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Review

Preparation, Properties, and Application of Biochar for Improving Sewage Sludge Dewatering Performance: A Review

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Abstract: Biochar is a widely available carbon-based material that has been used for soil remediation and sewage treatment. However, in recent years, biochar has received more attention as a conditioning agent to improve the dewatering performance of sewage sludge. The sludge from the secondary sedimentation tank of wastewater treatment plants has high microbial activity and poor dewatering performance, which poses a challenge to sludge dehydration. Biochar and modified biochar can be injected into sludge as a skeleton to effectively reduce sludge compressibility, increase permeability, and release bound water, thus improving the dewatering performance of sludge. In this review, the preparation and characteristics of biochar are described, the current methods of sludge dewatering and the properties of sludge are introduced, and the research on the application of biochar in sludge conditioning is summarized. In addition, the existing problems and future development directions of biochar in sludge conditioning are discussed.

Keywords: biochar; sewage sludge; dewatering performance; persulfate; advanced oxidation

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1. Introduction

Nowadays, most wastewater treatment plants (WWTPs) throughout the world use biological treatment as the core technology to treat municipal wastewater [1]. Despite the fact that biological treatment has the advantages of excellent adaptability to the water quality of the influent, a stable process performance, and high efficiency in removing organics, a lot of excess sludge is generated in this process [2]. It is estimated that the production of sewage sludge is 0.1–30.8 kg per population equivalent per year (kg/p.e/year) [3]. For example, China, with a large population, has more than 3900 WWTPs, which can produce about 200 million tons of sewage sludge every year [4]. The excess sludge of WWTPs derives from the primary sedimentation tank and the secondary sedimentation tank. The sludge usually contains heterogeneous mixtures of microorganisms, organic matter, colloidal particles, and heavy metals [5]. On one hand, there are many harmful substances in sewage sludge [6]. On the other hand, the water content of the sewage sludge is higher than 88% [7]. Therefore, the excess sludge must first be dewatered to reduce its volume, and then disposed in a centralized manner, such as by being landfilled or incinerated or used as agricultural fertilizer or building materials.

Conditioning technologies for enhancing sewage sludge dewaterability involve chemical conditioning and physical conditioning [8]. Usually, chemical agents are added to the sewage sludge to enhance the physico-chemical properties of the sludge so that the sludge is easily dewatered. Coagulation/flocculation [9], the advanced oxidation process [10], and an acid/base treatment [11] are all classified as chemical conditioning. Physical conditioning refers to the use of the porous materials [12], heating [13], freezing and thawing [14], ultrasonic treatment [15], or electric fields [16] to improve the dewatering capacity of sludge. Heating, freezing and thawing, ultrasonic treatment, and electric fields conditioning depend on the input of energy. Therefore, these methods are expensive and not suitable for the treatment of large amounts of sludge in WWTPs. Porous materials exhibit better application value in the conditioning of sludge because many of them are industrial or agricultural wastes, which can realize the effective use of wastes while conditioning sludge. It is reported that some porous materials, such as sawdust [17], coal fly ash [18], lignite [19], steel slag [20], gypsum [21], wood chips [22], rice husk [23], and biochars from plants, municipal wastes, or other biomass [24,25], were added to the sludge to assist in the dewatering of the sludge.

Among these sludge conditioning methods, biochar conditioning has received significant attention. Compared with other porous mineral materials, biochar can increase the permeability of sludge without reducing the calorific value of sludge, which is conducive to the incineration of dewatered sludge [26]. With the keywords "biochar" and "sludge" as search terms on the Web of Science (WOS), the total number of articles published in the past ten years is 700 (see Figure 1). In 2013, there were only 9 articles, while in 2022, the number of articles increased to 156. Some articles discuss using biochar made from agricultural wastes to assist sludge conditioning, and other articles review the application of biochar produced from sludge to improve sludge properties, which is an environmentally friendly sludge reuse style.

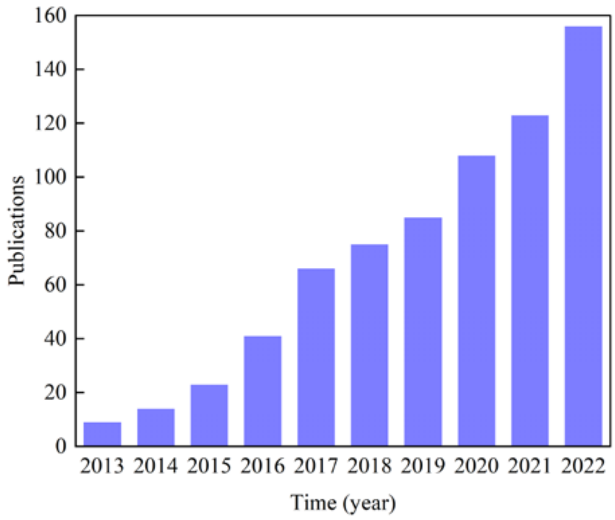

Figure 1. Analysis of published articles on biochar and sludge.

Biochar is a carbon-based material produced from carbon-rich biomass under limited-oxygen conditions [27]. A substantial amount of biomass can be adopted to produce biochar, such as woody and herbaceous biomass [28], watermelon rinds [29], potato peel waste [30], activated sludge [31,32], pig manure [33], and poultry litter [34]. Studies have shown that biochar can effectively improve sludge dewatering due to its rigid structure and high porosity. In addition, biochar can be employed to activate oxidants persulfate [35], peroxymonosulfate [36], and hydrogen peroxide [37] to generate free radicals. Both hydroxyl radical (•OH) and sulfate radical ($SO_4^{\bullet-}$) were able to disrupt the extracellular polymers and destroy activated sludge flocs structures to improve activated sludge dewatering. Therefore, the research about the advanced oxidation method based on biochar as a catalyst in sludge conditioning has also received extensive attention.

In this paper, the studies of different sources of biochar as the main materials for sludge conditioning and dewatering are reviewed. The main aim of the paper is to investigate the preparation methods and characteristics of biochar, to determine the methods of sludge treatment and sludge dewatering, to summarize the mechanism and effects of biochar and modified biochar on improving sludge dewatering performance, and to outline the current problems and research directions.

2. Preparation and Characteristics of Biochars

2.1. Preparation of Biochars

Biochar is commonly prepared by some thermochemical treatments on different biomass, including pyrolysis, gasification, hydrothermal carbonization, and torrefaction [38–40]. The major products in the thermochemical treatment of biomass include solid (biochar), liquid (bio-oil), and gas (syngas). Biochar from thermochemical treatment also has a high energy density. Figure 2 depicts the methods, conditions, and products for preparing biochar from different biomass, and the numbers next to the slashes in this figure represent the approximate percentages of the various products. Based on the heating rate, pyrolytic temperature, and residence time, the pyrolysis process can be classified as slow pyrolysis, fast pyrolysis, and intermediate pyrolysis [41]. Compared with fast pyrolysis, slow pyrolysis has a longer residence time but a larger biochar yield. The temperature and residence time required for intermediate pyrolysis are between the two above, and the biochar product is also in the middle. Gasification is the process of partial combustion of biomass in a high temperature range (600–1200 °C) with a short residence time (10–20 s) [38]. The main products of gasification are a gas mixture (CO, H_2, and CO_2) and a small amount of biochar [42]. Torrefaction usually refers to a mild dry pyrolysis process during which biomass is heated to a temperature of about 270–300 °C in an inert atmosphere for a residence time of 10–60 min [43]. This process results in about 80% of the biochar yield; the remainder is lost as gas. Hydrothermal carbonization (HTC), which is a wet torrefaction process, converts biomass into a carbon-rich solid product biochar [44]. In a confined system, the biomass is submerged in water and heated for 5–240 min at a temperature range of 180–300 °C and pressure of 2–6 MPa to complete the HTC process [45]. Compared to slow pyrolysis and dry torrefaction, the advantage of HTC is that it can operate in the presence of water and is not affected by the high moisture content of the biomass, eliminating the need to pre-dry wet biomass [46].

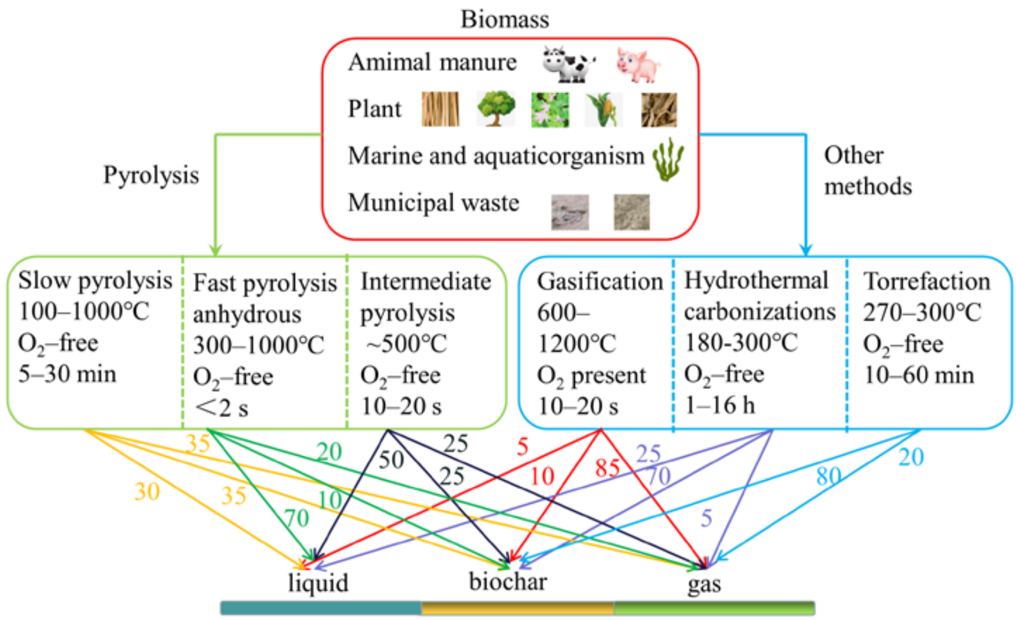

Figure 2. Various thermochemical approaches for biochar production.

2.2. Characteristics of Biochars

The properties of biochar determine its performance and effect on practical applications. There are certain differences in the physical and chemical properties of biochar from different biomass sources. The physical properties of biochar include its density, porosity, specific surface area, pore size, pore volume distribution, and mechanical stability. Its chemical properties are related to the elemental composition, surface charge, pH, electrical conductivity (EC), and cation exchange capacity (CEC). In general, biochar has a small bulk density (<0.6 g cm^{-3}) [47]. The surface area and porosity are important physical properties that directly affect the adsorption capacity of biochar towards pollutants. Their size depends on the biochar feedstock and pyrolysis temperature. Representative scanning electron microscope (SEM) images of spruce biochar and maple biochar are shown in Figure 3 [48]. Both spruce biochar and maple biochar form excellent pore structures, but the pores of the former are irregular. This indicates that the microstructure of biochar depends on the wood species and post-processing of the raw materials. The surface area of biochars extracted from most biomass ranges from 100 to 800 m^2 g^{-1}, while the surface area of biochars derived from sewage sludge is below 100 m^2 g^{-1} [49]. During the pyrolysis of biomass, biochar produces pores with different sizes, namely nano- (<0.9 nm), micro- (<2 nm), and macro- (>50 nm) biochar [50]. Biochar with larger pores can be produced at higher temperatures [51]. The chemical composition of biochar usually consists of carbon (C) (40–70%), oxygen (O) (10–45%), hydrogen (H) (1–5%), nitrogen (N) (0–3%), sulfur (S) (<1%), and other trace elements. The functional groups generated during biomass carbonization are closely related to their adsorption and catalytic performance, especially oxygen-containing groups. During pyrolysis, with the increase of temperature, the higher carbonization degree reduces the atomic ratio of H/C, O/C, and N/C, and the contents of the carboxyl group (–COOH), hydroxyl group (–OH), and amino group (–NH_2) decrease accordingly [52]. The surface charge and pH are also important properties of biochars. In general, the biochar produced via high temperature pyrolysis is alkaline, while the biochar generated by low temperature pyrolysis is acidic. Pyrolysis at high temperature results in the loss of the acidic functional groups and an increase in the content of alkaline earth metals, thus rendering biochar basic [53]. The result is the opposite at a low temperature. The charge on the biochar surface refers to the potential difference between the inner and outer surfaces of the particles in the solution. The surface charge of the particles is closely related to the pH of the solution. pH_{PZC} is the pH at which the net charge on the particle surface is zero [54]. When the solution pH is lower than pH_{PZC}, the biochar is positively charged; when the solution pH is higher than pH_{PZC}, the biochar is negatively charged [55]. At low pH values, functional groups such as amines can accept protons, and thus gain a positive charge, while with the increase of solution pH, the phenol and carboxyl groups gradually lose their protons, and thus become negatively charged [56]. For different usages of biochar, the pyrolysis temperature can be adjusted to produce biochar with different properties [57].

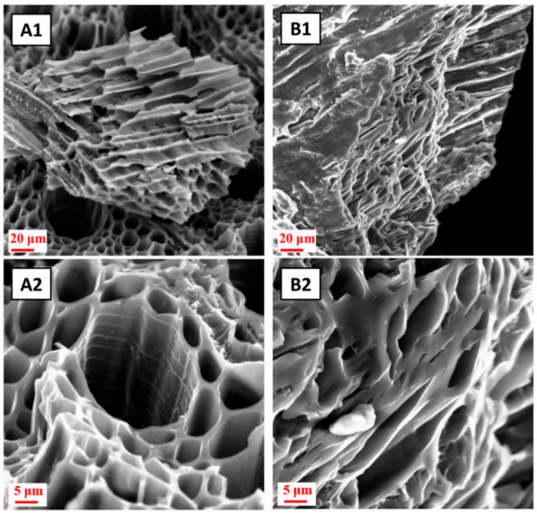

Figure 3. SEM image of biochar. The left is a maple sample (**A1**,**A2**) and the right is a spruce sample (**B1**,**B2**).

3. Sewage Sludge Treatment and Conditioning Method

3.1. Sewage Sludge Treatment Method

The WWTPs usually accept mixed water of domestic sewage and industrial wastewater, and the treatment method is mainly biological treatment, that is, the traditional activated sludge method and its deformation [58]. The wastewater and sludge treatment processes at the core of the activated sludge process are shown in Figure 4. Primary sludge and secondary sludge are produced in WWTPs. Primary sludge refers to the settleable solids in the primary sedimentation tank, including certain inorganic substances. Secondary sludge refers to the settled sludge after wastewater treatment with activated sludge, which is the result of net biological growth and accumulation of inert organic matter. WWTPs produce a large amount of sludge, even though it only accounts for 1% of the wastewater to be treated. The dewatered sludge still contains a high percentage of volatile solids and high water content, which results in a very large sludge volume. Sludge contains a large number of toxic and harmful microorganisms, bacteria, heavy metals, and various complex organic pollutants. If it is excreted and stacked at-will without proper treatment and disposal, it will cause serious secondary pollution to the water and atmospheric environment. More stringent local effluent regulations have brought about the increase of pipelines connected to WWTPs, the establishment of new plants, and the upgrading of old plants, and the final result is the continuous increase of sludge volume. A large amount of sewage sludge must be dewatered to reduce the volume of wet sludge before disposal via composting, landfill, drying, heat drying, or incineration. When the moisture in sludge is reduced to 50–60%, it can be disposed via composting, landfill, or incineration [59]. The current sewage sludge treatment process mainly focuses on the combination of thickening, digestion, and dehydration (Figure 4). Through thickening, the moisture content of activated sludge can be reduced from the original 99.5% to 94–96% [60]. In the process of sludge digestion, part of the organic matter is decomposed by anaerobic bacteria under anaerobic conditions, releasing methane and carbon dioxide. As a result, the sludge volume can be reduced by more than 50%, and the dewatering performance can be improved by 2–3% [61]. The dewatering method of sludge usually adopts mechanical dehydration, including vacuum suction filtration dehydration, pressure filtration dehydration, and centrifugal dehydration [62]. The dewatering performance of activated sludge is closely related to the previous sludge conditioning.

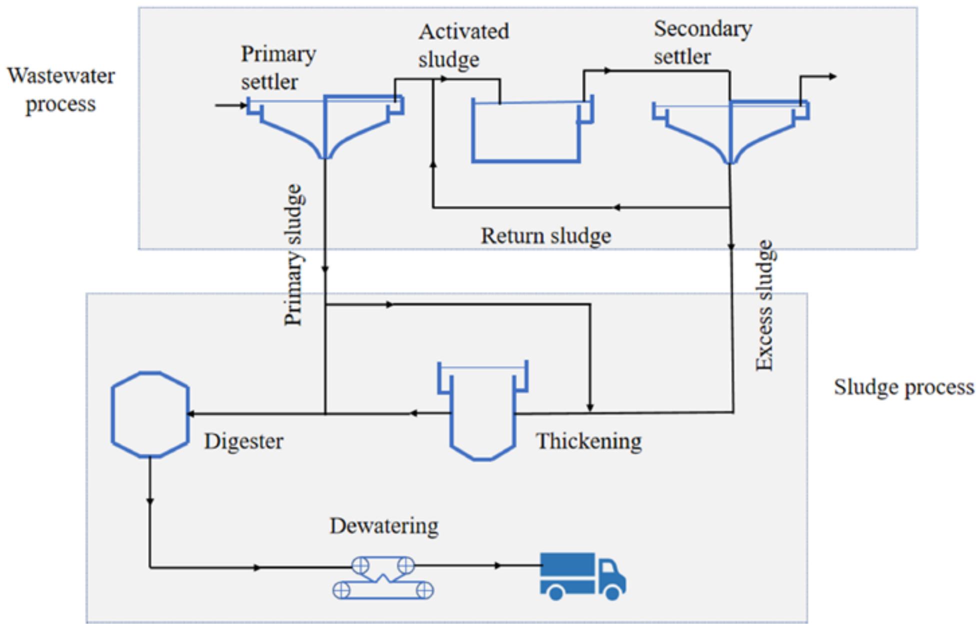

Figure 4. Process flow of WWTPs.

3.2. Sewage Sludge Conditioning Method

Sludge conditioning is usually required before sludge dewatering, which is determined by the characteristics of sewage sludge. Sewage sludge is a colloidal floc with a loose structure and high specific surface area and porosity, and the floc particles contain a high proportion of interstitial water and adsorbed water (Figure 5), which is difficult to remove during mechanical dehydration [63]. Therefore, physical, chemical, or biological conditioning methods are adopted to improve the hydrophilicity of the flocs by compressing the volume of the flocs so that the gaps and adsorbed water in the flocs are reduced, which is beneficial to sludge dewatering [64]. The sludge conditioning method plays an important role in the whole sludge dewatering process. Chemical conditioning is a common approach. In the sludge chemical conditioning process, inorganic coagulants (polyaluminum chloride or ferric chloride) and organic polymer coagulants (polyacrylamide) can be employed to improve the dewatering performance of sludge [65]. At the same time, coagulation aids (lime) can also be added to adjust the pH value of the sludge, alter the particle structure of the sludge, and destroy the stability of the colloid to improve the coagulation effect [66]. However, the consumption of chemical conditioning agents is large, resulting in high operating costs. Taking ferric chloride ($FeCl_3$) conditioning as an example, the national sludge output is calculated as 4.38×10^5 m^3/d, the dosage is set at 0.8 g/L, according to experience, and the market price of $FeCl_3$ is CNY 6000/ton, meaning the cost of ferric chloride is calculated as high as CNY 770 million/year [67]. In order to solve the problems of the high consumption of chemical conditioning agents and high operating costs in the current sludge preconditioning methods, some researchers have begun to explore various alternative sludge conditioning methods. The physical conditioning methods of sewage sludge without chemical additives have received significant of attention. Some structure-forming materials, such as fly ash [18], coal ashes [68], gypsum [69], rice husk [70], wheat dregs [71], walnut shells [72], wood chips [22], or biochar [73], have been confirmed as useful for sludge conditioning. These materials can act as framework builders or filter aids, and play an important role in reducing the compressibility and increasing the mechanical strength and permeability of the solids present in the sludge during compression [74]. These materials form solid, rigid lattice structures that can remain porous as they are compressed in a mechanical dehydration device. The dewatering capacity of activated sludge is improved by reducing the compressibility of activated sludge and converting the flocs into a more rigid structure, maintaining high porosity under pressure [75]. Biochar as a physical conditioning material is superior to other mineral materials due to its low ash content, high heating value, and high porosity [76]. The use of biochar is not only beneficial to improve sludge dewatering performance, but the solid mixture can also be disposed of by incineration, which will improve the overall economics of sludge treatment [26].

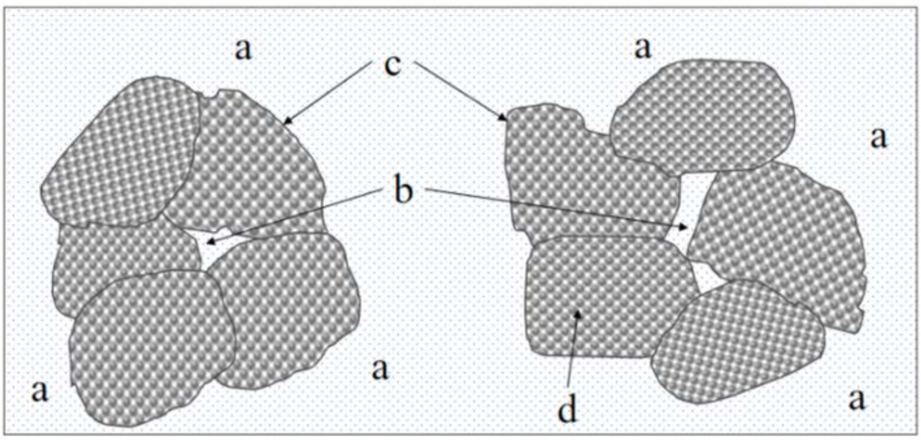

Figure 5. Schematic presentation of water in sewage sludge. a—free water; b—interstitial water; c—surface water; d—intracellular water.

4. Application of Biochar in Sludge Conditioning

Although a number of studies have demonstrated biochar can effectively remove heavy metals and organics from aqueous solutions, the use of biochar for sludge conditioning is still an emerging field. The relevant studies of biochar and modified biochar towards sludge conditioning are summarized in Table 1. Some biochar raw materials used for soil remediation and sewage treatment can also be used to produce biochar for sludge conditioning, including the branches, leaves, and husks of herbaceous plants (rice straw, rice husk, reed straw, wheat straw, corn straw, and waste tea powder and coconut shell), municipal and industrial sludge, etc. Biochar is usually obtained via anaerobic pyrolysis of these carbonaceous raw materials at either a low temperature or a high temperature. Among them, the activated sludge of the WWTPs is made into biochar and then adopted for the conditioning of activated sludge before dehydration. It is an economical approach to the rational utilization of activated sludge, and has attracted the attention of researchers. In addition, due to the small surface area and porosity of raw biochar, some modified biochar or a combination of biochar with other materials were employed for sludge conditioning to better improve the sludge dewatering performance.

Table 1. Research on biochar for sludge dewatering.

Feedstock	Biochar	Sewage Sludge	Dehydration Performance	Ref.
Sewage sludge	450 °C	MC = 78.8%, ash = 57.16%, VS = 38.95%, C = 16.01%, H = 3.02%, N = 2.53%, S = 0.88%, pH = 6.89	BC450: MC = 61.7%; BC450 + K_2FeO_4: MC = 58.7%.	[24]
Activated sludge	800 °C, sludge-derived Fe-rich BC	pH = 6.68, TSS = 32.71 g/L, VSS = 14.14 g/L, DS = 13.5 g/L, MC = 97.1%, SRF = 2.45 × 10^{13} m/kg, CST = 205.15 s	CST and SRF could be decreased by 23% and 44%, respectively.	[32]
Dried sludge cake	$KMnO_4$/$FeCl_3$/BC	MC = 89.9−99.5%, DS = 6.87–11.26 g/L, SRF = 6.13 × 10^{13}–8.01 × 10^{13} m/kg, YN= 0.81–1.56 kg/(m^2 h)	The optimal condition: $KMnO_4$ = 20 g/kg, $FeCl_3$ = 138.09 g/kg, BC = 70%DS; SRF decreased by 99.03%, YN increased by 24.6 times, MC decreased to 60.63%.	[77]
Coconut shell	600 °C, MCSB-$FeCl_3$, C 48.8%, O 48.6%	secondary sludge	MCSB-$FeCl_3$ = 41%DS, RMT = 10 min, SMT = 19 min; the best CST was 55.8 s.	[78]
Water supply sludge and industrial wastewater sludge	700 °C, SA= 49.39 m^2/g, total pore volume = 0.22 cc/g, pore diameters = 2–50 nm	MC = 99.4%, pH = 6.76, SRF= 12.69 × 10^{12} m/kg, TS = 6.478 g/L, VS = 4.426 g/L, SA = 28.18 m^2/g, total pore volume = 0.22 cc/g	The optimal conditions: 20% DS of BC with modified corn-core powder at a loading of 20% of DS, the largest YN and the lowest SRF reached.	[79]
Wheat straw	Heat/PS/BC	activated sludge	The optimal conditions: 70 °C, PS = 120 mg/g-VS, BC = 150 mg/g-VS, CST and CWR increased to 5.03 and 86.8%, MC decreased to 42.6%.	[80]
Sludge cake	400 °C, BC-conditioned with rice husk flour and $FeCl_3$	MC = 98.6–99.01%, DS = 9.52–13.97 g/L, SRF = 9.87 × 10^{12}–26 × 10^{12} m/kg, YN = 1.38–2.42 kg/(m^2·h)	The optimal biochar-conditioned dosage was 70% DS. SRF decreased by 63.9%, YN increased by 39.2%.	[81]
Rice straw	Fe^{2+}/PMS/rice straw BC (RSBC)		The optimal conditions: pH = 6.5, PMS = 0.6 mmol/g- VS, Fe^{2+}: PMS = 0.6, RSBC = 120 mg/g-VS.	[82]

Table 1. *Cont.*

Feedstock	Biochar	Sewage Sludge	Dehydration Performance	Ref.
Rice straw	500 °C, rice straw BC (RSB) modified by $AlCl_3$	pH = 6.8, TSS = 16.7 g/L, VSS = 10.4 g/L, DS = 13.5 g/L, MC = 98.7%, SRF = 13.8 × 10^{12} m/kg, CST = 126 s, SV30% = 96.4%, YN = 0.8 kg/(m^2·h), density = 1.02 g/cm^3	MRSB = 0.3 g(RSB)/g(DS), SV30%, SRF, MC and CST were decreased to 79.8%, 1.2 × 10^{12} m/kg, 81.4% and 38 s, respectively. YN was increased to 19.4 kg/(m^2·h).	[83]
Rice husk	500 °C, rice husk BC modified by $FeCl_3$	MC = 98.4–98.8%, DS = 12.05–16.25 g/L, SRF = 1.04 ×10^{13}–5.13 × 10^{13} m/kg, YN = 0.62–0.98 kg/(m^2·h)	SRF decreased by 97.9%, MC decreased to 77.9%, SV30% decreased to 60%, YN increased by 28 times.	[84]
Sludge	700 °C, corn-core powder and sludge-based BC	activated sludge	Aggregated strands and α -helix were released.	[85]
Sludge	200–900 °C, sludge-derived Fe-rich BC	thickened sludge	MS decreased to around 46%, the costs reduced by almost 29%.	[86]
Red mud and reed straw	800 °C, Fe-rich BC (RMRS-BC)	secondary sludge	The optimal conditions: 7.5% DS of RMRS-BC at a mass ratio of 1:1 combined with H_2O_2. MC 57.88.	[87]
Corn straw	800 °C, BC/PS	COD, VS, MC, CST and pH were 15, 824 mg/L, 14.4 g/L, 95.5%, 163.5 s and 6.5, respectively.	biochar = 2.1 g/L, PS = 7.5 mM, CST increased to 4.21 times, MC decreased to 43.4%.	[88]
Waste tea powder	500 °C, $MnFe_2O_4$-BC (MFB)	secondary sludge	MFB/PMS/TA, MC dropped to 40.80% at pH 5.0.	[89]

Note: TS: total solid; VS: volatile solid; SA: surface areas; MC: moisture content; BC: biochar; CST: capillary suction time; SRF: specific resistance to filterability; YN: net sludge solids yield; DS: dry solid; RMT: rapid mixing time; SMT: slow mixing time; PMS: peroxymonosulfate; TA: tannic acid; CWR: centrifuged weight reduction.

It is common to adopt aluminum-based and iron-based substances for the modification of biochar. Guo et al. [83] utilized rice straw biochar modified by $AlCl_3$ to enhance the dewatering performance of sewage sludge, and the results showed that the sludge conditioned by both the raw biochar and the modified biochar had improved dewatering performance compared with the unconditioned sludge, possibly due to their generally higher porosity, a desirable characteristic for efficient sludge dewatering. The conditioned sludge had a series of cracks, and the sludge was looser, especially the sludge conditioned by modified biochar. In subsequent experiments, the settling volume (SV30%), SRF, MC, CST, and YN of the conditioned sludge were examined, and it was confirmed that the dewatering ability of the sludge conditioned by the modified biochar was greatly improved. Wu et al. [84] prepared ferric chloride-modified rice husk biochar for sludge conditioning. The result was that the moisture content and SV30% of the conditioned sludge decreased by 19.36% and 37.5%, respectively, and the YN increased by 28 times. The aluminum or iron species on the surface of the aluminum- or iron-modified biochar are positively charged, which can counteract the negative charge of the sludge particles, thereby improving the sedimentation and dewatering performance of the sludge. The use of modified biochar based on iron or aluminum improves the incompressibility and permeability of the sludge, so that the sludge moisture can easily pass through the sludge cake.

The reason why activated sludge is not easily dewatered is that extracellular polymeric substances (EPSs) entangle with the sludge particles and prevent the bound water of the sludge system from flowing outward. A previous study [85] adopted a modified corn-core powder (MCCP) and sludge-based biochar (SBB) in sludge conditioning, and explored the concentration and morphological distribution of organic matter in EPS, as well as protein changes in the secondary structure of proteins. The results showed that there was a close relationship among the net sludge solids yield, the specific filtration resistance, and the zeta potential, and the dehydration properties were determined by the secondary structure of the protein. After the addition of SBB and MCCP to the sludge, the aggregated chains and α-helices were released, which indicated that the unfolding and de-helix effects of soluble

EPS were improved, the sludge network was disordered, and the flow resistance of the bound water was reduced, thereby improving the sludge dehydration ability.

In order to further destroy the stability and compactness of sludge, advanced oxidation methods based on oxidants, such as hydrogen peroxide or persulfate, are employed in sludge conditioning. Usually, biochar or modified biochar is used to activate the oxidant to obtain oxygen-containing free radicals to degrade the organic matter in the sludge so that the sludge flocculation is looser and the bound water can be effectively released. Tao et al. [86] investigated Fenton and Fenton-like approaches used for sludge conditioning. The occurrence of the Fenton reaction is based on iron and hydrogen peroxide. In this experiment, sludge-derived iron-rich biochar was used as an iron source and a catalyst to catalyze hydrogen peroxide to enhance the sludge dewatering performance. The inherent soluble Fe^{2+} of the sludge itself (256.21 mg/L) and the Fe^{2+} leached from the biochar (507.41 mg/L) reacted with hydrogen peroxide to generate hydroxyl radicals, which played a key role in degradation of the organic matter in the sludge. Li et al. [87] also proposed an iron-based biochar in activating hydrogen peroxide, triggering heterogeneous and homogeneous Fenton reactions and sludge conditioning. Fe_3O_4 supported on biochar acts as a catalyst for a heterogeneous reaction, and Fe^{2+} formed after acidification undergoes a homogeneous reaction. Bi-Fenton action enhanced the formation rate of •OH, and the sludge flocs were dispersed into smaller particles, releasing more extracellular polymer (EPS)-bound water, thereby improving the dewatering performance of the sludge. In addition, biochar, as a skeleton building agent, also played a major role in reducing the compressibility of the sludge cake. Free water outflow can be promoted due to the reduced compressibility of the sludge. Despite the obvious effect of activating hydrogen peroxide to condition the sludge, the too-low pH conditions (pH = 3.0) also caused some trouble in the operation process [88].

Compared with hydrogen peroxide, persulfate (including peroxodisulfate and peroxymonosulfate) is currently the most studied oxidant in advanced oxidation methods due to the stable nature of persulfate. A corn biochar was produced to activate peroxodisulfate to dewater waste-activated sludge [89]. Biochar can act as an activator to trigger peroxodisulfate to generate sulfate radicals, which can strongly degrade organic matter in sludge. The initial pH value of sludge has a great influence on the effect of biochar activation by peroxodisulfate. The results exhibited that the sludge dewatering performance was superior under acidic and neutral conditions, indicating that the effect of biochar activation on the peroxodisulfate system was stronger in this pH range. The experiments of free radical quenching under different pH conditions confirmed that the free radicals generated during the reaction were mainly sulfate radicals, which played the role of degrading organic matter. In addition, three-dimensional fluorescence spectroscopic analysis of EPS demonstrated that tryptophan protein and humic acid (a hydrophobic organic substance in EPS) were decomposed, making WAS more susceptible to dehydration.

Yang et al. [90] conducted peroxymonosulfate (PMS) activated by $MnFe_2O_4$-biochar (MFB) combined with tannic acid (TA) to improve sludge dewatering, and the SRF decreased by 83.68%. Figure 6 deduces the mechanism of sludge dewatering by MFB/PMS/TA. Firstly, the generation of some free radicals can oxidize the organic matter in the sludge and destroy the compact structure of the sludge. Then, Mn^{2+} and Fe^{2+} can activate PMS to generate sulfate radicals, and at the same time, they convert themselves into Mn^{3+} and Fe^{3+} (Equations (1) and (2)). Mn^{3+} and Fe^{3+} can be converted into Mn^{2+} and Fe^{2+}, respectively, under the action of TA (Equations (3) and (4)). Namely, there are interconversions between different valence states of iron (Fe^{3+}/Fe^{2+}) and different valence states of manganese (Mn^{3+}/Mn^{2+}) in the sludge (Figure 6). Because the redox potentials of Fe^{3+}/Fe^{2+} and Mn^{3+}/Mn^{2+} are 0.77 and 1.51 V, respectively [91], electron transfer would occur between Fe^{2+} and Mn^{3+} (Equation (5)). In addition, $SO_4^{-\bullet}$ could react with OH^- to form •OH (Equation (6)). Biochar materials can also activate PMS to generate $SO_4^{-\bullet}$ or $^1O_2$ [92]. $SO_4^{-\bullet}$, •OH, and $^1O_2$ are responsible for sludge degradation. Importantly, TA is a protein precipitant that binds to damaged cells in sludge microbes to form insoluble TA-protein complexes. Therefore, due to the advanced oxidation and the biochar skeleton and the composite of TA, the sludge dewatering performance was greatly improved.

$$\mathrm{Mn(II)} + \mathrm{HSO_5^-} \rightarrow \mathrm{Mn(III)} + \mathrm{SO_4^{\bullet-}} + \mathrm{OH^-} \tag{1}$$

$$\mathrm{Fe(II)} + \mathrm{HSO_5^-} \rightarrow \mathrm{Fe(III)} + \mathrm{SO_4^{\bullet-}} + \mathrm{OH^-} \tag{2}$$

$$\mathrm{Fe(III)} + \mathrm{TA} \rightarrow \mathrm{Fe(II)} + \mathrm{Q} \tag{3}$$

$$\mathrm{Mn(III)} + \mathrm{TA} \rightarrow \mathrm{Mn(II)} + \mathrm{Q} \tag{4}$$

$$\mathrm{Fe(II)} + \mathrm{Mn(III)} \rightarrow \mathrm{Fe(III)} + \mathrm{Mn(II)} \tag{5}$$

$$\mathrm{SO_4^{\bullet-}} + \mathrm{OH^-} \rightarrow \mathrm{SO_4^{2-}} + \bullet\mathrm{OH} \tag{6}$$

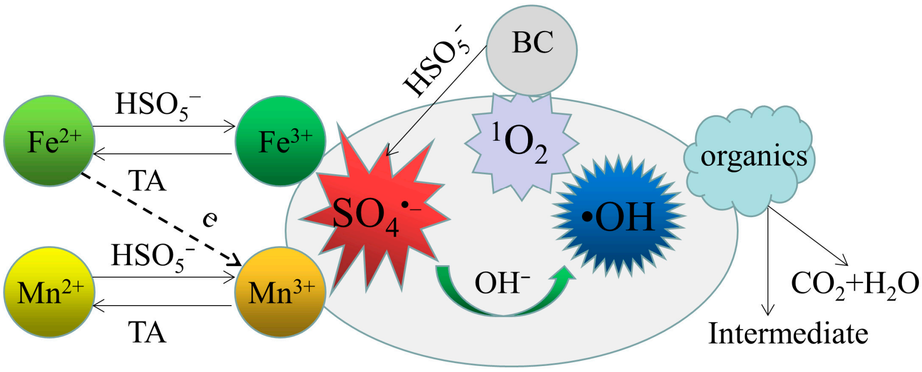

Figure 6. Schematic diagram of sludge dewatering mechanism.

In summary, it can be seen that biochar, modified biochar, and biochar combined with oxidants (hydrogen peroxide, peroxodisulfate, and peroxymonosulfate) can all improve the physico-chemical properties of sludge to varying degrees and facilitate subsequent dewatering treatment. Biochar as a physical conditioner is superior to other mineral materials owing to its low ash content, high calorific value, and normally high porosity. Biochar as a physical conditioner is superior to other mineral materials due to its low ash content, high calorific value, and generally high porosity. Its usage can not only enhance the sludge dewatering performance, but also increase the calorific value of the sludge during subsequent sludge incineration. Furthermore, the preparation of biochar from sewage sludge is reused for sludge conditioning, which enables waste recycling and helps to reduce carbon emissions. Although sludge conditioning via an advanced oxidation process based on biochar as an activator has been performed successfully in the lab, there are still several difficulties to overcome as it moves toward practical application. Biochar/Fenton systems require an acidic reaction condition (pH = 3.0), resulting in harsh operating condition and high costs. The design of the reactor and related piping should also include corrosion prevention. The data are still in short supply from pilot-scale tests to large-scale operations, especially for the conditioning of different types of waste sludge by biochar/persulfate systems. More importantly, some mechanisms and influencing factors of sludge conditioning via the biochar-based advanced oxidation processes need to be further studied and explored.

5. Concluding Remarks

In recent years, a large amount of sewage sludge has increased rapidly in WWTPs worldwide. Therefore, it is necessary to quickly develop and implement efficient sewage sludge dewatering technologies in industrial practice. The fact is that the dewatering of sewage sludge has always been a difficult problem due to the properties of sludge. Most of the moisture in sludge is bound water, resulting in the high-strength binding between water molecules and the solid surface of the sludge. Thus, the sludge must be conditioned to improve the dewatering performance before the sludge is dewatered in conventional dewatering equipment, such as centrifuges or filter presses. It has been found that there is abundant biomass waste rich in carbon to be treated. This biomass can be processed into biochar for soil remediation and wastewater treatment. It is a prospective direction to use a biochar framework material in conditioning sludge before dewatering.

This paper systematically reviewed the preparation methods and characteristics of different sources of biochar and summarized the sludge dewatering processes and conditioning methods. Furthermore, a detailed analysis and evaluation of the current research on biochar and modified biochar for sludge conditioning was carried out, and the application prospects of biochar as a sludge conditioner was proposed.

Although sludge conditioning by biochar and modified biochar materials has been successfully applied in the lab and a few pilot tests, the practical application of this method requires continuous experimentation and evaluation. At present, there are still several unsettled issues in conditioning sludge by biochar. The data are still lacking for biochars used in sludge conditioning, especially for different modified biochar produced from waste sludge. More fundamental research should be performed to understand the basic mechanisms of biochar-based materials in sludge conditioning. The mechanism and influencing factors of the combination of modified biochars and oxidants (H_2O_2, $S_2O_8{}^{2-}$, and $HSO_5{}^{-}$) in catalytic oxidation of sludge organic matter and auxiliary sludge dewatering need to be further discussed. Pyrolysis of sewage sludge into biochar for sewage sludge conditioning is a benign process of sludge recycling, which is beneficial to reducing operating costs and protecting the environment. In order to popularize the application of this recycling method, the expansion of biochar production technology and a better design of the sludge dewatering process need to be constantly updated and improved, and the life cycle assessment of sludge biochar should also be taken into consideration.

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