechanism, ecotoxicological impact and possible factors affecting biochar-based remediation are discussed. The review concludes by examining the drawbacks of biochar use in the remediation of hydrocarbon-contaminated soils and how to mitigate them. Biochar impacts soil microbes, which may result in the promotion of the degradation of petroleum hydrocarbons in the soil. Linear regression between bacterial population and degradation efficiency showed that R^2 was higher (0.50) and significant in treatment amended with biochar or both biochar and nutrient/fertiliser ($p < 0.01$), compared to treatment with nutrient/fertiliser only or no amendment ($R^2 = 0.11$). This suggest that one of the key impacts of biochar is enhancing microbial biomass and thus the biodegradation of petroleum hydrocarbons. Biochar represents a promising biostimulation agent for the remediation of hydrocarbon-contaminated soil. However, there remains key questions to be answered.

1. Petroleum contamination of soils

The widespread and increased use of petroleum hydrocarbons and derivatives in society makes its release into the environment inevitable (Sarkar et al., 2005). A recent BP report showed that global consumption continued to increase by 0.83–3.19% yearly between 2009 and 2019 (British Petroleum, 2020). Globally, soil contamination is one of the major environmental problems confronting modern society and hindering sustainable development (Hou and Al-Tabbaa, 2014; Mao et al., 2015). Petroleum hydrocarbons represent one of the most common soil contaminants; for example, 30–40% of the 80,000 estimated contaminated sites in Australia are contaminated by petroleum hydrocarbon (Asquith et al., 2012); in Europe, hydrocarbon contamination accounts for more than 30% of contaminated sites (Liedekerke et al., 2014).

Petroleum hydrocarbons are composed of a mixture of simple and complex hydrocarbons (Varjani, 2017) which can be broadly divided into saturates, resins, aromatics, and asphaltenes (Fig. 1). The presence of these contaminants in soils affects plant productivity negatively (Nie et al., 2011). Humans and animals also suffer from direct and indirect exposure to these pollutants (Ossai et al., 2019). Among the hydrocarbons, polycyclic aromatic hydrocarbons, and benzene, toluene, ethylbenzene and xylene (BTEX) have been listed among priority pollutants because of their frequency, toxicity and potential for human exposure (US Department of Health and Human Services, 2020).

The need to remediate hydrocarbon-contaminated soil is inevitable, considering the magnitude of the problem of hydrocarbon pollution and

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the negative impact on human health. A wide range of methods has been investigated to remediate hydrocarbon-contaminated soil (Ossai et al., 2019). However, because of the challenges associated with the use of some of these methods, hydrocarbon pollution persists globally. For example, physicochemical approaches (incineration, soil washing, etc.) are expensive, labour-intensive, and have a negative environmental impact (Xu and Lu, 2010). The challenges associated with the use of existing methods have led to the continued search for newer and more sustainable (environmentally friendly and cost-effective) techniques.

Among the techniques that have gained attention in recent times in soil remediation is the use of biochar (Gomez-Eyles et al., 2013; Zama et al., 2018; Varjani et al., 2019). Although the scientific term "biochar" appears to be recent, its origin is connected to the creation of *Terra preta* by the ancient Amerindian population using slash and char techniques (Lehmann, 2009; Lehmann and Joseph, 2009; Ahmad et al., 2014). Biochar is a dark and porous carbonaceous material, with excellent physicochemical characteristics such as extensive surface area, high porosity, presence of oxygen containing functional groups and favourable pH and cation exchange capacity (CEC) (Chen et al., 2011; Zama et al., 2018; Liu et al., 2018; Yuan et al., 2019). It is produced by heating biomass (organic materials) at high temperature in an oxygen-free/limited environment (Vijayaraghavan, 2019) and can be functionalised based on the application. Biochar application have found relevance in soil amendment, waste management, energy generation and climate change mitigation (Lehmann and Joseph, 2009).

Although there are many reviews that have focused on many other areas of biochar, to the best of our knowledge, no review has specifically focused on biochar for the remediation of hydrocarbon-contaminated soils. This review is relevant and timely because of the adverse impact of this class of pollutants on humans. Additionally, there are conflicting results regarding the efficacy of biochar to remediate petroleum hydrocarbon impacted soils, necessitating the identification of probable factors for these reported discrepancies through critical review. The main objective of this review is therefore, to assess: (i) the state of knowledge in the remediation of hydrocarbon-contaminated soil with biochar; (ii) properties of biochar; (iii) the mechanisms of remediation in biochar-amended soil; (iv) the factors affecting biochar application in the remediation of hydrocarbon-contaminated soil; (v) ecotoxicology and drawbacks of biochar use. The knowledge gained from this review will result in the improved success of biochar-based remediation of hydrocarbon impacted soils.

2. Biochar for the remediation of hydrocarbon-contaminated soil

Early research on biochar focused on its ability to improve the physical, biological or chemical properties of soil (Zama et al., 2018). Biochar gained popularity because of its environmentally friendly nature and because it can be sourced from different low-value raw materials, including waste biomass (Liu et al., 2018). As shown in Table 1, there have been several attempts to remediate hydrocarbon-contaminated soils with biochar derived from different feedstocks. These studies have demonstrated that the application of biochar to contaminated soil has been both beneficial and non-beneficial in terms of the remediation of hydrocarbon-contaminated soil. Kong et al. (2018) studied the effect of 5% (w/w) wheat straw and sawdust biochar on the remediation of polycyclic aromatic hydrocarbon (PAH)-contaminated soil. They found that the application of either biochar significantly enhanced PAH removal, (around 47.9–55.7%) compared to the non-amended treatment (27.7%). Similarly, Aziz et al. (2020) found that the efficiency of diesel degradation was at least two times higher in soils amended with either sewage sludge or vegetable/fruit waste biochar, compared to the non-amended soil (Table 1). Wang et al. (2017) showed that the application of bulrush straw biochar enhanced the degradation of petroleum in the soil with a removal efficiency of 46.9%, compared to the non-amended soil (28.2%). Interestingly, they found that biochar was more effective in TPH removal than the precursor material (bulrush straw) (39.5%). This may be due to the benefecial effect of biochar on soil properties (water holding capacity, nutrient status) and the total bacteria count (Wang et al., 2017). Also, biochar can provide better support for microbial growth compared to the precursor material because of the presence of pore spaces and a high surface area (Wang et al., 2017). A recent study also observed that biochar was more effective than the precursor material (ponderosa pine wood chips) in the degradation of a light oil in contaminated soil, with a concentration of 16,000 mg/kg (Mukome et al., 2020). However, both amendments were comparatively effective in soil contaminated with higher amount of hydrocarbon (21,000 mg/kg).

Other studies have compared the effect of applying biochar and activated carbon to hydrocarbon-contaminated soil (Agarry et al., 2015; Brown et al., 2017; Jia et al., 2017; Tazangi et al., 2020). TPH removal was found to be higher in soil amended with both biochar and fertiliser (44%) compared to soil amended with both activated carbon and fertiliser (29%) (Brown et al., 2017). In other studies, biochar was slightly

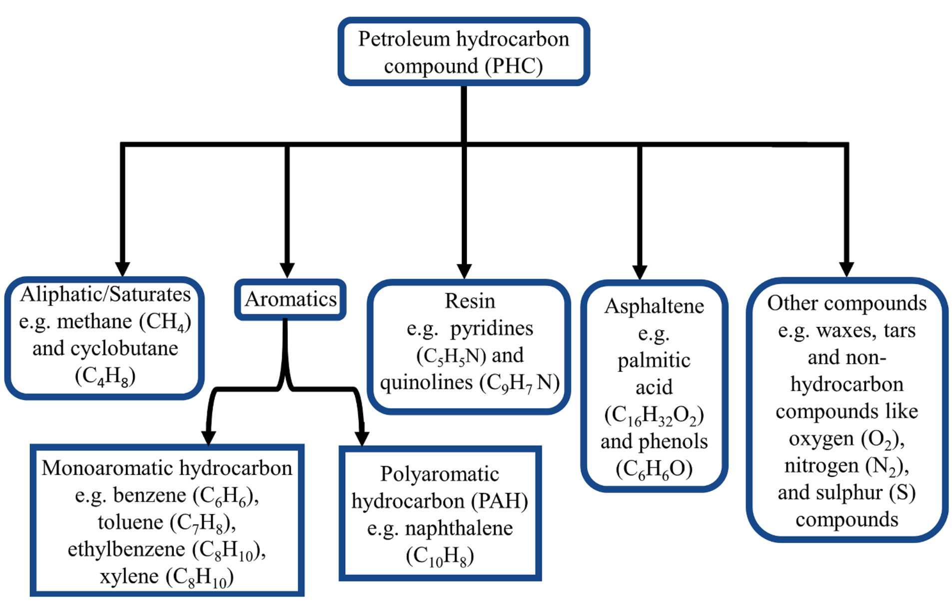

Fig. 1. Classification of petroleum hydrocarbon compounds and examples (Riazi, 2005; Khudur et al., 2018; Ossai et al., 2019).

Table 1
Studies showing the effect of biochar on the remediation of hydrocarbon contaminated soils.

Biomass	Temp. (°C)	Residence time (hour)	Surface Area (m^2/g)	Addition rate (%)[a]	Contaminant	Removal Efficiency (%)		Contaminant concentration (mg/kg)	Time (days)	Soil texture	Reference
						Non-biochar treatment[b]	Biochar treatment[b]				
Birch waste	450	–	49.7	1	Oil	56.0	59.0	47,000	84	Silt loam[c]	(Galitskaya et al., 2016)
Bulrush straw	300	3	–	5	Petroleum	28.2	46.9	9620	56	–	(Wang et al., 2017)
Corn cob	400	4	71.0	2.5	PAH	41.8[d]	39.3[d]	1.193	30	Loamy sandy	(Zhang et al., 2018)
	600	4	296.0	2.5	PAH	41.8[d]	26.9[d]	1.193	30	Loamy sandy	
Hardwood cordwood	400–430	10–12	–	2.5	Diesel	52.5	52.8	95,333	90	Loam	(Uyizeye et al., 2019)
Maize straw	500	–	36.4	1	PAH	39.3[d]	47.8[d]	11.85	21	Silt loam[c]	(Li et al., 2019c)
Oak leaves	500	12	–	0.1	Oil	9.4[e]	26.3[e]	16,790	50	Sandy loam[c]	(Abbaspour et al., 2020)
Ponderosa pine	900	–	127.0	5	Oil	39.4[de]	68.2[de]	24,000	60	Sand/silt/clay mix	(Mukome et al., 2020)
	900	–	127.0	10	Oil	39.4[de]	61.1[de]	24,000	60	Sand/silt/clay mix	
Plantain peels	350	5	–	20[f]	Oil	21.8	44.4–65.1	100,000	28	–	(Agarry et al., 2015)
Poultry manure	400	4	–	1	Petroleum	22.1	23.1	40,000	140	loam	(Barati et al., 2017)
			–	1	Petroleum	16.7	17.2	60,000	140	Sandy loam + Loam	
			–	1	Petroleum	13.0	13.8	80,000	140	Sandy loam + Loam	
Rice straw	500	–	1053.0	2	Petroleum	61.2[e]	77.8–84.8[e]	16, 300	180	Clay loam	(Qin et al., 2013)
	600	4	211.9	2	PAH	2.9[e]	50.1[e]	857	180	Loamy sandy	(Zhang et al., 2020)
Sawdust	300	3	4.8	5	PAH	27.7	47.9[d]	3596.4	84	Light clay	(Kong et al., 2018)
	500	3	28.5	5	PAH	27.7	55.7[d]	3596.4	84	Light clay	
Sewage sludge	550	2	46.9	5	Diesel	35.9	75.6	2.91[g]	180	–	(Aziz et al., 2020)
Sewage sludge digestate	350	0.25	–	5	Oil	9.8[d]	10.5[d]	6100	30	Loam	(Gielnik et al., 2019)
	350	0.25	–	5	Motor oil	25.4[d]	24.5[d]	32,600	30	Fine sandy	
Spent mushroom	550	3	109.3	5	Petroleum	8.7[e]	29.9[e]	47,700	60	–	(Zhang et al., 2019)
Vegetable/fruit waste	550	2	52.5	5	Diesel	35.9	72.3	2.91[g]	180	–	(Aziz et al., 2020)
Walnut shell	250	4	1.7	2.5	PAH	41.8[d]	30.3[d]	1.2	30	Loamy sandy	(Zhang et al., 2018)
	400	4	8.6	2.5	PAH	41.8[d]	35.9[d]	1.2	30	Loamy sandy	
	600	4	315.0	2.5	PAH	41.8[d]	12.4[d]	1.2	30	Loamy sandy	
Wheat straw	500	3	33.5	5	PAH	27.7	53.1[d]	3596.4	84	Light clay	(Kong et al., 2018)
	300	3	6.0	5	PAH	27.7	48.3[d]	3596.4	84	Light clay	
	450	1	6.9	1	Oil	36.1[e]	33.5[e]	7719	90	–	(Han et al., 2016)
–	–	–	–	5	PAH	58.0	61.4	2.2	77	–	(Bao et al., 2020)
–	–	–	10–12	5	Oil	43.0[e]	44.0[e]	10803–11474	110	Silty loam	(Brown et al., 2017)

Oil in this table was used to cover the terms oil and crude oil as used in papers.
[a] w/w, unless stated otherwise.
[b] Unless otherwise stated with ([e]), non-biochar treatment refers to study with no amendment added to the soil, while biochar treatment refers to soil with only biochar added.
[c] Soil texture was estimated using the soil texture triangle.
[d] Data was extracted from figure using GetData Graph Digitizer 2.26 software.
[e] Nutrient/fertiliser was amended to both the non-biochar and biochar treatment.
[f] Gram (g).
[g] g/100 kg.

more efficient than activated carbon, although higher removal efficiency was observed with both amendments in comparison to non-amended soil (Jia et al., 2017; Agarry et al., 2015; Tazangi et al., 2020). For example, the removal efficiency of biochar was between 44.4 and 68.5%, while for activated carbon, removal efficiency was between 40 and 66% (Agarry et al., 2015). Similarly, Jia et al. (2017) reported that the difference between both amendments was insignificant. Although biochar and activated carbon share some similarities in terms of adsorptive properties (Jia et al., 2017), the higher TPH removal in the biochar treatment compared to activated carbon may suggest the additional biological role of biochar. Agarry et al. (2015) reported a higher hydrocarbon-degrading bacterial population in the biochar treatment compared to the activated carbon. Also, comparing the economic cost, biochar represents a more cost-effective option. In terms of performance-based amendment cost, Brown et al. (2017) showed that the amendment cost to remediate 50% of initial TPH concentration was higher in soil amended with both activated carbon and fertiliser ($44/$m^3$ soil) than soil amended with both biochar and fertiliser ($12/$m^3$ soil).

Qin et al. (2013) examined the effect of 2% (w/w) rice straw-derived biochar on the remediation of petroleum-contaminated soil. They observed that there was no difference in the TPH removal between the nutrient-amended soil and the treatment amended with both biochar and nutrient (biochar added at day 0) until Day 60. The removal efficiency was significantly higher in the soil amended with both biochar and nutrient (77.8%) compared to the nutrient-amended soil (61.2%) at day 180 (Qin et al., 2013). The result of this study showed that there was a time lag before a significant difference in TPH removal was observed between the nutrient-amended treatment and soil amended with both biochar and nutrient. This suggests that short-term studies on the effect of biochar may be inadequate to understand the importance of biochar in soil remediation. In contrast, Galitskaya et al. (2016) observed that the addition of biochar significantly accelerated the remediation of crude oil-contaminated soil at the early stage, compared to the non-amended treatment. However, there was no significant difference after 84 days. A possible explanation for the observed discrepancy at the early stage may be because nutrients were added every two weeks in the former study (Qin et al., 2013), while no nutrient was added to the latter (Galitskaya et al., 2016). This explains the comparable remediation efficiency in the early stage observed in the former between the nutrient-amended treatment and the soil amended with both biochar and nutrient. The significant discrepancies in TPH removal efficiency after the early stage in the two studies may be attributed to differences in biochar production (feedstock and residence time) and soil contaminant-related (oil composition) factors, in addition to the differences in supplementary nutrient.

Biochar has also been applied to remediate hydrocarbon-contaminated frozen soil (−5 °C). Karppinen et al. (2017b) found that removal of the C_{16} – C_{34} petroleum fraction was higher in soil amended with both 3% (w/w) biochar (meat and bonemeal) and nitrogen fertiliser (28%) in comparison to soil amended with nitrogen and phosphorus fertiliser (approximately −3%). However, in the treatment with both biochar and nitrogen fertiliser, degradation of the C_{10} – C_{16} petroleum hydrocarbon fraction was no greater when compared to the nitrogen and phosphorus fertiliser treatment. Han et al. (2016) applied both wheat straw biochar and fertiliser to petroleum-contaminated soil and observed that compared to the fertiliser control (36.1%), the application of both biochar and fertiliser was detrimental to TPH removal (33.5%). Mukome et al. (2020) suggested that the low surface area and high ash content of the biochar could have contributed to the negative result in this study. However, Zhang et al. (2020) in their study suggested that although the surface area of rice straw produced at 400 °C was not large (6.5 m^2/g), the higher biodegradation efficiency of PAH (22.6–51.1%, except naphthalene) occurred due to the high ash content in the biochar. These contrasting views may be due to the differences in the soil contaminant. Ash content reflects the nutrient status of the biochar (Zhu et al., 2017), and may not be the factor responsible for the ineffectiveness of biochar in the study of Han et al. (2016). In another study, the effect of poultry manure biochar on the remediation of soil contaminated with different concentrations of hydrocarbon (40,000, 60,000 and 80,000 mg/kg) was examined (Barati et al., 2017, 2018). The authors observed that the application of biochar to unplanted soil did not significantly improve the remediation efficiency compared to the unplanted soil with no amendment; at a hydrocarbon concentration of 80,000 mg/kg, the removal efficiency in the unplanted soil amended with biochar was 13.8%, while the removal efficiency in the unplanted soil with no biochar was 13.0% (Barati et al., 2017).

Most studies have been carried out in the greenhouse, batch culture, or the laboratory. However, Karppinen et al. (2017a) examined the effect of biochar on the degradation of hydrocarbon contaminants in two farm field studies (Iqaluit and Whitehorse) and a laboratory study under frozen conditions. They reported that compared to the fertiliser-amended soil, the application of both biochar and fertiliser amendment did not enhance the removal of the soil contaminant under field conditions; however, a small increase in the degradation of C_{10} – C_{16} petroleum hydrocarbon fraction was observed over time. Under laboratory conditions, biochar performed better than in the field. This may be because unlike field studies, the environmental conditions (abiotic and biotic) can be controlled in the laboratory studies. Similarly, Ikiogha et al. (2019) evaluated the remediation efficiency of cow bone biochar on a 1.5 × 1.5 m area in a field study. Their result showed that after 8 weeks, TPH removal was considerably higher in the biochar treatment (above 50%) compared to non-amended treatment. Interestingly, the authors found that the results of biochar amendment on the contaminated soil was comparative with that of NPK fertiliser.

3. Properties of biochar

Biochar is suitable for remediation of contaminated soil because of its unique physicochemical properties. The changes in soil properties and the responses of microbes/biota in the soil are determined by the physicochemical properties of the biochar applied to the soil (Lehmann et al., 2011; Zhu et al., 2017). These properties are mainly a function of the biomass type and pyrolysis temperature (Table 2).

3.1. Surface area and porosity

The porous nature of biochar often provides a habitat for soil microbes (Zhu et al., 2017). Biochar surface area and porosity have been reported to link with a wide range of other properties of biochar (Leng et al., 2020). For example, Zhang and You (2013) found that the total pore volume (TPV) positively correlated with the water holding capacity of biochar, while both the average pore diameter and TPV influenced the water absorption rate of the biochar. Surface area and porosity are influenced by pyrolysis temperature (Liu et al., 2018). Surface area generally increases with increasing pyrolysis temperature. Wang et al. (2016) found that with increasing the temperature of maize straw-derived biochar from 250 °C to 600 °C, the surface area of the biochar increased from 110.2 m^2/g to 513.4 m^2/g. However, this increase reaches a plateau where further increase in temperature led to a decrease in the surface area (Chen et al., 2019). For example, Chun et al. (2004) observed that with increasing temperature, the surface area of wheat residue-derived biochar increased from 116 m^2/g at 300 °C to 438 m^2/g at 600 °C and decreased again to 363 m^2/g at 700 °C. The reasons for this decrease have been explained (Brown et al., 2006; Li et al., 2017; Weber and Quicker, 2018). Biochar derived from lignocellulosic biomass (agricultural, forestry and herbaceous) generally have higher surface areas in comparison to manure/litter and sludge-derived biochar, although a low surface area can be also found in biochar produced from lignocellulosic biomass (Table 2). The pore volume of biochar also increases with pyrolysis temperature; however, in some cases, there is an irregularity or decrease in the pore volume of biochar with increasing

Table 2
Influence of feedstock and pyrolysis temperature on some properties of biochar (Ahmad et al., 2014; Ahmed et al., 2016; Önal et al., 2014; Yang et al., 2017, 2020; UC Davies Biochar Database, 2021).

Feedstock categories	Pyrolysis Temp. (°C)	Surface Area (m^2/g)	pH	C (%)	H (%)	O (%)	N (%)	Ash (%)
Manure/litter[a]	<300	2.6–8.7	6.9–8.2	31.10–47.46	1.35–7.80	20.70–47.80	1.25–4.10	14.0–35.7
	300–399	0.9–92.6	6.5–9.7	25.20–66.30	1.40–6.70	8.60–51.50	1.30–7.80	7.7–51.2
	400–499	3.7–159.3	7.5–10.6	9.80–71.50	0.50–3.71	3.60–50.10	0.53–5.41	9.3–75.0
	500–599	3.9–150.0	7.8–11.0	23.00–74.30	0.30–3.44	0.52–58.40	0.60–5.50	10.4–67.5
	600–699	3.4–200.8	9.3–11.5	8.70–76.00	0.13–2.60	<0.01–40.27	0.33–4.24	10.6–69.6
	700–799	4.1–186.5	9.5–11.8	20.64–56.67	0.30–1.98	0.01–58.30	0.86–4.16	24.2–72.4
	800–899	63.0	11.4	42.10–43.60	0.80–1.10	13.50–21.70	1.10–1.60	51.8
	≥900	–	–	–	–	–	–	–
	<300–≥900	**0.9–200.8**	**6.5–11.8**	**8.70–76.00**	**0.13–7.80**	**<0.01–58.40**	**0.33–7.80**	**7.7–75.0**
Lignocellulose[b]	<300	0.4–139.7	4.7–8.0	37.30–67.10	2.43–10.50	26.43–48.30	0.04–4.30	0.3–18.5
	300–399	0.02–388.2	4.2–10.5	39.10–84.19	1.34–7.43	7.44–43.14	0.00–10.21	0.3–44.0
	400–499	0.1–551.7	4.6–10.5	33.20–94.00	1.21–15.10	5.26–36.10	0.00–4.04	0.4–58.0
	500–599	0.0–500.9	4.8–12.1	24.60–91.60	0.15–8.50	0.00–40.60	0.00–7.76	0.6–73.7
	600–699	0.4–548.9	3.1–11.6	7.91–94.61	0.60–3.24	0.40–59.14	0.00–4.80	1.0–64.2
	700–799	2.3–907.4	6.6–12.6	33.50–97.30	0.46–2.48	0.50–22.2	0.00–7.40	1.1–58.8
	800–899	2.0–652.0	6.2–11.5	29.17–97.40	0.25–1.71	0.50–17.29	0.10–2.21	3.9–60.8
	≥900	7.1–714.0	9.7–10.1	50.00–92.85	0.42–1.00	1.55–44.00	0.47–1.60	8.4–70.0
	<300–≥900	**0.0–907.4**	**3.1–12.6**	**7.91–97.40**	**0.15–15.10**	**0.00–59.14**	**0.00–10.21**	**0.3–73.7**
Sludge	<300	4.2	6.9–7.9	28.30–45.93	5.67	46.80	1.51–3.80	31.5–48.6
	300–399	4.0–4.9	6.0–8.8	21.20–60.00	1.00–4.35	11.16–33.81	0.30–7.10	37.4–58.1
	400–499	0.1–126.4	6.6–8.8	8.50–31.80	0.90–3.40	6.40–24.30	0.30–4.96	3.0–83.7
	500–599	3.2–71.6	7.1–10.0	9.80–30.60	0.40–3.30	5.91–22.70	0.20–4.32	46.2–74.2
	600–699	12.2–114.4	6.7–11.5	8.40–24.76	0.34–1.50	2.00–21.20	0.10–3.54	7.3–88.8
	700–799	18.3–145.6	7.7–11.1	8.10–59.88	0.21–0.89	0.60–37.89	0.20–3.08	66.7–90.7
	800–899	19.1–48.5	12.2	16.20	0.03–0.72	1.24–3.64	0.50–2.50	68.3–83.9
	≥900	34.2–67.6	10.2–12.2	15.92	0.11–0.64	1.16–2.44	0.53–1.24	71.2–88.1
	<300–≥900	**0.1–145.6**	**6.0–12.2**	8.10–60.00	**0.03–5.67**	**0.60–46.80**	**0.10–7.10**	**3.0–90.7**

(-: Not reported).
[a] Manure used here in some studies consist of bulking agents like sawdust, rice husk, wood.
[b] Agricultural, forestry and herbaceous feedstock.

pyrolysis temperature (Ahmad et al., 2014; Ahmed et al., 2016; Al-Wabel et al., 2018). Li et al. (2018) observed no change in pore volume when pyrolysis temperature increased from 200 °C to 300 °C. However, pore volume increased from 0.171 to 0.174 when temperature was increased from 300 °C to 400 °C. Further temperature increases to 500 °C, 600 °C and 700 °C resulted in a decrease, increase and decrease, respectively (Li et al., 2018).

3.2. pH

Apart from being an important property for agricultural applications, pH is a property that distinguishes chars produced through pyrolysis and hydrothermal carbonisation (Weber and Quicker, 2018). Biochar generally has a neutral or basic pH (Ahmad et al., 2014) although acidic pH has also been reported (Qi et al., 2017; Nguyen et al., 2010). Zhao et al. (2013) studied the physicochemical properties of biochar produced from different feedstock at different temperatures. They reported that pyrolysis temperature has a greater influence on biochar pH than the feedstock type (Zhao et al., 2013). The pH of biochar derived from manure/litters, sludge and lignocellulosics (agricultural, forestry and herbaceous) generally increases with pyrolysis temperature (Table 2). Srinivasan and Sarmah (2015) observed that the pH of green waste biochar increased from 5.3 at 350 °C to 8.4 at 550 °C. However, the pH of biochar has also been found to either decrease with increasing temperature or is irregular with temperature (Chen et al., 2015; Figueredo et al., 2017). For example, the pH of eucalyptus biochar decreased from 6.2 to 5.9 when pyrolysis temperature was increased from 350 °C to 500 °C (Figueredo et al., 2017). Zheng et al. (2013) and Jin et al. (2016) observed a positive correlation between biochar pH and ash content ($p < 0.01$). Zheng et al. (2013) suggested that the minerals of biochar may be the major factor responsible for the alkaline nature of the biochar.

3.3. Ash content and mineralogical content

The ash content/fraction constitutes a major component of biochar (Brewer and Brown, 2012; Lehmann et al., 2011). It is one of the important properties of biochar because the ash content is a reflection of the nutrient status of biochar (Zhu et al., 2017). Biochar contains both macro- and micro-nutrients that play a vital role in the soil food web (Lehmann et al., 2011). Ash content is affected by both the pyrolysis temperature and feedstock used (Laghari et al., 2016); however, it is more dependent on the feedstock than temperature (Zhao et al., 2013). Li et al. (2019a) determined that the ash content of biochar produced from herbaceous, biosolids, animal and wood feedstock increased linearly with temperature in all biochar groups. However, ash content has been found to decrease with increasing temperature or to be inconsistent with temperature (Figueredo et al., 2017; Zhang et al., 2017; Pariyar et al., 2020). In terms of the feedstock variation, higher ash content was found in biosolids and manure-derived biochar among the 4 feedstock categories, while herbaceous biochar had the lowest proportion (Li et al., 2019a). Similar to the ash content, the mineralogical content is also affected by the pyrolysis temperature and feedstock, but more sensitive to feedstock (Zhao et al., 2013).

3.4. Elemental analysis

Biochar is composed mainly of C, H, O and sometimes N (Liu et al., 2015b; Yuan et al., 2019). The exact content of each of these bulk elements is dependent on the biomass and pyrolytic condition used (Ahmad et al., 2014; Liu et al., 2015b). The C content of biochar, based on Table 2 is within the range of 8.7–76.0%, 8.1–60.0% and 7.9–97.4% for manure/litters, sludge and lignocellulosic (agricultural, forestry and herbaceous)-derived biochar, respectively. The C content is generally lower in biochar produced from sludge and manure/litters compared to biochar derived from agricultural, forestry and herbaceous biomass (Table 2). However, a lower C content of 7.9% and 15.1% were observed in corn stover-derived biochar with particle diameters of >500 μm and 300–500 μm, respectively (Jośko et al., 2013). The C content was higher in the biochar fraction with a diameter of <300 μm (39.3%) and the whole biochar (41.6%) (Jośko et al., 2013). This suggests the influence of particle size on the C content of biochar. Apart from the feedstock type, the C content is also influenced by pyrolysis temperature (Table 2). Hydrogen content, based on Table 2 varies between 0.13–7.8%, 0.03–5.7% and 0.15–15.1% for manure/litters, sludge and lignocellulosic (agricultural, forestry and herbaceous)-derived biochar, respectively. The H content is less dependent on the feedstock type and more dependent on the pyrolysis temperature (Li et al., 2019a). Generally, the H content decreases as temperature increases (Table 2). This is more evident in biochar derived from sludge and manure/litters than those derived from agricultural, forestry and herbaceous biomass (Table 2). Figueredo et al. (2017) observed that the H content of sugar cane increased from 1.0% at 350 °C to 2.7% at 500 °C. As can be seen in Table 2, the O content of biochar varied from <0.01–58.4%, 0.6–46.8% and 0.0–59.1% in biochar derived from animal manure/litter, sludge and lignocellulosic (agricultural, forestry and herbaceous) biomass, respectively. However, Figueredo et al. (2017) found that the O content in biochar derived from sewage sludge at 350 °C and 500 °C was as high as 75.2% and 70.8%, respectively. Like the H content, O content is more influenced by pyrolysis temperature than feedstock type (Li et al., 2019a). Oxygen content also generally decreases as temperature increases, but it is more pronounced in sludge derived biochar (Table 2). The decrease in O and H with increasing temperature have been suggested to occur due to breakdown of the oxygenated bond, reactions involving H_2O loss, as well as the liberation of low molecular weight by-products that contains O and H (Chatterjee et al., 2020). The N content varies from 0.3–7.8%, 0.1–7.1% and 0.0– 10.2% in biochar derived from manure/litter, sludge and lignocellulosic (agricultural, forestry and herbaceous) biomass, respectively (Table 2). The feedstock type determines the N content, while the pyrolysis temperature has an insignificant impact on N (Ahmad et al., 2014). However, Li et al. (2019a), based on the results of their analysis of biochar derived from herbaceous, biosolids, animal and wood feedstock reported that N content was heavily dependent on the pyrolysis temperature.

3.5. Functional groups

Biochar contains a wide range of functional groups on its surface which may include carbonyls, hydroxyls, phenols, carboxyl, nitriles, peptides, quinones, lactones and pyrones (Zama et al., 2018). The functional group is one of the properties of biochar that affects the physicochemical properties of contaminated soils (Yuan et al., 2019). Functional groups also play a role in modifying microbial habitat and supplying nutrients to microbes (Zhu et al., 2017). The abundance of functional groups in biochar is influenced by the pyrolysis conditions and biochar feedstock (Li et al., 2017). For example, biochar produced from slow pyrolysis is dominated by the C—H functional group, while the carboxylic and hydroxyl groups are most abundant in fast pyrolysis-derived biochar (Zama et al., 2018). Because of the higher degree of carbonisation in biochar produced at high temperatures, the abundance of the functional groups decreases with temperature increase (Li et al., 2017). Furthermore, the abundance of the carboxylic, amino and hydroxyl groups can decrease with temperature because the O/C, N/C, and H/C atomic ratio decreases with temperature (Li et al., 2017).

4. Mechanism of biochar-based remediation of petroleum hydrocarbons in the soil

In terms of the application of biochar to hydrocarbon-contaminated soil during remediation, studies have shown/speculated that biochar functions as a biostimulator (Kong et al., 2018; Mukome et al., 2020) or a sorbent (Wei et al., 2020a). As a biostimulator, biochar enhances the degradation of soil contaminants by stimulating soil microbes, while as a sorbent, biochar immobilises soil contaminants by reducing their chemical transport, leachability and bioavailability (Liu et al., 2018). What determines the mechanism in which biochar functions in the soil is still unknown. However, Chen et al. (2008) showed that adsorption was the dominant mechanism for higher temperature biochar, while partitioning played the dominant role for low temperature biochar. Under the partition mechanism, contaminants are bioavailable to microbes (Xia et al., 2010). Pyrolysis temperature may be a determining factor because the sorption capacity and nutrient status of the biochar is dependent on temperature. At higher temperatures, biochar may exhibit sorption because of higher sorption capacity (pore volume and surface area) (Beesley et al., 2011; Song et al., 2017). In contrast, because of the improved nutrient status at lower temperatures, biochar may function more as a biostimulator than a sorbent (Song et al., 2017). While evidence from some previous studies supports this claim (Song et al., 2017; Kong et al., 2018; Wei et al., 2020a), the findings from a recent study suggest that the pyrolysis temperature may not be the main factor (Mukome et al., 2020). There is a need for future studies to identify the factors that determine the mechanism of biochar function in contaminated soil, so that biochar application can be directed towards biostimulation rather than sorption. Since this review focuses on the role of biochar in the degradation of hydrocarbon-contaminated soil, the next sub-section will only examine how biochar operates as a biostimulator.

4.1. How does biochar acts as a biostimulator?

Microorganisms are instrumental in the degradation of hydrocarbon-contaminated soil. This section examines how biochar influences their activity in the soil to degrade the soil contaminants. Fig. 2 provides an overview of the proposed mechanism of biochar role in the remediation of hydrocarbon-contaminated soil.

4.1.1. Effect of biochar on soil microbes

The application of biochar to soil has been shown to improve soil physicochemical properties (Gul et al., 2015); this improvement in soil properties is a key factor responsible for the ability of biochar to stimulate soil microbial activity and increased biodegradation efficiency in biochar-amended soils (Hussain et al., 2018; Kong et al., 2018; Aziz et al., 2020; Tazangi et al., 2020; Zhang et al., 2020). However, in some studies, biochar application did not affect soil properties or the changes in soil properties did not influence the efficiency of hydrocarbon degradation (Song et al., 2017; Zhang et al., 2018, 2020). The influence of biochar on the properties of hydrocarbon-contaminated soil has not been widely studied. Lawson et al. (2019) and Zhang et al. (2019) observed that soil pH was higher in soil amended with biochar only or biochar with nutrient, in comparison to treatment with nutrient only or no amendment. For example, soil pH was found to be 9.31 in soil amended with both biochar and nutrient after 60 days of incubation, compared to a pH of 7.28 in nutrient-amended treatment (Zhang et al., 2019). The increase in pH following biochar application occurs because of the alkaline nature of biochar and because the biochar surface contains negatively charged functional groups (phenolic, carboxyl, and hydroxyl), which bind H^+ from the soil solution (Brewer and Brown, 2012; Gul et al., 2015). As soil pH increased in the soil amended with biochar or both biochar and nutrient, it was observed that the population of hydrocarbon utilising bacteria also either increased or significantly increased compared to the treatment with nutrient alone or no amendment (Lawson et al., 2019; Zhang et al., 2019). However, the addition of biochar to other contaminated soils slightly increased/decreased or showed no significant effect on soil pH (Song et al., 2017; Wang et al., 2017; Uyizeye et al., 2019). These different observations are likely due to the influence of many factors including biochar and soil properties (see Section 5).

Biochar feedstock is composed of mineral nutrients that remain in the biochar even after pyrolysis (Gorovtsov et al., 2019). Furthermore, biochar can also absorb and retain nutrients from the soil because of their surface chemistry (Anyika et al., 2015). These nutrients (inherent and adsorbed nutrients) can be released to the soil as slow-release fertiliser (Ding et al., 2016; Zhu et al., 2017), thus making more nutrients available to the soil microbes. Also, nutrients can be directly utilised by

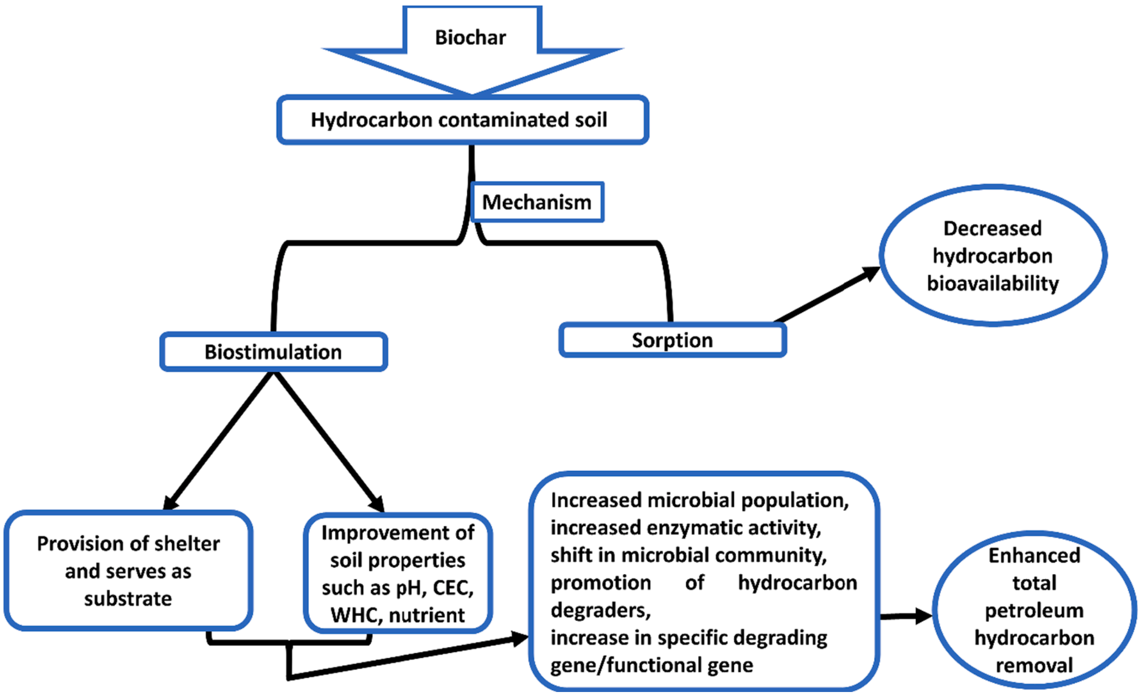

Fig. 2. Overview of the proposed mechanism and interaction of biochar in the remediation of hydrocarbon-contaminated soil. CEC: Cation Exchange Capacity; WHC: Water Holding Capacity (Liu et al. 2015a; Wang et al., 2017; Kong et al., 2018; Liu et al., 2018; Hussain et al., 2018; Lawson et al., 2019; Aziz et al., 2020; Tazangi et al., 2020; Zhang et al., 2020).

microbes attached to the biochar surface (Anyika et al., 2015). The nutrient content in petroleum-contaminated soil has been found to be higher in soils amended with biochar or both biochar and nutrients than in soils with nutrient only or no amendment (Wang et al., 2017, 2018; Aziz et al., 2020). The promotion of the growth and activities of soil biota in biochar-amended soil has been linked to an increase in soil nutrients following biochar addition (Palansooriya et al., 2019). This may explain why the bacterial population was significantly higher in the biochar treatment (7.5 $\log_{10}$ CFU/g) compared to the non-amended soil (approximately 6.0 $\log_{10}$ CFU/g) (Wang et al., 2017). Wang et al. (2018) observed a significant correlation between the nutrient status and TPH removal, which showed that an increase in soil nutrients contributed to increased TPH removal in soil amended with both biochar and nutrient. In another study, the concentration of available phosphorus and total nitrogen was found to increase and decrease, respectively following biochar application (Lawson et al., 2019). The authors believed that the increase in available phosphorus could be because of soil pH increase in the biochar treatment. A decrease in nitrogen occurred because of immobilisation resulting from a higher C:N ratio (Brewer and Brown, 2012; Lawson et al., 2019). Among other explanations, Zhang et al. (2020) suggested that enhanced PAH biodegradation in treatment with both biochar and fertiliser was likely due to an increase in soil mineral nutrients.

Lawson et al. (2019) found that the soil cation exchange capacity (CEC) increased following the application of biochar. Song et al. (2017) also found that the CEC was slightly higher after 24 weeks in the biochar treatment (15.5–16.1 cmol/kg), compared to non-amended soil (15.4 cmol/kg). The biochar in this study reduced the PAH toxicity and bioavailability in the soil instead of promoting their degradation. The water holding capacity has also been reported to be significantly higher in hydrocarbon-contaminated soil amended with biochar only or both biochar and nutrients relative to treatment with nutrient alone or no amendment (Wang et al., 2017, 2018). The increase in water holding capacity is due to an increase in soil porosity, reduction in bulk density and evapotranspiration following biochar application to the soil (Gul et al., 2015). Wang et al. (2018) found that soil porosity and bulk density in petroleum-contaminated soil was significantly lower and higher, respectively in nutrient-amended soil compared to soil amended with both biochar and nutrient. The results of their study showed that bulk density, soil porosity and water holding capacity exhibited a significant correlation with TPH removal and microbial population.

Kong et al. (2018) asserted that the porous structure and high surface area of biochar contributed to higher PAH removal efficiency in soil amended with biochar. Biochar can serve as a habitat for soil microbes and can also protect microbes from predators. According to Gul et al. (2015), the biochar surface and pores can support the growth of soil microbes, due to the presence of dissolved organic compounds (DOC) and nutrients released from the biochar, as well as a surface charge on the biochar (which allows for the immobilisation of microbial cells, chemical ions and compounds). Uchimiya et al. (2013) revealed that biochar contains structures similar to humic- and fulvic-like soil organic carbon. These observations suggest that biochar can be a suitable habitat for soil microbes. One of the reasons suggested by Zhang et al. (2020) for higher PAH biodegradation in soil amended with both biochar and inorganic fertiliser was that biochar enhanced the transfer of nutrients and water from the soil to the biochar pores. The resultant effect of this was the creation of a habitat that supported microbial growth and activity (Zhang et al., 2020). Jaafar et al. (2015) reported that biochar applied to the soil served as a potential habitat for soil microbes because of their high porosity and surface areas. Additionally, biochar can serve as a refuge for soil microbes from predators (Warnock et al., 2007; Thies and Rillig, 2009). Targeted experiments that focus on understanding how biochar provides protection/shelter for microbes in hydrocarbon-contaminated soil are required.

Young biochar has also been reported to serve as a source of energy for soil microbes within a short timeframe due to the presence of labile C (Smith et al., 2010). This observation is based on the findings from uncontaminated soil and whether this will still apply in hydrocarbon-contaminated soil is uncertain because microbes may not be able to consume both C-substrates simultaneously. It is possible that sequential consumption of C substrate may occur due to the creation of a hierarchy of C-consumption (Dal et al., 2002). Preference will be given by the organism for a carbon source that is more labile and energetically favourable (Dal et al., 2002). The biochar labile C will likely be preferred by the organism because aromatic hydrocarbon degradation genes have been reported to be downregulated in the presence of other alternate carbon sources (Mason, 1994; Dal et al., 2002; Kamath et al., 2004). Although there is no valid information on biochar studies in hydrocarbon-contaminated soils to validate this claim, findings from other carbon sources suggest this possibility (Mason, 1994; Dal et al., 2002). For example, Dal et al. (2002) reported that the consumption of aromatic compounds (p-hydroxybenzoic acid) by *Acinetobacter* sp. strain ADP1 was delayed until the second logarithmic growth phase in the presence of alternate C sources (acetate and succinate). In contrast, when only the aromatic compound (p-hydroxybenzoic acid) was present, there was clear evidence that the aromatic compound was consumed by the organism because the compound disappeared as the bacterial cell increased (Dal et al., 2002). This study implies that the consumption of the aromatic hydrocarbon was delayed in the presence of the alternate C sources until the depletion of the labile substrate because the organism showed a preference for the alternate C over the aromatic compound (Kamath et al., 2004). It is worth noting that the preference for labile C over hydrocarbon may not always apply due to the substrate type present in the labile C and the amount of substrate/labile C present in the biochar (Mason, 1994; Dal et al., 2002; Lehmann et al., 2011). Also, it is possible that the process of co-metabolism may be observed when simultaneous C is available in the soil. In co-metabolism, the organism oxidises a non-growth substrate (organic compounds) in the presence of a growth substrate (energy and carbon source) (Kuiper et al., 2004). However, co-metabolism is of more relevance to recalcitrant compounds such as high molecular weight (HMW) PAH because they cannot serve as growth substrate to soil microbes and are difficult to degrade (Soleimani et al., 2010; Nzila, 2013; Ghosal et al., 2016; Li et al., 2019b; Hoang et al., 2020). Although the term/idea of co-metabolism was previously opposed (Hulbert and Krawiec, 1977; Wackett, 1996), Nzila (2013) reported that there is evidence that show that different xenobiotics and chemical compounds are biodegraded by a broad spectrum of microbes through co-metabolism. In summary, whether labile biochar C is primarily consumed in the presence of hydrocarbon or consumed during co-metabolism of the more recalcitrant hydrocarbons requires further research.

4.1.2. Microbial responses to biochar-mediated changes in hydrocarbon-contaminated soil

The soil microbial community responds to the biochar-mediated changes resulting from the effect of biochar. This response is fundamental to the enhanced degradation of hydrocarbon. The changes reported include enzymatic activity, microbial abundance, and community structure.

4.1.2.1. Impact on enzymatic activities. Biochemical transformations and biodegradation of contaminants in the soil are facilitated by soil enzymes (Li et al., 2019c). To date there have been limited studies examining the influence of biochar on the activities of soil enzymes in hydrocarbon-contaminated soil; studies have examined the influence of biochar on the activity of enzymes such as dehydrogenase, polyphenol oxidase, fluorescein diacetate (FDA) hydrolase, urease, catechol 2,3-dioxygenase (C230), laccase, lignin-peroxidase (LIP) and manganese-dependent peroxidase (MnP) (Cao et al., 2016; Jia et al., 2017; Zhang et al., 2018, 2019; Li et al., 2019c; Aziz et al., 2020).

Dehydrogenases are important because of their role in the cyclic organic compound breakdown/conversion and in PAH degradation (Haritash and Kaushik, 2009; Lu et al., 2017). Studies have reported that dehydrogenase activities were higher in treatment amended with only biochar or both biochar and nutrient in comparison to treatment with nutrient alone or no amendment (Li et al., 2019c; Zhang et al., 2019; Aziz et al., 2020). In these studies, TPH removal was found to be either significantly higher or higher in treatment amended with only biochar or both biochar and nutrient compared to the treatment with only nutrient or no amendment. This implies that this increase in dehydrogenase activity with biochar addition contributed to the remediation of the soil contaminant. Cao et al. (2016) observed that dehydrogenase activity in biochar treatments was lower than the non-amended treatment before day 42 and did not differ significantly after day 42. The authors associated the decrease in the activity of this enzyme before day 42 to the toxicity of the biochar. Zhang et al. (2019) observed a positive correlation between dehydrogenase activity and TPH removal, suggesting the role of the enzyme in the remediation of the contaminants. In contrast, Li et al. (2019c) did not find a significant correlation between the enzyme and PAH removal. They concluded that since this enzyme is generally a marker of total microbial activity in soils, some microbes that are not PAH-degraders were also promoted by the biochar.

Polyphenol oxidase is an enzyme that plays a role in PAH degradation (Tang et al., 2010). The activity of polyphenol oxidase was found to be higher in hydrocarbon-contaminated soils amended with only biochar or both biochar and nutrient compared to the treatment with only nutrient or no amendment (Li et al., 2019c; Zhang et al., 2019). Li et al. (2019c) and Zhang et al. (2019) found a positive correlation between the enzyme and remediation of the contaminant. Cao et al. (2016) reported that the activities of this enzyme was higher in the first 42 days, relative to the non-amended treatment. However, at end of the study (day 56), enzyme activity was slightly lower in the biochar-amended soil (99.8 mg/kg) compared to the non-amended soil (101 mg/kg). The authors claimed that the stimulation of this enzyme due to biochar application was responsible for the removal of benzo[a]pyrene. Zhang et al. (2019) and Jia et al. (2017) found that FDA hydrolysis was higher in the treatment with biochar only or both biochar and nutrient than the treatment with only nutrient or no amendment. Zhang et al. (2019) reported that this enzyme positively correlated with TPH removal, which suggests their role in TPH removal. FDA is a general indicator of total microbial activity in soil microbes (Shahsavari et al., 2013). However, García-Delgado et al. (2015) did not detect the presence of this enzyme in their study, which agrees with the absence of PAH-degrading bacteria and low PAH degradation in their biochar-amended soil; they did not detect this enzyme in the non-amended soil at day 0. There may be factors other than the initial soil composition responsible for non-detection of FDA in biochar-amended treatment, because this enzyme was detected in the non-amended treatment at the end of incubation (day 42).

Zhang et al. (2018) found that in comparison to the soil with no amendment, the application of biochar had a negative effect on enzyme activity (LIP, MnP, C230 and laccase), especially for soil amended with biochar produced at high temperature. This finding agrees with the observation that biochar addition had little impact on PAH removal. The authors reported a negative correlation between the biochar surface area and all the enzymes (LIP, MnP, C230 and laccase) (Zhang et al., 2018). They claimed that this implied that enzymatic activities may be reduced by biochar with higher surface area (Zhang et al., 2018). However, Foster et al. (2018) suggest that apart from the biochar surface area, the pore size distribution also has an influence on the interaction of the biochar and the enzyme. Reduction in enzymatic activity have been either been shown or reported to be caused by the sorption of the enzyme (Lammirato et al., 2011; Wang et al., 2015; Foster et al., 2018) or substrate (Bailey et al., 2011; Foster et al., 2018) to the biochar. The sorption of the assay constituent to the biochar will compromise the ability to accurately estimate enzyme activities in biochar-amended soil (Swaine et al., 2013). Bailey et al. (2011) compared the colorimetric and fluorescent based assay and recommended the use of the fluorescent based assay for the determination of accurate result in biochar-amended soil, reporting that the fluorescent based assay is more robust than the colorimetric based assay in soils amended with biochar. However, Jin (2010) compared an Enzyme-Labelled Fluorescence (ELF) enzyme assay with fluorogenic substrates (4-methylumbelliferyl-β-D glucuronide

(MUF-G) and 4-methylumbelliferyl phosphate (MUF-P))-based assay. They found that while ELF was suitable to localise and detect enzymes, enzyme activities were underestimated by the MUF-based assay, probably because of fluorophore sorption to the biochar and the subsequent reduced extractability. They suggested that a correction strategy will be helpful in using the MUF-based assay for enzyme estimation (Jin, 2010). In another of their studies, they overcame the enzyme activity underestimation limitation associated with the fluorescent-based assay in biochar amended soil by measuring the equilibrium adsorption isotherm for the substrate (4-methylumbelliferone (MUF) and 7-amino-4-methylcoumarin (MCA)) and using a correction model (Jin, 2010).

In conclusion, the effects of biochar on enzymatic activities cannot be generalised due to the variability in soil condition, enzyme, biochar, incubation time and pyrolysis temperature (Bailey et al., 2011; Wang et al., 2015; Palansooriya et al., 2019). This methodological challenge associated with biochar due to sorption does not only apply to enzymatic activities estimation, but also to DNA extraction, molecular analysis, estimation of dissolved oxygen concentration, CO_2 evolution, soil biota abundance, activities and diversity (Lehmann et al., 2011; Thies et al., 2015). However, before any conclusion on this methodological challenge in hydrocarbon contaminated soil amended with biochar can be made, there is need for empirical findings in these soils.

4.1.2.2. Impact on microbial abundance and community structure. The improvement in soil properties and the provision of substrate/habitat/protection to soil microbes following biochar application to the soil can result in changes in the population, abundance and community structure of microbes. This change can result in enhanced TPH removal if this change is positive. Assessment of the bacterial population is one technique that has been used to study the impact of biochar on soil biota. Qin et al. (2013) and Wang et al. (2017), using culture-dependent approaches assessed the total bacterial count in a petroleum-contaminated soil amended with rice straw and bulrush straw biochar, respectively. The result of their study showed that the population of bacteria were either considerably or significantly higher in the treatment with biochar only or both biochar and nutrient than the soil with nutrient alone or no amendment. The higher TPH removal observed in the biochar or biochar with nutrient treatment may be attributed to the increased bacterial population; other authors (Onwosi et al., 2017; Liu et al., 2010) also observed increased TPH removal in treatments with a high bacterial population. Assessing the total bacteria population using a plate count may not be a good indicator of degradation because not all microbes present in the soil are hydrocarbon-degraders. Instead, Zhang et al. (2019) assessed the population of hydrocarbon-degrading bacteria and found that their population was higher in the treatment amended with biochar and nutrient (approximately 4.8 $\log_{10}$ CFU/g), compared to the nutrient-amended treatment (approximately 4.0 $\log_{10}$ CFU/g). Further, they observed a positive correlation between the hydrocarbon-degrading population and TPH removal, which suggests that an increased hydrocarbon-degrading population contributed to higher TPH degradation in soil amended with both biochar and nutrient.

In contrast, Han et al. (2016) found no significant difference in the total bacterial population between fertiliser-amended soil and soil amended with both biochar and fertiliser. García-Delgado et al. (2015) did not detect the presence of any PAH-degrading population; in addition, there was no significant difference in total heterotrophic bacterial population between the biochar treatment and the non-amended treatment. This may be attributed to the biological properties of the original contaminated soil because in the non-amended soil, a PAH-degrading population was detected only on day 21, but not on day 42. Han et al. (2016) observed that most of the biochar pores were below 1 μm in diameter, which are generally too small for microbial habitation.

Assessment of the impact of biochar on the fungal population in hydrocarbon-contaminated soil has not been well studied. However, in one study, Ikiogha et al. (2019) examined the impact of cow bone biochar applied at 3 different rates on the fungal population in hydrocarbon-contaminated soil. The results of the study showed that in comparison to the non-amended treatment, the hydrocarbon utilising fungal (HUF) population was higher in all biochar treatments throughout the incubation, except in week 1 and 2 where no HUF population was detected in the 0.5 and 3.5 kg biochar, respectively; in fact, no HUF population was detected in the non-amended treatment, except from week 4–8 when a negligible HUF population was detected. The enhancement of the HUF population in the biochar-amended treatment correlated with stimulation of the degradation efficiency observed in this study. However, in another study, the total fungal population was either significantly lower or showed no significant difference in the 12 different biochar treatments in comparison to the non-amended treatment ($p < 0.05$) (Zhang et al., 2018). A similar observation was also found in the total bacterial population. No obvious relationship was found between PAH degradation and microbial biomass (bacteria and fungi), correlating with the non-beneficial effect of biochar in PAH removal in this study. There is a need for more studies to examine the impact of biochar on the fungal population in hydrocarbon-contaminated soil.

To address whether improved biodegradation of petroleum hydrocarbons in contaminated soils in the presence of biochar may be due to increased bacterial biomass, a simple linear regression was used to predict the degradation efficiency based on published data on the bacterial population present in soils amended with biochar or biochar with nutrient/fertiliser amendment and soil with nutrient/fertiliser only or no amendment (Fig. 3). Counts comparing both total culturable bacteria heterotrophic plate counts, as well as culturable hydrocarbon-degrading bacteria, were included. The results of the study suggested that the bacterial population explained 50% of the variance, $R^2 = 0.50$, $p < 0.01$ in the treatments amended with biochar or both biochar and nutrient/fertiliser (Fig. 3b). The bacterial population in the treatments amended with biochar or both biochar and nutrient/fertiliser significantly predicted the degradation efficiency, $B = 10.98$, $p < 0.01$ (B is the coefficient of × (bacteria population) in the equation for the regression). However, in soil to which no biochar was added or only nutrient/fertiliser was added, the bacterial population explained only 11% of the variance, $R^2 = 0.11$, $p < 0.01$ (Fig. 3a). Unlike the treatment with biochar or both biochar and nutrient/fertiliser, the relationship between the bacterial population and degradation efficiency in the soil with nutrient/fertiliser alone or no amendment was not significant ($p < 0.01$). The result showed that compared to the soil with nutrient/fertiliser alone or no amendment, a higher correlation, and a significant relationship between the bacterial population and degradation was observed in the treatment with biochar or both biochar and nutrient/fertiliser. This confirms the suggestion that increased population arising from biochar played a vital role in influencing hydrocarbon degradation.

In addition to quantitative differences in soil bacteria in biochar-amended soil, changes in both soil microbial diversity and activity occur which may also affect the remediation of the soil contaminant. Culture-independent techniques such as phospholipid fatty acids (PLFA), quantitative polymerase chain reaction (qPCR), denaturing gradient gel electrophoresis (DGGE), deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) analyses have also been used in biochar-amended soils to assess the impacts of biochar addition on the soil microbial community (Palansooriya et al., 2019). PLFA analysis was used to assess the soil microbial communities in a PAH-contaminated soil amended with biochar (Li et al., 2019c). The study showed that the concentration of total PLFA and bacteria was significantly higher in the biochar treatment compared to the non-amended treatment, while the concentration of fungi and other eukaryotes was slightly higher but not significant in the non-amended treatment, compared with the biochar treatment. They observed a significant positive correlation between total PLFA and dehydrogenase activity, which showed that the application of biochar improved microbial biomass and activity (Li et al., 2019c). According to the authors, this is a possible reason why biochar

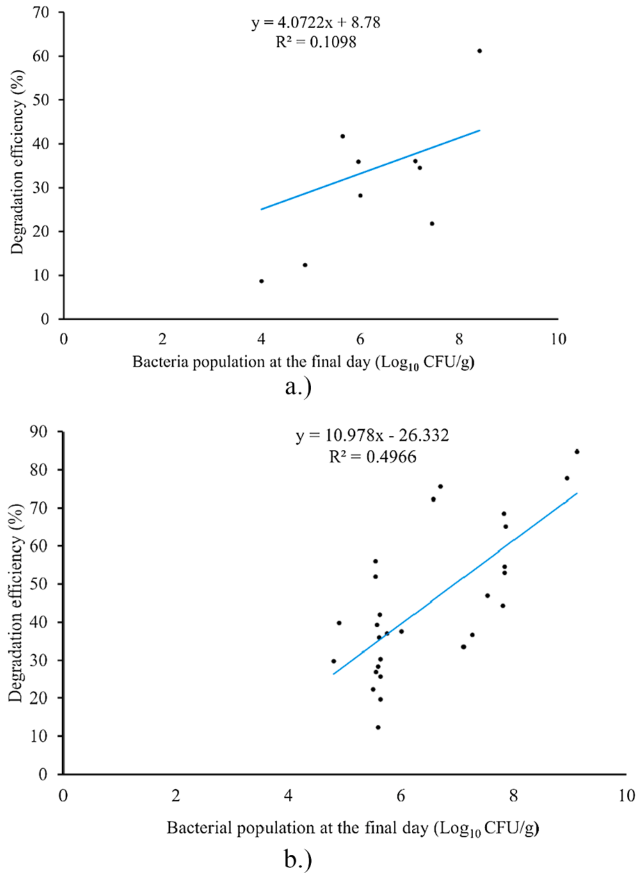

Fig. 3. Relationship between the bacterial population and degradation efficiency in (a) treatment with nutrient/fertiliser or no amendment, (b) treatment with biochar or both biochar and nutrient/fertiliser. The lower number of points in Fig. 3a (treatment with nutrient/fertiliser or no amendment) is due to the fact that in some studies, more than one biochar type was studied and compared with the same treatment with nutrient/fertiliser or no amendment. The bacterial population refers to either total heterotrophic or hydrocarbon-degrading populations. In studies where total heterotrophic or hydrocarbon-degrading population was provided, only the hydrocarbon-degrading population was used (Qin et al., 2013; Agarry et al., 2015; Han et al., 2016; Jia et al., 2017; Wang et al., 2017; Zhang et al., 2018, 2019; Piscitelli et al., 2019; Aziz et al., 2020).

enhanced PAH degradation in this study. In other studies, the fungal: bacteria ratio was found to be higher in biochar-amended treatment in comparison to the non-amended treatment (Li et al., 2019d; Wei et al., 2020b). This contrasting effect of biochar indicates that the effect of biochar on the fungal: bacterial ratio is not homogenous, and this may be due to factors mentioned in Section 5. Therefore, further work is required.

High-resolution techniques have been used to study the influence of biochar on bacterial communities (Palansooriya et al., 2019). Liu et al. (2015a) quantified the change in the number of gene copies of the bacterial community 16S rDNA, nitrogen cycle genes (*nirS*) and PAH-ring-hydroxylating dioxygenases alpha (*RHDα*) in a PAH-contaminated soil using terminal restriction fragment length polymorphism (T-RFLP) and qPCR. The study found that copy number of *nirS*, 16S rDNA and PAH-*RHDα* genes in the different biochar treatments were significantly higher than the non-amended non-sterilised soil. For example, the copy number of 16S rDNA was 4.1×10^8–5.1×10^8 copies g^{-1} dry soil, compared with 3.3×10^8 copies g^{-1} dry soil in the non-sterilised soil with no amendment. The first step in the metabolism of PAHs is mediated by a multi-component ring-hydroxylating dioxygenase (RHD) enzyme (Cébron et al., 2008). The catalytic domain is contained in the alpha subunits, and the encoding gene for this subunit is often used as a marker for the biodegradation of aromatic compounds (Marcos et al., 2009; Jurelevicius et al., 2012). This suggests that the significant increase of this gene copy number in the biochar treatments correlated with increased PAH removal in the biochar treatment. Furthermore, Sawulski et al. (2014) reported that the abundance of the PAH-*RHDα* gene from Gram-negative (GN) and Gram-positive (GP) bacteria shows that the soil bacterial community has the potential to degrade PAHs. The higher abundance of the PAH-*RHDα* gene from GP in the biochar treatments showed that the addition of biochar to the soil was beneficial in enhancing the degradation of the PAHs.

In addition, the number of *nir*S gene copies was reported by Guo et al. (2011) to positively correlate with potential denitrification activity, which negatively correlated with pyrene concentration in the soil. A significant increase in the degradation of two-ring to four-ring PAHs under denitrifying conditions was reported earlier (Lu et al., 2012). This finding confirms that the increase in the *nir*S gene following biochar addition contributed to the degradation of low molecular weight PAHs in this study (Liu et al., 2015a).

PCR-DGGE and sequencing analysis was used to elucidate the effect of biochar on the bacterial community composition in a PAH-contaminated soil (Kong et al., 2018). The authors reported that bacterial diversity reduced slightly in biochar treatments. However, some specific taxa increased in their abundance, including PAH degraders in the biochar treatment. Although bacterial diversity decreased following biochar addition, the increase in the abundance of PAH degraders suggests the influence of biochar on PAH degradation. Wei et al. (2020a), who also observed a decrease in bacterial diversity in petroleum-contaminated coastal marsh soil suggested that this decrease might be connected to the reduction in the extraction efficiency of bacteria present in biochar porous structure. However, Song et al. (2017) found that bacterial diversity was significantly higher following biochar addition in PAH-contaminated soils, relative to the non-amended treatment, except 1% biochar produced at 600 °C. Cao et al. (2016) observed that the microbial diversity (Shannon-Weiner index and evenness) was lower in the biochar treatment compared to the non-amended treatment on day 28. However, at day 56, the biochar treatment had a higher diversity than the non-amended treatment. In another study, Zhang et al. (2020) showed that the effect of biochar on the diversity (evenness and richness) of bacteria and fungi were not similar. In all treatments with both biochar and inorganic fertiliser, bacterial ACE and Chao1 indices were significantly higher in comparison to the inorganic fertiliser treatment, while most of the treatments with both biochar and fertiliser had little or negative effect on fungal Chao1 and ACE indices (Zhang et al., 2020). The fungal Shannon index was significantly higher in most of the treatments with both biochar and inorganic fertiliser, compared to the inorganic fertiliser-amended soil. In contrast, in most of the soil amended with both biochar and fertiliser, a significant decrease or little effect on the bacterial Shannon index was observed.

In another study, prediction of functional genes was carried out using Phylogenetic Investigation of Communities by Reconstruction of Unobserved States (PICRUSt) (Li et al., 2019c). The result of the mean proportion of the three most dominant genes showed that protocatechuate 4,5-dioxygenase significantly increased, while there was no significant difference in 4-hydroxyphenylpyruvate dioxygenase and acetyl-CoA C-acetyl transferase in biochar-treated soils compared to the non-amended treatment at day 21. The increase in this functional gene has also been associated with higher PAH degradation in a previous study (Bao et al., 2020). Liu et al. (2015a) carried out T-RFLP analysis of the specific homologous PAH-RHDα encoding gene from PAH-degraders in soils amended with biochar. They found that the bacterial community structure of the GP PAH degraders differed considerably between the different biochar treatments and the non-amended treatment. For example, T-RFs of 156, 14 and 9 bp did not appear in the non-amended treatment but was found in the biochar treatments (Liu et al., 2015a). Changes differed based on biochar type (feedstock and pyrolysis temperature). The number of T-RFs in GP bacteria in the different biochar treatments was higher, compared to the non-amended treatment, except the dairy manure-derived biochar produced at 350 °C.

The application of biochar has been reported to cause little or no shift in the taxonomical profile at the phylum level in soils amended with only biochar or biochar with nutrient/fertiliser compared to the soil with only nutrient/fertiliser or no amendment (Supplementary Table S1) (Wei et al., 2020a; Qin et al., 2013; Bao et al., 2020; Zhang et al., 2020, 2018; Song et al., 2017). To address whether improved biodegradation of petroleum hydrocarbons in contaminated soils in the presence of biochar or biochar with nutrient/fertiliser may be due to changes in the abundance of the dominant phylum, relationships between the changes in the dominant bacteria phylum abundance and degradation efficiency, in comparison with only nutrient/fertiliser or no amendment were examined (Supplementary Table S1). Although the data show variances in the dominant bacterial phylum among studies, there were some common bacterial phylum among the studies. Furthermore, the findings did not suggest an influence of the dominant phylum on biodegradation efficiency. However, it may be too early to conclude on the role of dominant bacterial phylum on biodegradation, since only a few studies have been carried out. Qin et al. (2013) found some variation between the nutrient-amended soil and soil amended with both biochar and nutrient at the phylum/class level, although taxonomic profiles were relatively similar. They reported that *Pseudomonas* species was responsible for the high abundance of *Gammaproteobacteria* in their study.

However, beyond the phylum level, a strong shift may occur. For example, Zhang et al. (2020) asserted that the strong shift in the bacterial community (except in rice-straw biochar produced at 600 °C) after biochar application was observed mainly at the genus level instead of the class or phylum level. In contrast, other authors did not find a significant change at the genus level (Bao et al., 2020; Wei et al., 2020a). Qin et al. (2013) observed that *Pseudomonas* sp. were higher in the soil amended with both biochar and nutrient compared to the nutrient-amended treatment. *Pseudomonas* are among bacterial genera that are classified as good hydrocarbon degraders (Kulkarni et al., 2012). In another study, Zhang et al. (2020) reported that the increased PAH removal observed in soil amended with both rice straw-derived biochar (produced at 600 °C) and inorganic fertiliser was related to the detection of some specific Acidobacteria-related genera, which only appeared in this treatment. The abundance of Acidobacteria-related genera (6.4%) also increased in this treatment, compared to the inorganic fertiliser treatment (0.1%) and other biochar treatments (with fertiliser addition). Other studies have observed that Acidobacteria was higher in hydrocarbon-contaminated soil amended with biochar, in comparison to the non-amended soil (Li et al., 2019c). Previously, Jiang et al. (2015) used DNA-stable isotope probing to show that Acidobacteria-related bacteria can be associated with PAH (phenanthrene) degradation. Additionally, Zhang et al. (2020) observed that most of the dominant genera in the soil amended with both rice straw biochar (produced at 600 °C) and fertiliser belonged to the class of Solibacteres which were not found in the fertiliser-amended soil and most other soils amended with both biochar and fertiliser. Examples include *Candidatus*, *Bryobacter*, *GOUTB8*, *PAUC26f* and *Paludibaculum*. Li et al. (2019c) showed that among bacteria genera with higher relative abundance in biochar-amended treatments (compared to the non-amended soil), *Stenotrophomonas and Pseudomonas* were the most highly enriched genera. These genera have been previously associated with PAH degradation (Juhasz et al., 2000; Ghosal et al., 2016). In the same study, the average relative abundances of the 47 PAH degrader genera were higher in the biochar-amended treatment compared to the non-amended treatment (Li et al., 2019c). However, there was no significant difference in the specific relative abundances of these genera ($p < 0.05$). In another study, Bao et al. (2020) observed that the relative abundance of 6 PAH degraders in the biochar treatment did not differ significantly from the non-amended treatment after 77 days, except *Sphingomonas* that decreased significantly ($p < 0.05$), in terms of abundance in the biochar treatment (Bao et al., 2020). Although PAH removal was significantly higher in the biochar-amended treatment relative to the non-amended treatment ($p < 0.05$), it differed by less than 4%. This may to an extent agree with the earlier observation in this study that biochar application did not benefit PAH degrading genera compared to the non-amended treatment. In other studies, observed changes in bacterial genera did not influence hydrocarbon degradation (Song et al., 2017; Li et al., 2019d). The variance in the response of bacteria to the biochar treatments and their effect on hydrocarbon degradation may be due to differences in the microbial community originally present in the contaminated soil as well as some of the factors identified in Section 5.

In contrast to reports on the impact of biochar on the bacterial community, the influence of biochar on the fungal community structure has not been well studied (Zhang et al., 2020, 2018; Li et al., 2019d). However, Zhang et al. (2020) reported a strong shift at the phylum, class and genus level in the fungal community composition in PAH-contaminated soil amended with both biochar and inorganic fertiliser. They also found that the application of biochar had a greater effect on the fungal community structure than that of the bacterial community. At the phylum level, they observed that *Ascomycota* (56.2–92.0%), *Basidiomycota* (3.9–27.5%) and *Zygomycota* (0.6–9.2%) were the dominant fungi in the fertiliser-amended soil and soil amended with both fertiliser and the different biochar types (Zhang et al., 2020). The dominance of the phylum *Ascomycota* (73–96%) is consistent with previous results from the same research group (Zhang et al., 2018). However, in addition to *Ascomycota*, other less representative phylum observed by Zhang et al. (2018) include *Ciliophora* (1.0–13%), *Chytridiomycota* (0.27–11%), *Basidiomycota* (0.34–7.0%), *Glomeromycota* (0.18–3.5%), *norank_k_fungi* (0.10–2.60%) and *Blastocladiomycota* (0.07–1.2%). Both studies differed in terms of PAH concentration, biochar dosage and fertilisers (presence/absence). The response of the fungal community to different biochar treatments with or without fertiliser in comparison to the soil with fertiliser or no amendment were not similar (Zhang et al., 2018, 2020). For example, the abundance of *Zygomycota* decreased by 3.0–31.2%, compared to the abundance in the fertiliser treatment, except for treatments amended with both wheat straw biochar (produced at 250 °C or 400 °C) and fertiliser, while the abundance of *Basidiomycota* increased in most of the treatments amended with both biochar and fertiliser (Zhang et al., 2020). The abundance of unidentified fungal sequences in the soils amended with fertiliser combined with either rice straw biochar (produced at 600 °C) or corn straw biochar (produced at 250 °C) were higher in comparison to other treatments (Zhang et al., 2020). More research is required not only on the influence of biochar on the fungal community structure but also how this influence affects petroleum hydrocarbon removal.

5. Factors influencing biochar's effect on the remediation of contaminated soil

The remediation of hydrocarbon-contaminated soil in the presence of biochar can be influenced by factors that can be categorised into (i) production, (ii) application, (iii) contaminant and (iv) soil-related. Production-related factors (feedstock type, pyrolysis temperature, residence time and particle size) can affect remediation because they determine the properties of biochar (Peng et al., 2011; Yavari et al., 2015). Application related factors, (e.g. the application rate, time and method) and contaminant-related factors (type, amount and composition of soil contaminant) also play a significant role in determining the response of biochar in contaminated soils. The existing soil condition (soil texture, physicochemical properties and microbial community) is also predicted to influence the effect of biochar. Although the influence of some of these factors have been studied (Table 3), further research in this area is required.

Table 3
Summary of factors influencing biochar in remediation of hydrocarbon-contaminated soil.

Factor	Description	Comment	References
Production-related			
Feedstock type	Ponderosa pine wood and walnut shell	In comparison to the fertiliser control, treatment with both pine wood biochar and fertiliser enhanced TPH removal, while TPH removal was inhibited in treatment with both walnut shell biochar and fertiliser.	(Mukome et al., 2020)
	Bonemeal, wood and fishmeal	Ranking of the removal efficiency of F3 (C_{16}–C_{34}) petroleum hydrocarbon in frozen soil was as follows: treatment with both bonemeal-derived biochar and fertiliser (73%) > treatment with both wood biochar and fertiliser (approximately 42%) > fishmeal biochar and fertiliser (approximately 4.7%).	(Karppinen et al., 2017a)
	Sewage-sludge and vegetable (fruit)	Removal efficiency was higher in sewage-sludge biochar (75.63%) than the vegetable (fruit) biochar (72.27%)	(Aziz et al., 2020)
Temperature	300 and 600 °C	Pyrolysis temperature influenced the effect of biochar application rate. Increasing the biochar application rate from 1 to 2% resulted in lower PAH residues and higher PAH residues in the soil treated with biochar at lower and higher temperature, respectively.	(Song et al., 2017)
Feedstock type and pyrolysis temperature	Wheat straw and saw dust; 300 and 500 °C	PAH removal was higher in biochar produced at 500 °C than 300 °C. In contrast, feedstock type had a little effect on PAH degradation	(Kong et al., 2018)
	Walnut shells, corn cobs, corn stems and rice straw; 250, 400 and 600 °C	Heatmap with clustering analysis of biodegradation showed that pyrolysis temperature and feedstock influenced PAH removal	(Zhang et al., 2020)
Particle size	480, 70 and 20 μm	TPH removal increased with decreasing particle size	(Agarry et al., 2015)
Application-related			
Application time	Day 0 and 80.	TPH degradation was higher when biochar was added on day 80 (84.8%) than on day 0 (77.8%).	(Qin et al., 2013)
Application rate	5 and 10%	TPH removal decreased with increasing application rate	(Mukome et al., 2020)
	20, 30 and 40 g	TPH removal increased with application rate	(Agarry et al., 2015)
Application method	Incorporation and injection	A significant decrease in F2 (C_{10}–C_{16}) and F3 (C_{16}–C_{34}) petroleum hydrocarbon occurred only at the 334th day with injection, while incorporation caused a rapid decrease within 31 days.	(Karppinen et al., 2017a)
Contaminant-related			
Concentration of hydrocarbon	16,000 and 21,000 mg/kg	TPH removal reached the US EPA standard (10,000 mg/kg) after 230 days in the heavily contaminated soil, while the light-contaminated soil reached that threshold on the 30th day.	(Mukome et al., 2020) *

* : Comparative study was carried using different soil sample.

6. Ecotoxicological impacts of biochar

Chemical analysis, which is the usual way of assessing soil contamination does not provide a true assessment of the efficiency of biodegradation, because a reduction in the amount of contaminants in the soil does not necessarily suggest a decrease in soil ecotoxicity (Molina-Barahona et al., 2005; Khudur et al., 2015). Moreover, concerns have been raised regarding the metals and PAHs found in biochar (Kuppusamy et al., 2016). This suggests the need to combine chemical analysis and ecotoxicological assessment (Lambolez et al., 1994). There is little data available on the ecotoxicological effect of biochar on hydrocarbon-contaminated soil. Qin et al. (2013), using the Microtox toxicity assay found higher EC_{50} values in soil amended with both biochar and nutrient (approximately 32.2–46.5%) relative to the nutrient-amended treatment (approximately 17.4%). This suggests that the application of biochar resulted in a reduction in soil toxicity. However, Wei et al. (2020b) found that algal biomass was higher in biochar treatment (about 5.6 μg/mL) compared to the non-amended treatment (about 4.4 μg/mL), while there was no significant effect on plant biomass and the shoot/root (S/R) ratio. Phytotoxicity assays revealed that biochar application to PAH-contaminated soil resulted in increased root length elongation (about 2.2–2.8 cm) compared to the non-amended treatment (about 1.7 cm) (Song et al., 2017). Other authors have assessed plant features (plant height, shoot height, chlorophyll content, etc.) after combining biochar and phytoremediation for the remediation of hydrocarbon-contaminated soil (Zhen et al., 2019; Abbaspour et al., 2020; Hussain et al., 2018; Barati et al., 2017; Han et al., 2016). Overall, the results have been both positive and negative/neutral compared to the non-amended treatment. Therefore, more studies should be carried out across different trophic levels using defined processes.

7. Challenges of biochar in the remediation of hydrocarbon-contaminated soils

While biochar is useful in soil remediation, its use in the soil has been associated with some challenges. Nitrogen/nutrient immobilisation may occur in the soil treated with biochar because of the high carbon: nitrogen (C:N) ratio, resulting from the high C content of biochar. Brewer and Brown (2012) reported that for every 5–10 mol of C consumed by microbes during their active stage, 1 mol of N will be required. Despite the high C:N ratio of biochar, the effective C:N ratio is much lower because a large amount of the C will be unavailable to microbes (Brewer and Brown, 2012). However, N immobilisation can still occur if biochar is not sufficiently pyrolysed because of the bioavailability of some of the C (Brewer and Brown, 2012). The high C:N ratio was reported by García-Delgado et al. (2015) as one of the reasons for low bacterial and fungal development and concomitant PAH degradation. This imbalance in the C:N ratio can be augmented by supplementing biochar treatments with N, which may enhance TPH removal (Saum et al., 2018). Other authors have found that TPH removal was higher in soil treated with both biochar and nutrients relative to when biochar is applied alone (Lawson et al., 2019; Wang et al., 2017; Wei et al., 2020a).

Biochar, because of its large surface area and porous nature can absorb contaminants in the soil. This may result in a reduction in hydrocarbon degradation because of reduced bioavailability. Song et al. (2017) and Rhodes et al. (2008) reported that the application of biochar reduced the bioavailability of soil contaminants. These observations contradict with the speculation of the beneficial effect of biochar pore on PAH biodegradation. This discrepancy points to the fact that biochar does not have a homogenous effect and further work is required to understand the factor/properties of biochar that promotes sorption and responsible for these discrepancies. Combining biochar with surfactant has been suggested to overcome the challenge of sorption because the surfactant can enhance the desorption of the hydrocarbon from the biochar without affecting the physical properties of biochar (Kang et al., 2019). Inoculating hydrocarbon-degrading organisms in biochar can also help to degrade the contaminants sorbed in the biochar. In doing this, the biochar pre-concentrates the contaminant and then reduces the distance between the contaminant and the introduced organism (Chen et al., 2012).

Kuppusamy et al. (2016) raised concerns that heavy metals and PAHs present in biochar can be released into the soil following the application of biochar. However, Freddo et al. (2012) found that the environmental impact attributable to biochar was likely minimal because they observed that the concentration of PAH, metals and metalloids were below the acceptable limit for sewage sludge and either lower or conforming to the limit for compost. Caution should be applied to this claim because the biochar assessed in their study was derived from less-toxic feedstock (Freddo et al., 2012). Cao et al. (2016) reported that the activity of dehydrogenase enzyme before day 42 decreased in the soil because of the toxicity of biochar. It may be important to assess the PAH and metal content of biochar before introducing it to the soil. Co-pyrolysis or modification of biochar can be used when biochar is derived from feedstock that is suspected to have a high level of toxicant.

8. Research gaps and future research need

Given the current knowledge on biochar for remediation of hydrocarbon-contaminated soil, the following are recommended for future studies:

- The influence of biochar on bacterial abundance and community structure in hydrocarbon-contaminated soil has not be well studied. Emphasis should also focus on fungi because little is known of their impact in the hydrocarbon-contaminated soil under biochar amendment.
- Evaluation of enzymatic activity and functional gene prediction has been used to assess the response of the microbial community to biochar application in hydrocarbon-contaminated soil. However, this has not been well studied and thus more work is required.
- Changes in the physicochemical properties of the soil following biochar addition to the soil is one of the major routes through which biochar improves degradation. Few studies have examined the influence of biochar on physiochemical properties in hydrocarbon-contaminated soil.
- Rates of degradation of the contaminant in hydrocarbon-contaminated soil to which biochar has been added is suggested to be a function of the properties of biochar. However, it is still unclear what are the most important properties (surface area, ash content, etc.) of biochar that influence the remediation. Understanding which properties of biochar is important in soil remediation will be vital in manipulating biochar for effective soil treatment.
- The effect of biochar on remediation of hydrocarbon-contaminated soil is a function of the production, soil, contaminant and application conditions. Despite the increasing research effort, the influence of these factors has not been well studied.
- Current research has shown that the ecotoxicological effect of biochar during remediation of hydrocarbon-contaminated soil has not been well studied. Such studies are important given that some biochar contain PAH and heavy metals which can have a negative effect on soil biota. This research deserves attention in future studies.
- Studies on biochar for the remediation of hydrocarbon contaminated soil have largely been focused on laboratory incubation and greenhouse experiments. Field trials are limited and thus it is recommended for researchers to study the influence of biochar on large-scale field trials before biochar will be deemed an effective tool.

9. Conclusion

In this review, we investigated whether biochar can serve as a stimulating agent for the bioremediation of hydrocarbon-contaminated soils. As part of this, the properties of biochar have been examined. The result of this review revealed that biochar can act as a biostimulator in the bioremediation of hydrocarbon-contaminated soils. However, in some studies, biochar was ineffective in stimulating hydrocarbon degradation. The ineffectiveness of biochar may be because of the drawbacks or factors identified in this review. Biochar can act as a biostimulator because it can have a positive effect on soil microbes by serving as a habitat, organic substrate, and improving the soil physicochemical properties. The result of this effect are changes in enzymatic activity, microbial abundance and community structure. Linear regression between bacterial population and degradation efficiency showed that R^2 was higher and significant ($p < 0.01$) in soil amended with biochar or biochar with nutrient (0.50), compared to the soil amended with nutrient/fertiliser only or no amendment (0.11). What this implies is that the increase in bacterial population following biochar addition may likely contribute to an increase in degradation of the soil contaminant. The efficiency of biochar in soil remediation can be affected by production, application, contaminant, and soil-related factors. Ecotoxicological studies revealed that biochar had both positive and negative ecotoxicological effects. Immobilisation of nitrogen, sorption of contaminants, and toxicity of biochar were identified as challenges of biochar use in the soil.

Author contribution

C.C.D wrote the manuscript. A.S.B. and E.S. supervised the planning, writing and reviewed the manuscript. A.S and K.S reviewed the manuscript.

Declaration of Competing Interest

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

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2021.106553.

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