

Recent Advances in Biochar Engineering for Soil Contaminated with Complex Chemical Mixtures: Remediation Strategies and Future Perspectives

Jerry Anae¹, Nafees Ahmad^{1,4}, Vinod Kumar¹, Vijay Kumar Thakur², Tony Gutierrez³, Xiao Jin Yang^{5,6}, Chao Cai⁷, Zhugen Yang¹ and Frederic Coulon¹

¹ School of Water, Energy and Environment, Cranfield University, Cranfield, MK43 0AL, UK

² Biorefining and Advanced Materials Research Centre, Scotland's Rural College, Edinburgh, EH9 3JG, UK

³ Institute of Mechanical, Process and Energy Engineering (IMPEE), School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK

⁴ Environmental Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh, 202002, India

⁵ State Key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

⁶ State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, 100029, PR China

⁷ Key Lab of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China

Abstract

Heavy metal/metalloids (HMs) and polycyclic aromatic hydrocarbons (PAHs) in soil have caused serious environmental problems, compromised agriculture quality, and have detrimental effects on all forms of life including humans. There is a need to develop appropriate and effective remediation methods to resolve combined contaminated problems. Although conventional technologies exist to tackle contaminated soils, application of biochar as an effective renewable adsorbent for enhanced bioremediation is considered by many scientific researchers as a promising strategy to mitigate HM/PAH co-contaminated soils. This review aims to: (i) provide an overview of biochar preparation and its application, and (ii) critically discuss and examine the prospects of (bio)engineered biochar for enhancing HMs/PAHs co-remediation efficacy by reducing their mobility and bioavailability. The adsorption effectiveness of a biochar largely depends on the type of biomass material, carbonisation method and pyrolysis conditions. Biochar induced soil immobilise and remove metal ions via various mechanisms including electrostatic attractions, ion exchange, complexation and precipitation. PAHs

remediation mechanisms is achieved via pore filling, hydrophobic effect, electrostatic attraction, hydrogen bond and partitioning. During last decade, biochar engineering (modification) via biological and chemical approaches to enhance contaminant removal efficiency has garnered greater interests. Hence, the development and application of (bio)engineered biochars in risk management, contaminant management associated with HM/PAH co-contaminated soil. In terms of (bio)engineered biochar, we review the prospects of amalgamating biochar with hydrogel, digestate and bioaugmentation to produce biochar composites

Keywords: Contaminated soil, biochar, (bio)engineering, hydrogel, digestate, bioaugmentation

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1 Introduction

1.1 Soil Contamination: A vital Life Supporting Resource

For generations, soil continues to be the foundation on which humans' source 90 % of their food, livestock feed, fibre and fuel. It provides raw materials and groundwater. It also serves as a water purifier and habitat for billions of living organisms, including humans (Gentile, 2000). Hence, soils are critical resources for achieving many of the 17 identified United Nation Sustainable Development (UNSDP) Goals, including food security, clean water, improve sanitation, and good health and wellbeing. In the last few decades, the exponential increase in human population and a substantial increase in industrialisation and urbanisation have resulted in the pollution of practically every environment on Earth, including soil (Ali et al., 2019; Tang et al., 2014). Typical soil pollutants include polycyclic aromatic hydrocarbons (PAHs), crude oil and its petrochemical derivatives, heavy metal/metalloids (HMs), pesticides, herbicides and chlorophenols (Chen et al., 2015). Among these pollutants, HMs and PAHs pose serious threats to food security and exert detrimental effects on human health and ecosystems (Perez et al., 2010). This is largely due to their toxicity, persistence and potential to bioaccumulate, and with respect to HMs their non-biodegradability properties (Hadia-e-Fatima, 2018).

1.2 Heavy Metal Classification and underlying Mechanism for their Toxicity

HMs can be divided into macro-nutrient (e.g. Co and Mg), micro-nutrient (e.g. Cu, Ni, Fe, Mn and Mb) elements, and those that are highly toxic (e.g. Hg, Cr, Cd, Pb, Ag, Pd, Bs, As, Se, Sn and Zn) (Selvi et al., 2019). Macro and micro-nutrient elements are also referred to as essential elements which are beneficial to the growth, development and reproduction of plants, but can be harmful when present in excessive quantities (Whitfield et al., 2010). Conversely, highly toxic elements can be harmful at trivial concentrations (Sall et al., 2020). Toxicity effects of HMs vary based on the specific HM ion species and the individual organisms that are exposed. However, the generation of free radicals is considered by many researchers as the common mechanism of HM toxicity, particularly in humans, which can cause oxidative stress, damage of biological molecules such as enzymes,

proteins, lipids, and nucleic acids (Engwa et al., 2019). Damage to DNA is a key process leading to carcinogenesis and neurotoxicity (Lu et al., 2015).

1.3 Polycyclic Aromatic Hydrocarbon Classification and Mechanism of Toxicity

In terms of PAHs, the 16 United States Environmental Protection Agency (USEPA) priority PAHs have been accepted as a representative and standardised set of compounds and were used extensively in environmental and analytical science in the last 50 years. But recently, there is a growing call to add additional compounds to this list. Compounds such as heterocyclic compounds, oxy-PAHs and nitro-PAHs (Pulleyblank et al., 2019; Andersson and Achten, 2015). One of the main reasons for this is to include these types of additional PAHs compounds that are of considerably higher toxicity than those currently present in the USEPA priority list (Andersson and Achten, 2015). From the many types of PAHs, some of the widely spread and commonly studied include naphthalene (Nap), anthracene (Ant), phenanthrene (Phe), pyrene (Pyr), chrysene (Chr), benzo[a]anthracene (B[a]A), fluoranthene (Flu), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenz[a,h]anthracene (D[a,h]A) and indeno[1,2,3-c,d]pyrene (I[c,d]P) (Pulleyblank et al., 2019; Bianco et al., 2020; Adel-Shafy et al., 2016). Generally, individual PAH compound is classified based on geno-toxic and carcinogenicity. According to International Agency for Research on Cancer-IARC (1983; 2010), PAHs are classified as carcinogenic to humans (Group 1), probably carcinogenic to humans (Group 2A), or possibly carcinogenic to humans (2B). Two-ringed PAHs, and to a lesser extent three-ringed PAHs, dissolve in water, making them more available for biological uptake and degradation (Choi et al., 2010; Johnsen et al., 2005). Further, two and three-ringed PAHs including some four-ringed PAHs depending on temperature can easily volatilise as gaseous into the atmosphere (Atkinson and Arey, 1994; Srogi, 2007). In contrast, compounds with four and five or more rings also referred to as High Molecular Weight PAHs (HMWPAHs) have low solubility in water and low volatility; they are therefore predominantly in solid-state, bound to soil and organic matter (Choi et al., 2010). In solid-state, these compounds are less accessible for biological uptake or degradation, which increases their persistence in the environment, and making them more detrimental

to the environment and human health (Johnson et al., 2005; Haritash and Kaushik, 2009; Xu et al., 2020). It is well-documented that the HMWPAHs are difficult to degrade, and they can be more detrimental to the environment and human health (Xu et al., 2020). Of all the HMWPAHs, B[a]P is considered the most toxic of the parent PAHs, common PAH to cause cancer in animals including humans and is widely used as a key marker PAH for environmental assessments (Cave et al., 2010; Latif et al., 2010).

Not all PAHs are carcinogenic. In fact, two and three-ringed (Lower Molecular Weight–LMW) PAHs have lower toxic equivalent factors and are non-carcinogens compared to HMWPAHs (Wu et al., 2019). The IARC Monographs Programme has reviewed experimental data for 60 individual PAHs (IARC, 2010). Of these 60 PAHs reviewed and with reference to the list of commonly widespread and studied PAHs mentioned above, one, B[a]P, is classified as carcinogenic to humans (Group 1). D[a,h]A is classified as probably carcinogenic to humans (Group 2A), and B[a]A, B[b]F, B[k]F, Chr and I[c,d]P are classified as possibly carcinogenic to humans (Group 2B). The toxicity mechanism of PAHs mainly affects the function of cellular membranes and enzyme systems which are associated with membranes (Zhang et al., 2019). The mechanism of PAH-induced carcinogenesis is believed to be via the binding of PAH metabolites to DNA (Zhang et al., 2019; Barnes et al., 2018). Briefly, PAHs are transported into cells due to their hydrophobicity characteristic. Once inside the cells, PAHs induce phase I and II gene expressions of cytochrome P450 (CYP) monooxygenase enzyme and an enzyme II (e.g. glutathione s-transferase) via aryl hydrocarbon receptor leading to the metabolism of PAHs into various metabolites or active carcinogens such as diol-epoxides and radical cations which can bind to DNA (DNA adduct) and become mutagenic or carcinogenic (Moorthy et al., 2015; Honda and Suzuki, 2020).

Generally, the toxicity of both pollutants (HMs and PAHs) depends on the absorbed dose, the route of exposure and duration of exposure (i.e. chronic or acute), which can lead to various effects and disorders (Jaishankar et al., 2014). Table 1 below shows various anthropogenic activities contributing to the release of HMs/PAHs into the environment and summarises the toxic effects of the various

pollutants to plants, soil microorganisms and humans. But the common anthropogenic sources of HMs/PAHs originate from mining, petroleum, agriculture and chemical industries and other operations. While HMs and PAHs in the soil environment originate from natural geological processes (Dixit et al., 2015; Gutierrez, 2019), significant amount stems from anthropogenic sources (Cristaldi et al., 2017).

Table 1. Detrimental effects of highly toxic HMs and carcinogenic PAHs (commonly widespread and studied) to living organisms

Pollutants	Anthropogenic Sources	Toxic Effects		
		Humans	Plants	Microorganisms
As	A, D, H, G, L & R	Skin and NS toxicity, carcinogenic, perforation of the nasal septum, peripheral neuropathy, congenital disabilities, damages the liver, bladder and gastrointestinal tract, birth defects, vomiting and diarrhoea (Hahladakis et al., 2018; Hansen et al., 2013; Jan et al., 2015; Anwar et al., 2002; ATSDR 2007).	Chlorosis, wilting, inhibits seed germination, plant growth, photosynthetic activity and translocation to shoots, alters chlorophyll and protein content, reduces transpiration intensity, electrolyte leakage, and induces oxidative stress (Rahman et al., 2007; Abedin et al., 2002; Barrachina et al., 1995; Singh et al., 2006).	Inhibits enzyme activities and damages DNA (Sankarammal et al., 2014; Khan et al., 2009).
Cd	A, B, D, H, K & P	Carcinogenic, mutagenic, endocrine disruptor, proteinuria, glucosuria, osteomalacia, emphysema, damages kidney, liver and lung (Mashitah et al., 2008; Malkor and Nuhoglu 2005; Sharma 1995; Aofolu 2005; Salem et al., 2000).	Chlorosis, necrosis, inhibits plant growth, root and shoot elongation, affects photosynthesis activity, membrane leakage, and inhibits enzyme activities (Wan et al., 2012; Ahmad et al., 2012; Yourtchi and Baya 2013; Wang et al., 2007); Versieren et a., 2017)	Inhibits enzyme activities, cell division and transcription, denatures protein, disrupts the cell membrane, damage DNA (Fashola et al., 2016; Khan et al., 2009).
Cr	A B, D, J & P	Liver, kidney and circulatory disorders, ulcer, perforation of nasal septum and respiratory cancer, severe cardiovascular and gastrointestinal disorders, genotoxic and alopecia (Engwa et al., 2019; Massos and Turner 2017; ATSDR 2004; Simate et al., 2016; Ali et al., 2013).	Inhibits root elongation and decrease the plant's nutrients (Vernay et al., 2007; Sharma and Sharma, 1993; Panda and Patra, 2000; Nematshahi et al., 2012).	Inhibits growth, elongation of lag phase and oxygen uptake (Cervantes et al., 2001).
Hg	A, B, C, F, H, K, L, M, N & R	Gastrointestinal ulceration, damages CNS, proteinuria, carcinogenic, disrupts DNA, memory problems, tremors, damages kidney and brain, and negative reproductive effects (Cook 2019; Hansen et al., 2013; Engwa et al., 2019; ATSDR, 2007; Abia and Igwe, 2005).	Chlorosis, decreases photosynthetic activity, antioxidant enzymes and water uptake, alters mitochondrial activity, inhibits plant growth, reduces tiller, panicle formation, flowering, root elongation, transpiration rate, water uptake and chlorophyll synthesis (Sridhar et al., 2007a&b; Han et al., 2004; Kibra, 2008; Du et al., 2005; Shekar et al., 2011; Sparks, 2005).	Denatures protein, disrupt the cell membrane, damages DNA, and inhibits enzyme activities, cell transcription and cell division (Fashola et al., 2016; Khan et al., 2009).
Pb	A, B, D, E, G, H, I, K, L, O & S	Encephalopathy, peripheral neuropathy, CNS disorders, hypertension, oxidative stress, infertility and damaged brain, kidney and cells (Hahladakis et al., 2018; Engwa et al., 2019; Massos and Turner, 2017; Jan et al., 2015; ATSDR, 2007).	Inhibits root elongation, enzyme activities, photosynthetic activity, chlorophyll biosynthesis and biomass production, suppresses growth, decreases plant protein content, changes lipid composition and cellular concentrations of micronutrients, and induces oxidative stress (Orcutt and Nielsen, 2000; Hussain et al., 2013; Sharma and Dubey, 2005; Patra et al., 2004).	Denatures protein, disrupts the cell membrane, inhibits cell division, enzyme activity and transcription, and damages DNA (Fashola et al., 2016; Khan et al., 2009).
Chr (4 rings)	H, L, U, V, W & X	Carcinogenic damages kidney and liver, induces jaundice cataracts, and causes germ cell effects (IARC, 2010; Luch, 2005; ATSDR, 1995; Jung et al., 2013).	Inhibits seed germination, plant growth and PSII photochemistry, decreases chlorophyll (a&b) content, phenolic, flavonoid, ascorbic acid, α -tocopherol, carotenoid and antioxidant, and induces oxidative stress (Tandey et al., 2020; Othman et al., 2018; Dubrovskaya et al., 2016).	Genotoxic, affects metabolic activities and alters microbial diversity (Szczepaniak et al., 2016; White, 2002).

B[a]A (4 rings)	H, L, U, V, W & X	Carcinogenic affects the nervous system and fertility, causes heart malformation, childhood asthma and skin irritations, and leads to embryotoxic effects (IARC, 2010; PHE, 2018; Igwe and Ukaogo, 2015; Luch, 2005; Wassenberg and Di-Giulio, 2004).	Inhibits plant growth and PSII photochemistry, decreases chlorophyll (a&b) content, phenolic, flavonoid, ascorbic acid, α -tocopherol, carotenoid and antioxidant, and induces oxidative stress (Tandey et al., 2020; Othman et al., 2018).	Affects metabolic activities, alters microbial diversity, damages cell wall disrupts membrane activities, and interferes with protein and enzymatic activities (Broniatowski et al., 2017; Abdel-Shafy and Mansour, 2016; Szczepaniak et al., 2016).
B[b]F (5 rings)	H, L, U, V, W & X	Carcinogenic, and causes eye irritation, nausea, vomiting and diarrhoea (IARC, 2010; Lawal, 2017).	Inhibits plant growth and PSII photochemistry, decreases chlorophyll (a&b) content, phenolic, flavonoid, ascorbic acid, α -tocopherol, carotenoid and antioxidant, and induces oxidative stress (Tandey et al., 2020; Othman et al., 2018).	Affects metabolic activities, alters microbial diversity, interferes with protein and enzymatic activities (Abdel-Shafy and Mansour, 2016; Szczepaniak et al., 2016).
B[k]F (5 rings)	H, L, U, V, W & X	Carcinogenic, and causes tumours of the gastrointestinal tract and lungs (IARC, 2010; ATSDR, 1995).	Inhibits plant growth and PSII photochemistry, decreases chlorophyll (a&b) content, phenolic, flavonoid, ascorbic acid, α -tocopherol, carotenoid and antioxidant, and induces oxidative stress (Tandey et al., 2020; Othman et al., 2018)	Affects metabolic activities and alters microbial diversity (Szczepaniak et al., 2016)
B[a]P (5 rings)	H, L, U, V, W & X	Carcinogenic, mutagenic and teratogenic, induces apoptosis of CD34+ stem cells, affects immune response, causes birth defects, leukaemia, heart malformation, childhood asthma, nausea, diarrhoea and DNA adduct, embryotoxic effects, and a skin irritant and sensitiser (IARC, 2010; Lawal, 2017; Luch, 2005; ATSDR, 1995; Giri et al., 2016); (Wassenberg and Di-Giulio, 2004; van Grevenynghe, 2005).	Affects membrane permeability and photosynthesis causes enzymatic dysfunction, decreases chlorophyll (a&b) content, phenolic, flavonoid, ascorbic acid, α -tocopherol, carotenoid and antioxidant, and induces oxidative stress (Tandey et al., 2020; Duxbury et al., 1997).	Genotoxic, affects metabolic activities and microbial diversity, damages DNA and interferes with protein and enzymatic activities (Abdel-Shafy and Mansour, 2016; Szczepaniak et al., 2016; Sowada et al., 2017; White, 2002).
D[a,h]A (5 rings)	H, L, U, V, W & X	Carcinogenic causes cataracts and jaundice cataracts and damages kidney and liver (IARC, 2010; ATSDR, 1995; Giri et al., 2016).	Decreases chlorophyll (a&b) content, phenolic, flavonoid, ascorbic acid, α -tocopherol, carotenoid and antioxidant, and induces oxidative stress (Tandey et al., 2020).	Damages cell wall, disrupts membrane activities and interferes with protein and enzymatic activities (Abdel-Shafy and Mansour, 2016; Broniatowski et al., 2017).
I[c,d]P (6 rings)	H, L, U, V, W & X	Carcinogenic, and induces jaundice cataracts (IARC, 2010; ATSDR, 1995).	Inhibits plant growth and PSII photochemistry (Othman et al., 2018).	Damages cell wall, disrupts membrane activities and interferes with protein and enzymatic activities (Abdel-Shafy and Mansour, 2016; Broniatowski et al., 2017).

A Mining industries	E Alloys	I Petroleum industries	M Hg amalgam	Q Stabiliser/flame retardants	V Sewage sludge
B Metallurgy/metal plating	F Pharmaceuticals	J Leather	N Chor-alkali	R Electrical/electronic	W Combustion process
C Chemical industries	G Textiles	K Battery	O Plumbing	S Welding/solder	X Mobile sources
D Dyes/paints/pigments	H Fertilizers/biocides	L Burning fossil fuel/coal	P Galvanised pipe/corrosion	U Petroleum spills	

Also, Table 1 shows the typical toxicity effects of HMs/PAHs on microorganisms which include disruption of cellular function and metabolic activities, oxidative stress, inhibition of enzyme activities, and damage of DNA. In the case of plants, chlorosis, necrosis, plant growth diminution, inhibition of enzyme activities, decreased chlorophyll, and inhibition of photosynthesis process and photosystem II activities are all common. Humans mostly suffer from HMs/PAHs toxicity by carcinogenic and mutagenic effects of the pollutants, including damage to important organs such as the liver, kidney, lung and brain.

HMs and PAHs are also capable of interacting with other naturally occurring inorganic compounds in soil that can form into toxic by-products with carcinogenic or mutagenic properties (Singh et al., 2017). Therefore, it is necessary to ascertain their bioavailable concentrations, exposure and potential toxicity in soil ecosystems which require suitable remediation strategies to effectively control these pollutants. While methods exist to remediate and control these pollutants, lately more attention has been directed towards the development of sustainably low-cost, environmentally friendly and effective remediation strategies. One such technology that has garnered increased interest is the application of biochar, particularly in environmental engineering. Biochar is a carbonaceous, solid and recalcitrant compound derived from the pyrolysis of waste biomass (Pandey et al., 2020). Most of the review articles published to date mainly focused on the sole application of biochar for the remediation of both or either HM ions and/or PAHs (e.g. Abbas et al., 2018; M. Guo et al., 2020; X. Guo et al., 2020 Cheng et al., 2020). Others have reviewed the potential of combining biochar with either digestate or bioaugmentation (e.g. B. Wang et al., 2017; Panahi et al., 2020). To the best of our knowledge, this review is the first of this kind that summarises the prospect of amalgamating biochar with hydrogel, digestate and bioaugmentation to enhancing remediation of co-contaminated (HMs and PAHs) soil. Herein, we review the remediation efficiency of biochar and engineered biochar. We also included remediation mechanisms of selected promising extraction techniques, as well as discuss its advantages and limitations. These techniques, in combination with biochar to enhance its remediation efficiency, are also discussed. Whilst biochar shows great promise for the remediation

of soil contaminated with HMs and/or PAHs, a view to its future success in this respect must take into account several important facets, concepts and knowledge gaps, such as (1) understanding the sorption mechanism of biochar and factors affecting its adsorption properties, particularly physicochemical factors, (2) implementing effective integrated (bio)engineered remediation approaches to enhance remediation efficacy of biochar, (3) understanding the pollutant removal mechanisms of the hydrogel, digestate and bioaugmentation, respectively, including factors influencing the remediation properties of the individual method, (4) promote environmentally friendly and sustainable approaches that embrace the circular bioeconomy concept, and (5) explore the applicability of (bio)engineered remediation strategies at regulatory and industry level.

2 A Need for Integrated Engineered Remediation Approaches

2.1 Conventional technologies and their Drawbacks

Existing conventional physical treatment (thermal treatment and soil replacement), chemical (leaching, precipitation, ion exchange and immobilisation) and physicochemical technologies (electro-kinetics, vitrification and soil washing) have proven, to some extent, effective in removing HMs and PAHs from contaminated soils (Sharma et al., 2018; Qayyum et al., 2020). Nevertheless, these technologies remain jeopardized by some minor and major shortcomings. This include poor feasibility, inefficiency, high cost, unsustainability and high secondary risk (Khalid et al., 2017; Lahori et al., 2017; Cao et al., 2004). Other existing technologies can also compromise soil quality (Khalid et al., 2017), can cause loss of other valuable metals (Tripp et al. 2002; Hou and Gao, 2003), or can only be effective under certain conditions such as low soil permeability and low carbonate conditions (Hanson et al. 1992). Other methods such as stabilization and solidification (S/S) and encapsulation can only stabilise and entrap pollutants in a solid form but does not destroy, transform or remove pollutants (Khalid et al., 2017) which are desirable outcomes for a successful remediation. Conversely, biological remediation (bioremediation) is often more economical and environmentally friendly, and as such has attracted increased interest in recent years. However, bioremediation

methods also have their limitations, for example, phytoremediation requires hyperaccumulators which are mostly quite slow-growing and, hence, their pollutant-accumulating rate is also slow. Hyperaccumulators are plant species with the ability to grow on contaminated soil and accumulate extraordinarily high concentrations of chemical contaminants, such as HMs and PAHs, without suffering phytotoxic effects compared to the majority of species (Rascio and Navari-Izzo, 2011). In addition, the use of invasive hyperaccumulator species can be a threat to native biodiversity (Chibuike and Obiora, 2014).

2.2 Biochar: A Promising Panacea

Other biological methods or materials (e.g. biochar), digestate and bioaugmentation have shown promising potential in the bioremediation of HMs and PAHs as has been demonstrated in laboratory-scale experiments (Tables 2 and 3). However, there are limited field and industrial applications that have been conducted to ascertain the feasibility and viability of these methods in the natural environment. Few field studies conducted so far which involve the application of biochar for removal of HMs and PAHs have shown promising results. For example, biochar treatment greatly reduced Cd content in rice grain by 20-90 %, resulting in a safe Cd level (<0.4 mg/kg) of rice grain from all Cd-contaminated rice fields at a biochar dosage of 40 t/ha (Bian et al., 2013). Another field study revealed exchangeable Cd decreased by 8.5 % and bioavailability of HMs (Cd, Cu and Pb) to plant shoots and roots were significantly reduced with increasing sugarcane bagasse biochar application rate (Nie et al., 2018). Biochar significantly reduced Cd and Zn availability by up to 85 % and 91 %, respectively, in an acidic paddy soil when incorporated at a rate of 20 and 40 t/ha (Chen et al., 2016). Similarly, a field experiment showed biochar increased the content of available nutrients in soils and decreased the content of exchangeable Pb in soils and biomass in above-ground parts of maize plants and grains; decreased the Cd contents in maize stems and grains by 27 % and 25 %, respectively; and decreased the Pb content in roots by 16 % (Zhan et al., 2019). A 6 months mesocosm scale study by Cippulo et al., (2018) amended genuine PAHs contaminated soil with 5 % w/w biochar (soil + biochar). The result showed TPH total content decreased by 18 % and bioavailable concentration decreased by 24-

28 %. In another study, the PAH sorptive efficiency of biochar was investigated in a five-years field experiment which involved biochar treatments of 16.5 t/ha of biochar application dosage in 2010. Thereafter, PAHs concentration decreased significantly with time from 153 ± 38 ng/g at first sampling to 80 ± 12 ng/g (Rombola et al., 2019). Stefanuik et al., (2017) experimented the removal of total PAHs ($\Sigma 16$ USEPA PAH) by 2.5 % biochar application rate on podzolic soil in an 18 months field experiment. After 12 months, up to 45 % reduction in $\Sigma 16$ PAHs concentrations in soil was recorded. Another field experiment with soil amended with 2.5 % biochar over an 18 months incubation period reported a maximum reduction of 4-6 rings PAHs by 18-67 % (Oleszczuk et al., 2019).

In most cases, the production of conventional biochars via pyrolysis has a relatively low surface area with subsequent low adsorption capacity (Rajapaksha et al. 2016). Purposive tailoring of their physicochemical properties can enhance their effectiveness in engineering applications (Rajapaksha et al. 2016). Biochar tailoring is also known as biochar modification. Massively produced biochars and their modified products are also referred to as engineered biochars (Duan et al., 2019). Engineering or modification of biochar (derived from biological feedstock materials) using applications of biological principles and engineering tools can be referred to as bioengineered biochars. Hence, a strategy is to integrate different methods to address some of the drawbacks associated with individual method whilst enhancing their remediation performance. For example, a promising strategy could be in integrating biological and chemical techniques, such as via the amalgamation of biochar with hydrogel, digestate and bioaugmentation to produce modified biochar composite or engineered biochars as demonstrated in Figure 1 below. Each of these remediation agents or methodologies involves various combinations of remediation mechanisms to remove HMs and PAHs, which are summarised in Table 4. Several researchers have classified biochar remediation techniques as either, or a combination, of chemical, physical and physicochemical methods depending on how each researcher understands the mechanism of the biochar-mediated remediation process.

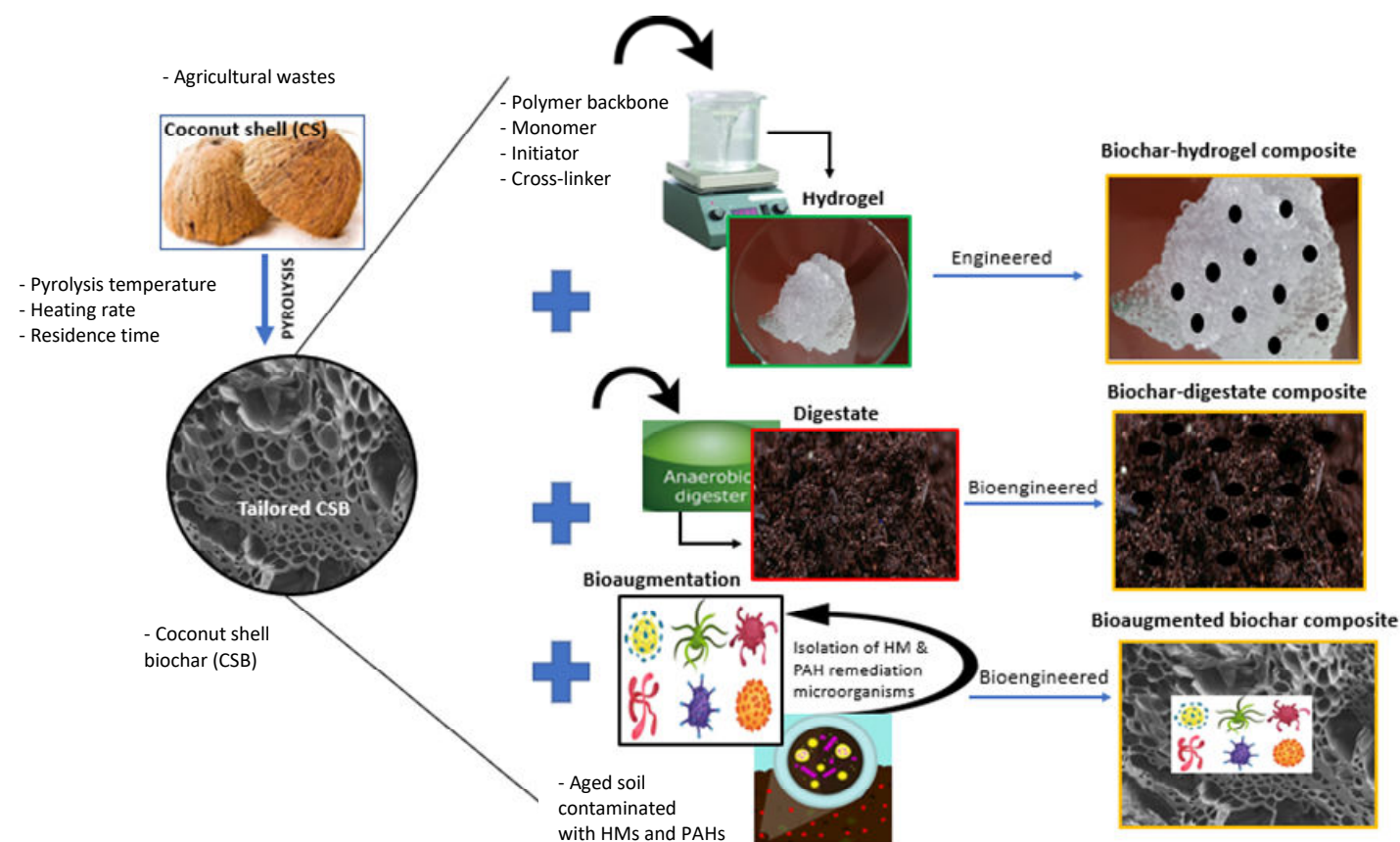


Figure 1. Production of (bio)engineered biochars (an integrated remediation approach)

The application of biochar, both conceptually and from short term studies at the laboratory scale, has proven to be effective depending on the type of biomass feedstock material, carbonisation method, pyrolysis conditions (Hassan et al., 2020) and biochar dosage (Chen et al., 2019a; Bian et al., 2013). It is economically feasible and sustainable at the lab scale (Gwenzi et al., 2017; Xiao et al., 2020; Xiang et al., 2020) in the sense that: (i) biomass are sourced from free or cheap renewable biowastes, (ii) no transportation cost is involved otherwise are ordered at low-cost given the small-size lab projects, and (iii) the capability of biochar to be regenerated and reused. Several studies have demonstrated that application of biochar during remediation does not lead to generation of secondary pollution or pollutants (Lahori et al., 2017). However, biochar can contain HMs and PAHs and subsequently act as carrier of these contaminants leading to secondary pollution after application (Kołtowski and Oleszczuk, 2015). A 6 years field experiment dealing with PAH contamination after biochar application showed biochar application increased soil B[a]P concentrations (de Resende et al., 2018). Secondary environmental risk associated with biochar application can be avoided

depending on the type of biochar, post-treatment measures, aging conditions, type of carbonisation method utilised, and specific pyrolysis conditions employed (Buss et al., 2015; Oleszczuk and Kołtowski, 2018). For example, Buss et al., (2016) concluded that straw-derived biochar contained 5.8 times higher PAH concentrations than softwood-derived biochar, and PAH concentration significantly decreased in case of straw-derived biochar (43 mg kg^{-1} to 4 mg kg^{-1}) when carriers gas flow of pyrolysis reactor was increased.

Table 2 and 3 show some recent lab-scale applications of biochar and HMs/PAHs decontamination efficiency. It also highlights key advantages of biochar as a bioadsorbent for enhancing remediation applications. It acts as a soil conditioner by improving soil quality, soil fertility and microbial activity (Wang et al., 2018; Safaei et al., 2018). Since biochar can also sequester greenhouse gases, such as CO_2 , CH_4 and N_2O , it could have a significant role in climate change mitigation if biochar production, such as for bioremediation, were to become more widely applied worldwide (Matušík et al., 2020; Dissanayake et al., 2020). Figure 2 below shows the reuse of various agricultural biomass wastes as feedstock materials to promote sustainability and cost-effective strategy, production of biochar and illustrates the four main applications of biochar.

Previous studies have shown that remediation using hydrogel, digestate and bioaugmentation are effective in removing HMs and PAHs when used individually (Table 2 and 4) owing to individual remediation mechanisms presented in Table 4. However, more work is needed to acquire a better understanding on the remediation efficiency and potential of amalgamating biochar with each of the aforementioned remediation agents and to evaluate their synergistic effects on the behaviour of pollutants and their bioavailability. The few adsorption studies conducted so far have shown promising results. For example, a biochar-hydrogel composite with 5% biochar was shown to significantly increase the swelling ratio of the hydrogel to 1506%, which is almost twice the size of the untreated hydrogel (818%), demonstrating great potential for the removal of Cd from soil (Li and Chen, 2018). Application of a biochar-digestate composite improved removal efficiency of Pb by nearly 100% when the composite dosage was applied at 1 g L^{-1} . The same trend was observed for Cd

in this dosage range, where the removal percentage increased from 13% to nearly 100% (Chen et al., 2019a). The digestate used in this study was prepared by anaerobic digestion of food waste and the biochar was prepared by pyrolysis of digestate granules at 700 °C for 15 minutes. Another study used a combination of maize biochar and bacterial strain *Pseudomonas sp. NT-2* (biochar-microbe composite) to investigate the dynamic effects and potential mechanisms of biochar alone and bacteria-loaded biochar on the immobilization of both Cd and Cu in soil by a 75-day pot experiment. Compared to the single biochar amendment, the results showed that the application of biochar inoculated with strain NT-2 significantly increased the proportion of total fraction of Cd and Cu, thus reducing the bioavailability of these metal ions in the soil. The application of bacterial-loaded biochar has also been shown to markedly enhance soil urease and catalase activities, and improved soil microbial community at the end of incubation indicating a recovery of soil function following metal stabilization (Tu et al., 2020).

Nonetheless, all these studies determined total concentrations of the contaminants rather than the bioavailable fraction. Bioavailability is defined as the fraction of freely available contaminant in the environment that is mobile and thus most likely to lead to human exposure (Dean and Scott, 2004). It influences the exposure of humans and ecological receptors to chemicals in soils, and because exposure is one aspect of risk assessment, measuring or modelling bioavailability is important for risk assessment and management of contaminated land. A similar trend is also observed in many other studies which employ total concentration of contaminants for risk assessment and management of contaminated land, as well as exposure risks. Total concentration does not address partitioning and associated toxicological effects of the partitioned fractions, such as the bioavailable fraction, and therefore can be misleading in terms of risk assessment and contaminant management (Cipullo et al., 2019). Table 2 below shows some main advantages and advantages of using biochar, hydrogel, digestate and bioaugmentation for remediation purposes. By nature of their bio-based genesis and composition, these remediation methods are deemed eco-friendly, economical and sustainable approaches for application to bioremediation.

2.3 Biochar Production, Properties and Applications

Biochar can be prepared using various methods. Some of these methods include pyrolysis, hydrothermal carbonization, microwave carbonization, flash carbonization, gasification, torrefaction, laser and plasma cracking (Liu et al., 2013; Xie et al., 2015). Pyrolysis, gasification and hydrothermal carbonisation are the common methods for biochar preparation (Wang and Wang, 2019). However, pyrolysis has been the go-to method because it is simple to operate, cost-effective and requires less energy compared to the other methods (Maguyon-Detras et al., 2020; L. Wang et al., 2020; X. Wang et al., 2020). Also, little data is available for carbonization (hydrothermal, microwave and flash), torrefaction and gasification as these technologies are commonly favoured for bio-oil, solid fuel or synthetic gas yield (Tomczyk et al. 2020; Biogreen, 2020). With respect to the pyrolysis method, biochars are produced under high temperature (typically between 350-800 °C) and in an inert atmosphere free of oxygen (Varma et al., 2018). The recent trend of pyrolysis studies is geared towards the development of new pyrolysis methods and modification of conventional pyrolysis methods. The primary aim is to synthesise engineered biochars with the excellent performance or to improve certain physicochemical properties of biochar, or to reduce the risks associated with the utilisation of contaminated biomass feedstock which could introduce contaminants into the environment during biochar application. For instance, in a recent study (Wang et al., 2020), the authors introduced new pyrolysis methods (e.g. microwave-assisted pyrolysis and steam-assisted pyrolysis) and new modified pyrolysis methods (e.g. magnetic modification and mineral modification). Biochars prepared by microwave-assisted pyrolysis can achieve higher degree of carbonisation, improved physicochemical properties (Mašek et al., 2013) and decrease oxygen-containing functional groups (Paunovic et al., 2019). Steam-assisted pyrolysis also generate low oxygen-containing functional groups (Braghiroli et al., 2019). Studies have shown that both microwave- and steam-assisted pyrolysis were effective in removing HMs (Kwak et al., 2019; Mohamed et al., 2017). The decrease of oxygen-containing functional groups may result in both electrostatic interactions and π - π interactions between aromatic rings of biochar and PAHs (Paunovic

et al., 2019; Zbair, Ahsaine, & Anfar, 2018) and effectively immobilising PAHs. The effectiveness of a biochar adsorbent depends on the type of biomass feedstock material and physicochemical properties of individual biochar, such as yield, ash, specific surface area, pore structure, type and number of functional groups and cation exchange capacity (Pandey et al., 2020; Xie et al., 2015). The physicochemical properties of biochar are influenced by several pyrolysis operating parameters, such as type of feedstock material, pyrolysis temperature, heating rate, residence time, and reaction atmosphere.

Generally, any form of organic material can be pyrolyzed to prepare biochar (Laird et al., 2009). However, due to increasing understanding of upcycling and the circular bioeconomy concept in recent years, more attention has been diverted towards utilisation of agricultural organic wastes, particularly agricultural food wastes. Table 3 below shows some common agricultural biomass wastes which have been used to produce biochar and their remediation effects on HMs and PAHs. Figure 2 below shows various agricultural biomass wastes which have been used to prepare biochars with multiple applications. Lignocellulose (cellulose, hemicellulose and lignin), which is an important structural component of biomass cell walls, plays a crucial role in the thermal stability and adsorptive properties of biochar (Jahirul et al., 2012), as well as influencing biochars' physicochemical properties that can, in turn, affect its adsorption efficiency. Hence, a variation in composition and proportion of lignocellulose in individual biomass material results in variations in physicochemical properties of biochars and stability (William and Besler, 1993; Crombie et al., 2013; Leng and Huang, 2018). The feedstock type also affects the carbon content of the biochar, carbon sequestration capacity, and ash content (Zhao et al., 2013). The reaction temperature is another important parameter which influences the physicochemical properties of biochar. Increasing the pyrolysis temperature increases the ash content, specific surface area, pore diameter and pH, while the biochar yield and acidic or oxygen-containing functional groups (e.g. -COH, -COOH and -OH) are reduced (Yang et al., 2019; Tomczyk et al., 2020) as a result of both depolymerisation and dehydration processes (Keiluweit et al., 2010). A decrease in acidic functional groups results in the reduction of negative charges. Low pyrolysis

temperatures, however, can maintain the structure of the biomass materials whilst undergoing dehydration (Liu and Han 2015).

The pyrolysis process can be divided into slow pyrolysis (SP) and fast pyrolysis (FP) depending on the heating rate (Figure 2). SP involves slow heating rate (minutes to hours, i.e. $<10\text{ }^{\circ}\text{C}/\text{min}$) of biochar material at high temperature ($400\text{--}600\text{ }^{\circ}\text{C}$) with a long solid and gas residence time (e.g. 1 hour) in the absence of oxygen (Varma et al., 2019; Bruun et al., 2012; Mohan et al., 2006). SP produces high biochar yield $>30\%$, which is time and energy efficient (Cong et al., 2018; Tomczyk et al., 2020). Conversely, FP occurs in a high-temperature range of $300\text{--}700\text{ }^{\circ}\text{C}$ at a faster heating rate (milliseconds to seconds, $>10\text{ }^{\circ}\text{C}/\text{s}$), with a short solid resistance time (0.5-10s) and fine particle size ($<1\text{mm}$) feedstock (Yang et al., 2019). In FP, solid biomass material decomposes into other forms, such as vapour, aerosol and char. Usually, the biochar yield is $<20\%$, while the bio-oil yield is $>50\%$ (Wang et al., 2020). As such, FP is recommended when the output is desired in liquid or gas forms (Laird et al., 2009; Tendero et al., 2006).

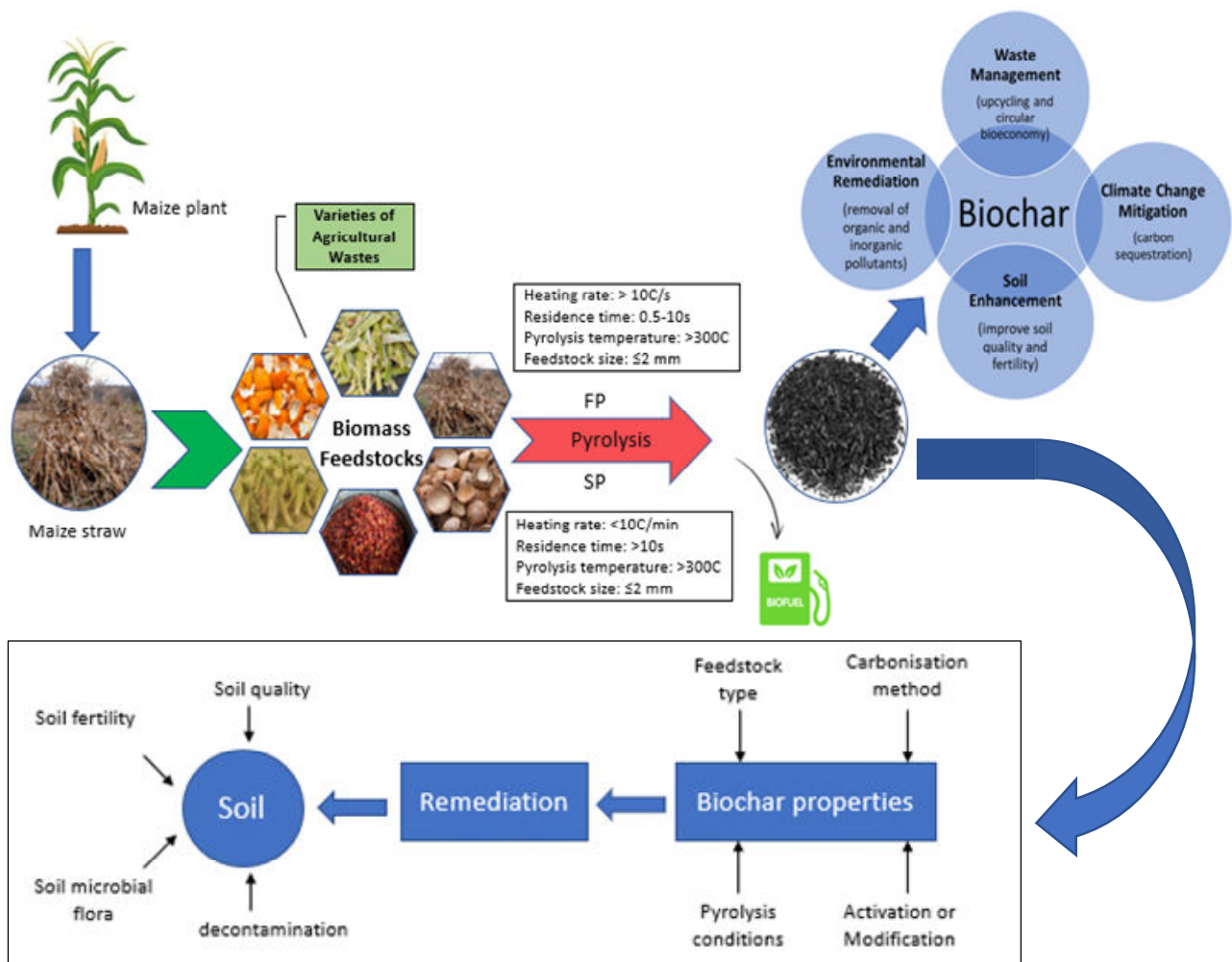


Figure 2. Preparation and application of biochar reusing agricultural waste biomass

The residence time mainly influences physical properties, particularly biochar yield. At a constant temperature, increasing the residence time decreases the biochar yield and enhances biochar carbonisation (Yang et al., 2019; Zornoma et al., 2016; Wang et al., 2020). Residence time can also affect the specific surface area and pore diameter of biochars (Bruun et al., 2012; Chen et al., 2011). Although the beneficial qualities of biochar are well documented by a plethora of studies in the literature, there are some limitations (Table 2). For instance, the ageing of biochar, or its residence time, in the soil is a growing concern. Ageing harms biochar's adsorption efficiency and growth of soil microorganisms. Therefore, the intermittent addition of fresh biochar is required for optimal nutrient cycling (Anyauwu et al., 2018). Several studies have reported weed problem associated with biochar application. For instance, Safaei et al., 2018 reported that biochar can lower herbicide efficacy, resulting in higher consumption of herbicides by weeds. In the same study, the addition of

7 t/ha bamboo biochar increased the weed biomass 1 and 2 years after biochar amendment approximately 65 % and 80 %, respectively. Theoretically, biochar is not a biodegradable substrate but the possibility of biochar undergoing deterioration as a result of aging, chemical oxidation and microbial processes due to potent labile carbon source in itself is a concern (Smith et al., 2010; Cross and Sohi, 2011). Moreover, most of the studies conducted so far originate from short-term experiments in laboratory conditions. Insights in the field application and the long-term effects of biochar remain lacking (Hardy et al., 2019; Maestrini et al., 2014; Sagrilo et al., 2015).

Table 2. Advantages and disadvantages of selected (bio)engineered remediation technologies of HMS and PAHs

(Bio)engineered Remediation	Advantages	Disadvantages	Efficiency	Ref
Biochar amendment	<ul style="list-style-type: none"> - Immobilise pollutants - Low cost & sustainable - Environmentally friendly - Sustainable - Sequestration of carbon - Improve soil fertility and quality - Promotes/Involves upcycling - Promote microbial activity - Retention of water 	<ul style="list-style-type: none"> - Reduce herbicide efficacy & promote weed growth - Could introduce HMs & PAHs into the soil - Possible biochar degradation by natural weathering - May form colloids affecting microbial activities - Can have an inhibitory effect on soil ageing thus requires intermediate biochar addition - Ageing biochar can affect soil microorganisms 	Biochar reduced bioavailability of Cd and Pb in contaminated soil by 85% and 29 %, respectively ^a and decreased bioavailable TPH concentration by 24-28 % ^b	Beesley et al., 2011; Manyà, 2012; Zhang et al., 2012; Anyanwu et al., 2018; Wang et al., 2018
				^a Alaboudi et al., 2019; ^b Cipullo et al., 2019
Hydrogel amendment	<ul style="list-style-type: none"> - Immobilise pollutants - Low cost & sustainable - Environmentally friendly - High water retention - Physiochemically & thermally stable - Good mechanical strength - Good reusability & biocompatibility - Wide modifiability - Moderate degradability 	<ul style="list-style-type: none"> - Difficulty recovering nano/micro-sized hydrogel - Selective removal and recovery of a targeted pollutant (e.g. HMs) is a challenge - The weak force of interaction could lead to reversible reactions & disintegration of hydrogel 	Hydrogel removed Pb ²⁺ and Zn ²⁺ from aqueous solutions with adsorption capacities of 146 mg/g and 287 mg/g, respectively ^c . Another study showed a high removal efficiency of both monocyclic and PAHs with a removal efficiency >60 % ^d	Yan et al., 2011; Shalla et al., 2019; Shen et al., 2011; Tang et al., 2014; B Wu et al., 2017; Tang et al., 2010; Tang et al., 2012 ; ^c Astrini et al., 2015 ^d Filho et al., 2020
Digestate amendment	<ul style="list-style-type: none"> - Immobilise pollutants - Low cost & sustainable - Environmentally friendly - Introduce various microorganisms - Improve soil fertility & quality - Low solubility & biodegradability - Promotes/Involves upcycling - Remove pathogens - Increase microbial diversity - Increase microbial activities 	<ul style="list-style-type: none"> - Could introduce organic and/or inorganic pollutants - Could introduce biological pollutants - Introduce indigested materials like stone/plastic/glass - Long-distance transportation can be costly - Can lead to nutrient leaching, increase soil salinity & NH₃ emission 	Digestate improved soil fertility and microbial activities (increased number of 16S rRNA genes and dehydrogenase activities) ^e . A study revealed the reduction of alkane and TPH by 99 % and 38-57 %, respectively. ^f	Montes et al., 2013; Möller & Müller, 2012; Aspray et al., 2017; Tella et al., 2016; Van Wezel et al., 2016; Insam et al., 2015 ^e Garcia et al., 2015 ^f Gielnik et al., 2020a,b
Bioaugmented amendment	<ul style="list-style-type: none"> - Immobilise pollutants - Low cost & sustainable - Environmentally friendly - Increase genetic diversity - Requires little equipment/technology - Applicable to in-situ and ex-situ 	<ul style="list-style-type: none"> - Competition between exogenous and indigenous microorganisms - Predation of exogeneous microorganisms by protozoa and bacteriophages - Difficulty delivering inoculant to sub-surface soil - Selection of suitable microorganisms or their consortia is a challenge - Process sensitive to toxicity and physicochemical condition of the soil 	<i>Streptomyces flavomacrosporus</i> significantly decreased Hg from contaminated media ^g . Gram-positive bacteria showed a significant reduction (99 %) in PAHs concentration ^h	Kapahi & Sachdeva 2019; Azubuike et al., 2016; Rapper et al., 2018; Megharaj and Naidu 2017; Mrozik & Piotrowska-Seget ,2010; ^g Sunil et al., 2015 ^h Haleyur et al., 2019

2.4 Engineered Modification of Biochar for Tailored and Enhanced Remediation Approaches

One way to reduce the mobility and bioavailability of HMs and PAHs is to increase the binding sites (lessens competitive adsorption) and to introduce HM/PAH tolerant microorganisms capable of removing HMs and degrading PAHs. Biochars can be modified with other materials to produce engineered biochars with increased binding sites and microbial activities. Engineered biochar is the derivative of pristine biochar that is modified to improve its physical, chemical and biological properties (e.g., specific surface area, porosity, cation exchange capacity, surface functional group, pH etc.) and adsorption capacity compared to pristine biochar (Mohamed, Ellis, Kim, Bi, and Emam, 2016; Rajapaksha et al. 2016). The four common engineered methods in which biochars can be modified are physical modification, chemical modification, biological modification and other modification treatments such as UV and magnetic exposures (Peng et al., 2019; Liu et al., 2020; Panahi et al., 2020). Physical modifications mainly affect physical structure of biochar while chemical modification has large effect on biochar's chemical structure including bonds and functional groups (Sajjadi et al., 2019a), and biological modification promote microbial diversity and activities (Gielnik et al., 2019a,b).

2.4.1 Physical modification

Physical modification includes traditional gas (e.g. steam, CO₂ or ozone), thermal, ultrasound, plasma, and electrochemical modification. Physical modification greatly affects the physicochemical properties of biochar such as surface area, pore volume ash content, pH, aromaticity (H/C), and polarity (O + N)/C (Sajjadi et al., 2019b).

2.4.2 Biological modification (bioengineered biochar)

Biological modification of biochar is done to produce bioengineered biochar (Wang et al., 2017). Bioengineered biochar can be produced by amalgamating biochar with biologically pre-treated biomass feedstocks (digestate) through anaerobic digestion (Inyang et al., 2010; Gielnik et al., 2020a,b), or inoculation of contaminant degrading microorganisms onto the surface of biochar (Tu et al., 2020) for enhanced remediation performance.

2.4.3 Chemical modification

Chemical modification, in which char is doped with a chemical agent, is the most common method to modify surface functional groups, though its mechanism is not well understood (Sjjadi et al., 2019a). Chemical modification can be further categorised into oxidation, amination, sulfonation, and impregnation of nanomaterial (metal oxides) into biochar structure (Sajjadi et al., 2019a; Yin et al., 2018). The processes of surface oxidation can be sub-divided into two categories, which uses oxidants (e.g. HCl, HNO₃ or H₂O₂) and reductants (e.g. NaOH, KOH or NH₄OH) to increase the hydrophilic properties of the biochar (Liu et al., 2012). Surface oxidation is purposely done to create oxygen-containing functional groups on the surface of biochar. Carboxyl, phenolic hydroxyl, lactones, and peroxides are the most common oxygen containing functional groups formed on biochar after oxidation. Among these groups, hydroxyl and carboxyl groups remarkably improve the adsorption capacity when biochar is utilised for HM removal (Sajjadi et al., 2019a). The use of amino group (e.g. NH₃) and/or sulfonic (-SO₃H) groups is the most commonly used method for the surface amination and sulfonation of biochar for acidic materials (Sajjadi, et al., 2019a). The metal impregnation, which uses heteroatoms (e.g. Mg, Mn, Ca, Cu, Ni, and Fe) oxides to increase the specific surface area of the biochar and, thus, improving its general adsorptive properties (Yin et al., 2018; Li et al., 2016; H. Wu et al., 2017). However, the cost associated with the number and volume of chemicals can be costly and there is a greater risk of these chemicals becoming released into the environment, thus generating secondary pollution.

2.5 Hydrogel Assisted Remediation

2.5.1 Application and properties

A hydrogel is a three-dimensional network of hydrophilic polymers which are cross-linked and flexible, and that can swell in water or biological fluid and retain a large volume of water while maintaining its structure (Chai et al., 2017; Ahmed, 2015). Apart from its widespread applications in bioengineering, biomedicine, agriculture, sensors, food industry and water purification and separation

processes (Annabi et al., 2014; Zhou et al., 2017; Liu and Li 2017; Xu et al., 2017), hydrogels have been recently used as a sorbent for the removal of metal ions from water and aqueous media (Rehman et al., 2019; Pathan and Bose, 2018, Du et al., 2020). The application of hydrogels in metal removal is attributed to its hydrophilic properties, largely conferred by hydrophilic functional groups, such as hydroxyl, carboxyl, sulfonic acid and amide (Rehman 2019; Askari et al., 1993).

2.5.2 Adsorption process and mechanism

Generally, the adsorption process of hydrogels can be divided into two sub-systems called chemical sorption and physical sorption. Chemical sorption is an irreversible system characterised by the formation of a chemical bond between the adsorbate (e.g. HMs) and the adsorbent (the hydrogel), while physical sorption is a reversible system characterised by weak physical interactions between the adsorbate and adsorbent – these include electrostatic interactions, hydrogen bonding, van der Waals bonds, co-ordination bonds and hydrophobic interactions (Holback et al., 2011; Buenger et al., 2012; Abeer et al., 2014; Liu et al., 2014; Pourbeyram and Mohammadi, 2014).

2.5.3 Synthesis: method and key ingredients

Hydrogels are synthesised by various methods, such as by freeze-drying, pyrogenation, microemulsion formation and segment separation (Butylina et al., 2016; Badiger et al., 1993; Ghayempour and Montazer, 2018; Omidian et al., 2005). However, free radical polymerisation (FRP) is regarded as the most widely used method to prepare hydrogels and also other polymers with successive addition of free-radical building blocks (Shinde et al., 2013; Thakur and Thakur, 2014). FRP is widely used because it acts as a synthesis route for obtaining a wide variety of different polymers and material composites. Also, the relatively non-specific nature of free-radical chemical interactions makes FRP one of the most versatile of methods for manufacturing polymers (Tessinova, 2011; Kim and Sikes, 2020; Gao et al., 2020). In general, a typical hydrogel synthesis requires a backbone polymer (e.g. sodium alginate), monomer (e.g. acrylic acid), crosslinker (N-N' methylene bis-acrylamide) and an initiator (e.g. potassium persulfate) (Verma et al., 2020). The formation of a gel is a result of weak and strong interactions tethering the properties of the hydrogel construct (Ajdari et al., 2020). Other researchers have argued that the use of synthetic chemical backbone polymers could lead to secondary pollution, and as such have recommended the use of biopolymers (biosorbents), such as cellulose and lignin, which are more eco-friendly and foster the circular bioeconomy concept (Coviello et al., 2007; Klein and Poverenov, 2020; Kabir et al., 2018; Ajdari et al., 2020). Recent advances have explored the use of natural biopolymers, such as polysaccharides, proteins and lipids among others. For instance, several hydrogels have been used as biosorbents, for

example cellulose graft acrylic acid (C-g-AA), chitosan hydrogel, PVA-hydrogel biomass of *Penicillium cyclopium*, and starch graft acrylic acid/montmorillonite (S-g-AA/MMT) (Jamnongkan et al., 2014). However, the application of biosorbent polymers to treat contaminated soils can result in their degradation by soil microorganisms, thus shortening their remediation life span without achieving their expected function (Nair et al., 2017). On the other hand, synthetic polymers are less susceptible to natural and biological degradation, often making them an ideal choice for contaminated soil remediation (Leja and Lewandowicz, 2010).

2.5.4 Factors affecting the adsorption capacity

The swelling and sorptive behaviour of a hydrogel is largely influenced by factors such as pH of contaminated media (Cao et al., 2011), ionic energy, the composition of adsorbate and adsorbent, contact time, initial concentration, temperature, light chemical species, electric and magnetic fields (Chen et al., 2013; Bekin et al., 2014; Chatterjee et al., 2010). However, pH has been reported to have a significant influence, particularly in having selective adsorption for metal species compared to other factors. Studies have shown that maximum adsorption efficiency can be achieved at a pH range between 4 and 6 (Hua et al., 2012; Dragan, 2014).

2.5.5 Hydrogel-assisted remediation studies

Hence, by amalgamating biochar with hydrogel (i.e. biochar-hydrogel composite) would enhance the adsorption efficiency of biochar. Enhanced remediation could lead to the less intermittent application of ageing biochars or quicker remediation output time compared to biochar when applied alone. Also, the mechanical stability of hydrogels could provide stability to biochar when subjected to natural degradation, thus improving its life span. Moreover, the reusability (sustainably economical), low-cost associated with the purchase of chemicals needed for hydrogel synthesis, and biocompatibility (harmless to the physiology of biological organisms) of hydrogels add to the advantage of hydrogel (Table 2). The most common monomer for polymerizing hydrogel is acrylamide, whose market price can be as low as \$1/kg (Li and Chen, 2018). Several studies of biochar-hydrogel composite applications investigated for remediation of PAHs and HMs have yield positive results. M. Zhang et al. (2020) and W. Zhang et al. (2020) used waste biomass based hydrogel soybean residue-poly(acrylic acid) (SR-PAA) to remove Cd^{2+} and Pb^{2+} ions from aqueous solutions. It was found that

the adsorption equilibrium was achieved within 20 min, and maximum adsorption for Cd^{2+} and Pb^{2+} ions were 1.43 and 2.04 mmol g^{-1} , respectively. The adsorption of metal ions was not much affected during the subsequent adsorption-desorption cycles. After 5 cycles of regeneration and reuse, the adsorption for Cd^{2+} and Pb^{2+} ions were 1.01 and 1.50 mmol g^{-1} which corresponded to 70.6% and 73.9% of adsorption capacity of the first cycle, respectively. Li and Chen (2018) investigated the adsorption behaviour of wood waste biochar-hydrogel composite to remove Cd^{2+} from aqueous media. The composite achieved a swelling capacity of 1,506 % compared to the hydrogel (818 %) when used alone. The maximum adsorption capacity of the composite was reported 63.58 mg g^{-1} compared to untreated hydrogel (24.72 mg g^{-1}). The increased maximum adsorption capacities of the hydrogel composite to remove Cd^{2+} was attributed to synergistic effect of polyacrylamide hydrogel-biochar composite. The reason for the synergistic effect was linked to each single biochar particle scattered in the composite creating an ionic attraction field for attracting and retaining metallic ions such as Cd^{2+} . This ionic attraction field significantly extended the potential of each biochar particle to entrap ions within the cross-linked composite structure against large concentration gradient of ions (Li and Chen, 2018). The formation of many ionic attraction fields around the scattered biochar particles made it possible to overcome the ionic osmotic stress, the main factor regulating the sorption and release of ions in hydrogel materials (Wang et al., 2014). Another study used a novel three dimensional MnO_2 modified biochar-based porous hydrogel (MBCG) composite to eliminate Cd^{2+} and Pb^{2+} ions. The maximum MBCG adsorption capacity on Cd^{2+} and Pb^{2+} was 85 and 71 mg g^{-1} , respectively. Just like SR-PPA, MBCG was separated and regenerated with an excellent reusability, which retained 92.1% and 80.5% of the initial adsorption capacities of Cd^{2+} and Pb^{2+} after 5 cycles (Wu et al., 2020). A hydrogel-biochar (rice husk) composite (HBC-RH) was utilised for the removal of zinc from wastewater. The maximum monolayer sorption capacity of HBC-RH for Zn^{2+} was 35.75 mg g^{-1} (Sanyang et al., 2014). The nanosorbent (N-PSPB/SHGL) was fabricated based on encapsulation of derived nanoscale spherical biochar from *Pisum sativum* pods (N-PSPB) with starch hydrogel (SHGL). N-PSPB/SHGL attained a high swelling capacity of 500 % with excellent stability

for ten cycles with respect to regeneration by 0.1 mol L⁻¹ HCl (Mohamed and Mahmoud, 2020). Biochar/pectin/alginate hydrogel beads (BPA) derived from grapefruit peel were synthesised and used for Cu²⁺ removal from aqueous solution. The adsorption capacity of Cu²⁺ onto optimised BPA-9 reached maximum values of 36.25 ± 0.33 mg g⁻¹ at pH 6 (Zhang et al., 2020).

Table 3. Remediation of contaminated soil by biochars derived from various agricultural biomass wastes

Biomass Feedstock	Soil Texture	Pollutants		Remediation Effect	Ref
		HMs	PAHs		
Wheat chaff	Sandy-loam	√		>96 % of extractable soil Cd was significantly immobilised after the biochar application	Zhang et al., 2013
Soybean stover	Loam-sandy	√		Reduction of >90 % in Pb leachability was achieved after application of biochar in firing range soil	Moon et al., 2013
Wheat straw	Clay	√		Soil extractable Cd decreased by 55-71% and Pb by 65-80%	Bian et al., 2014
Dates	Sandy-loam	√		A reduction of 53 % in the soil Ni was recorded compared to unamended treatment	Ehsan et al., 2014
Cassava stem	Silty-clay-loam	√		Cd accumulation in shoots decrease by about 35 %	Prapagdee et al., 2014
Peanut, soybean, canola, rice	Oxisol	√		Pb adsorption increased by 67%, 57%, 51% and 43% for the treatments with each biochar, respectively.	Jiang et al., 2014
Sugarcane straw	Clay-loam	√		Decreased the available concentrations of Cd, Pb and Zn by 56, 50 and 54% respectively, in the mine contaminated soil	Puga et al., 2015
Rice hull	Sandy-loam	√		Application of biochar reduced Cd by 97 %, Cu (90 %), Pb (100 %) and Zn (100%)	Kim et al., 2015
Coconut shell, sugarcane bagasse	clay	√		Cd adsorption increased after application of coconut shell biochar (13 %) sugarcane bagasse (24 %)	Tan et al., 2015
Wine lees	n.a.	√		Cr, Ni, Cu, Pb, Zn, and Cd decreased by 19, 30, 26, 23, 23 and 48 %, respectively in contaminated soil while Zn, Cd, and Pb decreased by 12, 9 and 8 %, respectively in rice plant	Zhu et al., 2015
Wheat straw	n.a.	√		Soil available Cd and Zn decreased by 85% and 91%, respectively. Translocation of Cd from rice roots to shoots reduced from 20 to 80% and reduced rice grain Cd by 86 %	Chen et al., 2016
Soybean stover	Sandy-loam	√		Effective in immobilizing Pb (88%) and Cu (87%) in a contaminated shooting range soil	Ahmad et al., 2016
Rice straw	Red clay	√		Cd and Pb decreased in soil and plant after applications of the biochar	Shen X et al., 2016
Rice straw	Sandy-loam	√		Decreased extractable Cu and Zn by 97 % and 62 %, respectively	Yang X et al., 2016
Tomato green waste	Sandy-clay-loam	√		Reduced Cd mobilization in soil by 35–54% and reduced its accumulation in shoots of Pak Choi cultivars by 34–76%	Khan et al., 2017
Peanut vine and rice straw	latosolic red soil			Biochars amendment led to 35.80% and 28.48% lower rates of exchangeable Cd content in the soil, respectively of two biochars	Chen et al., 2020
Tobacco stalk	Clay-loam	√		The concentration of extractable Cd and Zn decreased by 64 % and 95 %, respectively	Yang et al., 2017
Sugarcane bagasse and orange peel	Silt loam	√		Reduced the concentrations of As below regulatory limit	Abdelhafez et al., 2014
Beet	n.a.	√		Effectively reduced Cd, Cu, Ni and Pb by 57, 98, 26 and 87%, respectively	Inyang et al., 2012
Fruit biochar	na	√		Significantly reduced total and bioavailable HM concentrations	Beesley et al., 2014
Grape prune residue	Calcisols			The mobility factor values of Cd, Pb, Cu and Zn decreased by 47, 62, 70 and 49%, respectively	Hamzenejad and Sepehr, 2018
Rice straw, husk and bran	n.a.	√		Significantly reduced the transport coefficient of Cd and Pb in the aerial parts of plants and promote the transfer coefficient of As	Zheng et al., 2012
Sugarcane bagasse	Sandy loam silty clay	√		Cd decreased by 62-76%, Pb decreased by 17-49% and Cu by 15-38% in shoots	Nie et al., 2018
Rice straw	Red loam soil	√		Significant reduction in the bioavailable fraction of Cd, Cu and Zn Metal bioavailability by 24–65% and increased vegetable yield by 34–67%	Niu et al., 2015
Palm silk	n.a.	√		Cd and Pb decreased by 45% and 49% in corn, respectively	Li et al., 2017
Wheat straw	n.a.	√		Cd decreased by 20-90%	Bian et al., 2013

Rice husk	n.a.	√		Cd decrease by 69%	Guo et al., 2016
Rice straw	ultisol			Decreased Cu and Pb by 20–100% and 19–77%, respectively	Jiang et al., 2012
Beanstalk and rice straw	n.a.	√		Cd, Zn and As decreased by 21-67%	Meng et al., 2018
Agriculture residues	Loamy sand	√		Achieved reduction of expendable Pb and Cd by 28.68% and 85.14%, respectively	Alaboudi et al., 2019
Pecan shell	na	√		Adsorbed 61% more Pb	Crisler et al., 2019
Vegetable wastes	sandy loam	√		Achieved Pb immobilization of 87%	Igalavithana et al., 2019
Miscanthus straw	Sandy loam	√		Reduction of bioavailable fraction reached 92 %, 87% and 71 % for Cd, Zn ²⁺ and Pb ²⁺ , respectively	Houben et al., 2013
Rice straw	Sandy loam	√		Reduced Pb ²⁺ and Cu ²⁺ by 71 % and 46 %, respectively in <i>Sedum plumbizincicola</i>	Lu et al., 2014
Coconut shells	n.a.		√	Decreased phenanthrene by 95%, anthracene 98%, fluoranthene 97%, pyrene 98%, benzo(a) pyrene 88%, chrysene 95%, benzo(b) fluoranthene 86%, benzo(k)fluoranthene 88%, benzo(a) anthracene 95%, indeno (1,2,3-cd) pyrene 73%, and Benzo(g,h,i) perylene by 69%	Amstaetter et al., 2012
Maize stover	n.a.		√	Decreased PAHs by ≤57%. Studied PAHs include: naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo(a) pyrene, indeno(1,2,3cd) pyrene, Benzo(g,h,i) perylene	Oleszczuk et al., 2012
Soybean stalk	n.a.		√	Removed naphthalene by 100%, phenanthrene by 100% and acenaphthene by 96%	Kong et al., 2011
Wheat straw	n.a.		√	Phenanthrene, fluoranthene, pyrene achieved 96-99% removal efficiency	Li et al., 2014
Sugarcane bagasse	n.a.		√	Increased removal of PAHs contained in highly polluted soil by up to 40%	Trejo-Hernandez. 2007
Sugar beet tailing	Sandy soil		√	Immobilised PAHs in the contaminated soil and replenished the bioavailability of the soil, compared to unamended soil	Wang et al., 2018
Plant residues and empty fruit bunches	Sandy-loam		√	PAHs accumulation was reduced concerning time for organic waste/plant residues. Thus, it enhanced soil modification on application	Zeng et al., 2018;
Olive pomace	n.a.		√	Pyrene concentration was reduced by 70 % after 28 days of biochar application	Piscitelli et al., 2019
Rice straw	Sandy soil		√	Addition of biochar achieved highest biodegradation rate of PAHs by 40-59 %	Zhang et al., 2020
Peanut shell			√	Bioaccumulation reduction of PAHs by 71-84 %	Khan et al., 2015
Walnut shell, corn straw & rice straw	Sandy loam		√	increased biodegradation rate of chrysene by 3–45%	Zhang et al., 2018
Corn straw	Sandy loam silty clay		√	Reduced bioavailable 2(+3)-, 4-, and 5-ring PAHs in rice roots by 10 %, 40 % and 40 %, respectively	Ni et al., 2018
Maize straw	Sandy loam silty clay		√	Decreased PAH from contaminated soil by 30 %	Li et al., 2019a,b
Wheat straw	n.a.		√	Degradation of ΣPAHs in contaminated soil increased by 38 %	Cao et al., 2016
Rice hull	n.a.		√	Increased removal efficiencies of all two-ring to four-ring PAHs by 35 to 37 %	Liu et al., 2015

n.a. not available

2.6 Digestate Amendment

2.6.1 Source and classification

From the many years of bioremediation studies and research, little remains unknown about the contribution of microorganisms from digestate to the overall efficiency of contaminant removal and the role of digestate as biostimulant in the remediation of HMs and PAHs. Digestate as a biostimulant is mainly attributed to the rich nutrient content of digestate contributing to increase microbial population and activities, in return, the microorganisms remove the pollutants (Gielnik et al., 2019a,b). Digestate is produced by anaerobic digestion (AD) of organic fraction of municipal solid wastes (OFMSW) and agricultural food wastes (AFW). Digestate is composed of three parts: undigested feedstock, microbial organisms, and microbial metabolites. The solid part of digestate after mechanical solid-liquid separation or natural sedimentation is called solid digestate, while the liquid part is called liquid digestate (Deng et al., 2020). Like biochar, the application of digestate employs and promotes the concept of upcycling and circular bioeconomy by utilising OFMSW and AFW to enhance pollution remediation, with environmental, agricultural and economic benefits (Logan and Visvanathan, 2019). Unlike AFW, which entirely consists of organic wastes, MSW consists of various types of wastes like paper, glass, metal, plastic, textiles and other organic wastes. The composition and proportion (proportional % of an individual type of waste) of MSW varies across the world. In the developing world, MSW contains a rich organic fraction, while in more developed countries the major fraction of MSW comes from plastic and paper. For example, organic wastes constitute more than 50 % of Thailand's MSW (Thi et al., 2015). Poor management and disposal of OFMSW and AFW in landfills can lead to uncontrolled anaerobic decomposition, thus resulting in soil and water pollution, bad odour, and production of methane and other pollutant gases released to the atmosphere (Sisto et al., 2017; Psomopoulos et al., 2009). For instance, the Food and Agriculture Organization (FAO) of the United Nations estimated that 1.3 billion tons of edible food is wasted globally each year resulting in 250 km³ of corresponding wasted water and an addition of 3.3 billion tons of CO₂ emissions to the atmosphere (FAO, 2013). Instead, the OFMSW and AFW

can be upcycled to produce digestate with rich nutrients (organic fertilizers) that is cheaper compared to inorganic fertilizers. It can act as the carrier of microorganisms capable of removing HMs and degrading PAHs. Moreover, it supports carbon sequestration in soil organic matter (SOM), thereby reducing the emission of greenhouse gasses such as CO₂.

2.6.2 Nutritional properties (bio-fertiliser)

The nutrient-rich digestate usually contains a dense and diverse microbial population which can degrade PAHs and remove HMs (Mrozik and Piotrowska-Seget, 2010; Agnello et al., 2016). Nutrients from digestate and exogenous microorganisms (respective to indigenous microorganisms in the soil) inhabiting the digestate can promote microbial abundance, diversity and activities (Gielnik et al., 2019a,b; Ogbonna et al., 2018). Recently, the use of digestate as an organic fertilizer has generated interest in soil science due to its high concentration of nutrients that are present in bioavailable form and low level of easily degradable carbon (Tambone et al., 2010; Walsh et al., 2012; Kataki et al., 2017).

2.6.3 Digestate-assisted remediation with biochar

A 60-day incubation experiment was set up on a French technosol which was heavily contaminated with Pb due to former mining activities. After 30 days of incubation, cow manure biochar reduced Cd and Zn by 90 % and 80 %, respectively, and digestate by 63 % and 73%, respectively, compared to the control (Van Poucke et al., 2020). Bianco et al., (2020) showed that contaminated soil amended with digestate after 120 days reduced PAHs by 43 %. Several laboratory-scale studies added digestate and organic matter (OM) to contaminated soil have shown significant improvement in the rate of hydrocarbon biodegradation (Namkoong et al., 2002; Juteau et al., 2003; Kriipsalu et al., 2007; Sayara et al., 2010). A 2 months incubation of soil with digestate increased *alkB* genes (encoding enzymes responsible for the degradation of saturated hydrocarbons) to 11.5 % and after the addition of hydrocarbon degrading bacteria immobilised onto biochar, this value increased up to 60 %. The application of digestate positively affected soil respiration and bacterial density, and decreased petroleum hydrocarbons by 74%, while extra addition of bacteria immobilised onto biochar increased

this value up to 95% (Gielnik et al., 2020a,b). A similar study examined digestate as a potential nutrient and microbial seeding for bioremediation of weathered (aged) petroleum hydrocarbon contaminated (TPH) soils (Gielnik et al., 2019a,b). After 30 days of incubation, the TPH removal was observed in microcosms containing digestate together with a bulking agent (18 % and 13 % higher than control in clay-rich soil and sandy soil, respectively) or digestate together with immobilised bacteria (13% and 9% higher than control in clay-rich soil and sandy soil, respectively). Quantification of *alkB* genes in the digestate was extremely high application of digestate. The same study revealed the promising potential of digestate as a source of nutrients and bacteria for soil bioremediation. Hence, biochar-digestate composite can be bioengineered to harbour selected microbial consortia that will comprise a biochemical system that will enhance the reclamation of contaminated soil beyond conventional methods. In addition to its advantages, it is deemed cost-effective, environmentally friendly, sustainable and requires less effort and equipment (Table 2).

2.7 Microbe-Assisted Remediation

2.7.1 Remediation process and mechanism

Another bioremediation technique is bioaugmentation which employs adding microorganisms to immobilise HMs and PAHs, including to degrade the latter. Just like hydrogels and digestate, microorganisms (e.g. bacteria, fungi and/or alga) can be seeded with biochar to enhance its remediation efficiency. Microorganisms can release contaminant-degradative enzymes into the environment to break-down organic contaminants such as PAHs. During microbial degradation, PAHs are degraded, which is complete will become mineralised to CO₂ and H₂O (Yakimov et al., 2007). The uptake and storage of HMs by microorganisms can be achieved through either by an active process called bioaccumulation (i.e. absorption of HMs at a faster rate than at which it is lost by catabolism and excretion) or passively via adsorption process (binding of metals ions to anionic functional groups). The cell walls of microorganisms consist of various functional groups such as carboxylate, hydroxyl, amino, sulfate, amine, and phosphate, which provides a negatively charged

surface that can attract positively charged metal ions from soil (Abdi and Kazemi, 2015; Vijayaraghavan and Yun, 2008). The opposite charges facilitate for one or a combination of various interactions like electrostatic forces, and van der Waals forces (Rajendra et al., 2003). Table 4 summarise various chemical interactions involved in the remediation mechanism of biochar and bioaugmentation. Microorganisms which have the capability of accumulating HMs in their bodies pose an inherent characteristic for converting toxic forms of HMs into non-toxic or less toxic forms through various mechanisms to avoid potential health effects of metal toxicity. The bioaccumulation mechanisms can be grouped into an extrusion system (e.g. removal of metal-mediated by chromosomal or plasmid actions), biotransformation (biological conversion of metals from toxic to non-toxic form), enzyme utilization (e.g. the conversion of toxic metal to the metabolic product by oxidase and reductase), exopolysaccharide (EPS) production (a physiological adaptation of hydrophobic cell membrane via secretion of EPS), and synthesis of metallothioneins which form complexes with metals (Dixit et al., 2015; Garbisu and Alkorta, 2003; Singh and Ward, 2004; Wu et al., 2010). Whilst a metal tolerant microorganism which can undergo all the bioaccumulation mechanisms would be considered an ideal species for the remediation of soil polluted with HMs and/or PAHs, such an organism remains undiscovered or not yet bioengineered. Therefore, microorganisms possessing various mechanisms are combined to form a mixed culture with improved mechanisms and features.

2.7.2 Bactoremediation, mycoremediation and phycoremediation

In recent years, bactoremediation (employ bacteria for detoxification) using actinobacteria have received special attention as candidates for bioremediation due to their proven versatility and abundance in the environment. Actinobacteria are a group of Gram-positive bacteria with high guanine and cytosine content in their DNA and constitute the largest bacterial phyla (Barka et al., 2016). For example, Alvarez et al., (2017) reported the ability of actinobacteria in removing HMs and pesticides simultaneously. Generally, Gram-positive bacteria are recognised as most effective in the removal of HMs due to presence of glycoproteins compared to Gram-negative bacteria comprising

phospholipids and lipopolysaccharides (Das et al., 2008; Gourdon et al., 1990). Chang et al., (2019) had shown that augmenting biochar with *Pseudomonas* sp. DC-B1 and *Bacillus* sp. DC-B2 performed well in reducing Hg^{2+} contents in soil, lettuce shoots and roots, achieving a decrease of 12-27%, 25-58 % and 2-49 %, respectively. Similarly, Gram-positive bacteria are quite effective PAH degraders and are often found as the dominant group of species over other bacterial species that are present in PAH-contaminated soil (Haleyur et al., 2019). Apart from commonly used bacteria for microbial remediation, the capabilities of fungi and alga to remove HMs and PAHs in contaminated soils had been studied. For example, A mycoremediation (employing fungi for detoxification) study by Lakkireddy and Kues (2017) utilised mushroom *Coprinopsis atramentaria* to achieve a Cd removal efficiency of 76% at 1 mg L^{-1} and Pb^{2+} (9%) at 800 mg L^{-1} . A similar study by Fernandez et al., (2017) used psychrotolerant yeasts reported having removed 80% of 1 nM of Cr^{6+} , 55% of Cd^{2+} and 80% of Cu^{2+} . The ability of algae has also been reported to remediate HMs in several studies. The term ‘phycoremediation’ is used to denote macro-algal-, micro-algal- or cyanobacterial-mediated remediation, either through the removal (e.g. biosorption) or degradation and assimilation of HMs (Chabukdhara et al., 2017). Like bacteria, the surface of algal cells consists of various functional groups (e.g. $-\text{OH}$, $-\text{COOH}$, NH_2CO and PO_4^{3-}), which form the negatively charged surface that acts as metal-binding sites to attract positively charged toxic metal/metalloid ions (Abbas et al., 2014; He and Chen, 2014). For example, the cell wall of brown macro-algae (Phaeophyta) possess a significant level of carboxyl groups which acts as a sink for HMs via electrostatic attraction, thus behaving as a hyperaccumulator species (Ali et al., 2017; Sharma et al., 2018).

2.7.3 Microbe-assisted remediation studies

In a 75 days pot experiment, biochar was used as a carrier for immobilising Cd-Cu tolerant strain NT-2 (*Pseudomonas* sp.). The bacteria NT-2 loaded biochar decreased the bioavailability of Cd^{2+} and Cu^{2+} from 29.5 mg kg^{-1} to 20.8 mg kg^{-1} and from 127.3 mg kg^{-1} to 73.4 mg kg^{-1} , respectively. The enriched biochar also increased soil enzyme activity and greatly improved soil microbial community profile (Tu et al., 2020). Chen et al., (2019) applied phosphate-solubilising bacteria (PSB) modified

biochar to enhance immobilisation of Pb^{2+} by rice biochar (RB) and sludge biochar (SB). The study showed that the RB and SB effectively removed Pb^{2+} (18.61 % and 53.89 %, respectively). But, the higher reduction of Pb^{2+} was achieved from colonisation of RB and SB with PSB (24.11 % and 60.85 %, respectively). Similarly, corn straw biochar and pig manure biochar were studied as carriers of a mutant genotype from *Bacillus subtilis* (B38) for heavy metal contaminated soil remediation. After amendment with bacteria loaded biochars, the heavy metal (Cd, Cr, Hg and Pb) concentrations in the edible part of lettuce decreased by 70 – 96 % (Wang et al., 2017). Ejaz (2016) applied biochar at the rate of 1 % and 2 % in each pot containing 10 kg heavy metal (Ni, Cd and Pb) contaminated soil. Three different strains of endophytic bacteria i.e. FD-17, KS-54 and PsJN were applied. The levels of Ni, Cd and Pb decreased up to 40 %, 59 % and 14 %, respectively, over control, by combined application of FD-17 and KS-54 in 2% biochar amended soil. Another study mixed three strains *Bacillus subtilis*, *Bacillus cereus*, and *Citrobacter sp.* in a 3:3:2 proportion as a kind of mixed bacteria (MB9) consortium to detoxify co-contaminated soil with U and Cd. Two types of MB9-loaded biochar were synthesised namely AIB and EIB. After 75 days, the highest reduction in the extractable U (69 %) and Cd (56%) was achieved with the 3% AIB amendment (Qi et al., 2020). Another study demonstrated enhanced bioremediation of contaminated soil having a long history of PAH contamination by immobilising bacteria (*Pseudomonas putida* and an unidentified indigenous bacterium) onto biochars as carriers. The individual removal percentages of phenanthrene and pyrene were 22–38 % and 39–40 % in the treatment amended with free bacteria and increased to 46–47 % and 77–78 % after amended with immobilised-bacteria, respectively (Chen et al., 2012). Xiong and Co-workers (2017) inoculated rice straw biochar with PAH-degrading *Mycobacterium gilvum*, and the subsequent amendment of this composite material to PAHs contaminated soil. The microbe-biochar composite showed superior degradation capacity for phenanthrene (62.6 ± 3.2 %), fluoranthene (52.1 ± 2.3 %) and pyrene (62.1 ± 0.9 %).

Although bioaugmentation has shown great potential in immobilizing HMs and PAHs, there are limitations associated with its application. For example, it initiates competition between exogenous

and indigenous microorganisms for nutrient and/or predation of exogenous microorganisms by inhabiting protozoa and bacteriophages. Inoculation of exogenous microorganisms to sub-surface soil could be problematic. It is easy to disperse into surface soil, but it is difficult to do the same in the subsurface soil environment (Mrozik and Piotrowska-Seget, 2010). Also, the selection of a suitable effective strain of microorganisms or their consortia could be a challenge. Successful soil augmentation does not entirely require a sound knowledge on type and level of contaminants but suitable strains of microorganisms and their consortia. Mrozik and Piotrowska-Seget (2010) reported specific features of microorganisms to be considered during the selection of proper cultures. This includes fast-growing, easy cultured, to withstand high concentration of contaminants, and the ability to survive in a wide range of environmental conditions.

2.8 Remediation Mechanism of Biochar

In recent years, numerous studies have documented the remediation or sorption mechanisms of biochar (e.g. Wang et al., 2020; Cheng et al., 2020; Oliveira et al., 2017). However, little has been done to understand the remediation mechanism of (bio)engineered biochar and how the integrated material could improve biochar's sorption abilities; thus, contributing to enhancing pollutant removal efficiency. Generally, remediation mechanisms differ based on the type of contaminant and the type of biochar feedstock material. Similarly, the remediation mechanism varies based on the type of hydrogel, digestate and bioaugmentation microorganisms. The dominant remediation mechanisms of biochar involve in the removal of both organic (e.g. PAHs) and inorganic (e.g. HMs) are illustrated in Figure 3 and summarised in Table 4 below. The removal mechanisms are often governed by the interactions of pollutants with various attributes of biochar.

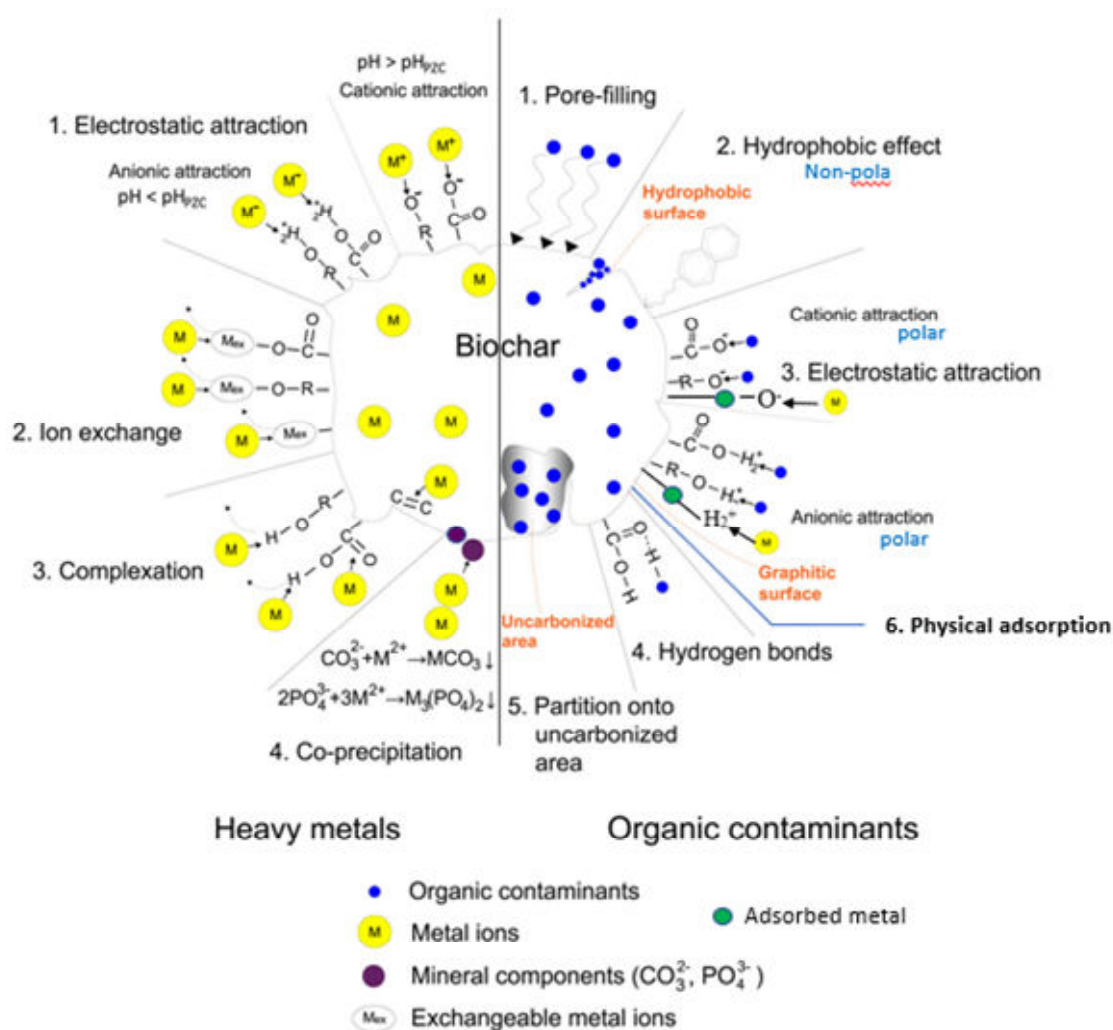


Figure 3. Sorption interactions between biochar and pollutants (Modified from Wang et al., 2020b)

For inorganic pollutants, such as HMs, the remediation mechanisms of biochar very much depend on the valence state of the target metal ion(s) of interest at different pH (Li et al., 2017). Although several sorption mechanisms have been reported by different researchers, the four dominant HM removal mechanisms are (Qian et al., 2015; Reesa et al., 2014; Li et al., 2017): (i) Electrostatic attraction between positively charged metal ions and negatively charged biochar surface – the larger surface area and higher surface energy are helpful for biochars to strongly absorb the HM ions and remove them from the soil; (ii) Ion exchange between HM ions in soil and alkali and alkaline earth metals or protons on biochar surface – the higher the cation exchange capacity value, the stronger the retention of HMs; (iii) Complexation with π electron- or surface functional groups (e.g. $-\text{COOH}$, $-\text{OH}$ and $-\text{NH}_2$) – complexation is significant for the fixation of HM ions with strong affinity; and (iv) Co-

precipitation to form insoluble compounds. Addition of biochar can increase the pH of the soil, and the reaction of HM ions with -OH , PO_4^{3-} , CO_3^{2-} can form hydroxide, carbonate or phosphate precipitation, which effectively solidifies HM pollutants. The sorption interaction of HM ions with biochar is influenced by pyrolysis temperature, feedstock type, pH of soil and biochar, physical and chemical properties of HM ions, and application rate (Patel et al., 2018; Wang et al., 2020; Oliveira et al., 2017). In comparison, five dominant PAH-remediation mechanisms are mediated by biochar (Wang et al., 2020; Oliveira et al., 2017), and these are: (i) Pore-filling, where sorption capacity is directly proportional to the micropores' surface area; (ii) Hydrophobic effect, which relates to the reduction of H- and O-containing functional groups on biochar during pyrolysis enhance its hydrophobicity and improve sorption efficiency; (iii) Electrostatic attraction, which is governed mainly by interactions via π - π electron donor-acceptor; (iv) Hydrogen bonds, mainly intermolecular hydrogen bonds between H atom and COOH , OH , and R-OH functional groups on biochar surface and (v) Partitioning, where the non-carbonised organic matrix of biochar initiates partitioning of PAHs due to reduction of substrate polarity. The sorption ability of biochar and its interactions with PAHs are influenced by several factors. Typical factors influencing sorption interactions between biochar and pollutants include pH, pyrolysis temperature, feedstock type and ratios of pollutant-to-biochar (Patel et al., 2018). Given the aforementioned remediation mechanisms of biochar, many studies have reported positive results of biochar application in removing of HM and PAH pollutants (Table 3). However, remediation work involving biochar alone could require more time and/or larger quantities of biochar to be effective in removing certain pollutants (selective adsorption) compared to (bio)engineered biochar. Selective adsorption as a result of competition among HM ions and/or PAH compounds for binding sites on biochar may favour pollutants sequestration over others (Mahdi et al., 2019). The outcompeted pollutants could possibly be accommodated via other remediation agent or material engineered with biochar to provide a wider range of binding sites. For example, in a multicomponent system, the adsorption of Pb^{2+} , Cu^{2+} , and Ni^{2+} by date seed biochar exhibited competitive behaviour. Compared to single component systems, the adsorption capacities of each ion

were reduced by 48–75 % in both batch and column experiments (Mahdi et al., 2019). Park et al., (2016) reported maximum adsorption capacities (mg g^{-1}) of metals by sesame straw biochar which were in the order of $\text{Pb (102)} > \text{Cd (86)} > \text{Cr (65)} > \text{Cu (55)} > \text{Zn (34)}$ in the mono-metal adsorption isotherm and $\text{Pb (88)} > \text{Cu (40)} > \text{Cr (21)} > \text{Zn (7)} > \text{Cd (5)}$ in the multi-metal adsorption isotherm. In this case, the amalgamation of biochar with hydrogel, digestate and bioaugmentation, respectively, could speed up the process of removing these pollutants, reduce the amount of biochar usage, and further result in remediating other types of recalcitrant pollutants. As shown in Table 4, HMs/PAHs remediation mechanisms of hydrogel include complexation, ion exchange, chelation, and electrostatic attraction. Similarly, dominant remediation mechanisms of digestate and bioaugmentation include precipitation, ion exchange, electrostatic interaction, complexation, redox reaction, and Van der Waals forces. Although digestate does not directly remove pollutants, it acts as a carrier of exogenous microorganism. Also, it acts as a source of nutrients, thus promoting microbial diversity and abundance, which the microorganisms, in turn, remove the pollutants.

Table 4. Remediation of HMs and PAHs by different methods

Technique	Mechanism	Ref	Remediation efficiency of HMs and PAHs removal	Ref
Biochar	Physical adsorption, ion exchange, electrostatic interaction, complexation, precipitation, hydrophobic effect, hydrogen bond and pore-filling	Xie et al., 2015; Zhou et al., 2018; Beesley et al., 2014	Biochar decreased Cd and Zn content by 99% compared to untreated soil and significantly increased biomass	Brendova et al., 2015
			Biochar reduced PAHs in coal contaminated soil by 86% and reduced bioaccessible PAHs by almost 100% compared with the untreated soil	Kořtowski et al., 2016
Hydrogel	Chemisorption, complexation, adsorption on surface and pores, ion exchange, chelation, adsorption by physical forces, electrostatic interactions, and entrapment in inter- and intra-fibrillar capillaries and spaces of the structural polysaccharide network,	Omidian et al., 2015; Ahmed, 2015; Adjary et al., 2020Pan	A lignin-based poly(acrylic acid) hydrogel showed a reduction in Cu, Zn, Cd and Pb concentrations by 23%, 53%, 14% and 18%, respectively	Zhao, 2019
			Poly(vinyl alcohol)/chitosan/maleic anhydride- β -cyclodextrin hydrogels reduced PAHs concentrations by 43%, 69%, and 19% for low, intermediate, and high swelling hydrogels, respectively	Filho et al., 2020
Digestate	Slight alkaline property neutralises acidic soil thus enhance immobilisation of pollutants. Acts as a source of nutrient, carbon and microorganisms. Hence, promote microbial activity and immobilisation of pollutants	Smith et al., 2010; Zeng et al., 2015	Application of digestate showed a significant reduction in concentrations of Cu, Zn, Fe, Pb and Cr in the mining soil	Guo et al., 2020
			Application of digestate (OFMSW) to petroleum-contaminated soil revealed a high proportion of <i>alkB</i> genes with diesel removal efficiency rate of 78 %	Gielnik et al., 2019 a,b
Bioaugmentation	Precipitation, chemical adsorption, ion exchange, electrostatic interaction, complexation, covalent bonding and redox reaction and van der Waals Force	Agnello et al., 2016; Rajendra, 2003	<i>Bacillus subtilis</i> efficiently immobilised Cr, Cu and Zn in contaminated soil, transforming from bioavailable-fraction (high-mobility) (60–90% reduction) to residual-fraction (low-mobility) (50–80% increment). Increased urease and dehydrogenase activities by 41% and 8 %) respectively, compared to control	Maity et al., 2019
			<i>Pseudomonas aeruginosa</i> degraded fluorene, phenanthrene and pyrene with the efficiency of 96%, 50% and 41%, respectively, at initial concentrations of 20 mg L ⁻¹ in seven days	Medic et al., 2020

3 Biochar/Digestate-Based Circular Bioeconomy

Conversion of waste to biochar and digestate is a sustainable pathway to circular bioeconomy (Hu et al., 2020). Circular bioeconomy can be defined as the exploration and exploitation of waste bio-resources, which involves the use of biotechnology to convert into bio-products of economic value in a sustainable manner (Bugge et al., 2016; Stegmann, et al., 2020). In this case, biomass material from agricultural wastes is the bio-resource while the resultant biochar/digestate is the bio-product. The biochar/digestate can be used for agricultural and environmental applications with added economical value (Figure 4). This concept in principle promotes sustainability compared to the traditional ‘take-make-dispose’ linear model. Essentially, the production, marketing, awareness campaigns and commercialization activities of converting the waste bio-resource into a valuable bio-product are imperative for the sustainability of bioeconomy (Oni et al., 2019). All these activities in bioeconomy is an avenue for employment opportunities both direct and indirect employment. Several reviews (e.g. Dahal et al., 2018; Oni et al., 2019; Jindo et al. 2020) have been published addressing utilisation of biochar in agriculture and environment including its implications in promoting a circular bioeconomy framework.

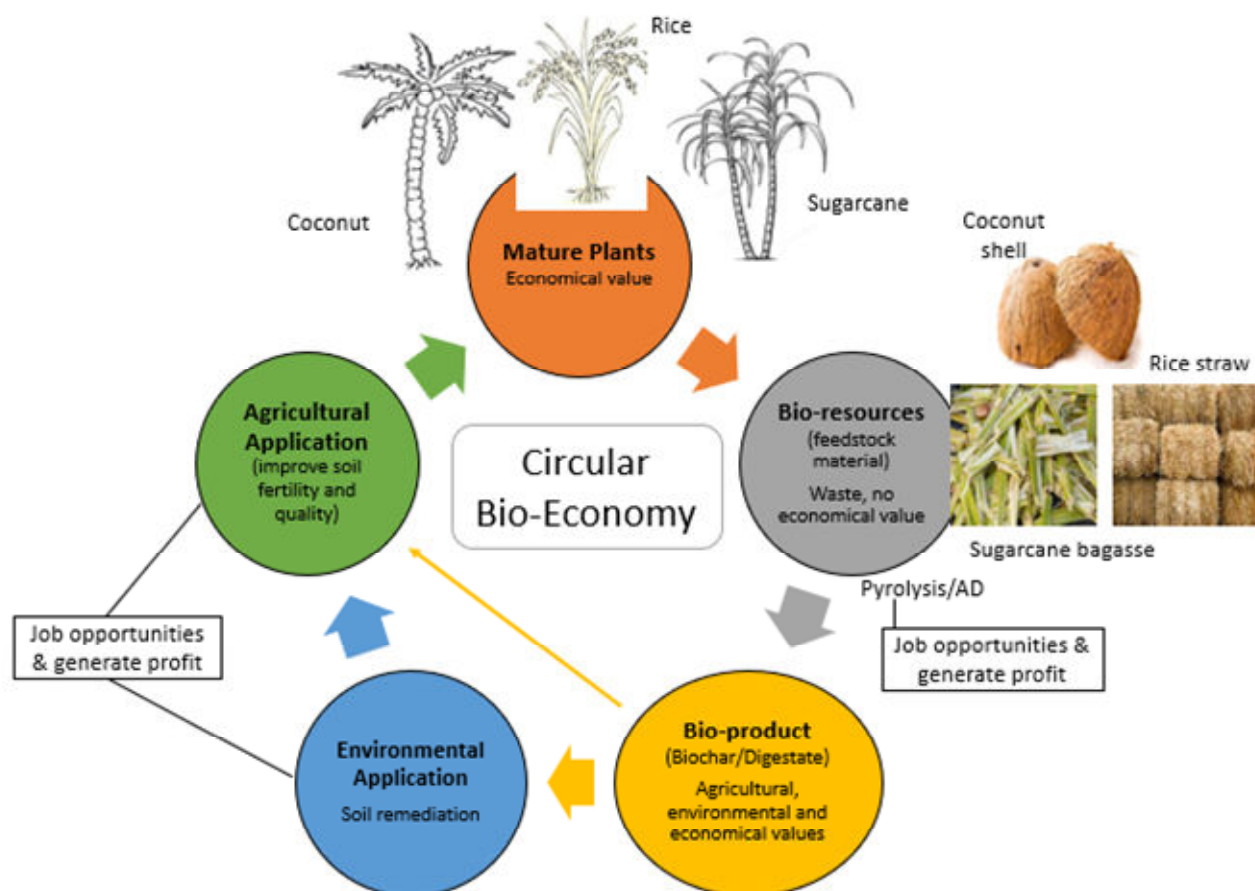


Figure 4. Promoting circular bioeconomy via use of biochar for decontamination

4 Large-Scale Field Application and Challenges

Biochar adsorptive studies at laboratory (Alaboudi et al., 2019), greenhouse (Khan et al., 2015) and small-scale field trials (Nie et al., 2018) have shown great potential. But challenges remain in terms of practicality, effectiveness, cost and sustainability at large-scale field application at commercial levels. Large-scale field trials are essential before implementation of operational scale remediation projects (Zhang et al., 2013; Antonangelo and Zhang, 2020). One of the key challenges associated with large-scale field trials is to achieve comparable or better remediation results compared to small-scale experiments considering the prevailing real-world environmental parameters. At small-scale, experimental and environmental parameters are controlled, therefore, the result does not necessarily mimic the real-world field conditions (Van Zwieten et al., 2010; Beesley et al., 2010). Cost involved in up-scaling of project is another factor. The cost associated with production (raw biowaste and pyrolysis), transportation (raw biowaste and biochar), equipment purchases, and biochar application presents a major hurdle in the implementation of large-scale field applications (Xiao et al., 2020; Marousěk et al. 2017; Shackley et al., 2011). Typical reported production costs range between \$222 and \$584 ton^{-1} (Huang et al. 2014; Shabangu et al. 2014), while the profit made in improving soil condition is only of \$96.13 ton^{-1} (Campbell et al. 2018). Thus, this calls for a sustainable approach to mitigate economical infeasibility of biochar usage for soil remediation. However, due to limited large-scale field trials of biochar, little findings are available to understand commercial sustainability of its application (Fytili and Zabaniotou, 2018). Most authors understand the improvement in the biochar economy in the perspective of proposing new types of cheaper feedstock instead of as a purpose-grown biomass (El-Naggar et al. 2019). Few others (e.g. Zhou et al., 2019) support the idea of employing new pyrolysis methods (e.g. wet pyrolysis) for producing tailored made biochars at low-cost compared to traditional high energy consumption pyrolysis method. An option would be to combine different strategies to address economic feasibility and practicality. For instance:

- Utilise free or cheap readily and locally available waste biomass with high remediation efficiency,
- The selected biomass should require trivial or no artificial fertilisation and herbicide/pesticide treatments to grow in large quantities,
- The selected biomass should generate profit by marketing certain edible parts of the plant, while the non-edible parts could be used for biochar production,
- Employ low-cost carbonisation method,
- The biochar should be produced in the vicinity of the feedstock production area or within its application site to reduce logistical costs,

- Biochar derived from the selected biomass feedstock should have good regeneration and reusability cycles, and
- Combine biochar with other cheap adsorbent or degradation material/organisms to reduce cost and enhance remediation performance

Although the biochar price is proportional to labour cost, it varies across the world. In general, global biochar price and labour cost are high in the USA and UK (about 500 USD t⁻¹) and low in India and the Philippines (90 USD t⁻¹ on average), thus, making biochar application more economically feasible for low income countries (Vochozka et al., 2016).

5 Conclusion and Future Perspectives

Biochar has the potential to be developed as a viable technology for remediation of co-contaminated soils. Numerous studies have shown that biochar can conceivably reduce the level of both HMs and PAHs in soil. In addition to biochar's function as a soil conditioner and sequester of greenhouse gases, it is sustainably economical and environmentally friendly, thus making it a suitable option over physical and chemical remediation technologies. The efficacy and effectiveness of biochar to remove contaminants from contaminated soil depends on the physicochemical properties of the biochar, which are influenced by the type of feedstock (biomass) material, type of carbonisation method used, and pyrolysis conditions employed. However, the efficacy of biochar to remediate contaminants can potentially be improved with specific engineered modifications of the biochar. In conclusion, this review has provided a positive outlook for the implementation of biochar and enhanced biochar remediation with hydrogel amendment, digestate amendment and microbial amendment, for remediation of HMs-PAHs co-contaminated soil. The prospect and research on biochar for soil treatment applications are reported in large quantities, but the study on soil application using the aforementioned engineered biochar amendments is a major knowledge gap at present. As a potential technology for remediation of contaminated soils, many aspects are still yet to be developed. Several knowledge gaps have been identified, and further research is required to close these gaps.

- So far, studies that explore biochar and biochar composites for remediation of contaminated soils have mainly been conducted at the laboratory scale. Field-scale trials are essential before large-scale and operational scale remediation projects are implemented
- The biochar characteristics vary with different biomass materials and pyrolysis conditions. It is important to optimise production systems to produce tailored biochar with desired characteristics to effectively remediate co-contaminated soil with HMs and PAHs
- The capacity of biochar to adsorb or sequester pollutants increases with time, reaching an equilibrium and then decreasing due to the ageing process. Additional understanding of the ageing process is required to provide a better understanding of the long-term environmental fate of the sequestered contaminants, biochar application rate and frequency to improve remediation efficiency
- An optimised hydrogel can effectively immobilise HMs and PAHs. Little, however, is known about the synergic adsorption efficiency of amalgamating biochar with desired optimised hydrogels (i.e. as a biochar-hydrogel composite).
- Several studies have shown that biochar and digestate promote immobilization of pollutants. However, limited studies have demonstrated that biochar-digestate composite improves microbial population, diversity and activity in the soil, and reducing the total and bioavailable concentrations of HMs and PAHs in situ
- Inoculation of microorganisms (bioaugmentation) with biochar has shown promising results for cleaning up soils contaminated with HMs and PAHs. Selection of suitable metal removal and PAHs degradation microorganisms and their consortia could be a challenge. Also, there is a need in finding sources of microbial agents able to degrade PAHs which may serve as species pools for enrichments during inoculum preparation
- Short term and long-term effects of biochar and biochar-based composites on soil physicochemical properties, and their influence in soil, need to be monitored and evaluated over time.

- The regeneration of used biochar and biochar-based composites, and the possibility of its reusability and quality, must be assessed to achieve sustainability
- The addition of exogenous microorganisms has been shown to enhance the removal of pollutants in soil. However, it is important to perform initial characterisation of digestate microbiota (exogenous) to understand and compare the effects of exogenous and indigenous microorganisms after digestate application and during the remediation incubation period

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Anae, Jerry

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