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Review

Impacts of Polyvinyl Alcohol and Chitosan-Modified Biochar on the Anaerobic Digestion of Sewage Sludge and Valuable Resource Recovery

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Abstract: The accumulation of organic dyes and heavy metals (HMs) in sewage sludge (SS) after wastewater treatment is a significant problem due to the non-degradable nature of these pollutants. Moreover, the simultaneous removal of HMs and dyes in the complex process of SS treatment, such as anaerobic digestion (AD), has become attractive. HMs and dyes present in SS can have a detrimental effect on anaerobic digesters. These pollutants not only inhibit the production of methane, which is crucial for biogas generation, but also affect the stability of AD treatment, which can result in failure or inadequate performance of the AD process. This review highlights a novel method of removing HMs and dyes from the AD process of SS through the use of biochar modified with polyvinyl alcohol (PVA) and chitosan (CTS). The applications of conventional biochar have been limited due to poor adsorption capacity. However, modification using PVA/CTS composites enhances properties such as surface functional groups, adsorption capacity, porosity, surface area selectivity, and stability. Furthermore, this modified version can function as an additive in AD of SS treatment to boost biogas production, which is a viable source for heat generation or electricity supply. In addition, the digestates can be further processed through plasma pyrolysis for the removal of HMs and dyes bound to the modified biochar. Plasma pyrolysis generates two major products: syngas and slag. The syngas produced can then be used as a source of hydrogen, heat, and electricity, while the slag can potentially be reused as an AD additive or as a biofertilizer in the agricultural sector. Additionally, this study addresses the challenges associated with this integration and biochar modifications, and offers an outlook on understanding the interactions between the modified biochar properties, microbial dynamics, and the presence of micropollutants to ensure the economic viability and scalability of this technology. This comprehensive review provides insights into the potential of PVA/CTS-modified biochar as an effective additive in AD systems, offering a sustainable approach to SS treatment and valuable resource recovery.

Keywords: modified biochar; heavy metals and dyes removal; sewage sludge; biogas production; integrated techniques; resource recovery

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1. Introduction

Industrial development and population growth have resulted in increasing amounts of wastewater, leading to the construction of a large number of wastewater treatment plants. In addition, these plants generate large amounts of sewage sludge (SS) after treatment of wastewater [1]. Nowadays, the disposal of sludge has been identified as a major problem due to its potential health risks and environmental challenges, as it contains HMs such as Cu (236.67 mg/kg), Ni (26.67 mg/kg), Mn (433.33 mg/kg), Cr (53.33 mg/kg), Pb (33.33 mg/kg), Zn (1166.67 mg/kg) [2], dyes [3], pathogens, and other chemical substances from municipal and industrial wastewater treatment plants. Based on Raheem et al. [4], chemical elements and other harmful substances remain in SS even after thermochemical and biological treatment. Thus, it is crucial to treat sludge in an economical and environmentally friendly manner to avoid secondary pollution or underutilization of resources.

The improper discharge or poor treatment of SS, including open dumping, agricultural use, and landfilling, can cause serious environmental problems. This is because heavy metals (HMs) and dyes are non-degradable, which allows them to persist in the environment for incredibly long periods of time. Once they are discharged into waterways, the pollution does not only remain in the water, but also permeates from water to soil, affecting all living systems and organisms [5]. Other treatment technologies such as incineration, pyrolysis, AD, and various chemical degradation methods have limitations. They often fail to completely break down hazardous organic materials into harmless smaller compounds, and are insufficient in minimizing waste volumes and immobilizing heavy metals. Indeed, it is highly challenging to simultaneously achieve multiple objectives for ideal SS treatment, including complete decomposition of organic materials, waste weight/volume minimization, and efficient immobilization of toxic HMs below permissible limits for land-based applications. Moreover, the treatment of dye-containing sludge from textile industries is crucial to prevent pollution of aquatic ecosystems. Untreated effluent adversely affects the biochemical properties of water bodies, impairing processes such as photosynthesis. It also poses potential toxicity threats to flora and fauna, which can eventually enter the human food chain, thereby affecting public health overall [6]. Thus, eco-friendly technologies are recommended for SS waste management reducing the environmental footprint alongside ensuring safety standards while conserving natural resources.

AD is a treatment process that involves the breakdown of organic matter in an oxygen-free environment. It is an attractive technology for disposing of SS due to its efficiency in decomposing approximately 60% of organic substances to produce biogas and nutrient-rich residue [7]. Additionally, plasma pyrolysis has gained significant attention, as it allows for the production of syngas and slag by thermally decomposing waste materials in an environmentally friendly manner without oxygen contact [8]. Conventional treatment methods, including AD, have shown limitations in effectively removing pollutants while maintaining process stability and efficiency, while the application of plasma technology alone would incur additional drying costs [1]. Recent years have seen growing interest in the application of biochar as an adsorbent for pollutant removal in various environmental remediation processes. However, the use of unmodified biochar in AD systems has been constrained by its limited adsorption capacity and potential negative impacts on microbial communities. This has led to the exploration of biochar modification techniques to enhance its performance and compatibility with AD processes.

Chitosan (CTS) is a natural biopolymer derived from chitin, which has remarkable characteristics such as biocompatibility, biodegradability, and non-toxicity. Consequently, it has broad application prospects. Pujol Pozo et al. [9] reported CTS as a suitable material for HM removal due to its hydroxyl and amino groups, which act as active sites for radionuclide and HM ion adsorption. Furthermore, polyvinyl alcohol (PVA) is affordable, chemically stable, biocompatible, and environmentally friendly, containing a high amount of hydroxyl functional groups. PVA/CTS composites have attracted much attention owing to their excellent biocompatibility, good hydrophilicity, and high mechanical stability. While several reviews have addressed the use of biochar in wastewater treatment and soil

remediation, there is a notable gap in the literature regarding the specific application of PVA/CTS-modified biochar in AD systems for simultaneous HM and dye removal from SS.

The procedures for data collection in this review were conducted in English by searching various scientific citation indexing services, including Web of Science (https://www.webofscience.com/ accessed on 15 May 2024) Google Scholar, and other online resources. The search keywords used were "PVA/CTS modified biochar in AD" and "modified biochars in AD". Several hundred articles were initially retrieved and subsequently refined to focus on specific content related to modified biochar, pyrolysis, plasma pyrolysis, AD, resource recovery from organic waste and SS, public health, HM and dyes ecological issues, and integrated technologies. Finally, six papers published within the past ten years and sixty-six papers published within the last five years were selected for inclusion in this review.

Therefore, this review recommends the application of PVA/CTS-modified biochar as an additive in AD treatment to enhance the decomposition of SS organic substrates, promote electron transfer, remove inhibitors, regulate pH, increase biogas production, and improve nutrient-rich digestate recovery. The produced digestate can be introduced into plasma pyrolysis to generate syngas and slag, significantly reducing digestate volume and immobilizing HMs, dyes, and other toxic materials. The biogas and syngas produced by AD and plasma pyrolysis, respectively, can be used to generate electricity, fuel, and heat energy, while the slag can be recycled as an additive for AD treatment or as a biofertilizer to improve soil properties. The proposed technologies are energy-consuming processes. However, AD requires lower temperatures compared to plasma pyrolysis. Despite their energy demands due to high operating temperatures, these combined technologies could present promising future prospects for sustainable treatment of SS. The energy generated may offset operational costs or even provide additional revenue when sold off-grid.

2. Pyrolysis Process and Modification of Biochar

The pyrolysis process is thermal conversion of organic and inorganic wastes into syngas, bio-oil, and biochar in the absence of oxygen [10]. Biomass, when heated with limited oxygen, breaks down into biochar, bio-oil, and syngas, as shown in Equation (1)

$$\text{Biomass} + \text{Pyrolysis} \rightarrow \text{Biochar} + \text{Bio-oil} + \text{Syngas} \quad (1)$$

The yield and properties of these products are strongly affected by pyrolysis conditions such as temperature and residence time, and also depend on the type of waste feedstock. This thermochemical treatment is divided into the three categories of conventional pyrolysis, fast pyrolysis, and flash pyrolysis, with the temperature ranges being 300–490 °C, 500–750 °C, and 800–1300 °C, respectively. Equation (2) represents the pyrolysis of lignocellulose, a major component of plant-based biomass. The exact composition of biochar and the hydrocarbons produced will vary depending on the specific pyrolysis conditions.

$$\text{Pyrolysis (300–700 °C)}$$

$$(C_6H_{10}O_5)n \rightarrow CxHyOz + \text{Biochar} + CO + CO_2 + H_2O + \text{Hydrocarbons} \quad (2)$$

Furthermore, pyrolysis should not be confused with torrefaction, which is performed at lower temperatures of 200–300 °C under oxygen-free conditions [11]. The pyrolytic products can be applied to different purposes. For example, biochar can be used as an additive in the AD process to remove inhibitors (such as ammonia nitrogen, dyes, HMs, etc.), accelerate electron transfer, enhance buffering capacity, provide microbial habitat, and promote interactions between fermentation bacteria and methanogens and improved nutrient recovery [12]. It can also be used for soil improvement due to its most valuable compounds being beneficial for growing crops. Syngas and bio-oil can be upgraded to produce hydrogen, electricity, and fuel, respectively.

According to Amalina et al. [13], biomass is the best feed for pyrolysis to produce biochar with high adsorption rates for toxic HMs and other organic pollutants. Since the types of pyrolysis differ from their operating temperature and heating rate, this will also significantly affect the yield of biochar produced. The main components of biomass are cellulose, hemicellulose, and lignin, which are thermally converted into other compounds. Pyrolysis of lignin requires a higher temperature range than cellulose and hemicellulose. Hemicellulose has the lowest thermal decomposition, with a temperature range of 220–315 °C [14]. Thus, conventional pyrolysis undergoes partial decomposition of substrate, which could reduce the specific surface area of biochar. This is because the processes occur slowly at lower temperatures, allowing more time for solids to form from volatile precursors before they evaporate away [15]. In addition, the temperature range used by flash pyrolysis is more conducive to the production of syngas than biochar, which results in a lower yield of biochar. This makes fast pyrolysis the best option, as it can thermally decompose biomass components and produce high quality/quantity biochar [16]. The produced biochar is then modified with polyvinyl PVA and CTS, as shown in Equation (3).

$$\text{Biochar} + \text{PVA} + \text{Chitosan} \rightarrow \text{PVA Chitosan Modified Biochar} \quad (3)$$

Biochar, as a stable form of carbon derived from biomass by thermochemical conversion, has been increasingly used in environmental applications due to its high adsorption capacity for various pollutants [12]. The simple synthesis route of PVA/CTS-modified biochar is shown in Figure 1.

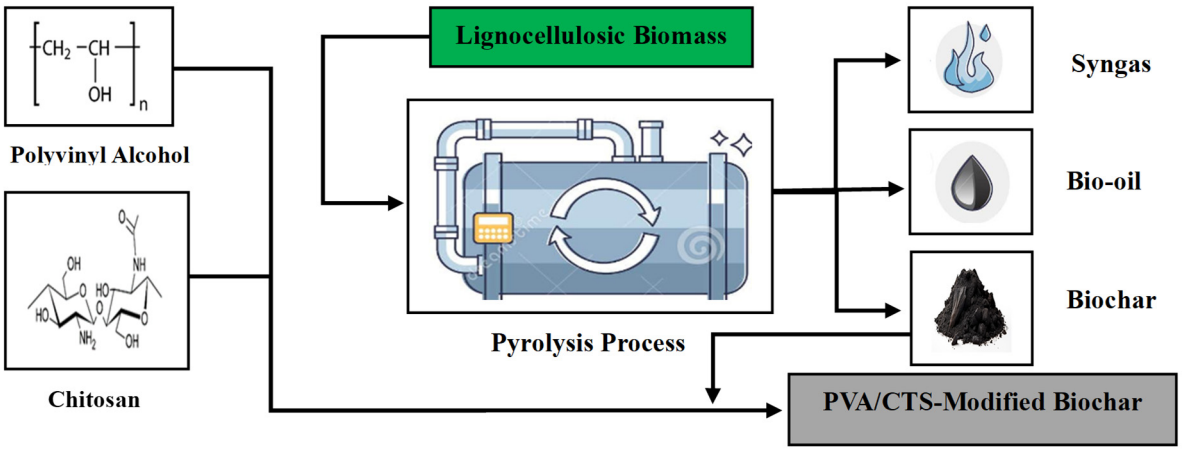

Figure 1. Simple synthesis route of PVA/CTS-modified biochar.

However, direct use of biochar can cause operational issues such as loss during operation, and low recovery rate post-application [17]. To address these problems while enhancing the pollutant adsorption capability, biochar modification with PVA and CTS emerges as a solution. This modification enhances the biochar's surface properties and adsorption capacity. PVA is versatile, as it forms insoluble complexes when cross-linked, making it ideal for supporting biochar. Meanwhile, CTS is a naturally abundant biopolymer rich in amino groups that potentially increase the available binding sites, thus improving the removal efficiency of contaminants [18]. The PVA/CTS-modified biochar exhibits enhanced physicochemical properties like higher surface area compared to unmodified ones, along with more functional groups capable of interacting with different pollutants, resulting in improved contaminant uptake ability [19].

As presented in Figure 1, the preparation of PVA/CTS-modified biochar involves several steps: The first step is to prepare the raw biomass into biochar by pyrolysis, a process in which organic materials are heated in an oxygen-free environment [17]. The feedstock can be derived from various types of biomass including woodchips, straw, bamboo, etc. After preparing the biochar, it should be washed with distilled water until the

pH becomes neutral, then dried at 70–100 °C for about 24 h to remove moisture content [20]. Modification of biochar can be performed by two techniques: (i) the modification with PVA or CTS and then impregnating the previous biochar with one of aforementioned modifiers, and (ii) the formation of PVA and CTS solutions to modify biochar. The modified biochar displays better performance than plain biochar in various applications, including AD treatment involving HM ions or organic dyes removal [21–23], soil amendment to reduce nutrient leaching [24], removal of ammonia nitrogen [25], and emission control via CO_2 capture [26]. This improved performance is largely due to the enhanced stability brought about through polymer modifications. These modifications effectively address conventional hurdles faced by unmodified biochar, such as poor hydrodynamic behavior. The resulting modified biochar is far easier to handle practically, thereby expanding possible future utilization scenarios.

2.1. Physicochemical Characteristics of Modified Biochar

The physicochemical properties of PVA/CTS-modified biochar greatly enhance its potential to adsorb dyes, HMs, and other pollutants that might destabilize the AD process. They also increase methane production and nutrient recovery throughout the SS treatment process. The properties of biochar greatly depend on pyrolysis parameters, substrates, and coated chemical compounds, which immensely affect the functional groups, specific surface area, pore arrangements, ion exchange capacity, electrostatic attraction, physical adsorption, π-electrons, complexation, and reduction. Some of these chemical and physical properties are discussed in detail below.

2.1.1. pH and Surface Charge

One important aspect during the AD treatment is maintaining appropriate pH levels, because different groups of microorganisms involved have specific optimal pH ranges for their growth [27]. PVA/CTS-modified biochar has been shown to efficiently regulate pH levels in this scenario. In conventional AD processes, maintaining the desired pH level is challenging due to volatile fatty acids produced during fermentation, which often cause acidification, leading to low system efficiency or even failure [28]. This problem could potentially be overcome with coating PVA/CTS on biochar surfaces, as these polymeric materials are known to be capable of absorbing excessive ions caused by acidification, thereby stabilizing the overall system PH values and ensuring high efficiencies without major interruptions [29]. Based on Zhang et al. [30], using PVA/CTS hydrogels instead of traditional lime buffering methods results in improved performance, reflected in longer operation periods, higher biogas production rates, and reduced risk of unstable operational conditions such as sudden pH drops. This provides a more robust and reliable way of managing treatment processes involving AD for various types of wastes, including sludge.

By modifying the surface properties of traditional biochar, some studies have been able to increase its affinity for certain pollutants [31,32]. One way in which PVA and CTS modify the surface properties is by increasing their overall charge. When these chemicals are applied on the surface of raw biochar, they introduce new functional groups which carry either positive or negative charges [33], resulting in an enhanced electrostatic interaction between contaminants and adsorbents. In addition, an increase of this charge enhances its pollutant-capturing capabilities, as it improves the capacity for ion exchange reactions with oppositely charged substances such as dyes [34], metal ions [35], or organic compounds typically found in wastewater streams [25]. Moreover, by enhancing the surface charge with PVA/CTS, it improves hydrophilic characteristics that make it easier for microorganism attachment leading to better efficiency in waste degradation [36]. Therefore, modifying biochars with polymeric substances like PVA/CTS not only makes them effective as adsorbents, but also potentially boosts their capability as an additive promoting microbial activity essential within anaerobic reactors.

A simplified equation that illustrates the introduction of new functional groups and the resulting change in surface charge can be represented as thus:

$$\text{BC-OH} + \text{PVA-R} + \text{CTS-NH}_2 \rightarrow \text{BC-(O-PVA-R)-(NH-CTS)} + \text{H}_2\text{O} \quad (4)$$

where

- BC-OH represents the raw biochar surface with hydroxyl groups;
- PVA-R represents polyvinyl alcohol, where R is the polymer chain;
- CTS-NH_2 represents chitosan with its amine groups;
- BC-(O-PVA-R)-(NH-CTS) represents the modified biochar surface.

This simple equation shows the raw biochar surface (BC-OH) interacting with PVA and CTS, as well as the formation of new bonds, replacing the -OH group with PVA and CTS and the introduction of new functional groups from PVA (represented by -R) and CTS (represented by -NH). The resulting modified surface (BC-(O-PVA-R)-(NH-CTS)) would have an altered charge distribution due to the new functional groups, enhancing electrostatic interactions with contaminants. However, this is a simplified representation and does not show all possible interactions or the exact stoichiometry, which would depend on the specific PVA and CTS used and the reaction conditions.

2.1.2. Specific Surface Area and Functional Groups

The application of biochar has gained significant attention in recent years. Its high specific surface area is one of its desirable properties, as it facilitates the adsorption and retention of nutrients. In an effort to further improve this characteristic, studies have explored modifying biochar using different substances [18,32]. When PVA or CTS is coated onto biochar particles, they act like a binder that increases the porosity [37], thus increasing specific surface area while also improving other characteristics like nutrient loading capacity [24]. The increase in specific surface area enhances AD processes because of more surface being available for microorganisms involved in anaerobic processes to work upon, leading to better breakdown of organic matter into biogas essential for green energy production [38]. This modification process does not only improve performance, but can be environmentally beneficial too; reducing sludge waste by utilizing low-cost materials derived from biomass wastes, simultaneously creating a sustainable solution tackling both environmental protection and generation of renewable energy.

Furthermore, functionalization of biochar with other compounds leads to an increase in functional groups on the biochar surface. Many researchers, including [19,31,32], have used different chemical materials to modify biochar to improve its adsorption and selectivity properties. For instance, Wang et al. [39] constructed magnetic xanthate-modified PVA and CTS composites for efficient removal of metal ions from wastewater. The hydroxyl and amino acid groups on the surface of biochar play an important role in the adsorption of HMs and dyes by providing some additional binding sites. Based on Cui et al. [27], functional groups allow complexation and electrostatic interactions, thereby enhancing the ability to adsorb HMs. Moreover, amino and carboxylic acid functional groups allow them to react with various molecules through either end of the structure. Through these interactions, they can form complex compounds, where they bond together via covalent bonds. This shows that functional groups on the surface of biochar can be protonated to form positive charges, which can bind metal anions to the adsorbent surface through electrostatic interactions. Additionally, Zhang et al. [29] reported that hydroxyl groups can engage not only in hydrogen bonding, but also act as donor or acceptor sites for electrostatic interactions because it consists of a polar oxygen–hydrogen bond that gives rise to partial positive and negative charges at each pole, respectively.

3. Polyvinyl Alcohol/Chitosan-Based Absorbent for Pollutants

Industrial sludge refers to the residual, semi-solid material that is produced as a by-product during wastewater treatment [3]. The composition of industrial SS can vary

greatly depending on the source industry, but it usually contains various pollutants such as HMs [1], dyes [3], pathogens, and other harmful chemical substances. This type of sludge needs to be treated and disposed of safely in order to prevent environmental damage or health risks from exposure. In addition, PVA and CTS are two natural polymers that have been attracting attention due to their excellent properties including non-toxicity, biocompatibility, biodegradability, and adsorption capabilities [21]. They can be used for various environmental applications, including wastewater treatment, because they can attach themselves to harmful particles through physical absorption or chemical reactions making them safe for disposal [35,40]. The effectiveness and the application of PVA and CTS in adsorbing different pollutants is well discussed in the following sections.

3.1. Adsorption of Dyes

Based on Malek et al. [34], PVA and CTS can be used in the adsorption of dyes, including those found in wastewaters from the textile industry. These substances form a hybrid adsorbent film that removes different dyes from SS when subjected to differing combinations of time and temperature during a curing process [41]. For instance, the hydroxyl groups of PVA, which is situated along the chain, provide high affinity towards water, making it highly useful for dye removal [42]. It also has good chemical stability, non-toxicity, and excellent film forming properties, making them preferable as an effective absorbent material. Similarly, the structure of CTS comprises amino functional groups that can easily form bonds with dye molecules, resulting in high adsorption rates [43]. CTS's unique properties such as its hydrophilicity, non-toxic nature, and large surface area per unit mass make it ideal to be used in the treatment of sludge containing different types of dyes by means of adsorption techniques.

Different studies have employed PVA or CTS for dye removal. For example, Elzahar and Bassyouni [43] studied the adsorption efficiency of CTS micro-beads, polyacrylamide, and CTS powder for removing direct blue 78 dye. It was found that increasing the powdered CTS dose to 4.5 g/L and extending the contact time up to 40 min significantly increased the dye removal efficiency to 94%. Perez-Calderon et al. [22] used the biodegradable polymers PVA/CTS to remove Acid Orange 7 (AO7) from aqueous solution. The ATR-FTIR confirmed the electrostatic interactions by hydrogen bonds between PVA and CTS, and the maximum adsorption capacity of AO7 was 678 mg/g. Zhang et al. [29] reported EDTA/CTS-functionalized bamboo magnetic biochar as adsorbent material for the removal of methyl orange (MO). The MO is adsorbed through π–π interaction, hydrogen bonding, and electrostatic attraction, and the optimal capture capacity was 305.4 mg/g at room temperature. Furthermore, Wang et al. [42] reported Zeolite imidazole framework-8 (ZIF-8)-modified PVA/CTS composite material was developed as an affordable adsorbent material with high removal efficiency for dye residues in wastewater. The addition of PVA improves the mechanical properties of CTS. The results show that the constructed composite material has high water stability and compression resilience, and the optimal adsorption capacity for Congo red is 1216.5 mg/g. After five repeated adsorption experiments, the removal rate still reached more than 91%. This is significantly higher than previously reported for most different adsorbents. Table 1 presents different characterization techniques and adsorption capacity for dye removal by using PVA/CTS-based absorbents.

As shown in Table 1, PVA/CTS-based composites were highly efficient in removing dyes. In addition, different concentrations of PVA or CTS used as functionalizing substances will significantly change the physical and chemical properties of biochar. Therefore, perfect dosages are recommended for future studies to maximize removal efficiency of dyes from SS. Furthermore, the optimal pyrolysis parameters based on the specific biomass feedstock should also be considered to produce initial biochar with high specific surface area and a large number of pores, which will help optimize the adsorption process. Malek et al. [34] developed CTS/PVA/FA as an adsorbent for the removal of reactive orange 16 (RO16) from wastewater by adding fly ash (FA) particles into the polymer matrix of magnetic CTS/PVA. The adsorption isotherm results showed that the multilayer adsorption

process also conformed to the Freundlich model; the optimal CTS/PVA/FA dosage was 0.06 g, and the maximum removal capacity of RO16 was 123.8 mg/g. The adsorbent was successfully recovered by applying an external magnetic field. In addition, Wu et al. [21] prepared CTS/polyvinylpyrrolidone/PVA to adsorb methylene blue and malachite green, with removal efficiencies of 13.27 mg/g and 17.86 mg/g, respectively. Thus, PVA/CTS composites have good adsorption properties for many dye species, and can serve as a safe and economical recycling method to recycle dyes for various industrial applications and reduce ecological problems associated with free discharge into the environment.

Table 1. Different characterization techniques and adsorption capacity for polyvinyl alcohol/chitosan-based adsorbents for dyes.

Absorbent Composition	Methodology	Characterization Techniques	Dyes	Adsorption Capacity (mg/g)	Reference
PVA/L-cysteine	Doehlert experimental design	FTIR, elemental analysis, SEM, AFM, and TGA analysis	Crystal Violet	197	[44]
Zeolitic imidazole framework-8-PVA/CTS	freeze-drying and situ growth	FT-IR and XRD	Congo Red	1216.5	[42]
CTS/polyvinylpyrrolidone/PVA	Ultrasonic mixing, electrospinning	FTIR, XRD, SEM	Methylene blue	13.27	[21]
EDTA/CTS	Solvent casting	XRD, FT-IR	Methyl orange	305.4	[29]
PVA/CTS	Solvent casting	Modulated differential scanning calorimetry and thermogravimetric analysis, ATR-FTIR	Acid orange 7	678	[22]
CTS/polyvinylpyrrolidone/PVA	Ultrasonic mixing, electrospinning	FTIR, XRD, SEM	Malachite green	17.86	[21]
CTS-PVA/fly ash	Solvent casting	XRD, SEM, FTIR	Reactive orange 16	123.8	[34]

3.2. Adsorption of Heavy Metals

Adsorption is a commonly used method for the removal of HMs from wastewater. PVA and CTS are two types of adsorbents that have been studied extensively due to their high adsorption capacities, biocompatibility, and ease of modification [18,21,23,39]. Based on Patel et al. [19], the hydroxyl groups present in PVA make it highly reactive with different toxic metal ions such as Pb, Cu, Ni, Zn, etc. Zhong et al. [45] experimented on grafting various functional groups onto PVA chains, which increases its ability to interact with different pollutants effectively. CTS, on the other hand, is a natural polysaccharide derived from the de-acetylation of chitin, which has excellent properties like non-toxicity, biodegradability, and enhanced mechanical strength, making it suitable for use in water treatment processes [38]. It has abundant amino and hydroxyl groups responsible for binding metal ions by coordination bonds, resulting in stable structures, thereby enabling efficient removal of pollution-causing substances, including HMs.

In addition, PVA/CTS-based materials have been used for the removal of metals ions. For example [46], bilayer mixed matrix membranes were prepared for the removal of Cr and Pb ions by incorporating aminated Fe_3O_4 nanoparticles into CTS/PVA nanofibers on polyether sulfone membranes. Sopanrao and Sreedhar et al. [18] reported that a new efficient adsorbent derived from PVA-modified CTS composite was developed for the removal of Zn, Ni, and Cu. The composite was characterized and showed to be rich in functional groups, thermally stable, and contained a large number of pores. The best fit of pseudo-second-order kinetic model and Langmuir isotherm shows that the maximum adsorption capacity of Zn, Ni, and Cu was 173.39, 209.08, and 303.29 mg/g, respectively. Moreover, Zhu et al. [23] employed a PVA/CTS magnetic composite for adsorption of Co,

and the highest sorption capacity was 14.39 mg/g at pH 6.0. FTIR and SEM-EDAX analysis before and after adsorption of Co on PVA/CTS magnetic beads showed that the functional groups played a major role in the Co adsorption process. In the pH range of 5.0–6.0, the maximum adsorption capacity of U ions was 156 mg/g [47]. Patel et al. [40] used CTS/PVA to remove Cu, Pb, and Fe in a marine environment. Further, Wang et al. [39] constructed a magnetic xanthate-modified PVA/CTS composite material for the recovery and efficient removal of HM ions. The adsorption equilibrium is reached at 303 K within 120 min, and the Cd removal rate is 307 mg/g. Table 2 presents different characterization techniques and adsorption capacities for HMs removal using PVA/CTS-based absorbents.

Table 2. Different characterization techniques and adsorption capacity for polyvinyl alcohol/chitosan-based adsorbents for heavy metals.

Absorbent Composition	Methodology	Characterization Techniques	Heavy Metals	Adsorption Capacity (mg/g)	Reference
PVA/CTS	Solvent casting	BET, TGA, FTIR, FE-SEM	Zn	173.39	[18]
Xanthate-magnetic PVA/CTS	Instantaneous gelation method	FTIR, Raman, SEM, TGA, DSC, BET, XRD	Cd	307	[39]
CTS/PVA	Fe_3O_4 nanoparticles: co-precipitation method	XRD, SEM, FTIR, TGA, BET	Cu	243.90	[40]
Magnetic CTS/PVA	Gelation method	FTIR, SEM-EDX	Co	14.39	[23]
CTS/PVA	Solvent casting	XRD and FTIR	Fe	135.14	[19]
PVA/CTS/ A-Fe_3O_4	-PVA/CS/A-Fe_3O_4 membrane: electrospinning process	SEM, TEM, and AFM analysis	Cr	509.7	[46]
PVA/CTS	Solvent casting	FTIR, FE-SEM BET, TGA	Ni	209.08	[18]
PVA/CTS	Fe_3O_4 nanoparticles	FTIR and SEM-EDAX	Co	14.39	[23]
EDTA/CTS	Solvent casting	XRD, FT-IR	Zn	50.8	[29]
CTS/PVA/CuO	Precipitation into anti-solvent	XRD, FTIR, SEM with EDS, TEM	Pb	116.84	[35]
CTS/PVA	Iron oxide nanoparticles	XRD, SEM, and FTIR	Cu	500	[33]
CTS/polyvinylpy-rrolidone/PVA	Ultrasonic mixing, electrospinning	FTIR, XRD, SEM and BET	Ni	25.24	[21]
PVA/CTS	Solvent casting	FE-SEM BET, TGA, FTIR	Cu	303.29	[18]
CTS/PVA resin	Fe_3O_4 nanoparticles: co-precipitation method	FTIR, TGA, BET, XRD, SEM	Fe	87.72	[40]
CTS/PVA	Solvent casting	FTIR and XRD	Zn	222.21	[19]

3.3. Potential Adsorption Mechanisms for Removal of Heavy Metals and Dyes Using PVA-CTS-Modified Biochar in Anaerobic Digestion

The adsorption of HMs and dyes by PVA/CTS-modified biochar in anaerobic digestion (AD) systems involves multiple mechanisms working synergistically [48]. Surface complexation is a key mechanism, where the oxygen-containing functional groups (e.g., -OH, -COOH) introduced by PVA and the amino groups (-NH_2) from CTS act as Lewis bases, forming coordinate covalent bonds with heavy metal ions (Lewis acids) [48,49]. This mechanism is particularly effective for multivalent metal ions like Pb^{2+}, Cu^{2+}, and Cd^{2+} [49,50]. The reaction between a carboxyl group and a divalent metal ion (M^{2+}) can be represented as:

$$\text{R-COOH} + M^{2+} \rightarrow \text{R-COO-}M^{+} + H^{+} \quad (5a)$$

Ion exchange is another important mechanism, where the functional groups on the modified biochar surface participate in exchange reactions with metal cations [48,49]. For example, the protons (H^+) of carboxyl groups can be exchanged with metal cations:

$$2(\text{Biochar-COOH}) + M^{2+} \leftrightarrow (\text{Biochar-COO})2M + 2H^+ \quad (5b)$$

This mechanism is pH-dependent and generally more effective at higher pH values where more functional groups are deprotonated [49,50]. Electrostatic attraction plays a significant role, as the PVA/CTS modification typically results in a net negative surface charge on the biochar under neutral to alkaline conditions, enhancing the attraction of positively charged metal ions and cationic dyes [48–50]. The strength of this interaction is influenced by the ionic strength of the solution and can be described by the Gouy–Chapman theory of the electrical double layer. Hydrogen bonding is facilitated by the abundant hydroxyl (-OH) and amino (-NH_2) groups introduced by PVA and CTS, which can form hydrogen bonds with appropriate functional groups on dye molecules [48,51]. This is particularly important for the adsorption of large organic molecules that may not be effectively removed by other mechanisms. For aromatic dyes, π–π stacking interactions can occur between the aromatic rings of the dye and the graphene-like structures in biochar [48,51]. This interaction is strengthened by the electron-withdrawing or electron-donating groups on the aromatic rings. Physical adsorption is enhanced by the PVA/CTS modification, which often increases the specific surface area and pore volume of the biochar [48–50]. This can be described by various isotherm models (e.g., Langmuir, Freundlich), with the adsorption capacity influenced by factors such as pore size distribution, surface area, and the size of the adsorbate molecules [49,50]. Precipitation can occur due to local pH changes near the biochar surface, often resulting from the release of alkaline minerals or functional groups, inducing the precipitation of metal hydroxides or other insoluble compounds [49,50]. This mechanism is particularly relevant for metals that form stable precipitates at neutral to alkaline pH, such as lead and copper. Reduction is another mechanism where some functional groups on the biochar surface, particularly those containing sulfur or nitrogen, can act as electron donors, reducing certain metal ions to less soluble forms [49,51]. For example:

$$2\text{Biochar-SH} + Hg^{2+} \rightarrow \text{Biochar-S-Hg-S-Biochar} + 2H^+ \quad (6)$$

This mechanism is particularly important for mercury and chromium removal. In the context of AD systems, these mechanisms work synergistically to remove heavy metals and dyes. The modified biochar not only adsorbs contaminants, but also provides a supportive surface for microbial growth, with the increased surface area and functional groups potentially enhancing biofilm formation and improving the overall efficiency of the AD process [48–50].

4. Performance of Polyvinyl Alcohol/Chitosan Modified Biochar in Anaerobic Digestion and Co-Processing with Plasma Pyrolysis

Generally, AD is a series of biological processes in which microorganisms breakdown biodegradable material in the absence of oxygen to generate biogas and digestates [10]. The modified biochar is then used in the AD. The general process can be represented as:

$$\text{Organic Matter} \xrightarrow[\text{PVA/CTS-Modified Biochar.}]{\text{AD-Micro-organism}} CH_4 + CO_2 + NH_3 + H_2S + \text{Digestate} \quad (7)$$

This process of AD occurs in four main stages, as extensively described by [10]. The biogas production from AD requires control or treatment of inhibitory substances including dyes, HMs, ammonia, etc. This process holds great promise for waste treatment due to its ability to produce methane from organic waste materials in an eco-friendly way, which

can serve as a great source of bioenergy. Several studies have reported biochar as a great additive to the AD process because its helps in pH regulation, enhances thermochemical conversion of bio-waste, facilitates cation exchange, has high absorption of inhibitors, stabilizes the reactor, and increases nutrients recovery. For instance, Shi et al. [52] studied the dosage–effect of biochar in the AD treatment process of oily sludge. With adding the maximal dose of biochar, the production yield of methane was 2.19-fold compared to the control. However, it can be improved with the help of various materials and chemicals that enhance methane yield and stabilization time.

PVA/CTS-modified biochar has been found to have several positive effects on AD of SS. Due to SS from wastewater treatment of textile industries being highly loaded with dyes, pathogens, HMs, and other chemical substances [3], Giwa et al. [1] did not recommend direct feed of sludge into AD treatment, as it contains some materials such as HMs, ammonia nitrogen, dyes, and other compounds which can inhibit or destabilize the AD process. The present study recommends against the direct introduction of SS into AD treatment. Instead, it suggests using PVA/CTS-modified biochar, which has great potential to adsorb inhibitory materials from the AD of SS. Moreover, this modified biochar not only removes HMs and dyes from sludge, but can also enhance methane production. Yin and Chen [38] investigated the effect of CTS in AD treatment of waste activated sludge. The results show that the methane production potential was positively correlated with the CTS content. The addition of 30 g/kg total suspended solids CTS increased the methane yield from 215 to 272 mL/g volatile suspended solids. Since CTS contains amino acid functional groups, it neutralizes the carboxyl and hydroxyl groups of the extracellular polymers, resulting in a reduction of negative charges on the sludge surface, enhancing sludge aggregation agglomeration, thereby inhibiting the release of organic matter. It also increases the abundance of methanogens and biodegradability of substrates, thereby promoting methane production.

In addition, the role of PVA in the production of methane and the effect of direct interspecies electron transfer on the anaerobic syntrophic degradation of propionate were studied by [53]. The results showed that PVA mixed with activated carbon had the highest methane conversion of 72%, while the control (sludge) had a methane conversion of 61%. It was also reported that the syntrophic propionate-degrading microorganisms in modified PVA beads were *methanobacterium* and *syntrophobacter*, either *methanosaeta* or *methanoculleus*. The authors concluded that composite PVA with conductive materials can enhance electron transfer by related microbial species and accelerate propionate consumption, which promotes methane production. Moreover, Li et al. [36] prepared a sustained-release agent using PVA and calcium compounds (PVA-Ca) to improve the degradation of the long-chain fatty acids in food waste and increase the production of methane. Due to the addition of PVA-Ca, the lag phase duration was significantly shortened to 10 days, the AD kinetic constant was 0.083 day^{-1}, and the unit load methane production increased from 238.2 to 489.3 mL/g volatile solids. Therefore, PVA leads to an increase in surface area, which promotes efficient adsorption of organic matter from substrates. This helps to concentrate the nutrients required for microbial activities, leading to improved degradation of organic material.

Moreover, the modified biochar with PVA/CTS also enhances methane production by reducing toxic substances in the anaerobic digester. Biochars are well known for their capacity as adsorbents; when coated with these polymers, they exhibit increased efficiency in sequestering potential toxicants within AD systems. This reduces inhibitory effects on resident microorganisms, leading to stabilized digester performance even under loading stress situations [37]. Based on this, many studies have been conducted regarding their ability to remove HMs and dyes. For example, Patel et al. [19] studied the effectiveness of PVA/CTS derivatives for cyclic multi-metals removal. Both Fourier transform infrared (FT-IR) and XRD (X-ray diffraction) results confirmed a strong interaction between PVA and CTS. The highest adsorption efficiency of Zn, Fe, and Pb was 222.21, 135.14, and 4.02 mg/g, respectively. Wang et al. [39] synthesized a magnetic xanthate-modified PVA

and CTS composite for the efficient removal and recovery of metal ions from aqueous solutions. The equilibrium adsorption isotherm was well described by the Langmuir and Freundlich equations. The results showed that the maximum removal of Cd was 307 mg/g. Patel et al. [40] reported that the optimum absorption capacity was 6.85, 243.90, and 87.72 mg/g for Pb, Cu, and Fe, respectively. In addition, Wu et al. [48] prepared CTS/polyvinylpyrrolidone/PVA to remove metal ions and organic dyes from wastewater. The optimal adsorption of Cu, Ni, Cd, Pb, malachite green, and methylene blue were 34.79, 25.24, 18.07, 16.05, 17.86, and 13.27 mg/g, respectively. Furthermore, Khalifa et al. [44] reported PVA as a good absorbent in the removal of dyes such as crystal violet, where the maximum adsorption capacity reaches 197 mg/g. An application of this process on doped real wastewater demonstrates its efficacy and selectivity with a percentage of removal up to 85%. This shows that the porous structure of polymer-coated biochar provides ample housekeeping functions of harmful compounds including HMs, dyes, and other substances like ammonia [54], which is a common inhibitor of methanogens in the digestion process. By reducing these inhibitors, modified biochars enhance the survival and optimize metabolic activities of methanogens, ultimately leading to increased methane yield.

Furthermore, biochar-coated PVA/CTS-modified biochar improves nutrient recycling efficiency. The digestate produced from AD contains valuable nutrients such as nitrogen (in the form of ammonium) and phosphorus (in the form of phosphate). The modified biochar can adsorb these nutrients, facilitating their recovery and reuse as simply represented in Equations (8) and (9).

$$\text{Ammonium Adsorption: } NH_4^+ + \text{Modified Biochar} \rightleftharpoons NH_4^+ - \text{Biochar} \quad (8)$$

$$\text{Phosphate Adsorption: } PO_4^{3-} + \text{Modified Biochar} \rightleftharpoons PO_4^{3-} - \text{Biochar} \quad (9)$$

Nutrient recovery is crucial for sustainable waste management. The adsorbed nutrients can be used as fertilizers, reducing the need for synthetic fertilizers and promoting a circular economy. The ability of the modified biochar to adsorb and retain nutrients from the digestate allows for their recovery and reuse, contributing to sustainable nutrient management and reducing environmental pollution.

Yin and Chen et al. [38] examined the effect of CTS in AD of waste activated sludge. The methane yield from the AD with CTS was 272 mL/g, while that of the control digester was 215 mL/g. This confirms that CTS enhances biogas production in AD of sludge. Due to the biodegradable nature of CTS, it can also break down to produce methane throughout the AD process. The chemical equation for the decomposition of CTS shows that 1 mole of CTS can produce 3 moles of methane, which means that 0.415 g of CTS can produce about 173 mL of methane. The total amount of CH_4 produced by AD was 93.7 mL, which is only 54.2% of the expected methane production calculated from the equation. This indicates that the CTS is partially degraded, and the remainder can be recovered from the digestate. CTS has been reported to activate the metabolic and physiological pathways of plants and improve soil properties [55]. Furthermore, the addition of NPK (Nitrogen, Phosphorous, and Potassium)-loaded PVA/CTS reduced soil zeta potential, which promotes the carbon cycle by increasing soil organic carbon from 9.71 to 11.68 g/kg [24]. Therefore, using PVA/CTS-functionalized magnetic biochar as an additive in the AD process can not only increase the production of biogas, but also improve the properties of the digestate. The schematic diagram of PVA/CTS-modified biochar as an additive for AD treatment and co-processing with plasma pyrolysis is shown in Figure 2.

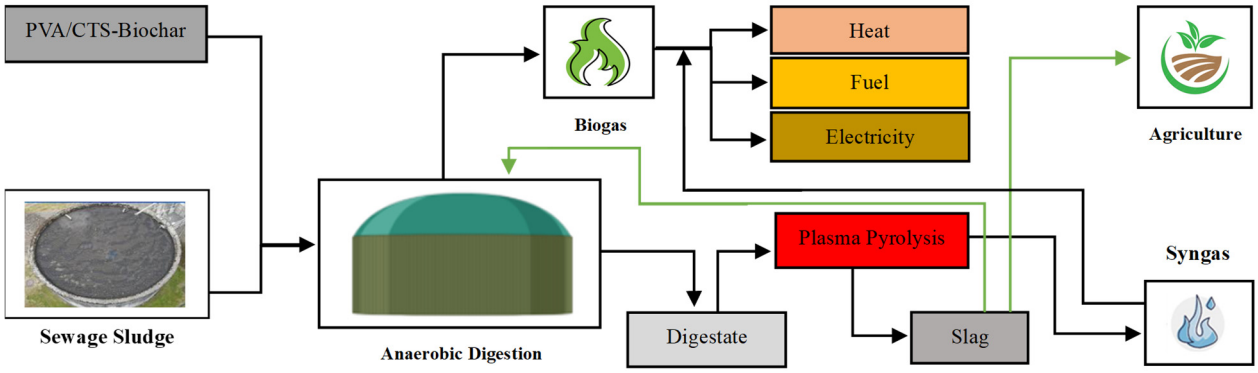

Figure 2. Schematic diagram of PVA/CTS-modified biochar as an additive in mesophilic anaerobic digestion (30–38 °C) treatment and co-processing with plasma pyrolysis.

The temperature of the AD chamber is a critical factor when using PVA- and CTS-modified biochar as additives. Since both PVA and CTS are temperature-sensitive, a mesophilic temperature range would be most suitable for this application. Mesophilic AD typically operates at temperatures between 30 and 38 °C. This temperature range is recommended for several reasons, including stability, material integrity, microbial activity, and energy efficiency. Mesophilic conditions provide a more stable and less complex process compared to thermophilic conditions (50–57 °C). At these temperatures, PVA and CTS are less likely to degrade, maintaining their beneficial properties as biochar modifiers. Additionally, mesophilic temperatures support a diverse and robust microbial community, which is essential for efficient AD [10]. Lower temperatures also require less energy input for heating, making the process more economical. Furthermore, mesophilic digesters are generally more tolerant to temperature fluctuations and other environmental changes.

Plasma pyrolysis is a thermal process used to convert waste materials into useful products such as syngas and slag [3]. Through the application of high temperatures (generated using plasma), waste material undergoes significant molecular breakdown, resulting in the formation of smaller molecules [1]. This technology has been viewed as an environmentally friendly alternative for solid waste management because it not only reduces the volume of waste, but also decreases pollution by neutralizing harmful emissions before they are released into the air [56]. Such systems have found applications in managing municipal waste, medical wastes, and hazardous industrial wastes. This process can be used in the treatment of digestate from AD treatment, due to the digestate from AD of SS containing HMs, dyes, and other toxic substances that are bonded on the PVA/CTS-modified biochar. Therefore, to enhance the production of bio-energy and lower the chance of secondary pollution, digestate should be fed into plasma pyrolysis, hence the full treatment of digestate through generation of syngas, slag, and adsorption of HMs, dyes, and fixing other harmful chemical substances.

The process involves rapidly heating the digestate in an oxygen-free environment using a plasma torch as the heat source. This intense heat initiates chemical reactions which decompose complex molecules within the digestate into useful outputs, including syngas (mixture mainly comprising hydrogen and carbon monoxide) and slag. In addition, the produced syngas can be used for energy generation either directly as fuel or through conversion mechanisms like Fischer–Tropsch synthesis for biofuel production [57]. In addition, the slag residue contains carbon and nutrients, making it potentially useful as a soil amendment or fertilizer component [58], and it can also be employed as an additive in the AD process [59]. Furthermore, plasma pyrolysis allows immobilization of dyes [3], HMs [1], and other hazardous chemical substances. This technique of introducing digestate into plasma pyrolysis can significantly reduce volumes of digestate needing disposal while unlocking additional resource efficiency gains from what would otherwise be considered as waste. It also contributes towards circular economy models where outputs feedback beneficially into other processes without resorting much on conventional

landfilling methods that are space-intensive or environmentally problematic, given their propensity towards greenhouse gases emissions, contamination of ground water, etc.

5. Techno-Economics of the Proposed Technology

The integration of PVA/CTS-modified biochar into the AD of SS presents a promising approach for enhancing both the efficiency of the digestion process and the recovery of valuable resources. AD and plasma pyrolysis are two prominent waste-to-energy technologies that can contribute significantly towards sustainable development. Therefore, understanding the techno-economics of these processes is crucial for industrial implementations, policy making, and investment decisions. This present review recommends co-processing of both methods for treating SS in an economic and eco-friendly way. Biochar, produced through pyrolysis at high temperatures, has been shown to improve methane production and reduce volatile fatty acids (VFAs) and chemical oxygen demand (COD) when used in AD systems. Specifically, a concentration of 6.67 g/L of biochar produced at 888 °C increased methane production by 18% and reduced COD by 88%, alongside a 42.75% reduction in VFAs, indicating its potential to stabilize the digestion process and enhance biogas yield [60].

Additionally, Bhatt et al. [61] compared AD integrated with plasma pyrolysis of sludge with other methods such as carbonization, gasification, hydrothermal treatment, farmland application, and composting. Their analysis revealed that the recommended technology offers many advantages in terms of bioenergy generation, adsorption of dyes and HMs, reduction of waste volume, and nutrient recovery. SS is regarded as hazardous waste, as it contains many toxic materials including HMs, pathogens, dyes, and other chemical compounds. Therefore, direct feeding of SS into AD with PVA/CTS-modified biochar as an additive enhances treatments and leads to high biogas yield. The produced biogas can be used for heating or electricity generation purposes once cleaned of contaminants [10], creating additional income streams when sold to different markets.

Different studies have reported digestate from AD treatment as the best biofertilizer to improve soil properties [62]. However, this study does not recommend direct use of digestates from SS as organic fertilizer, as it contains some toxic materials such as HMs, hazardous chemical substances, dyes, and other pollutants that are bonded to the PVA/CTS biochar. Therefore, the digestates must be introduced into plasma pyrolysis to produce syngas and slag. Furthermore, syngas mainly comprises hydrogen gas and carbon monoxide, but also includes small amounts of other gases like methane, carbon dioxide, etc. [61]. It can be employed as fuel, heat, and electricity generation, or further processed to produce chemicals/fuels such as methanol, diesel, etc. [63]. The slag is the non-combustible materials that remain after plasma pyrolysis. The molten residue cools down, forming a vitrified solid containing valuable minor metals, which can be recovered and sold for use in various industrial applications [64]. The inert part can be reclaimed for use as an additive in other treatment processes such as AD [59], or applied as a fertilizer to improve soil properties [58,62,65]. This material poses no toxic hazard due to the complete destruction of harmful substances at very high temperatures during the vitrification process. Furthermore, plasma pyrolysis will allow for the adsorption of heavy metals HMs [1] and dyes [3], while fully destroying pathogens and other toxic substances that may be contained in digestates after AD treatment of SS.

Generally, treatment of SS using PVA/CTS-modified biochar as an additive in AD leads to high biogas yield. The resulting digestate can then be introduced into plasma pyrolysis to produce syngas and slag. However, integrating these processes requires higher temperatures, which can raise concerns about energy demand. These concerns are counterbalanced by the generated energies that may create additional income when supplied back into the grid system. This process also enhances resource utilization to produce bioenergy, promotes nutrient recovery, and creates a safe disposal method for large quantities of SS in an environmentally and economically sound manner.

The economic evaluation of PVA/CTS-functionalized magnetic biochar as an additive to the AD process, including operating costs, sales prices, production costs, and revenue, will depend on plant capacity and the cost of pyrolysis and AD byproducts. The economic feasibility of biochar as an additive in AD treatment has recently been studied by [66]. It was revealed that significant economic benefits can be achieved by adding biochar. The total annual methane production of AD with biochar added and AD without biochar was 1.01×10^8 m^3 and 7.39×10^7 m^3, respectively. An extra 2.71×10^7 m^3 of methane is produced annually, which can contribute to the production of electricity, fuel, and heat energy. In addition, the management and operating costs of the above-mentioned entire plant are approximately USD 4.1 to USD 6.1 million, and the electricity revenue produced from combustion of biogas was around USD 10 million.

In addition, Rida Galaly et al. [67] evaluated the environmental and economic feasibility of plasma gasification treatment of plastic waste in the Middle East, especially in Saudi Arabia. The author found that plasma gasification is the greenest technology for plastic waste treatment in terms of environmental, economic, and strategic perspectives, as it recovers 3.17×10^5 tons of bio-oil, equivalent to 12.55×10^9 MJ of energy. Additionally, an economic and environmental vision roadmap was introduced, resulting in financial benefits with a rate of return of 80%, a payback period of 1.2 years, and a gross profit of 129%. Galaly [8] reported that plasma pyrolysis of medical waste was also found to be more profitable. In 2022, the sales profits from electricity generated using diesel oil reached up to USD 1020 million for households and USD 1445 million for factories. Additionally, the sales profits from pyrolysis oil were USD 34.44 million, while the cost of syngas was USD 354 per ton, with an annual production of 1500 tons. This analysis shows how plasma pyrolysis can be more profitable, and can also be referenced for the treatment of AD digestate to provide a means for syngas and slag production. It is important to note that while financial returns are crucial when assessing feasibility, environmental benefits like reduced greenhouse gas emissions and resource conservation add more dimensions towards the overall advantages, making it even more appealing, economically feasible, and eco-friendly [68].

Hydrothermal carbonization of organic waste into hydrochar, which is rich in surface functionalities, further supports the potential of biochar in AD systems. Hydrochar-based technology not only improves AD performance, but also facilitates nutrient recovery, contributing to sustainability goals such as clean water, zero hunger, and climate action [69]. However, the presence of emerging micropollutants like endocrine-disrupting compounds (EDCs), microplastics (MPs), and engineered nanoparticles in wastewater streams poses challenges to the AD process. These contaminants can affect microbial activity and enzyme functions, potentially hindering the valorization of SS and the production of biogas and other valuable byproducts [70]. Therefore, the modification of biochar with PVA and CTS could enhance its adsorption capacity for these micropollutants, thereby mitigating their negative effects and improving the overall efficiency of the AD process. Techno-economic analyses and life cycle assessments are crucial to evaluate the commercial viability and environmental impact of using modified biochar in AD systems, ensuring that the benefits outweigh the costs and contribute to a circular economy. This integrated approach aligns with the broader goals of sustainable waste management and resource recovery (biogas and nutrients), offering significant socioeconomic benefits, particularly for developing economies.

6. Challenges and Future Outlooks

The integration of PVA- and CTS-modified biochar as additives into AD of SS presents both promising opportunities and notable challenges. AD, along with plasma pyrolysis, is a promising waste management technology with significant potential for renewable energy generation. AD breaks down organic matter in an oxygen-free environment, producing biogas primarily composed of methane and carbon dioxide for energy, as well as nutrient-rich digestate that can be used as a soil amendment or fertilizer [10]. On the other hand, plasma pyrolysis uses high temperatures to convert complex materials into simple molecules to

produce syngas and slag in an environmental way, as it emits negligible greenhouse gas compared to traditional disposal methods such as incineration and gasification [3]. In addition, biochar, as a carbon-rich product obtained from the pyrolysis of biomass, has gained significant attention as an additive in AD due to its beneficial properties such as high porosity, large surface area, and inherent microbial activity [12]. Biochar has been shown to enhance AD performance by mitigating issues such as acidification and volatile fatty acid (VFA) accumulation, which can inhibit methane production. The modification of biochar with PVA and CTS could potentially enhance these benefits by improving microbial colonization and supporting direct interspecies electron transfer (DIET), which is crucial for efficient AD. However, the effectiveness of biochar in AD is highly dependent on its properties, which are influenced by the feedstock and production process. Studies have shown that different types and doses of biochar can have varying effects on methane yield, with some types increasing production and others decreasing it.

In this review, PVA and CTS as two types of biopolymers with excellent film-forming capabilities and good compatibility with other substances have been recommended for modifying biochar to enhance its performance in AD of sludge. The operational temperature of the AD reactor plays a crucial role when incorporating PVA- and CTS-modified biochar as additives. Given the temperature sensitivity of both PVA and CTS, a mesophilic temperature regime, typically ranging from 30 °C to 38 °C, is considered optimal for this application. Within this temperature range, the structural integrities of PVA and CTS are better preserved, allowing them to maintain their advantageous characteristics as biochar modifiers. This temperature-controlled environment ensures the stability of the modified biochar while simultaneously promoting efficient microbial activity for the AD process.

However, like all emerging technologies, they have their challenges. For instance, when using these polymers, the preparation procedure should be carefully controlled, as improper handling may result in a loss of stability, thereby reducing their activity [71]. Additionally, the recovery process after capturing pollutants can be challenging when dealing with micro-sized particles, which can affect overall efficiency. Furthermore, the effective stoichiometric ratio for modifying biochar with PVA and CTS must be thoroughly studied [72]. Despite promising initial results in research studies involving PVA/CTS-modified biochar on AD process outcomes like increased methane yield or enhancing nitrogen removal capacity, systematic understanding is yet missing about exact mechanisms by which these materials exert their effects inside AD systems. Although both PVA and CTS can bind well onto surfaces, they may not adhere evenly across different types of feedstock-derived biochar, owing to variations in physical characteristics such as the constituent's particle size distribution patterns, etc., leading to potentially uneven modification efficiency levels per batch processed. Therefore, the perfect feedstock to produce biochar, which can be effectively modified, is highly needed. The operating temperature of plasma pyrolysis is a key factor that can significantly affect quality/quantity of syngas and slag produced [61], hence the optimal operating condition must be well examined with respect to digestate from AD treatment. There should be a comprehensive assessment of relevant environmental aspects related to slag disposal considerations when used as a fertilizer or soil amendment. This assessment should include potential leakage scenarios, such as if certain harmful trace elements get adsorbed during the operation phase and are subsequently released into the environment, especially after long-term usage.

In conclusion, despite a few challenges, both polymeric substances show promising results in SS treatment via AD and plasma pyrolysis. However, further research and optimization are needed to enhance their application across a wide range of industries. Additionally, the presence of emerging micropollutants such as EDCs, MPs, and engineered nanoparticles (NPs) in SS and wastewater streams poses a significant challenge. These compounds can affect the microbial community and enzyme activity, potentially disrupting the AD process and reducing the efficiency of resource recovery. Therefore, while PVA- and CTS-modified biochar hold potential for improving AD performance and resource recovery, further research is needed to understand the interactions between biochar properties,

microbial dynamics, and the presence of micropollutants. This further research will help to optimize the process and ensure its economic viability.

7. Conclusions

The application of PVA- and CTS-modified biochar in the AD of SS demonstrates significant potential for enhancing biogas production and nutrient recovery. The modification of biochar with PVA and CTS introduces functional groups that increase the overall surface charge, thereby improving the adsorption of dyes, HMs, and other pollutants. This enhanced adsorption capacity helps stabilize the AD process by mitigating the negative effects of these contaminants on microbial activity. PVA/CTS-modified biochar has been shown to effectively regulate pH levels, which is crucial for maintaining optimal conditions for microbial communities involved in AD. This regulation addresses one of the primary challenges in conventional AD processes, where volatile fatty acids can cause acidification and system instability. The modified biochar's ability to absorb excess ions and stabilize pH ensures higher efficiencies and reduces the risk of process interruptions. Furthermore, the presence of emerging micropollutants in SS and wastewater streams poses a significant challenge to AD processes. These micropollutants can disrupt microbial communities and enzyme activities, thereby reducing the efficiency of resource recovery. The use of PVA- and CTS-modified biochar offers a promising solution to mitigate these effects, as it enhances the stability and performance of the AD process. Despite these promising results, further research is needed to optimize the application of PVA- and CTS-modified biochar across a wide range of industries. Subsequent research endeavors should prioritize elucidating the complex interplay among biochar physicochemical characteristics, microbial community structure and function, and the occurrence of trace organic contaminants to optimize process efficiency, enhance economic feasibility, and facilitate the scale-up of this innovative technology for widespread implementation. By addressing these challenges, PVA- and CTS-modified biochar can play a crucial role in advancing sustainable SS treatment and valuable resource recovery.

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