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Production of Biochar from Biomass Pyrolysis for Removal of PFAS from Wastewater and Biosolids: A Critical Review

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Abstract: Biochar is an inexpensive and effective carbon sequestration technology produced by slow and fast pyrolysis of biomass feedstock at elevated temperatures in inert conditions producing large quantities of solid residue (i.e., biochar), condensable liquids (bio-oil) and hydrocarbon gases. Biochar have shown excellent adsorption capabilities. Biochar has shown excellent adsorption capabilities for short-chain PFAS and short chain PFAS. This paper suggests optimal pyrolysis reaction conditions to adsorb PFAS to maximum allowable concentrations in wastewater up to Environmental Protection Agency (EPA) is 70 ng/L. The paper highlights the operation conditions and influential reaction conditions to control the microporous structures in Biochar. The paper also aims to summarize the fundamentals of production of Biochar from biomass slow pyrolysis as well as optimal conditions for extraction of PFAS from wastewater streams and destruction of PFAS in biosolids. The scientific contributions for production of Biochar from biomass pyrolysis are highlighted. The paper also highlights the advantages of biochar over activated carbon in terms of low manufacturing costs and higher adsorption rates.

Keywords: biochar; PFAS; biomass pyrolysis; fluidized bed reactors; wastewater; biosolids

1. Introduction

Polyfluoroalkyl substances (PFAS) are a group of undesired chemical compounds including PFOA (Perfluorooctanoic acid), PFOS (Perfluorooctane sulfonic acid), GenX (HFPO dimer acid and its ammonium salt) that can be found in packaged foods, commercial household products and drinking water [1–3]. The aforementioned chemical compounds exist in many manufactured products and consequently pose persisting environmental risks because of their high chemical stability and bioaccumulation potential in living organisms. Due to the high concentrations of PFAS in wastewater and biosolids that have been found in many sites in North America, global concern is raised illustrating the toxicological hazards on reproductive, immunological, and biological effects on animals and other living organisms. The expected PFAS concentration in biosolids are 403 ± 127 ng g^{-1}dry weight for PFOS and 34 ± 22 ng g^{-1}dry weight in PFOA, while other types of PFAS chemical compounds were lower typically in the range of 2 to 25 ng g^{-1}dry weight [16]. Biochar production varies depending on operating conditions of slow, fast, and flash pyrolysis that are discussed in this research work. Biochar produced from slow pyrolysis exceed 85 wt. % which is the most recommended method for production of biochar.

The environmental persistence of PFAS caused by its complex chemical structure raises a global concern and requires sustainable solutions for the chemical's destruction with minimal environmental effects [4]. This paper illustrates characteristics of biosolids including their typical chemical compositions and concentrations of organic pollutants and pathogens. Different operating parameters for destruction of PFAS in biosolids and wastewater streams are also discussed, in congruence with ideal operating conditions during pyrolysis to produce biochar that achieves high adsorption of PFAS [10–15]. The PFAS molecule is made up of long-chain networks of linked carbon and fluorine bonds. The environmental persistence of PFAS are due to the strong carbon fluorine bond that makes these molecules non-biodegradable with very long half-life. The degradation of PFAS requires high operating temperatures to overcome the intrinsically stable thermodynamics of the carbon-fluorine bond.[17]. Therefore, sustainable technologies for destruction of PFAS in biosolids and removal of PFAS from wastewater using biochar is essential to ensure safety of environmental habitats. Biochar possesses exceptional properties such as resistance to biodegradation, high cation-exchange capacity and high porosity that makes it an excellent substance for usage in many industrial applications such as extraction of PFAS from wastewater. The objective of this paper is to illustrate current optimal operating conditions as well as conducting risk assessment for PFAS contamination and wastewater treatment. The degree of PFAS extraction using activated biochar is proportional to the operating temperature and conditions of the activation process [18–20].

Synthesis of biochar using biomass pyrolysis for adsorption of PFAS have been investigated with various feedstocks such as switchgrass, water oak leaves and have been experimented to adsorb PFAS compounds. Experimental investigations have shown that biosolid biochar is recommended for PFOA adsorption compared to biomass feedstocks such as switchgrass or water oak leaves due to higher O (26 - 36 wt.%), S (1 - 3.8 wt.%) and heavy metal content such as Ca, Cu, and Fe [4,5,7,8]. Addition of additive materials such as carbon nanotube significantly enhanced the overall surface area as well as increased porosity [1–20].

The focus of this work is to summarize the chemical treatment methods and operating conditions for PFAS destruction to eliminate the dangers and adverse health effects of PFAS accumulation in habitats. Operating conditions for destruction of PFAS in biosolids and adsorption using biochar is the focus of this research work. The current statistics and concentrations of organic pollutants in biosolids and wastewater is illustrated. Biomass feedstock from agricultural waste such as corn, rice, peels and forest wood contain high lignocellulosic content that is recommended for biochar production. By definition, pyrolysis is an endothermic process that includes thermal degradation of solid organic materials in complete absence of oxygen to convert it wide range of products including biochar, bio-oil and syngas in a batch, semi-batch or continuous process depending on heating rate [5]. There are three classifications of biomass pyrolysis: slow pyrolysis (300 - 700°C), fast pyrolysis (600 - 1000°C), and flash pyrolysis (> 1000 °C) [5–10]. Slow pyrolysis has heating rates between 5-20 °C/min and has the highest yield of biochar from 50 - 85 wt. % biochar. Fast and flash pyrolysis has heating rates above 30°C/min and yields 10 - 20 wt.% hydrocarbon gases and 60 -75 wt.% bio-oil with expected biochar range 10 - 15 wt.% [8–12].

During the pyrolysis process, slow pyrolysis with lower heating rates yield higher biochar between 50-85 wt.% with highest cation-exchange capacity. Higher operating conditions produce biochar with higher surface area and microporosity [6]. Also, biomass with higher natural fiber concentration and higher lignin content produces higher biochar product yield [8–12]. Thermochemical reactions with different operating conditions for intermediate pyrolysis, flash pyrolysis, gasification and hydrothermal carbonization are used for biochar production with different physical characteristics and microporous structure properties [7].

In addition, other alternative techniques such as intermediate pyrolysis, flash pyrolysis, gasification and hydrothermal carbonization for used for production of biochar. Thermochemical reactions such as slow pyrolysis, flash pyrolysis, hydrothermal carbonization and gasification methods have also been employed but less frequently compared to slow and fast pyrolysis [7]. Depending upon the residence time, type of biomass feedstock, operating temperature, and heating rate the pyrolysis process, the biochar intermolecular characteristics and product yield are determined. Slow pyrolysis is recommended for production of biochar with higher product yield between 30 - 80 wt. % depending on heating rates [8,9]. Slow pyrolysis has the highest yield of biochar and can accept wide range of biomass particle size. The optimal operating temperatures for biomass slow pyrolysis that has the highest yield of biochar occurs between 600°C - 700 °C [7,8,12,22]. Biochar produced at these temperatures has high hydrophobic characteristics while biochar produced at lower operating temperatures (300 - 400 °C) has more diversified organic content due to existence of aliphatic and cellulose structures [4,9,12].

Biochar produced at these operating conditions demonstrated high aromaticity with fewer functional groups whereas biochar produced at lower operating temperature between (300°C -400°C) have numerous organic contents with high functional group concentrations [11]. The most influential factors that control the chemical and physical characteristics of biochar are the lignin content and chemical composition of biomass feedstock as well as the reactor operating temperature and heating rates [12].The influential factors of the microstructural arrangements and physical properties of biochar are the operating temperature and reaction residence time[3,4,10,16]. Fluidized bed reactors are recommended for higher product yield of biochar achieving 36 - 45 wt.% biochar yield at operating temperatures between 500°C- 600 °C. Biochar produced at these operating conditions demonstrated more than 80 wt.% adsorption capacity of long-chain PFAS and more than 30 wt.% adsorption of short-chain PFAS compounds from contaminated wastewater streams. Integrated incineration-pyrolysis chemical processes have shown highest PFAS destruction by more than 90 wt. % [16]. PFAS chemical compounds have many forms where some are illustrated to table 1 as below:

Table 1. PFAS chemical compounds and abbreviation.

Chemical Name	Abbreviation
Perfluoro octane sulfonic acid	PFOS
Perfluorooctanoic acid	PFOA
Perfluoro nonanoic acid	PFNA
Perfluoro decanoic acid	PFDA
Perfluoro hexane sulfonic acid	PFHxS

The operating conditions of the biochar production during biomass pyrolysis determines the physical characteristics such as internal surface area and biochar porosity that determines the adsorption capacity and performance towards PFAS adsorption [18]. The activation process can improve the sorption ability of biochar and expands its surface area through creation of nanopores (< 2 nm) and aromatic surfaces. The biochar activation process can be achieved either by chemical or physical activation. Physical activation involved oxidation either by steam (H_2O) or carbon dioxide (CO_2) preferably at 850°C [18]. Chemical activation involves mixing biochar with oxidizing agents such as $ZnCl_2$, H_2PO_4 or KOH [18]. The biochar chemical activation occurs at a lower operating temperature at 500 °C while physical activation occurs at higher temperatures around 850 °C by considered less toxic [5].

1.1. Physical and Chemical Activation of Biochar

Physical activation of biochar is preferred due to less harmful pollutants and lack of usage of separating agents. In addition, another advantage is that for physical activation carbonization and activation are two separate steps that reduce operating costs and using less harmful chemicals compared to chemical activation. The primary objective of physical activation of biochar is increasing the internal surface area using oxidizing agent such as steam, CO_2 or inert agents such as H_2 and N_2. These methods are energy intensive and require high temperature as well as improves the adsorption capacity but less harmful to the environment compared to chemical agents used in chemical activation. Physical activation occurs between 500 °C to 1000 °C using oxidizing agents such as steam and carbon dioxide. Steam activation is mainly used to improve reaction rates and pore size penetration of biochar. The operating temperature and heating rates during biomass pyrolysis process are the limiting factors that determine the biochar properties. The influencing factors that affect the biochar adsorption rate are porosity, surface area, pore size distribution, alkalinity, and cation-exchange capacity [19]. Chemical activation of biochar is performed using zinc chloride, sodium hydroxide, potassium hydroxide or phosphoric acid. Chemical activation is achieved by exposing biochar to desired amount of zinc chloride or potassium hydroxide with 100 mL and allowing the mixture to settle for 2 hours. Chemical activation form pores in the carbon structure to increase the surface area and natural adsorption capacity.

The production of activated carbon from biochar is recommended since it has higher adsorption PFAS rates and withstand higher operating pressures. Physical activation involves carbonization of biochar in inert atmosphere and partial gasification with steam or CO_2 in range of 800 - 1000 °C to form complex micropores and mesopores structures [9,20–22].

1.2. Expected Product Yields of Biochar from Slow and Fast Pyrolysis

Biomass slow pyrolysis at moderate operating temperatures (1-30 ℃/min and long residence time achieves the highest product yield for biochar while fast and flash pyrolysis produces more bio-oil [5,7,26,27]. Experimental investigations show that highest biochar yield at 50 wt.% is achieved at slow pyrolysis at 300 °C at heating rate 5 °C/min and 30 minutes residence time. Biomass with fine aromatic structure and high lignin content is highly desirable for highest biochar yield [7,8,18,19,22].

The influential factors are biomass feedstock, heating rate, pyrolysis temperature and vapor residence time. Also, the highest treatment temperature known as (HTT) has the greatest effect on the final product characteristics [23]. The operating temperature ranges between 350 - 600 °C in absence of oxygen for biomass pyrolysis. The final products from slow pyrolysis: biochar (50- 85 wt.%), bio-oil (i.e., a volatile matter than can be further condensed to liquid phase) (20 - 60 wt.%), and non-condensable gases like CO, CO_2, CH_4 and H_2 (5 - 40 wt.%) [8,9,24,25]. Biomass can be utilized in a high energy source, but this energy production is dissipated due to unsustainable exploitation and inefficient use [26]. For slow pyrolysis, the highest product yield is biochar around 60 wt.% of the final product and most recommended chemical reactors are bubbling, circulating or fluidized beds [26]. The product yield is dependent upon mass composition and lignin concentration of feedstock, process type, heating rate and condition and thermal efficiency.

For fast pyrolysis, at heating rates (10 - 200°C/s), biochar yield is between 36 - 45 %at operating temperatures between (500 °C - 600 °C). The produced biochar was found to have high stability and achieved over 90 wt. % removal of PFOS and PFOA substances from biosolids. In addition, integrated pyrolysis-combustion process combined pyrolysis-combustion integrated process enhances biochar properties and achieve over 80 % adsorption of long PFAS molecules and 19-28 % adsorption of short chain PFAS molecules from contaminated wastewater [16]. In slow pyrolysis, slow heating rates (< 10 ℃/min) and low operating temperatures (450–500 °C), yield more than 65 wt.% of biochar [27]. Highest bio-oil yield was achieved at 500 °C around 45 wt.% and biochar and syngas 33 wt.% and 22 wt.% respectively. At high operating temperatures (600 - 800 °C) yields 35 - 40 wt. biochar and 50 – 60 wt.% syngas [20–25]. The produced biochar is characterized using proximate analysis, CHN elemental analysis, bomb calorimetry for high heating value (HHV), nitrogen adsorption for Brunauer-Emmett-Teller (BET) which calculates the physical adsorption and surface area of materials [29]. Other methods of pyrolysis such as intermediate pyrolysis, flash pyrolysis and hydrothermal carbonization have also been used [7].

The major two groups of acids produced are sulphonic acids and carboxylic acids. The chemical formula of is $R{-}S(=O)_2{-}OH$, where R is an organic alkyl or aryl group and the $S(=O)_2(OH)$ group a sulfonyl hydroxide. On the other hand, are carboxylic acids, which is an organic acid that contains carboxyl group (C(=O) OH) attached to an R-group. The formula for carboxylic acid is R-COOH or $R{-}CO_2H$ which R referring to alkyl, alkenyl, aryl, or other groups.

On the other hand, production of biochar from fast pyrolysis includes high heating rates and has higher yield of liquid and gaseous products with lower reaction residence time [7]. Fast pyrolysis requires feedstock with smaller particle size to obtain higher yields of single-phase bio-oil. Fast pyrolysis yields 50-85 % bio-oil which mainly consists of lighter hydrocarbon products and yield only 5-25 % solid char depending on the nature of the feedstock [30]. Since the fast pyrolysis process yields higher concentrations of volatiles, its value for soil applications is limited. Fast pyrolysis produces 50-85 % of bio-oil, 5-25 % of solid char, and 10–20 % of gases, depending on the nature of feedstock and operating conditions [31].

Fast pyrolysis involves high heating rates and short vapor residence times with highest product yield of bio-oil. The pyrolysis reaction temperature applied in this process is usually around 500°C. Fast pyrolysis requires feedstock with smaller particle size and heating rate of (300 °C/min) and used specifically to obtain high yields of single-phase bio-oil. Torrefaction of biomass is a mild pyrolysis process between 200°C and 350°C resulting in a torrefied biomass that contains typically 60-70 % of the initial mass and 90% of LHV with no water content and is a common process to produce biochar [32]. Torrefaction of biomass is a thermochemical process that upgrades biomass feedstock as well as reduce moisture content which is known to increase the biochar quality. Torrified biomass enhances the biochar quality since feedstock has higher energy density, homogeneity, grindability and reactivity. The benefits of torrefied biomass compared with green biomass are increased energy density and homogeneity, improved grindability, pronounced hydrophobic character, and enhanced reactivity. Benefits of torrefied biomass compared with green biomass are increased energy density and homogeneity, improved grindability, pronounced hydrophobic character, and enhanced reactivity.

Alternative heating methods are used for biomass pyrolysis including inductive heating, microwave assisted heating, and furnaces. Advantages of microwave heating includes lower energy consumption, shorter residence time and internal heating. The most recommended heating method for biomass pyrolysis is inductive heating. Below is illustration of reaction conditions and biochar characteristics including product yield and BET surface area as shown below in table 2:

Table 2. -Reaction conditions for production of biochar from different biomass feedstock [18,25,26,37].

Heating Method	Feedstock	Temperature (°C)	Heating Rate (°C/min)	Biochar Yield (%)	BET Surface Area (m²/g)
Fast pyrolysis	Palm kernel shells	480 - 550	100	21-23	19 - 40
Slow pyrolysis	Halophyte grass	500 - 700	10	24 - 45	2-13
Fast pyrolysis	Jerusalem Artichoke	550-850	100-300	32 - 35	
Slow and fast pyrolysis	Beech wood	600 - 2000	5 - 450	6 - 14	7-128
Slow pyrolysis	Maple leaves	350 -750	10	17 -35	2 - 190

1.3. Process Stages for Biochar Production for Removal of PFAS

The biomass feedstock selection plays a vital role in the characteristics of biochar produced which affects the rate of absorption of PFAS chemical compounds. The first process stage includes selection of biomass feedstock based on composition, particle size and type of feedstock. The second stage includes selection of operating temperatures and heating methods such as microwave thermal plasma, conventional heating methods and heating rate. The final stage includes selection of activation method either physical or chemical based on desired biochar properties.

1.4. Experimental Results of PFAS Adsorption using Biochar

Biochar produced from biosolids are known to have better adsorption characteristics PFAS chemical compounds found from experimental investigations. Biochar produced from biosolids achieve high PFOA adsorption and better adsorption performance than biochar produced from switchgrass and water oak leaves. This is due to higher oxygen, sulphur and metal ion contents in biochar produced from biosolids. Also, PFOA adsorption is enhanced by addition of $FeCl_3$ to biochar during the adsorption process [16–18].

Experimental investigations using biochar produced from various biomass resources are being investigated. For example, according to (W. Guo, S.Huo, 2017), experimental results for biochar produced from corn straw is being investigated at different operating temperatures including 250, 400, 550, and 700°C. Biochar produced at high pyrolytic temperature resulted in biochar with larger surface area and higher aromaticity. The adsorption behavior according to (W. Guo, S.Huo, 2017) fits pseudo-second order model following Langmuir adsorption isotherm ($R_2 > 0.949$). Biochar produced at higher operating temperatures is found to have higher adsorption capacities reaching 170 mg/g. It was found that biochar produced at higher operating temperatures enhances the hydrophobicity; thus, increase PFOS adsorption [4,16–18].

In addition, several chemical treatments using acid or alkali, metal salts impregnation and nanoparticle coating have been proved through experimental investigations to enhance micro-porosity. Biochar produced from phosphate-functional bamboo sawdust is treated with phytic acid prior to pyrolysis have shown improvement in microporous structure and enriched surface phosphate functionality leading to higher adsorption capacity reaching 229 mg/g (Y.Wu, L.Q.G.Chen, 2022).

2. Biochar Desired Properties for Extraction of PFAS

Low heating rates increase the yield of biochar due to avoidance of secondary pyrolysis reactions. For example, reducing the heating rate from 50 to 10 °C / min in poplar wood pyrolysis, the yield of biochar increases from 3 wt.% to 6 wt.% [33]. Also, highest recorded biochar surface area S_{BET} was recorded 411 m^2/g at 600 °C at heating rate 30 °C /min.

While, in fast pyrolysis, secondary cracking reactions between volatiles and charcoal favors bio-oil production and reduces biochar production. The other factor that affects biochar yield is the reaction residence time. Longer reaction times supply sufficient time for repolymerization reactions and maximizes the biochar yield. Also, high vapor residence time provide sufficient time for repolymerization reactions and maximize the biochar yield [33].The biochar properties are controlled by key factors including pore size composition, hydrophobicity and pyrolysis temperature and biomass feedstock. Currently, biochar exhibits lower properties than granular activated carbon (GAC) for sorptive purposes. The current desired properties of biochar are excellent physicochemical properties such as high surface area, porosity, and diversified surface function groups which achieves high contaminant removal efficiency [7].

2.1. Biochar Physical Characteristics and Chemical Composition

The important physical properties of biochar include bulk density, particle density, particle size, macro and microporosity as well as water holding capacity. The chemical analysis of biochar determines its behavior and this includes mineral contents such as N,P,K, S, Ca, Mg and heavy metal contents such as Fe, Mn, Zn, Mo, B, Cl and Na. Measuring the solubility of these elements at different soil PH will provide indication of absorptivity of PFAS chemical compounds. The physical properties of biochar have an impact on the mobility, interaction with soli water, suitability for soil, surfaces and adsorption rate of biochar.

The physical properties of biochar include the bulk density, porosity against pyrolysis temperature and hydrophobicity which determines the adsorption rate and performance. The proximate and ultimate analysis of biochar determines the chemical composition of carbon, hydrogen, nitrogen and sulfur in biochar samples. The proximate and ultimate analysis of biochar are used to determine the physical composition and characteristics. For example, proximate analysis determines the moisture content, water content and fixed carbon content in biochar samples.

2.2. Heavy Metals, Pathogens and Organic Pollutants in Biosolids

The heavy metals existing in biosolids originate from industrial wastewater and sewage system. Concentration of these heavy metals affect the physical behavior of biosolids and depends in their contents in the wastewater. Thermal treatments such as microwave irradiation is used for release of heavy metals from biosolids. Thermal treatments are recommended for metal removal before land applications [9,34,35]. Several adsorption and membrane technologies are used for removal of organic pollutants from biosolids. Pyrolysis of biosolids over several advantages including significant volume reduction, destruction of pathogens, and organic pollutants as well as removal of heavy metals. Pyrolysis at elevated temperatures also increase the carbon stability of biochar [1].

2.3. Operating Conditions for Physical Activation of Biochar

The physical activation is a process that increases the surface area and porosity of the carbonaceous elements in the biochar. The activating agent exposes the reactive carbon element and is converted to carbon monoxide (CO) resulting on opening and widening the existing pores in the biochar [24,25]. Physical activation occurs by treating biochar with oxidizing agents using either steam or carbon dioxide at temperature between 500 °C and 1000 °C. Physical activation using steam is at a faster reaction rate and achieves higher penetration into the pores of the biochar [39]. In physical activation, the oxidizing agent such as oxygen penetrate the internal structure of char and gasify the carbon atoms which results in widening of the porous structures and increasing functional groups that serve as active sites. In steam reforming, the reaction between carbon and steam is an endothermic process using superheated steam (800-900°C) for 30 minutes to 3 hours. The overall reaction between carbon and steam includes chemisorption of water, carbon gasification, water shift and gasification by super-heated steam.

2.4. Advantages of Biochar over Activated Carbon for PFAS Removal from Wastewater

The environmental benigness of biochar is recommended over granular activated carbon (GAC) as well as being more cost-effective. Biochar outperform fossil based activated carbon in the production and price however PFAS adsorption capacity requires improvement [40]. Typical concentrations of PFOA range from 70 ng/L to 1000 ng/L while PFOS range 10 to 600 ng/L.

Granular activated carbon (GAC) is more energy intensive and expensive on comparison with biochar. The life cycle assessment results favor biochar in terms of environmental benefits including global warming, respiratory and noncarcinogenic benefits with lower carbon footprint [2]. Overall, biochar is an environmental superior alternative to coal based GAC and its use offsets wastewater facility carbon footprint.

3. Current Challenges for PFAS Removal from Wastewater

Currently in the US, PFAS contaminated biosolids are treated using three methods: (1) Treatment of biosolids by land applications; (2) Disposal at landfill; (3) Destruction using sewage sludge incinerators. Also, contaminated biosolids are rich in nutrients and most common practice for removal of PFAS is aerobic or anaerobic digestion to produce stabilized biosolids that could be used as farmland fertilizers [16,41].

The amount of incinerated biosolids is 16 wt.% while incineration isn't advised due to additional costs and other environmental considerations [42]. Treated biosolids could be beneficial after thermal destruction of PFAS compounds. Currently 54 % of treated biosolids are used in agricultural practices after removal of PFAS using aerobic and anaerobic digestion to produce stabilized biosolid products that can be applied for land usage as fertilizers after treatment of biosolids whereas the nutrient biosolids includes nitrogen, phosphorous and other traceable metals are used as a land applied fertilizer after treatment of PFAS chemical compounds [43].

The current technologies for removal of PFAS compounds from wastewater includes activated carbon adsorption, ion exchange, and high-pressure membranes. Granular activated carbon (GAC) is most used and is made from organic materials with high carbon contents such as biomass, wood or coal [44,45]. Granular activated carbon is recommended on long chain PFAS compounds such as PFOA and PFOS but doesn't perform well on short chain PFAS family compounds such as perflourobutanesulfonic acid (PFBS) and perfluoro-butyrate (PFBA) [3]. Carbon sorbents for PFAS removal are classified intro three groups: Granular activated carbon (GAC), powdered activated carbon (PAC) and multi-walled carbon nanotubes (CNTs) [4]. Granular activated carbon products are available commercially including Filtrasorb 400 (F400), Filtrasorb 600 (F600), GAC400 and GCN1240. The recorded BET surface area varies from 600 to 1100 m^2g^{-1} [4].

4. Expected PFAS Concentration Levels in Biosolids

The most common PFAS chemical compounds in biosolids are PFOS, PFOA, and other long chain PFAS compounds [42]. The most persistent PFAS compounds in sludge are PFOS (<10 to 1,100 ng/g dry weight) and PFOA (1 to 240 ng/g dry weight). Perfluoro decanoate (PFDA) compounds dominate the overall PFAS-fluorine (ΣPFAS-F) primary sludge feedstock. The PFAS group of compounds are divided into two groups: an alkyl carbon chain with multiple carbon fluorine bond and a hydrophilic functional group. The PFAS group of chemicals contain a group of 5000 chemical compounds that has been reported until now [36]. Majority of PFAS molecules ad different chemical structures are detected in biosolids. PFOS has the highest concentrations and are the most abundant chemical followed by PFOA [27,37]. There is a dire need to remove PFAS from biosolids using thermal destruction to prevent its contamination in edible crops and dairy products [37]. The expected PFAS levels in biosolids are 2.5 ppb for PFOA, 5.2 ppb for PFOS, and 1900 ppb for PFBS [38].

Sewage sludge is a major bio-waste that has significant challenges in wastewater management including organic contaminants and chemical compounds such as PFAS chemical compounds [45]. Incineration of biosolids reduce solid waste volume by 70 % and results in the thermal destruction of toxic organic compounds such as PFAS. Sludge also has a calorific value equivalent to coal and incineration of bio-waste under energy recovery conditions could be used for energy generation and reduction of CO_2 emissions [45]. Sludge incineration should comply with 2000/76/EEC standards. The ash produced from incineration of biosolids are more toxic in comparison with coal combustion and includes high quantity of metals including Cr, Cu, Ni, Pb, Zn and Fe [45].

Wastewater sludge are found to be contaminated with perfluoroalkyl carboxylates (PFCAs) and perfluoro-alkane sulfonates (PFSAs) and additional FAS compounds such as Genx. The fate and transport of PFAS compounds from biosolids have shown possible transport and uptake of PFAS to soil and plants [7], [33]. Due to the highly oxidizing nature of PFOA and PFOS, thermal incineration of PFAS in biosolids occurs higher than 1000 °C, more than 99 wt.% of PFAS is degraded above 600°C [46]. The behavior of per-and poly-fluorinated alkyl substances in biosolids and wastewater is influenced by length of alkyl chain and functional groups. The high cation content in biochar decreases the sorption of PFAS molecules. Hence, current thermal processes can't achieve high conversion rate of PFAS destruction [33]. Below is the expected mean, median and range of detected concentrations in biosolids for PFAS molecules as shown in table 3:

Table 3. Mean, median and range for detected concentrations in biosolids μg/kg [5–7,40].

	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFOS	PFDS
Mean	8.27	7.71	5.12	23.5	25.1	22.5	5.61
Median	6.85	7.03	0.414	2.53	17.6	19.3	5.41
Range	1.54 - 7.7	21.1	67.7	601	218	68.1	14.2

5. PFAS Destruction Mechanisms in Biosolids

PFAS compounds are present in sewage and wastewater systems from the industry. Therefore, they are found on concentrated solutions during the production of biosolids [32,33]. The presence of PFAS in biosolids possess both a potential health risk and shall be removed from biosolids and wastewater systems. There is an interest to study the relative concentrations of PFAS in various materials to estimate the exposure of PFAS in these chemicals. Biosolids are the solid organic matter recovered from sewage wastewater systems and could be utilized as a fertilizer to improve soil fertility.

Several reactor designs are used for large-scale pyrolysis of biosolids including heating systems such as microwave heating systems which were applied to transform sewage sludge (i.e., biosolids) using chemical additives such as KOH, H_2SO_4, H_3BO_3, $ZnCl_2$and $FeSO_4$ [16]. Most recommended reactor design for removal of PFAS from biosolids are fixed bed reactors [16].

Out of the 6.5 million tonnes of biosolids, 45 % sent to disposal while rest of biosolids are recycled for agricultural use. Sludge landfill practices account for 63 wt.% while incineration and surface disposal accounts for 33 wt.% and 4 wt.% respectively as shown [52,53]. The expected PFAS concentrations in biosolids are PFOS at concentrations above 403 ng/g while remaining 11 PFAS compounds range between 2 to 25 ng/g. The average PFAS concentration detected are 660 ng/g [34]. High concentrations in sludge samples are showed high PFAS concentration between 5.6 to 963 ng/g [35]. The concentrations of PFAS within biosolids are dependent on the nature of the treatment processes from where PFAS are released. Treatment of sludge is necessary to reduce PFAS to acceptable levels to meet EPA 403 biosolids regulations. Heating and composting treatments breakdown PFAA concentrations during the thermal treatment process. The current post treatments chemical processes are not effective in achieving high destruction concentration of PFAS in biosolids to acceptable levels [36,42]. The most common PFAS compounds in sludge are PFOS (<10 to 1,100 ng/g dry weight) and PFOA (1 to 240 ng/g dry weight). The overall PFAS-fluorine (ΣPFAS-F) primary sludge feedstock is dominated by perfluoro decanoate (PFDA) compounds. The PFAS group of compounds are divided into two distinct groups: an alkyl carbon chain with multiple carbon fluorine bond and a hydrophilic functional group.

The behavior of per-and poly-fluorinated alkyl substances in biosolids and wastewater is governed by the length of the alkyl chain and functional group. The high cation content in biochar could decrease the sorption of PFAS molecules. PFAS molecule contains long chain carbon chains with covalently bonded fluorine molecules making them chemically and thermally stable. Hence, current thermal processes make PFAS difficult to degrade via chemical and biological processes [33].

Thermal oxidation (Incineration is the most common method for destruction of PFAS in biosolids. When combustion, PFAS compounds break down into scrubbed and separated gases including CO_2, H_2O, and HF [55,56]. PFAS compounds, such as PFOS when combusted, breaks down into easily scrubbed and separated gases such as CO_2, H_2O and HF. In the early 2000s, previous studies have indicated that degradation of PFOS occurs at temperatures above 600°C. This also, however resulted in the formation of potent greenhouse gases CF_4 and C_2F_6.

Destruction is not applicable in case of PFAS due to the strong C-F bond and the very high melting point of PFAS [35]. The average PFOS concentration ranges from concentrations from 15 to 600 ng/g in sludge [35]. Two groups of PFAS are of particular concern for human health and the environmental perspectives, namely perfluoroalkyl sulphonates (PFOS) and perfluorooctanoate (PFOA), especially regarding their persistent and bio accumulative nature. The thermal oxidation of PFAS compounds breaks PFAS molecules to separated gases such as CO_2, H_2O, and HF. Thermal degradation of PFAS occurs at temperatures higher than 600 °C and breaks down to molecules such as CF_4 and C_2F_6 [27,37]. Below are the recommended reactor setups for thermochemical conversion of biomass to biochar as shown in table 4:

Table 4. Recommended reactor setups for thermochemical conversion of biomass to biochar [39,51,53].

Reactor Type	Reactor Specification	Feedstock	Final Product	Operational Features
Dual fluidized bed for combustion and reduction reaction	40 kg/h reactor fluidized bed using silica bed can reach 500°C, the moving bed operates between 600-650 °C	Biomass, sludge	Bio-oil reached 45 wt.% using catalytic pyrolysis using HZSM-5 catalyst with < 10wt.	High yield of bio-oil is due to usage of HZSM-5 catalyst
Double auger setup for fast pyrolysis	Consists of a horizontal auger reactor coupled with a secondary inclined auger tube reactor	Biomass	Biochar, Bio-oil and gas	The first horizontal auger reactor operates at 450 - 550 ◦C and the second inclined reactor operates at 400 ◦C. The second inclined reactor has higher reaction residence time.
Mechanically fluidized reactor	Recommended at larger flow rates	Biomass	Power, biochar, and ash	Has highest wall-to-bed heat transfer ratio

The most abundant PFAS in biosolids are PFOS with average concentrations 400 ± 120 ng/g followed by PFOA 35 ± 20 ng/g. The remaining eleven PFAS concentration range between 2 and 25 ng/g and the mean total concentration of PFASs detected in random PFAS samples was 530 ± 224 ng/g dw [37,40]. Biosolids tend to accumulate heavy metals and organic compounds due to physical-chemical processes involved in wastewater treatment [44]. Destruction of PFAS in biosolids are temperature dependent and requires high thermal control and high temperature [1–20].

According to EPA, high temperature and long residence time achieved by biomass pyrolysis or gasification followed by direct combustion of hydrogen rich syngas in an after burner or thermal oxidizer destroys PFAS by breaking apart chemicals into inert chemicals [58].

Pyrolysis and gasification thermal decomposition chemical reactions convert solid waste feedstocks into combustible gases. Pyrolysis operating conditions are between 200 to 1100 °C in absence of oxygen generating carbonaceous rich porous material known as biochar. On the other side, gasification is thermal cracking in limited oxygen supply yielding syngas which consists of CO and H_2. Co-gasification of coal with biomass is also under investigation since co-gasification operates at 700 °C. Below are the recommended reactor setups for thermal conversion of biomass.

Biosolids properties varies and may affect PFAS release and contamination. The expected properties in biosolids are:

- Moisture content
- Al content (1400 to 53,000 mg/kg),
- Fe content (1,575 to 299,000 mg/kg),
- PH between 6.5 to 8 and ionic composition [16].

Destruction of PFAS molecules is performed by breaking chemicals into less inert constituents and can be achieved to fully destruct PFAS in biosolids the following two steps as shown below:

- High temperature slow pyrolysis or gasification
- Second step is incineration of the hydrogen rich syngas stream in a thermal oxidizer or afterburner to destroy PFAS by breaking the chemicals into inert final products.

The high temperatures and residence time achieved by biosolids destroys PFAS by breaking apart the chemicals into inert or less recalcitrant chemicals. The most predominant PFAS chemical compounds are polybrominated diphenyl ethers (PBDEs) and hexabromocyclodecane (HBCDDs). Expected concentration of Perfluoro hexanoate (PFHxA) vary between (12-5700 ng/L) [16,50]. The most detected PFAS compounds in biosolids are decabro-modiphenyl ether (BDE-209) between 0.4-2300 ng/g and perfluorooctanesulfonate (PFOS) < 380 ng/g and PBTs are detected in biosolids [59]. The most abundant PFAS in biosolids was PFOS, detected at a concentration of400 ± 125 ng/g dw, followed by PFOA (35 ± 20 ng/g dw). The remaining eleven PFASs ranged between 2 and 25 ng/g (Table 2) and the mean total concentration of PFASs (ΣPFAS) detected in the five composite samples was 530 ± 220 ng/g dw. Most detected PFAS compounds in biosolids are Decabro-modiphenyl ether (BDE-209) (<0.4-2300 ng/g) and perfluorooctanesulfonate (PFOS) (< LOD 400 ng/g) were the predominant PBTs detected in biosolids. [1–20]

6. Recommended Reactor Configurations for PFAS Destruction in Biosolids

There are four reactor configurations used for biochar production from biomass pyrolysis that includes fluidized bed reactors, circulating fluid bed reactors, vacuum and ablative pyrolizer. Fluidized bed and circulating bed reactors are recommended for ease of operations and collection of biochar. Vortex pyrolysis reactors are used for easy collection of biochar and recommended for fast pyrolysis process.

7. Conclusions

In conclusion, biomass slow pyrolysis is recommended for high production yield of biochar taking into account biomass with high lignin content. Highest biochar yield is achieved at 300 °C at heating rate 5 °C/min for 30 minutes yielding higher than 50 wt.% biochar. Biomass with high lignin content and fine aromatic structure is recommended for biochar production. PFOA and PFOS has the highest concentrations in biosolid contaminations and are destructed using pyrolysis slow pyrolysis between 500 and 800℃.Paddle kiln, auger reactors, and bubbling fluidized bed reactors are recommended for highest yield of biochar production.

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Abbreviation

BET	Brunuaer-Emmett-Teller surface area analysis
GAC	Granular activated carbon
HF	Hydrogen fluoride
PFOA	Perfluorooctanoic acid
PFAS	Per-flouro alkyl substances
PFOS	Perfluorooctane sulfonate

Symbols

S_{BET}	Biochar surface area using BET device

References

1. J. Broman *et al.*, "Destruction of Per- And Polyfluoroalkyl Substances (PFAS) via Lacasse Enzymatic Degradation and Electrochemical Advanced Oxidation," 2021. https://doi.org/10.1109/WERC52047.2021.9477539.
2. N. Bolan *et al.*, "Remediation of poly- and perfluoroalkyl substances (PFAS) contaminated soils – To mobilize or to immobilize or to degrade?," *Journal of Hazardous Materials*, vol. 401, 2021. https://doi.org/10.1016/j.jhazmat.2020.123892.
3. L. J. Winchell, J. J. Ross, M. J. M. Wells, X. Fonoll, J. W. Norton, and K. Y. Bell, "Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review," *Water Environment Research*, vol. 93, no. 6. 2021. https://doi.org/10.1002/wer.1483.
4. A. K. Sakhiya, A. Anand, and P. Kaushal, "Production, activation, and applications of biochar in recent times," *Biochar*, vol. 2, no. 3, 2020. https://doi.org/10.1007/s42773-020-00047-1.
5. B. R. Patra, A. Mukherjee, S. Nanda, and A. K. Dalai, "Biochar production, activation and adsorptive applications: a review," *Environmental Chemistry Letters*, vol. 19, no. 3. 2021. https://doi.org/10.1007/s10311-020-01165-9.
6. V. Mulabagal*et al.*, "Biochar from Biomass: A Strategy for Carbon Dioxide Sequestration, Soil Amendment, Power Generation, CO2 Utilization, and Removal of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in the Environment," in *Handbook of Climate Change Mitigation and Adaptation*, 2021. https://doi.org/10.1007/978-1-4614-6431-0_80-2.
7. J. J. Manyà, M. Azuara, and J. A. Manso, "Biochar production through slow pyrolysis of different biomass materials: Seeking the best operating conditions," *Biomass and Bioenergy*, vol. 117, 2018. https://doi.org/10.1016/j.biombioe.2018.07.019.
8. Y. N. Guragain and P. v. Vadlani, "Renewable Biomass Utilization: A Way Forward to Establish Sustainable Chemical and Processing Industries," *Clean Technologies*, vol. 3, no. 1, 2021. https://doi.org/10.3390/cleantechnol3010014.
9. N. B. Saleh *et al.*, "Removal of poly- and per-fluoroalkyl substances from aqueous systems by nano-enabled water treatment strategies," *Environmental Science: Water Research and Technology*, vol. 5, no. 2, 2019. https://doi.org/10.1039/c8ew00621k.
10. A. Ashiq and M. Vithanage, "Biochar-mediated soils for efficient use of agrochemicals," in *Agrochemicals Detection, Treatment and Remediation*, 2020. https://doi.org/10.1016/b978-0-08-103017-2.00023-4.
11. J. J. Zhao, X. J. Shen, X. Domene, J. M. Alcañiz, X. Liao, and C. Palet, "Comparison of biochars derived from different types of feedstock and their potential for heavy metal removal in multiple-metal solutions," *Scientific Reports*, vol. 9, no. 1, 2019. https://doi.org/10.1038/s41598-019-46234-4.
12. J. Horst, J. McDonough, I. Ross, and E. Houtz, "Understanding and Managing the Potential By-Products of PFAS Destruction," *Groundwater Monitoring and Remediation*, vol. 40, no. 2, 2020. https://doi.org/10.1111/gwmr.12372.
13. E. W. Tow *et al.*, "Managing and treating per-and polyfluoroalkyl substances (Pfas) in membrane concentrates," *AWWA Water Science*, vol. 3, no. 5. 2021. https://doi.org/10.1002/aws2.1233.
14. B. N. Nzeribe, M. Crimi, S. MededovicThagard, and T. M. Holsen, "Physico-Chemical Processes for the Treatment of Per- And Polyfluoroalkyl Substances (PFAS): A review," *Critical Reviews in Environmental Science and Technology*, vol. 49, no. 10, 2019. https://doi.org/10.1080/10643389.2018.1542916.
15. S. Kundu *et al.*, "Removal of PFASs from biosolids using a semi-pilot scale pyrolysis reactor and the application of biosolids derived biochar for the removal of PFASs from contaminated water," *Environmental Science: Water Research and Technology*, vol. 7, no. 3, 2021. https://doi.org/10.1039/d0ew00763c.
16. M. J. Bentel *et al.*, "Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management," *Environmental Science and Technology*, vol. 53, no. 7, 2019. https://doi.org/10.1021/acs.est.8b06648.

17. E. Sørmo*et al.*, "Stabilization of PFAS-contaminated soil with activated biochar," *Science of the Total Environment*, vol. 763, 2021. https://doi.org/10.1016/j.scitotenv.2020.144034.
18. S. Nanda, A. K. Dalai, F. Berruti, and J. A. Kozinski, "Biochar as an Exceptional Bioresource for Energy, Agronomy, Carbon Sequestration, Activated Carbon and Specialty Materials," *Waste and Biomass Valorization*, vol. 7, no. 2. 2016. https://doi.org/10.1007/s12649-015-9459-z.
19. E. Gagliano, M. Sgroi, P. P. Falciglia, F. G. A. Vagliasindi, and P. Roccaro, "Removal of poly- and perfluoroalkyl substances (PFAS) from water by adsorption: Role of PFAS chain length, effect of organic matter and challenges in adsorbent regeneration," *Water Research*, vol. 171. 2020. https://doi.org/10.1016/j.watres.2019.115381.
20. S. F. Nakayama *et al.*, "Worldwide trends in tracing poly- and perfluoroalkyl substances (PFAS) in the environment," *TrAC - Trends in Analytical Chemistry*, vol. 121. 2019. https://doi.org/10.1016/j.trac.2019.02.011.
21. J. Cui, P. Gao, and Y. Deng, "Destruction of Per- A nd Polyfluoroalkyl Substances (PFAS) with Advanced Reduction Processes (ARPs): A Critical Review," *Environmental Science and Technology*, vol. 54, no. 7. 2020. https://doi.org/10.1021/acs.est.9b05565.
22. F. Ronsse, S. van Hecke, D. Dickinson, and W. Prins, "Production and characterization of slow pyrolysis biochar: Influence of feedstock type and pyrolysis conditions," *GCB Bioenergy*, vol. 5, no. 2, 2013. https://doi.org/10.1111/gcbb.12018.
23. A. K. Dalai, N. Batta, I. Eswaramoorthi, and G. J. Schoenau, "Gasification of refuse derived fuel in a fixed bed reactor for syngas production," *Waste Management*, 2009. https://doi.org/10.1016/j.wasman.2008.02.009.
24. N. Abdoulmoumine, S. Adhikari, A. Kulkarni, and S. Chattanathan, "A review on biomass gasification syngas cleanup," *Applied Energy*. 2015. https://doi.org/10.1016/j.apenergy.2015.05.095.
25. N. Cai, H. Zhang, J. Nie, Y. Deng, and J. Baeyens, "Biochar from Biomass Slow Pyrolysis," in *IOP Conference Series: Earth and Environmental Science*, 2020, vol. 586, no. 1. https://doi.org/10.1088/1755-1315/586/1/012001.
26. M. Tripathi, J. N. Sahu, and P. Ganesan, "Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review," *Renewable and Sustainable Energy Reviews*, vol. 55. 2016. https://doi.org/10.1016/j.rser.2015.10.122.
27. C. Z. Zaman *et al.*, "Pyrolysis: A Sustainable Way to Generate Energy from Waste," in *Pyrolysis*, 2017. https://doi.org/10.5772/intechopen.69036.
28. P. Sinha, A. Datar, C. Jeong, X. Deng, Y. G. Chung, and L. C. Lin, "Surface Area Determination of Porous Materials Using the Brunauer-Emmett-Teller (BET) Method: Limitations and Improvements," *Journal of Physical Chemistry C*, vol. 123, no. 33, 2019. https://doi.org/10.1021/acs.jpcc.9b02116.
29. M. I. Jahirul, M. G. Rasul, A. A. Chowdhury, and N. Ashwath, "Biofuels production through biomass pyrolysis- A technological review," *Energies*, vol. 5, no. 12. 2012. https://doi.org/10.3390/en5124952.
30. A. v. Bridgwater, "Pyrolysis of Solid Biomass: Basics, Processes and Products," in *Energy from Organic Materials (Biomass)*, 2019. https://doi.org/10.1007/978-1-4939-7813-7_984.
31. T. A. Mamvura and G. Danha, "Biomass torrefaction as an emerging technology to aid in energy production," *Heliyon*, vol. 6, no. 3. 2020. https://doi.org/10.1016/j.heliyon.2020.e03531.
32. J. L. Klinger *et al.*, "Effect of biomass type, heating rate, and sample size on microwave-enhanced fast pyrolysis product yields and qualities," *Applied Energy*, vol. 228, 2018. https://doi.org/10.1016/j.apenergy.2018.06.107.
33. D. Barraoui, J. F. Blais, and M. Labrecque, "Cleanup of sewage sludge spiked with Cd, Cu, and Zn: Sludge quality and distribution of metals in the 'soil-plant-water' system," *Chemosphere*, vol. 267, 2021. https://doi.org/10.1016/j.chemosphere.2020.129223.
34. S. Li, R. Li, Y. Tang, and G. Chen, "Microwave-induced heavy metal removal from dewatered biosolids for cost-effective composting," *Journal of Cleaner Production*, vol. 241, 2019. https://doi.org/10.1016/j.jclepro.2019.118342.
35. E. Antunes, J. Schumann, G. Brodie, M. v. Jacob, and P. A. Schneider, "Biochar produced from biosolids using a single-mode microwave: Characterisation and its potential for phosphorus removal," *Journal of Environmental Management*, vol. 196, 2017. https://doi.org/10.1016/j.jenvman.2017.02.080.
36. P. Basu, Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory. 2013. https://doi.org/10.1016/C2011-0-07564-6.
37. P. Basu, Biomass gasification, pyrolysis and torrefaction: Practical design and theory. 2018. https://doi.org/10.1016/C2016-0-04056-1.
38. B. Sajjadi, W. Y. Chen, and N. O. Egiebor, "A comprehensive review on physical activation of biochar for energy and environmental applications," *Reviews in Chemical Engineering*, vol. 35, no. 6, 2019. https://doi.org/10.1515/revce-2017-0113.
39. K. A. Thompson, K. K. Shimabuku, J. P. Kearns, D. R. U. Knappe, R. S. Summers, and S. M. Cook, "Environmental Comparison of Biochar and Activated Carbon for Tertiary Wastewater Treatment," *Environmental Science and Technology*, vol. 50, no. 20, 2016. https://doi.org/10.1021/acs.est.6b03239.

40. D. Cui, X. Li, and N. Quinete, "Occurrence, fate, sources and toxicity of PFAS: What we know so far in Florida and major gaps," *TrAC - Trends in Analytical Chemistry*, vol. 130. 2020. https://doi.org/10.1016/j.trac.2020.115976.
41. H. Hall, D. Moodie, and C. Vero, "PFAS in biosolids: A review of international regulations," *Water e-Journal*, vol. 5, no. 4, 2021. https://doi.org/10.21139/wej.2020.026.
42. H. Wijesekara*et al.*, "The impact of biosolids application on organic carbon and carbon dioxide fluxes in soil," *Chemosphere*, vol. 189, 2017. https://doi.org/10.1016/j.chemosphere.2017.09.090.
43. P. Westreich, R. Mimna, J. Brewer, and F. Forrester, "The removal of short-chain and long-chain perfluoroalkyl acids and sulfonates via granular activated carbons: A comparative column study," *Remediation*, vol. 29, no. 1, 2018. https://doi.org/10.1002/rem.21579.
44. C. C. Murray *et al.*, "Removal of per- and polyfluoroalkyl substances using super-fine powder activated carbon and ceramic membrane filtration," *Journal of Hazardous Materials*, vol. 366, 2019. https://doi.org/10.1016/j.jhazmat.2018.11.050.
45. C. J. Liu, D. Werner, and C. Bellona, "Removal of per- And polyfluoroalkyl substances (PFASs) from contaminated groundwater using granular activated carbon: A pilot-scale study with breakthrough modeling," *Environmental Science: Water Research and Technology*, vol. 5, no. 11, 2019. https://doi.org/10.1039/c9ew00349e.
46. N. Lakshminarasimman, S. B. Gewurtz, W. J. Parker, and S. A. Smyth, "Removal and formation of perfluoroalkyl substances in Canadian sludge treatment systems – A mass balance approach," *Science of the Total Environment*, vol. 754, 2021. https://doi.org/10.1016/j.scitotenv.2020.142431.
47. H. Lee and S. A. Mabury, "Global Distribution of Polyfluoroalkyl and Perfluoroalkyl Substances and their Transformation Products in Environmental Solids," in *Transformation Products of Emerging Contaminants in the Environment: Analysis, Processes, Occurrence, Effects and Risks*, 2014. https://doi.org/10.1002/9781118339558.ch27.
48. R. Kim Lazcano, C. de Perre, M. L. Mashtare, and L. S. Lee, "Per- and polyfluoroalkyl substances in commercially available biosolid-based products: The effect of treatment processes," *Water Environment Research*, vol. 91, no. 12, 2019. https://doi.org/10.1002/wer.1174.
49. H. Hall, D. Moodie, and C. Vero, "PFAS in biosolids: A review of international regulations," *Water e-Journal*, vol. 5, no. 4, 2021. https://doi.org/10.21139/wej.2020.026.
50. R. J. Letcher, S. Chu, and S. A. Smyth, "Side-chain fluorinated polymer surfactants in biosolids from wastewater treatment plants," *Journal of Hazardous Materials*, vol. 388, 2020. https://doi.org/10.1016/j.jhazmat.2020.122044.
51. B. Xu *et al.*, "PFAS and their substitutes in groundwater: Occurrence, transformation and remediation," *Journal of Hazardous Materials*, vol. 412, 2021. https://doi.org/10.1016/j.jhazmat.2021.125159.
52. I. T. Cousins *et al.*, "The high persistence of PFAS is sufficient for their management as a chemical class," *Environmental Science: Processes and Impacts*, vol. 22, no. 12. 2020. https://doi.org/10.1039/d0em00355g.
53. N. Bolan *et al.*, "Distribution, behaviour, bioavailability and remediation of poly- and per-fluoroalkyl substances (PFAS) in solid biowastes and biowaste-treated soil," *Environment International*, vol. 155, 2021. https://doi.org/10.1016/j.envint.2021.106600.
54. B. Chandramouli, "PFAS in waste: Occurrence, risks and treatment," 2019.
55. L. J. Winchell, J. J. Ross, M. J. M. Wells, X. Fonoll, J. W. Norton, and K. Y. Bell, "Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review," *Water Environment Research*, vol. 93, no. 6. 2021. https://doi.org/10.1002/wer.1483.
56. J. Paz-Ferreiro, A. Nieto, A. Méndez, M. P. J. Askeland, and G. Gascó, "Biochar from biosolids pyrolysis: A review," *International Journal of Environmental Research and Public Health*, vol. 15, no. 5. 2018. https://doi.org/10.3390/ijerph15050956.
57. J. Horst, J. McDonough, I. Ross, and E. Houtz, "Understanding and Managing the Potential By-Products of PFAS Destruction," *Groundwater Monitoring and Remediation*, vol. 40, no. 2, 2020. https://doi.org/10.1111/gwmr.12372.
58. D. Moodie *et al.*, "Legacy and emerging per- and polyfluoroalkyl substances (PFASs) in Australian biosolids," *Chemosphere*, vol. 270, 2021. https://doi.org/10.1016/j.chemosphere.2020.129143.