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Review

Recent Progress in Sludge-Derived Biochar and Its Role in Wastewater Purification

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Abstract: As the by-product of wastewater treatment, a large amount of sludge is generated annually. Turning this waste into a resource is a feasible and sustainable strategy to reduce potential environmental risks and recover energy. As a way to realize the international goal of carbon dioxide emission peak and carbon neutrality, producing biochar from sludge has gained worldwide attention. This review evaluates recent progress in synthesis techniques for biochar of sludge origin. Different preparation techniques and their key affecting factors are compared and described. The obtained sludge-derived biochar could be employed for eliminating aqueous pollution or purifying wastewater, mainly through adsorption and catalytic reactions. The removal of various pollutants by sludge-derived biochar and its related mechanisms are discussed and summarized in detail. This review will be conducive for a comprehensive understanding of recent progress in sludge-derived biochar study and for guiding the purposeful production of biochar, as well as for developing wastewater purification technology based on sludge-derived biochar.

Keywords: sludge; biochar; pyrolysis; wastewater; adsorption; advanced oxidation process

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1. Introduction

With accelerated urbanization and industrialization, the amount of sludge generated from municipal wastewater treatment plants (WWTPs) has increased significantly, which has led to serious environmental problems. According to data from the Ministry of Housing and Urban–Rural Development of China, in 2021 alone, the treatment capacity of municipal WWTPs in China reached 70.6 billion cubic meters, and the amount of sludge cakes with a moisture content of about 80% exceeded 56 million tons. With the steady growth in sewage treatment, the amount of sludge will continue to rise in the future. Sludge, as a by-product of the sewage treatment process, contains a variety of pollutants including pathogens, toxic organic chemicals, and heavy metals, which need to be treated appropriately [1]. On the other hand, sewage sludge can also act as a resource, for applications such as soil amendment, due to its high contents of organic matter, nutrients (e.g., N and P), and some trace elements. Thus, converting waste into resources for reuse is a future global trend.

For the purpose of realizing the goal of international "Carbon Dioxide Emission Peak" and "Carbon Neutrality", producing biochar based on biomass waste and its utilization can lower the industry's carbon footprint and mitigate the effects of climate change. Sludge is an ideal raw material for biochar manufacturing because of its intrinsic floc structure and richness in carbon and other reactive elements. Compared to conventional sludge treatment methods, including anaerobic digestion, composting, and incineration, producing biochar

using sludge has gained increasing attention. As calculated and summarized in Figure 1, publications focusing on biochar and sludge-derived biochar in the past decade have been increasing drastically. Transforming sludge into functional biochar is an environmentally friendly technique, which can not only remove hazardous compounds such as pathogens and organic pollutants from sludge and reduce the volume of sludge, but can also convert the organic matter in sludge into bio-oil and bio-gas, for use as fuels [2]. Meanwhile, the residual solid, which is called sludge-derived biochar, is proven to have a porous structure with a large specific surface area and abundant oxygen-containing functional groups with good metal-binding affinity, which can be further developed as adsorbents and catalysts [3]. This review provides a deep insight into the progress in the sludge-derived biochar production process and its applications in aqueous contaminant removal through adsorption and advanced oxidation processes (AOPs). The production methods and the key factors are systemically reviewed. The obtained biochar can be utilized as adsorbents and catalytic material; herein, its removal mechanisms are carefully studied.

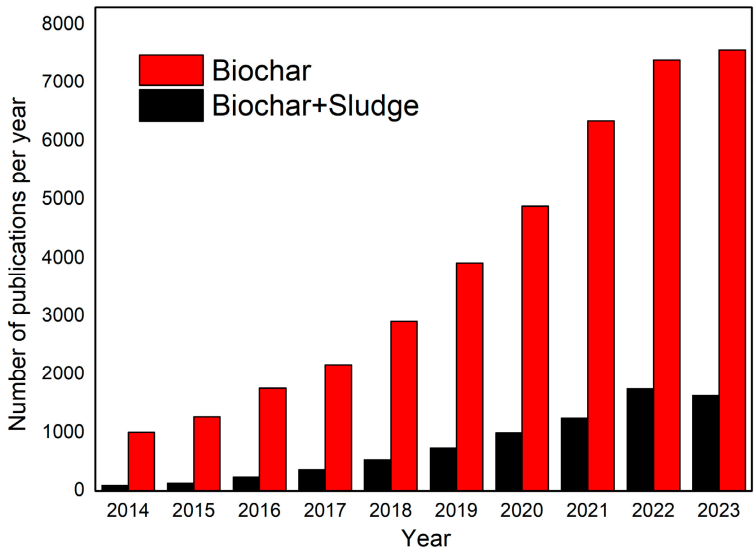

Figure 1. Evolution of the number of publications on biochar and sludge-based biochar between 2014 and 2023 (data from Web of Science; keywords used for search were "biochar" and "biochar and sludge").

2. Production of Sludge-Derived Biochar

The method for preparing sludge-derived biochar follows a similar routine, which mainly includes preprocessing, pyrolysis, collection, and characterization. In the preprocessing stage, the sludge will undergo drying, sieving, and activating. The drying process is often performed at 105 °C for 24 h with the purpose of reducing the volume of sludge and saving energy consumption for the subsequent pyrolysis. During the whole production process, the properties of sludge-derived biochar are affected by many factors, such as sludge moisture content, sludge modification and/or activation method, pyrolysis temperature, retention time, heating rate, pyrolysis atmosphere, etc. In general, the production of sludge-derived biochar can be determined mainly by two categories: (1) the sludge's inherent properties and (2) the production process parameters.

2.1. Effects of Sludge's Inherent Properties

As the sludge-derived biochar's precursor, raw sludge will directly affect the physicochemical properties of as-obtained biochar. Compared to conventional lignocellulosic biomass, sludge usually has a relatively higher nitrogen content (around 3.8% on average) because of peptides and proteins. The content and type of elements vary in sludges obtained from different wastewater and treatment sections. For example, compared with municipal sludge, the composition of industrial sludge is more complicated and polluted.

Papermaking sludge contains lots of organic matter such as lignin and cellulose, higher inorganic contents (Ca, Si), and low heavy metal contents. These biochars showed excellent performance in phosphate adsorption. Printing and dyeing sludge contains many dyeing agents, polycyclic aromatic hydrocarbons, and relatively high heavy metal contents (Cu, Ni, Cr), and the derived biochar could be utilized as catalysts for AOPs after careful treatment [4]. Basically, the sludge contains conventional elements (C, H, O, and N), bio-elements (P and S), inorganic elements (Ca, Mg, Si, Fe, Al, and Cl), and toxic heavy metal elements (Cu, Ni, Pb, Cd, Zn, As, Cd...). Among them, carbon is the dominant element and its content is the most basic and key index for measuring the quality of biochar [5].

During the thermochemical process, the organic components undergo a serious complicated chain reaction and convert into aliphatic carbons (at 100–300 °C), aromatic carbons (at 400–700 °C), and graphite carbon at high temperatures [6]. The carbon in its existing form and carbon-based chemical bonds will further affect the surface functional groups and affinities of the obtained sludge-derived biochar in practical applications. Despite the low carbon content in the original sludge (around 20%), the average carbon content could be enhanced dramatically, up to 75.01%, after carbonization [7]. Different contents of organic nitrogen will convert into pyridine-N, pyrrole-N, graphitized-N, and oxidized-N through a thermochemical process. The proportions of the nitrogen species will affect the derived biochar's adsorption ability and catalytic reaction kinetics, since it could modulate the electronic properties of the sp2-hybridized carbon layer and, thus, new active sites may be created [8]. Moreover, the inorganic elements in sludge are closely related to the pollutant's removal ability, while the metal elements can facilitate the graphitization process and act as the active sites for the pollutants' catalytic reactions [9]. For example, some sludges are abundant in element iron. The obtained Fe-rich sludge-derived biochar can be utilized as a catalyst for organic pollutant removal through Fenton-like reactions.

Considering the composition of sludge will directly affect the characteristics of sludge-derived biochar. Many research studies focus on the modification and conditioning of sludge through metal-doping, co-pyrolysis with other feedstocks, or introducing active substances. Yu et al. [10] fabricated Cu-doped sludge biochar (CSBC) for peroxydisulfate (PDS) activation to degrade Bisphenol A (100 mg/L, PDS = 0.5 g/L, catalysts = 0.7 g/L) in high-salinity wastewater. The introduced Cu species has a valence state of Cu^0, Cu^I, and Cu^{II}, which could greatly promote catalytic kinetics. The process was found to be dominated by singlet oxygen ($^1O_2$). Wang et al. [11] prepared $CuFe_2O_4$-doped sludge-derived biochar for Bisphenol S removal through a PDS activation process. It was found that 84.5% Bisphenol S (20 mg/L, PS = 8×10^{-3} mol·dm^{-3}, catalysts = 0.8 g/L) could be removed within 120 min. The introduction of metal elements benefit from the PDS activation and generate reactive oxygen species, such as sulfate radical ($SO_4\cdot^-$), hydroxyl radical (·OH), and singlet oxygen($^1O_2$). Chen et al. [12] mixed sewage sludge with rice husk (Mass ratio of 1:1) (SRHB) and then performed co-pyrolysis at 500 °C. The obtained SRHB showed an excellent adsorption ability towards various dyes. It had a maximum sorption capacity of 59.77 mg/g (for direct red), 42.12 mg/g (for acid orange), 38.46 mg/g (for react blue), and 22.59 mg/g (for methylene blue). Furthermore, SRHB with biomass added can form an aromatic structure and strengthen the π-π stacking interaction for dye removal. Yu et al. [13] introduced nitrogen into sludge-derived biochar production. The obtained nitrogen-doped biochar showed an excellent performance on tetracycline (TC) removal using a peroxymonosulfate (PMS) activation process. Under acidic conditions, 82.2% of TC at a rather high concentration (100 mg/L) was degraded within 120 min (PMS = 1.6×10^{-3} mol·dm^{-3}, catalysts = 0.2 g/L). ·OH and $SO_4\cdot^-$ were the dominant active species for TC removal.

Nevertheless, the biochar obtained from sludge suffers from an undeveloped pore structure and a low specific area, which limits its further application. The activation of sludge as a pre-treatment is considered to be an effective method for optimizing the pore structure and functional groups. In general, the activators include sodium hydroxide (NaOH), potassium hydroxide (KOH), phosphoric acid (H_3PO_4), water vapor (H_2O), and

zinc compounds [14,15]. Min et al. [16] found that zinc chloride ($ZnCl_2$) impregnation could lead to an increase in sludge-derived biochar yield and in the content of S and O elements. Increased specific functional groups were obtained and the aromaticity and hydrophilicity of the biochar were improved. In addition, $ZnCl_2$ also could act as chlorinating agent to passivate and reduce the total content of heavy metals in sludge through chlorination, thereby lowering the ecological risks. Li et al. [17] produced KOH-activated biochars derived from a mixture of sewage sludge and pine sawdust. The textual properties and functional groups were found to be significantly enhanced after KOH activation. Meanwhile, the specific surface area was increased by 3.9–14.5 times and the microporosity was fully developed, which contributed to an increased adsorption capacity for CO_2 capture (136.7–182.0 mg/g).

Notably, some researchers found that the above activators may damage industrial equipment or cause secondary pollution. Studies on milder activators have been investigated and carried out. Zhang et al. [18] produced sludge-derived biochar from cassava ethanol sludge for the first time by using $NaHCO_3$, an environmentally friendly weak alkali, as an activator. The $NaHCO_3$-activated biochar showed an enhanced adsorption capacity (154.45 mg/g) for TC, compared to raw biochar (34.04 mg/g). This novel activator could not only increase the contents of C, H, N, and O, but also efficiently removed ash from the obtained biochar in the thermal activation process, which benefitted the BET surface area and resulted in an enhanced adsorption capacity. Gu et al. [19] replaced NaOH with CaO, a gas-hardening inorganic gel, as an activator for sludge-based biochar production. The obtained CaO-activated biochar showed superior adsorption capacity for Cd (II) (43 mg/g), and its mechanical strength was improved. It was observed that CaO can increase the specific surface area and calcium ion content of the sludge-based biochar, which can improve the effective sites and surface functional groups.

2.2. Effects of Production Process Parameters

Dewatered sludge can be transformed into biochar through various thermochemical methods including gasification, conventional thermal pyrolysis, microwave pyrolysis, and hydrothermal carbonization (HTC, which is also called wet pyrolysis) [20]. The selection of production techniques is crucial to the obtained biochar's structure, morphology, composition, and other chemical properties. The various operating conditions and processes have unique intrinsic advantages, which are summarized in Table 1.

Table 1. Processes of biochar production from sludge and their advantages.

Production Method	Operation Conditions	Advantages
Gasification	>700 °C, <1 min	Rapid, stable, low volatile matter content
Conventional pyrolysis	300–1000 °C, >1 h	Easy operation, rapid heat, most mature technology
Microwave pyrolysis	0.3–300 GHz	Flexibility, not affected by sludge moisture
HTC	180–250 °C, 1–4 MPa	No pretreatment, low energy consumption

Gasification is a thermochemical method that occurs in gaseous media such as nitrogen, carbon dioxide, or limited oxygen and air, etc., and turns the carbonaceous biomass into gaseous fuel. In comparison to other processes, the biochars obtained through gasification are more stable under thermal conditions and generate less volatile matter.

The conventional pyrolysis method is the most widely studied and used method. The pyrolysis parameters, such as temperature, heating rates, residue time, and atmospheric pressure, are pivotal for determining the pyrolysis process [21]. According to the temperature range, classical pyrolysis is divided into fast pyrolysis (temperature > 500 °C), moderate pyrolysis (temperature 300–500 °C), and slow pyrolysis (temperature < 300 °C) [22]. Fast and moderate pyrolysis can facilitate the decomposition of organic materials, which enhances the

liquid and gaseous fractions, resulting in a higher yield of bio-oil. In contrast, slow pyrolysis results in a higher solid fraction owing to the longer residue times. Moreover, compared to slow pyrolysis, in the fast pyrolysis process, more carboxyl and hydroxyl groups can be formed, and the particle size of sludge-derived biochar is relatively small, which benefits the active sites' exposure. The temperature of pyrolysis directly affects the carbon content and the properties of sludge-derived biochar. Generally, a low temperature favors the biochar yield, while a higher temperature results in better catalytic and adsorption performances [23].

In the low-temperature pyrolysis process, the cross-linkage in carbon atoms is hard to break due to the low energy inputs; thus, the macrostructure in raw sludge remains. Polar functional groups, such as -COOH, -C=O, and -CO-, are more easily obtained in sludge-derived biochar with a low-temperature pyrolysis process [24]. With the increase in temperature, the C, H, N, and S contents decrease while the heavy metal contents increase. Meanwhile, the specific surface area of the obtained biochar increases with the elevating temperature, but the particle sizes are greatly reduced. Pore size distribution changes also ensued. At high temperatures, the obtained biochar tends to become more porous and more prone to metal adsorption. Liang et al. [25] produced biochar via the pyrolysis of a sewage sludge and red mud mixture for catalytic reactions. They found that, when the pyrolysis temperature increased from 500 °C to 700 °C, the catalytic reaction kinetics of sulfamethoxazole (SMX) degradation through PMS activation increased by 1.9 times. A higher temperature resulted in an increase in the specific surface area and in the content of C=O, Fe(II), and active sites such as pyridinic N and graphite N sites, which jointly contributed to the enhanced pollutant degradation performance. The pyrolysis temperature largely determined the output and quality of the sludge-derived biochar. In addition, the pyrolysis atmosphere also affected the physico-chemical properties of sludge-derived biochar. In most cases, the pyrolysis carried out in an inert atmosphere (N_2) removed the specific elements, modified the products' properties, and mitigated the emission of polluting gases. NH_3, CO_2, and Ar were also used as flux gases for biochar synthesis [26].

Hydrothermal carbonization (HTC), which is also called wet pyrolysis, is a relatively gentle thermal transformation process. It can convert the wet raw sludge into carbonaceous biochar without dewatering and avoids costly drying steps, considering its adaptability for high moisture. Compared to conventional pyrolysis, the energy consumption for the HTC process is significantly lower. Since HTC operates below 250 °C, the biochar or so-called hydrochar obtained can rarely attain high levels of carbonization and has a lower carbon content [27]. However, a higher oxygen content exists, as oxygenated function groups can be found in sludge-derived biochar obtained through the HTC process. HTC has been proven to be a suitable and effective method for producing sludge-derived biochar and for further applications. Marin-Batista et al. [28] used anaerobically digested sewage sludge as a raw material for phosphorus recovery through HTC at 180–240 °C. The reaction temperature affected the organic P and inorganic P retention yields. A mild temperature of 180–210 °C is recommended for HTC. Malhotra et al. [29] obtained biochar through HTC, based on the mixed centrifuged sewage sludge for energy recovery and the extraction of value-added compounds. HTC was performed under high pressure at 200 °C for 1–8 h. It was found that the oxygen content was significantly reduced and the fuel properties were improved when treated for 3 h or longer. The reaction duration in the HTC process is of great importance to the products' properties. Apart from producing biochar, HTC can also be an excellent method for improving the sludge dewaterability and reducing the volume of high-moisture sludge.

Overall, the choice of methods and treatment parameters are vital for the production of sludge-derived biochar. Optimizing the production process is the first step for utilizing the useful substances in sludge and obtaining high-quality sludge-derived biochar.

3. Application of Sludge-Derived Biochar in Wastewater Treatment

3.1. Adsorption

Compared to conventional wastewater treatment technologies, such as membrane separation, ion exchange, coagulation, and chemical precipitation, the adsorption process is simple and feasible [30]. Biochar has long been regarded as an excellent adsorbent material due to its large specific area and abundant oxygen-containing functional groups [31]. The sludge-derived biochar, which has a good carbon matrix, is proven to have a good adsorption ability for heavy metals, dyes, pharmaceuticals, ammonia nitrogen, phosphorus, emerging contaminants, oils, and other organic pollutants. In this process, the adsorption capacity is the pivotal index for assessing the adsorption performance. Usually, the characteristics of raw sludge and the pyrolysis conditions will jointly affect the adsorption capacity, by bringing in different element contents, porosities, pore size distributions, available surface areas, and surface functional groups. Table 2 presents the different experimental conditions, the characteristics of sludge-derived biochar, and their adsorption performance for different contaminants.

Table 2. Preparation of sludge-derived biochar and its adsorption performance.

Material	Conditions	Type	Contaminants	Specific Surface Area	Adsorption Capacity	Ref.
Sewage sludge modified by hydroxyapatite	Pyrolysis temperature: 550 °C, 2 h, pH 4–8	Heavy metal	Cu(II); Cd(II).	/	89.98 mg/g; 114.68 mg/g.	[32]
Sewage sludge/$MnFe_2O_4$ loaded	Hydrothermal temperature: 180 °C, 10 h, pH 5–6	Heavy metal	Pb(II)	129.29 m^2/g	174.22 mg/g	[33]
Sewage sludge	Pyrolysis temperature: 600 °C, 2 h, pH 1–2	Heavy metal	Cr(VI)	487.59 m^2/g	150.84 mg/g	[34]
Sewage sludge activated by $ZnCl_2$	Pyrolysis temperature: 750 °C, 2 h, pH 5–6	Dyes	Methylene blue	461.44 m^2/g	24.83 mg/g	[35]
Tannery sludge activated by melamine and KOH	Pyrolysis temperature: 550 °C, 3 h	Dyes	Active red X-3B; direct yellow RS; cationic blue X-GRL; acid blue 2GL.	47.67 m^2/g	45.13 mg/g; 84.10 mg/g; 154.80 mg/g; 120.92 mg/g.	[36]
Industrial sludge activated by $ZnCl_2$	Pyrolysis temperature: 800 °C, 1 h, pH 5–6	Dyes	Reactive black 5; green alizarin.	702.4 m^2/g	256.02 mg/g; 312.69 mg/g.	[37]
Dyeing sludge activated by KOH	Pyrolysis temperature: 800 °C, 3 h, pH 5	Antibiotics	Tetracycline	1178.4 m^2/g	1081.3 mg/g	[38]
Pharmaceutical sludge activated by NaOH	Pyrolysis temperature: 600 °C, pH 3–8	Antibiotics	Tetracycline	/	379.8 mg/g	[39]
Beverage sludge	Pyrolysis temperature: 800 °C	Pharmaceuticals	Paracetamol; ibuprofen; ketoprofen.	642.00 m^2/g	145 mg/g (pH 8); 105 mg/g (pH 4); 57 mg/g (pH 6).	[40]
Septic tank sludge activated by KOH	Pyrolysis temperature: 800 °C	Inorganic substance	Phosphate	82.90 m^2/g	42.51 mg/g	[41]

Table 2. *Cont.*

Material	Conditions	Type	Contaminants	Specific Surface Area	Adsorption Capacity	Ref.
Dewatered dry sludge	Pyrolysis temperature: 700 °C, 1 h, pH 11	Inorganic substance	Phosphate	20.93 m^2/g	51.79 mg/g	[42]
Oil sludge activated by $ZnCl_2$	Pyrolysis temperature: 800 °C, 1 h, pH 9	Oil	Gasoil	110.00 m^2/g	406.8 mg/g	[43]
Paper sludge/wheat husks, Austria	Pyrolysis temperature: 500 °C, 20 min, pH 2.8	Pesticides	2,4-DCP	63.80 m^2/g	17.51 mg/g	[44]
Activated sludge pretreated by $FeCl_3 \cdot 6H_2O$	Pyrolysis temperature: 600 °C 2 h, pH 3	Pesticides	Tebuconazole; linuron.	79.24 m^2/g	12.37 mg/g; 9.06 mg/g.	[45]
Sewage sludge	Pyrolysis temperature: 550 °C, 2 h, pH 7.5	Other organic pollutants	Tetrabromobisphenol A (TBBPA)	/	87.02 mg/g	[46]
Sewage sludge/Layered double hydroxides composited	Pyrolysis temperature: 550 °C, 2 h, pH 3–4	Other organic pollutants	Benzotriazole (BTA)	111.74 m^2/g	239.6 mg/g	[47]

It can be inferred that sludge-derived biochar has a good adsorption performance for all kinds of pollutants from the table. Notably, pollutants often coexist in contaminated wastewater systems, where competitive sorption always occurs. The decrease or the increase in adsorption performance is determined by the nature of the biochar and the pollutants. Despite the competitive adsorption between target pollutants, the sludge-derived biochar shows excellent adsorption behavior in complicated conditions. Ni et al. [48] obtained biochar derived from anaerobically digested sludge and studied its adsorption ability for Pb(II) and Cd(II). The mechanisms of the adsorption were investigated via single-metal and binary-metal systems. In the single-metal system, a higher adsorption capacity was found for Pb(II) (0.75×10^{-3} mol·dm^{-3}·g^{-1}) compared to Cd(II) (0.55×10^{-3} mol·dm^{-3}·g^{-1}). Meanwhile, in the binary-metal systems, the Cd (II) adsorption was inhibited to some extent, due to the competing adsorption sites, while Pb(II) had a greater affinity for obtained biochar. The obtained sludge-derived biochar still worked when heavy metal ions coexisted in the untreated water. According to the different pollutants treated, there were different adsorption mechanisms or multiple adsorption mechanisms involved. At present, electrostatic attractions, π-π bond interactions, and H-bonding are the three main adsorption mechanisms widely studied, especially for organic pollutant removal [20]. For heavy metal ion adsorption, the mechanism is more complicated, considering the heterogeneity and chemical properties of the biochar surface, the ionic environment of the aqueous solution, and the surface charge of the pollutants [49,50]. The adsorption between heavy metals and sludge-derived biochar may be driven by hydrophobic processes, ion exchange, pore-filling, precipitation, and functional group complexation [51] (Figure 2a). For inorganic pollutants such as phosphates, diffusion, ligand exchange, ion exchange, and electrostatic attraction jointly contribute to the adsorption process. The pharmaceuticals adsorption process involved pore-filling, electrostatic attraction, π-π stacking, and H-bonding and complexation (Figure 2c). The adsorption mechanisms involved in typical organic pollutant adsorption are summarized in Figure 2d.

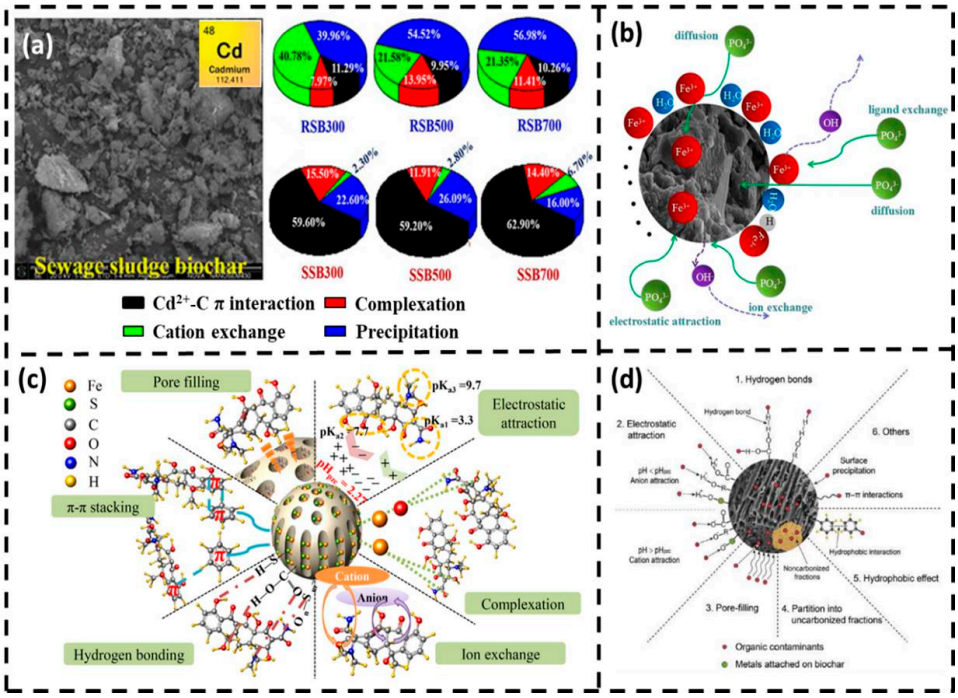

Figure 2. Mechanisms involved in the adsorption of (**a**) heavy metals, (**b**) phosphates, (**c**) pharmaceuticals, and (**d**) organic contaminates into sludge-derived biochar [52–55].

Electrostatic attraction occurs when two atoms or molecules are charged oppositely. The strength of these electrostatic forces is determined by the amount of surface charge and is closely related to the solution's pH and ionic strength, as well as the pH point of zero charge (pH_{pzc}) of the sorbent [22,56]. As a rule, the electrostatic attraction is relatively weak and it is the main mechanism for ionizable organic contaminant adsorption. Elkhlifi et al. [57] obtained sludge-derived biochar for phosphate adsorption and found that the value of pH and pHpzc would directly affect the adsorption performance. The uptake of phosphate is more pronounced when the pH is below the pH_{pzc}, while the adsorption kinetics become slower when it exceeds pH_{pzc}. Therefore, electrostatic attraction occurs at a specific pH and strongly depends on the zero-point charge of the biochar and the solution pH.

π-π interaction is a nonbonded interaction with plane structure and exists when the pollutants have aromatic rings or functional groups, as the pollutants contain C=C functional groups or benzene rings [58]. However, the spatial structure of the organic pollutants may be affected by environmental pH, coexisting anions, temperature, etc. As a result, the π-π interaction and the removal efficiency will change. Li et al. [46] produced sludge-derived biochar for tetrabromobisphenol A (TBBPA) adsorption. Based on the Fourier transform infrared spectrometer (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis, the C=C functional group was abundant on the surface of the obtained biochar [59]. After TBBPA adsorption, the stretching vibration absorption peak of C=C functional group was significantly changed, indicating that the absorption process took place through π-π interaction. The TBBPA benzene ring structure provided π electrons, and the obtained biochar provided adsorption sites for target pollutants.

The hydrogen bonding mechanism refers to forming an intermolecular hydrogen bond between the oxygen-containing functional group on the biochar surface and the functional group on the organic substance [60,61]. Hydrogen bonding commonly exists in the adsorption process and always occurs with the π-π interaction mechanism. Wei et al. [62] produced iron-loaded sludge-derived biochar for TC and doxycycline (DOX) co-adsorption. A hydrogen bond forms between the oxygenated carbon group on obtained biochar and the phenolic group of TC, which is responsible for its excellent adsorption performance. Besides environmental factors such as pH and temperature, humic acid

(HA) in real-life aqueous environments also influences the strength of hydrogen bonding interactions, since HA consists of various functional groups, including phenolic, carboxyl, and aromatic groups [63]. Luo et al. [64] found that low concentrations of HA could promote ciprofloxacin (CIP) removal, while a higher concentration would hinder the removal efficiency. An appropriate amount of HA is considered to be enough to facilitate the formation of oxygen-containing functional groups on the biochar surface and strengthen the hydrogen bonding force for adsorption. However, excessive HA may encapsulate the surface of sludge-derived biochar and occupy adsorption active sites.

Apart from the three main adsorption mechanisms discussed in detail, other mechanism cannot be neglected. The adsorption mechanisms for various kinds of contaminants may be obviously different in all aspects [65], but identifying adsorption mechanisms is indispensable. This is not only for a better understanding of the interactions between the adsorbent and the adsorbate interface; more importantly, it can facilitate the desorption process optimization [66] and benefit the obtained biochar regeneration.

3.2. Advanced Oxidation Processes (AOPs)

AOP technology, which has the advantages of selective oxidation and limited harmful by-products, is a type of important wastewater purification technology. It is especially efficient for organic pollutants, which are hard to biodegrade. According to the type of catalytic reaction, AOPs generally include PMS-, PDS-, hydrogen peroxide (H_2O_2)-, and peracetic acid (PAA)-activated oxidation processes (Figure 3). The mechanism of AOPs in sludge-derived biochar are more complicated because the catalytic sites are quite different from regular carbon material, considering the complex composition of sewage sludge as a precursor. During the AOPs, pollutants are degraded via radical and/or nonradical pathways. In the radical pathway, the highly reactive oxygen species ·OH, $SO_4{\cdot}^-$, and $^1O_2$ are produced and oxidize the pollutants into CO_2 and H_2O, eventually. In the non-free radical pathway, $^1O_2$ and the mediated electron transfer between pollutants and catalysts play a main role in pollutant degradation. Some AOPs based on different activation processes are summarized in Table 3.

Table 3. Different AOPs process for aqueous pollutant removal.

Material	Agents	Contaminants	Experimental Conditions	Removal Kinetics/Efficiency	Ref.
Fe-rich sludge-derived biochar	H_2O_2	4-chlorophenol	Pollutants 0.78 mM/L, catalysts 2 g/L, pH 2, H_2O_2 30 mM	0.51 min^{-1}	[67]
Municipal sewage sludge	H_2O_2	Ofloxacin	Pollutants 30 mg/L, catalysts 0.1 g/L, pH 6, H_2O_2 4 mM	91.5 ± 1.4%,	[10]
Zero-valent iron (ZVI) sludge	PS	Acid orange	Pollutants 0.06 mM, catalysts 0.5 g/L, pH 5.22, PS 0.925 mM	0.0718 min^{-1}	[68]
Red mud–sewage sludge	PMS	Sulfamethoxazole	Pollutants 0.02 mM, catalysts 1.5 g/L, PMS 0.15 mM	0.0481 min^{-1}	[69]
Secondary sewage sludge	PDS	Sulfamethoxazole	Pollutants 0.04 mM, catalysts 2.0 g/L, pH 5, PDS 1.5 mM	0.0145 min^{-1}	[70]
Mixture of primary and secondary sludge	PAA	4-chlorophenol	Pollutants 5 mg/L, catalysts 0.3 g/L, pH 7, PAA 1.8 mM	0.051 min^{-1}	[71]

3.2.1. AOPs Based on H_2O_2

During the H_2O_2 activation process, the strong oxidizing species ·OH are generated and effectively attack contaminants. Since iron is present in sludge, sludge-derived biochar has been regarded as a Fenton-like catalyst or is modulated, via various methods for adding iron groups, to catalyze the production of ·OH from H_2O_2. The iron content, as well as the surface functional structure, of sludge-derived biochar jointly affect the activation efficiency of H_2O_2, and directly determine the pollutant degradation performance.

Gan et al. [67] pyrolyzed a sludge cake conditioned using Fenton's reagent and red mud and obtained Fe-rich biochar with multivalent iron compounds for 4-chlorophenol (4-CP) removal. Under different pyrolysis temperatures, the valence of Fe is varied and its catalytic ability for the H_2O_2 activation and 4-CP degradation pathways are completely different. Apart from affecting the H_2O_2 activation reactive sites, the iron in the sludge-derived biochar can also act as an electronic mediator in the H_2O_2 activation process. Wu et al. [71] prepared iron-rich sludge-derived hydrochar and used it for triclosan oxidation through Fenton-like reactions. Both persistent free radicals (PFRs; 19.7%) and iron (80.3%) were found to activate H_2O_2 and to benefit pollutant oxidation. Additionally, other modified methods, including metal and non-metal-co-doped, heteroatom-doped, and acid/alkaline-modified sludge-derived biochar, as well as the biochar's internal structural changes, could also affect the H_2O_2 activation process.

3.2.2. AOPs Based on Persulfate

Persulfate-based advanced oxidation processes (PS-AOPs), represented by PMS and PDS activation, have gained a boost in attention for wastewater treatment [61]. In the PS-AOPs, $SO_4\cdot^-$ is the primary reactive oxygen species. Compared to ·OH (2.7 V, <1 μs), $SO_4\cdot^-$ has a higher redox potential (2.5–3.1 V) for organic mineralization, a longer half-life (30–40 μs), and a wider pH tolerance [72]. PMS and PDS are two representative agents and can be activated and decomposed into reactive species ($SO_4\cdot^-$, ·OH, $^1O_2$, and $O_2\cdot^-$) through various types of activation, including ultraviolet (UV) irradiation, microwave activation, transition metal ion activation, etc. To be more specific, PDS has the advantages of cheaper and easier transportation, higher water solubility, and higher stability than PMS, and, thus, has broader applications in wastewater and soil remediation [70]. The generated reactive species, as well as the nonradical pathways, can effectively break down the chemical bonds in organic pollutants for wastewater purification. Notably, the degradation of organic pollutants (antibiotics, dyes, phenolic compounds, pharmaceuticals, etc.) through the PS system is more easily facilitated than in the H_2O_2 system.

In addition to the above radical-based AOPs, non-free radical pathways participate in the oxidation process. At present, the number of studies on non-free radical pathways are increasing, and some researchers have found that non-free radical pathways play an even more important role. $^1O_2$ is the first excited electronic state of molecular oxygen and is highly reactive. It can be generated through the oxygen vacancies on sludge-derived biochar in the PMS activation process [69]. In addition, carbonyl groups and metals can also be active sites for $^1O_2$ generation [73]. Yin et al. [70] pyrolyzed sewage sludge at 700 °C to produce sludge-derived biochar for sulfamethoxazole (SMX) removal through PDS activation. In contrast to the traditional radical oxidation pathways in the biochar/PDS system, $SO_4\cdot^-$ and ·OH were not produced. The excellent SMX degradation performance was on account of the non-free radical processes dominated by singlet oxygen.

It is noted that both free radical and non-free radical processes exist, but the proportion and dominance are different. At present, the effect and mechanism of pollutant degradation in sludge-derived biochar/PS systems has been widely studied. Zang et al. [74] produced Fe-doped biochar from waste sludge for rhodamine B removal via PMS activation. Using electron spin resonance spectroscopy detection and a free radical quenching test, $SO_4\cdot^-$, ·OH, $^1O_2$, and $O_2\cdot^-$-were proven to be generated in the process. Large quantities of free-flowing electrons in sludge-derived biochar were believed to facilitate $SO_4\cdot^-$ and ·OH generation. Qian et al. [75] obtained sludge-derived biochar from petrochemical sludge for chloramphenicol (CAP) removal through PMS activation. The excellent CAP removal performance was the combination of adsorption with a catalytic degradation reaction. In the biochar/PMS system, free radical and non-free radical pathways simultaneously occur, and $SO_4\cdot^-$, ·OH, and $^1O_2$ were the main reactive species contributing to CAP degradation. Fang et al. [76] prepared N-modified sludge-derived biochar (N-SDBC) for fluoroquinolone antibiotics (FQs) degradation through PDS activation. Seven commonly used FQs were proven to be degraded by the N-SDBC/PDS system, as the graphite-N and Fe^0 on the

N-SDBC provided active sites for PDS activation. It was found that $^1O_2$ was the dominant reactive species, while the $SO_4\cdot^-$ and ·OH played minor roles. The non-free radical pathway was shown to contribute more than the free radical pathway.

3.2.3. AOPs Based on PAA

Peracetic acid (PAA)-based AOPs are emerging and have been identified as an alternative technology for wastewater treatment. They are especially effective for the degradation of chlorophenols and micropollutants such as naphthyl compounds and sulfa drugs [77]. Compared to PMS and H_2O_2, PAA has lower O-O bond energy (PAA 159 kJ/mol, PMS 317 kJ/mol, H_2O_2 213 kJ/mol) and, therefore, is thermally more feasible for multiple reactive species generation [78]. PAA can be activated by transition metals such as Co^{2+}, Fe^{2+}, Mn^{2+}, and $CoFe_2O_4$ to generate free radicals (·OH, $CH_3C(O)O\cdot$, and $CH_3C(O)OO\cdot$) [79,80]. Wu et al. [71] obtained sludge-derived biochar through the pyrolysis of a mixture of primary sludge and secondary sludge. The optimized biochar/PAA system exhibited an outstanding catalytic performance for 4-CP under a wide range of pH conditions through dichlorination, hydroxylation, and a ring-opening pathway. Persistent free radicals (PFRs), rather than the chemical composition or the material structure, dominated PAA activation, and RO· was found to be the major reactive species. During the pyrolysis process, organic matter and inorganic metals in the two sludges synergized and resulted in more abundant electron donation groups (C=O, -OH), which promoted PFR formation, and eventually facilitates 4-CP oxidation degradation. So far, little information on the PAA-based activation of sludge-derived biochar is available, but it is expected to be further investigated and have a large application potential in the future.

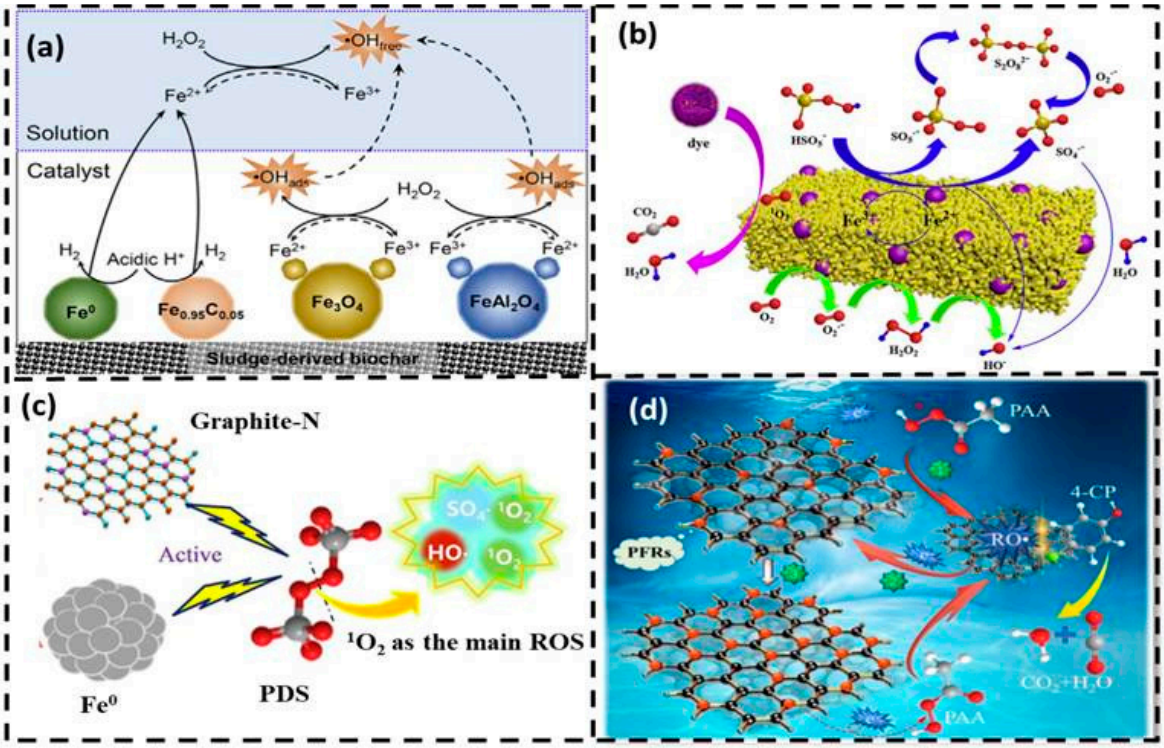

Figure 3. Activating mechanisms of (**a**) H_2O_2, (**b**) PDS, (**c**) PMS, and (**d**) PAA on sludge-derived biochar ([67,71,74,76]).

In addition to its excellent contaminant removal performance through adsorption and AOPs, its recycling and regeneration ability is vital to evaluate sludge-derived biochar. Gao et al. [38] found that the obtained sludge-derived biochar could maintain an 86.35% tetracycline removal efficiency after five adsorption–regeneration cycles with Fenton

reaction regeneration. The morphology of the biochar was not obviously damaged. Lv et al. [81] used microwaves, coupled with hydrogen peroxide, to regenerate functional sludge-derived biochar (MSBC) after Bisphenol S adsorption. They found that the regenerated MSBC remained stable after three cycles. Ma et al. [82] reused sludge-derived biochar using NaOH regeneration and found that the adsorption ability could still reach up to 98.5% after five cycles. Through different regeneration methods, sludge-derived biochar has been proven to have long-term running stability and reusability, which make it more cost-effective and broaden its potential applications in practical wastewater treatment.

4. Challenges and Future Recommendations

Nowadays, huge amounts of sludge are produced yearly, and they remain challenging to treat appropriately. Converting waste sludge into functional biochar has been proven to be a value-added strategy, which benefits sustainable waste management, as well as sustainable environmental development. In this process, several aspects should be especially noticed. Firstly, sewage sludge from different origins and industries exhibits profound differences in its chemical properties, which leads to completely different characteristics of the obtained biochar. Therefore, the factors correlating with the sludge's chemical properties need be quantitatively analyzed. This could allow us to distinguish between and make full use of the components in sludge. Secondly, to achieve specific properties of the obtained biochar and to further match it to specific applications, the production process should be consciously regulated. Parameters ranging from pyrolysis temperature, pyrolysis atmosphere, heating rates, and activation method to additive substances should be deliberately modulated and designed, in order to aim for a sludge-derived biochar with specific functions.

Furthermore, the sludge-derived biochar used for environmental remediation has some challenges and restrictions, such as economic problems and possible environmental risks. Compared to traditional sewage sludge disposal methods, pyrolyzing sewage sludge to create biochar inevitably requires more heat and energy consumption, resulting in higher costs. The production price of biochar is determined by the whole production process, including feedstock supply, sludge drying, pyrolysis, transportation, storage, the cost of labor, etc. For example, seeking cheaper raw materials or using industrial waste heat to dry the sludge could lower the cost, to some extent. The pyrolysis temperature and heating time can directly affect the biochar yield. Therefore, future development of sludge-derived biochar needs to seek a better balance between the quality, yield, and cost of biochar. Also, the raw sludge contains heavy metals, toxic substances, nitrogen, and phosphorus. When using sludge-derived biochar as an adsorbent or catalyst, it may cause eutrophication or secondary pollution. Therefore, in the preparation process of biochar, harmful substances and heavy metals need to be removed or immobilized by means of pretreatment. Also, the quantity of pollutants should be accurately determined based on the biochar's characterization and degradation capacity.

5. Conclusions

This review summarizes the recent progress in sludge-derived biochar production processes, including the synthesis methods and the key factors affecting the quality of obtained biochar. It is concluded that the selection of the appropriate thermochemical process and the operation parameters are of great significance. The obtained biochar has potential for practical applications, especially for wastewater purification through adsorption and advanced oxidation processes. Clarifying the adsorption and catalytic reaction mechanism would be helpful in better understanding pollutant degradation and mineralization, and would also purposefully guide the production of sludge-derived biochar in turn.

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