



Article Harnessing Digestate Potential: Impact of Biochar and Reagent Addition on Biomethane Production in Anaerobic Digestion Systems

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Abstract: This article reports on an experiment that aimed to investigate the effects of digestate and cosubstrate input with varying biochar concentrations on methane production in anaerobic digestion processes. The findings revealed distinct trends in methane production among the substrates. Further investigations were conducted to evaluate the effects of different types of biochars on biomethane production from raw cattle manure digestate. Four conditions were tested: one raw digestate condition and three digestate conditions containing 1% of a different biochar type to one another. BC1 (PEFC-certified spruce BC) and BC2 (oak wood BC) showed promising results in enhancing biomethane production. About 884.23 NmL of methane was produced, with a yield and productivity of 22.80 NmL.g⁻¹ and 1.62 NmL.g⁻¹.day⁻¹ with BC1. However, BC3 (cow and chicken manure digestate BC) demonstrated lower biomethane production compared to raw digestate. Additionally, the study explored the effects of adding reagents to digestate. Hematite and iron chloride salt did not show any positive effects on biomethane production when biochar was introduced, while activated carbon powder significantly improved biomethane production rates by approximately 11.18%.

Keywords: biochar; biomethane production; anaerobic digestion; cattle manure digestate; cosubstrates

1. Introduction

Anaerobic digestion (AD) is a sustainable technology that can effectively manage organic waste, reduce sludge, and generate renewable energy in the form of biogas and a nutrient-rich residue called digestate [1]. AD offers numerous benefits such as the reduction of greenhouse gas emissions (GHGs), additional income from farmers, recycling of nutrients, and a pollution reduction [2,3]. However, maintaining the stability of AD reactors can be challenging due to the accumulation of toxic inhibitors, unsteady pH, or other key factors [4]. To improve the efficiency of AD technology, different methods such as mechanical [5], physical [6], chemical [7], or biological have been developed [8,9].

Biochar (BC) is a type of charcoal that is produced from biomass, such as wood chips, agricultural waste, manure, and other organic materials [10]. It is produced through a process called pyrolysis, which involves heating the biomass in the absence of oxygen [11]. The quality of the BC produced depends on several factors, including the type of organic matter used, the temperature and duration of pyrolysis, and the conditions in the kiln or container [12].

These materials can be used as a soil amendment, as well as for various other applications [13]. One of the main benefits of BC is its ability to improve soil fertility and plant growth [14,15]. It also has the potential to sequester carbon in the soil, which can help mitigate climate change by reducing the amount of carbon dioxide in the atmosphere [16]. BC has also been shown to have potential in other areas, such as water treatment [17], energy production [18], and the remediation of contaminated soils [19]. Overall, the use of



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). BC has been a subject of considerable interest and research in the modern age owing to its potential to address a range of environmental and agricultural issues.

BC can be used to address some of the limitations of AD, such as stabilizing carbon, retaining nutrients, high-level Ammonia (NH₃), and buffering pH, while the organic waste material from AD can serve as a feedstock for BC production [20]. The AD process involves a varied assemblage of archaea and bacteria [21]. Direct interspecies electron transfer (DIET) among bacteria and methanogenic archaea has lately been explored to accelerate the syntrophic conversion of various organic compounds to methane [22]. BC, due to its conductive properties, has been found to stimulate DIET and is a possible external additive for enhancing methanogenesis [23]. Various researchers have investigated AD feasibility enhanced by BC, and have demonstrated that BC can notably increase the methane yield of multiple feedstocks [24].

BC can have a positive impact on microbiological activity in AD by creating a more hospitable environment for microorganisms that are involved in the AD process [25]. The porous structure of BC provides a habitat for microorganisms, which can enhance their activity and growth [26]. The high surface area of BC allows for more microorganisms to attach to its surface, which can increase their overall activity [27]. BC can also improve the nutrient availability and retention in the digestate, which is the residue that remains after the AD process is complete [28]. This can provide a sustained source of nutrition for the microorganisms, which can promote their growth and activity [29]. Furthermore, BC can help regulate the pH and moisture content of the digestate, creating a more stable environment for the microorganisms, which lead to more consistent and efficient microbiological activity [30]. BC can also decrease the lag time required for methane formation, enhance the production and degradation of intermediate acids, and increase the levels of macroand micronutrients in the digestate [24,31]. Overall, research has shown that the addition of BC to AD systems can increase the population and diversity of microorganisms during the process, which can lead to improved stability and higher yields of biogas [32]. The physicochemical properties of BC, which are attributed to the feedstock types and pyrolysis conditions used for its production, control the variability of these specific effects [33]. Studies on the behavior of different types of BC during AD remain uncommon [31], further research is needed to fully understand its potential in these areas.

The study aims to investigate the impact of BC on biomethane production by working with two different input materials (digestate and a preshredded cosubstrate prior to its integration into the digester). In the first case, BC is introduced along with the digestate, while in the second case, it is introduced with the cosubstrate before it becomes digestate. In addition, we assess the effects of BC concentration and type on methane production and explore the potential benefits of reagent addition such as hematite, iron chloride, and activated carbon powder to enhance biomethane production. The findings aimed to contribute to the optimization of AD processes, with the goal of promoting sustainable waste management practices and renewable energy generation.

2. Materials and Methods

2.1. Digestats, Cosubstrates, Biochars, and Reagents

In the conducted experiment, two different input materials, namely digestate and cosubstrates, were used. The digestate used in the experiment was obtained from the Castel Metha AD plant located in Brittany, France, which operates at a biogas production flow rate of 125 Nm³/h and is located approximately 20 min away from the laboratory. The primary input for this unit comprised young cattle manure reared on straw, which was stored in opaque containers at room temperature until use. Notably, the Castel Metha unit actively feeds biomethane into the natural gas grid.

The cosubstrates used for the experiment came from the SAS Biogaz-IFF plant, also located in Brittany, France. This unit has a biogas production flow rate of 65 Nm³/h and is situated approximately 30 min away from the laboratory. The cosubstrate's composition consisted of various components, including cattle slurry (10 m³ day⁻¹), pig slurry

 $(5 \text{ m}^3 \text{ day}^{-1})$, cattle manure (4 tons), pig manure (2 tons), poultry manure (3.5 tons), and maize silage (5 tons). In our study, raw digestate and cosubstrates were employed as the control variable.

Furthermore, the experiment involved the utilization of three types of biochars, namely BC1, BC2, and BC3. BC1 was PEFC-certified spruce biochar, BC2 was derived from oak wood by the University of Cassel, and BC3 was digestate biochar sourced from the Netherlands. These biochars were employed in different proportions depending on their specific application. The differences between the three types of biochars are presented in Table 1. Additionally, activated carbon, hematite (Ouenza, 70 km of Tebessa, Algeria), and iron (III) chloride salt were incorporated into the experiment.

ВС Туре	Source Material	Production Method	Brunauer Emmett-Teller (BET m ² /g)	Density (kg/m ³)	Ash Content (%)	Production T° (°C)	Residence Time (min)
BC 1	PEFC- certified Spruce	Auger Pyrolysis	420	115	2.5	600	<10
BC 2	Oak Wood	Auger Pyrolysis	160	110	3	400	30
BC 3	Cow and chicken manure digestate	Gasification	105	533	59	650–750	10–20

Table 1. Type and Characteristics of BC.

2.2. Process Monitoring of AMPT II

The Automatic Methanization Potential Test II (AMPT II) is an automated process that involves monitoring various parameters such as substrate and inoculum mass, pH and temperature, monitoring biogas production, and calculating methane yield. Twelve parallel, completely mixed anaerobic digesters are used to conduct batch experiments on anaerobic digestion. Each digester had a working volume of 400 g and was equipped with a gas-sampling bag and a sludge-sampling pore. These digesters are placed in a shaker at a temperature of 37 °C and a speed of 140 rpm for a defined time. Throughout the experiments, the volume of biomethane produced is continuously measured using the Gas-Volume Measuring Device of AMPTS II and recorded in the AMPTS II software (bcp instruments version 1.04) from the start of experiments (day 0) until the last day of experiments. The temperature of the sample incubation unit is maintained at 37 °C to ensure mesophilic conditions. The experiment was conducted in triplicate for each trial.

2.3. Analytical Methods

Physicochemical analyses were conducted in triplicate for each experiment, both at the end of each experiment after centrifuge at 4 °C and 5000 rpm/min for 15 min using centrifugation (ThermoFisher Scientific Heraeus Megafuge, Porton, UK). Six analyses were performed, which included the % of dry matter (% DM), Chemical Oxygen Demand (COD), pH, Complete Alkalimetric Title (CAT), and volatile fatty acids (VFAs).

The protocol of measuring dry matter (DM) involves the following steps:

Three masses were weighed for each essay, including the mass of the empty aluminum container (m0), the mass of the sample with the aluminum container (m1), and finally the mass of the dried sample with the aluminum container (m2) after being placed in the oven for 2 days at 105 °C until it reaches a constant weight. The samples were dried using a drying oven (VWR[®] DRY-Line[®], UK).

The dry matter content is calculated as follows:

Dry Matter (DM %) = (Dry weight / wet weight) \times 100

After centrifugation, the centrifuged samples can be used for COD analysis using COD reagent vials, a thermoreactor (Spectroquant TR 420, Merck, Frankfurt, Germany), and colorimeter (Spectroquant Move 100, Merck, Frankfurt, Germany). A volume of 0.5 mL was extracted from each assay (blank control, control, and essays) and then diluted with 10 mL of distilled water. The resulting mixtures were further diluted with an adapted dilution factor. Next 3 mL of each diluted supernatant was transferred into a COD tube and then placed in the thermoreactor at 150 °C for a period of 2 h. After 2 h, the COD tubes were removed and allowed to cool in a test tube rack for 40 min before reading the results with the colorimeter.

2.3.2. pH Measurement

The pH of samples was determined using a pH meter (pH 3110, pH electrode SenTix[®] 21, Grosseron, WTW, France) at the start and end of the experiments following centrifugation of the samples at 4 °C and 5000 rpm/min for 15 min.

2.3.3. Complete Alkalimetric Title (CAT) and Volatile Fatty Acid (VFA) Measurement

In this study, the CAT and VFA were measured using an Automatic titrator (ThermoFisher Scientific TM Orion Star TM T910 Series Potentiometric Titrators, France). To perform the measurement, 5 mL of supernatant from each of the samples were taken and then diluted to 100 mL with distilled water and mixed thoroughly in glass beakers. The measurement was conducted following the manufacturer's instructions for the automatic titrator. VFA and CAT were determined according to the method described by [34]. Therefore, the VFA/CAT ratio is used to assess the stability and health of the AD system.

3. Results and Discussion

3.1. Experimental Investigation of Digestate and Cosubstrates Input with Different Biochar Concentration in Anaerobic Digestion

The experimental investigation involved the utilization of digestate and cosubstrates as input materials in AD processes, with varying doses of BC 1 (1%, 2%, and 4% based on the mass of the sample) added to the feedstocks. The primary parameter measured in this study was the accumulated biomethane volume after a period of 9 days. Analysis of the obtained data revealed distinct trends in methane production among the different substrates (Figure 1a,b). Specifically, the raw digestate showed higher methane production (around 548.0 \pm 49.6 NmL) compared to the cosubstrates (341.5 \pm 16.5 NmL). This could be attributed depending on the composition and characteristics of the feedstock use; in terms of complexity and degradability, the cosubstrates with its multiple organic materials would generally be considered more complex and potentially harder to degrade compared to digestate, which primarily consists of raw cattle manure. Moreover, the addition of 1% BC to digestate resulted in similar methane production levels (550.5 ± 22.2 NmL), albeit slightly lower than that of the cosubstrates (299.96 \pm 9.7 NmL) when compared to their respective control groups. However, the introduction of 2% and 4% BC doses appeared to inhibit methane production, as the volume of methane generated was noticeably reduced compared to the other experimental conditions. These observations indicate that the influence of BC on methane production varied depending on the substrate used, with the higher BC concentrations negatively impacting methane production.



Figure 1. Effect of different doses of BC on biomethane production using digestate (**a**) as a material input and cosubstrates (**b**) as a material input after 9 days of AD.

The addition of 1% BC resulting in similar methane production for raw digestate, although slightly lower than cosubstrates, corresponds to studies suggesting that low concentrations of biochar can enhance anaerobic digestion performance [35]. BC, with its porous structure and high surface area, has the potential to adsorb and retain volatile fatty acids, improving process stability and methane production [30]. However, the slight reduction in methane production compared to cosubstrates could be attributed to variations in substrate composition and biochar's specific interaction with different feedstocks [36].

The inhibitory effect of higher BC concentrations (2% and 4%) on methane production aligns with literature highlighting the potential negative impact of excessive BC doses [37]. High concentrations of BC can lead to increased pH levels, nutrient immobilization, and reduced microbial activity, thereby impeding AD efficiency [32]. These findings emphasize the importance of optimal BC dosing to avoid potential negative consequences on methane production. The compelling results obtained from the experimental investigation strongly warrant further pursuit of experiment focused on digestate as a primary feedstock in AD processes.

3.2. Effects of Different Type of Biochars on Biomethane Production of Digestate

The experiment aimed to evaluate the impact of different types of BC (1, 2, and 3) on biomethane production when added to raw cattle manure digestate. The results varied depending on the type of BC used.

Four different conditions were tested: raw digestate, digestate + 1% BC 1 (PEFCcertified spruce BC), digestate + 1% BC 2 (oak wood BC), and digestate + 1% BC 3 (cow and chicken manure digestate BC). The experiment measured the accumulated biomethane volume against days, as shown in Figure 2a. The results showed that BC1 was the most effective in enhancing biomethane production (884.23 \pm 62.0 NmL at the end of experiment), yielding 22.80 NmL.g⁻¹ which correspond to a productivity of 1.62 NmL.g⁻¹.day⁻¹. This is likely due to the high porosity and surface area of the spruce BC, which provide more sites for the colonization of methanogenic bacteria that produce biomethane [33]. Interestingly, BC 2 showed a similar performance to BC 1, with some fluctuations in biomethane production. However, as the experiment progressed, BC2 caught up and eventually outperformed BC 1 yield by 2.4%, indicating that adding BC2 can have a positive impact on biomethane production over the long term, although it may not provide immediate benefits. On the other hand, BC 3 showed less performance in biomethane production (around 742.0 \pm 22.0 NmL) compared to raw digestate (870.20 \pm 37.0 NmL). The yield and productivity of biomethane for BC 3 were 21.66 $NmL \cdot g^{-1}$ and 1.50 $NmL \cdot g^{-1} \cdot day^{-1}$, while the yield and productivity for raw digestate were 21.25 NmL \cdot g⁻¹ and 1.51 NmL \cdot g⁻¹·day⁻¹, respectively (Figure 2b). This could be attributed to the high ash content (see Table 1) and the presence of copper in the BC 3, which may have a negative impact on microbial activity in the AD process.



Figure 2. Cont.



(**b**)

Figure 2. (a) Effect of different type of biochar on cumulative biomethane (NmL) volume per day. (b) Cumulated biomethane yield and productivity of different biochar in AD.

Table 2 shows the productivity (measured in NmL g^{-1} dry matter day⁻¹), pH, COD, and VFA/CAT ratio values for the four different conditions: raw digestate, digestate + 1% BC 1, digestate + 1% BC 2, and digestate + 1% BC 3.

Productivity Yield Methane COD pН (NmL·g⁻¹ DM·day⁻¹) DM% (NmL·g⁻ DM) VFA/CAT (NmL) $(g O_2/L)$ t₀ tf t_0 tf t₀ tf Raw 0.49 870.20 ± 37.0 22.45 9.69 ± 0.20 8.36 8.19 ± 0.08 26.23 31.30 ± 5.1 0.67 ± 0.05 1.60digestate Digestate + 1% BC 1 884.23 ± 62.0 22.80 1.62 10.68 ± 0.1 8.36 8.12 ± 0.10 23.56 33.20 ± 2.4 0.62 0.62 ± 0.03 Digestate 856.93 ± 94.0 23.36 10.16 ± 0.50 8.42 8.07 ± 0.04 33.00 ± 2.1 0.50 0.59 ± 0.04 1.66 24.88 + 1% BC 2 Digestate 742.0 ± 22.0 21.66 1.50 9.79 ± 0.10 8.01 ± 0.04 27.80 34.00 ± 0.6 0.33 0.71 ± 0.01 8.61 + 1% BC 3

Table 2. Parameter values at the end of anaerobic digestion after 14 days.

From the Table 2, we can see that the productivity values of all four conditions are relatively similar, ranging from 1.50 to 1.78 NmL g⁻¹ dry matter day⁻¹. However, it is worth noting that the addition of BC 2 appears to have a positive impact on productivity and enhance the biomethane production by 9% compared to raw digestate. At the end of the experiment, the pH level decreased for all conditions, but to varying degrees. The pH level of raw digestate decreased from 8.65 to 8.14, while the pH levels for digestate with BC 1, 2, and 3 decreased from 8.36 to 8.12, 8.42 to 8.07, and 8.61 to 8.10, respectively. The decrease in pH level can be an indication of the production of acidic byproducts such as volatile fatty acids (VFAs) during the anaerobic digestion process. It is also possible that the BC addition affected the pH buffering capacity of the digestate, resulting in a less significant decrease in pH level for some conditions.

The COD values for all four conditions show an increase from t_0 (initial time) to t_f (final time). BC 1 and BC 3 show the highest increase in COD values, indicating that they may have a more significant impact on organic matter degradation. During the AD process, microorganisms break down organic compounds, leading to the consumption of oxygen in the sample, which is reflected in higher COD values. In some situations, biochar can

support microbial activity, providing a favorable environment for microorganisms to break down organic matter. While this can be beneficial in certain agricultural or composting settings, excessive microbial breakdown of organic matter can lead to increased COD levels in the environment. In terms of process stability, the VFA/CAT ratio results showed varying degrees of effectiveness in enhancing process stability depending on the type of BC used. BC 3 shows the highest VFA/CAT ratio (0.71), indicating a less stable process. Meanwhile, BC 1 (0.62) and BC 2 (0.59) show similar VFA/CAT ratios, which suggests a more stable process.

However, the effect of different types of BC on biomethane production from raw cattle manure digestate can also depend on the conditions used to produce the BC. For example, BC produced at higher temperatures may have a more stable carbon structure that is less accessible to the microbial community responsible for AD, which could reduce biomethane production (BC3). Biochar has gained attention for its potential applications in agriculture and environmental management [25]. One intriguing area of research is its possible effect as an in situ CO_2 adsorbent and its relation to the enhancement of methane production [38]. This discussion aims to explore the hypothesis that the addition of biochar to methane production systems could act as a CO_2 adsorbent, potentially leading to improved methane yields. Biochar's unique physical and chemical properties contribute to its CO_2 adsorption capacity. Its high surface area and porous structure provide ample sites for CO_2 molecules to bind through physisorption and chemisorption mechanisms [33]. The presence of functional groups on the biochar surface also enhances its ability to attract and retain CO₂ molecules. The absence of any improvement in methane production, despite the addition of biochar as an in situ CO_2 adsorbent, could be attributed to several factors [39]. It is possible that the biochar used lacked sufficient CO_2 adsorption capacity or faced competition from other substances for adsorption sites. Moreover, microbial adaptation to CO₂ presence, potential inhibition of methanogens by biochar properties, and altered experimental conditions might have influenced the outcomes. Additionally, complex interactions with the environment, variations in biochar types, and the short-term nature of experiments could have obscured any positive effects on methane production. Understanding these factors is crucial for refining our comprehension of biochar's role in methane production systems.

3.3. Effects of Addition of Reagents on Biomethane Production of Digestate

Numerous studies have been conducted to ascertain the potential benefits of introducing various reagents to biochar to enhance its characteristics and expand its potential applications, particularly in environmental remediation, agriculture, and energy production. This experiment sought to investigate the impact of adding specific reagents (namely, iron (III) oxide (hematite), iron (III) chloride salt, and activated carbon powder) on the biomethane production of digestate. The results presented in Figure 3 demonstrate the effects of these reagents on the accumulated biomethane volume yield and productivity at the end of the process.

Based on the information illustrated in the Figure 3, it appears that the addition of hematite and iron chloride salt did not lead to any positive effects on biomethane production in terms of yield and productivity when compared to the raw digestate (control). This indicates that these additives do not enhance or improve the methane production process when digestate is used as an input material.

The results present in Table 3 show an overall increase in the value of COD at the end of AD. The study also found an increase in volatile fatty acids (VFA) except when 1% biochar 1 + 200 mg hematite was used. However, as we can see in the Table 3, the VFA/CAT ratio increased for all tested substrates, except for 1% biochar 1 + 200 mg iron oxide. It is worth noting that this ratio ranged from 0.4 to 0.8, indicating that the AD process was unstable. Furthermore, the pH values were above the optimal range for AD (6.5–7.5).



Figure 3. Cumulated biomethane yield and productivity of digestate using biochar and different reagent in anaerobic digestion.

Table 3.	Outcomes	of a resear	ch study e	examining	the impact	of reagent	addition or	n biomethane
producti	on.							

	Methane (Nml)	Yield (NmL∙g ^{−1} DM)	Productivity (NmL·g ^{−1} DM·day ^{−1})	% DM	pH		COD (g O ₂ /L)		VFA/CAT	
					t ₀	t _f	t ₀	t _f	t ₀	t _f
Raw digestate	870.20 ± 37.0	22.45	1.60	9.69 ± 0.20	8.36	8.19 ± 0.08	26.23	31.30 ± 5.1	0.49	0.67 ± 0.05
Digestate + 200 mg hematite	885.13 ± 25.6	23.42	1.67	9.13 ± 0.04	8.71	8.09 ± 0.06	25.60	33.00 ± 0.7	0.35	0.54 ± 0.02
Digestate + 1% BC1+ 200 mg hematite	813.13 ± 147.0	22.60	1.61	9.98 ± 0.2	8.42	8.06 ± 0.07	20.76	34.60 ± 0.6	0.56	0.47 ± 0.05
Digestate + 0.25 g iron (III) chloride salt	823.46 ± 171.0	22.03	1.57	9.34 ± 0.10	8.33	7.85 ± 0.07	19.96	31.86 ± 4.9	0.55	0.87 ± 0.03
Digestate + 1% BC1+ 0.25 g iron (III) chloride salt	789.00 ± 191.0	21.38	1.52	10.25 ± 0.09	8.70	7.83 ± 0.01	23.40	32.13 ± 2.0	0.64	0.84 ± 0.10
Digestate + 1% BC1+ 0.5 g iron (III) chloride salt	741.00 ± 114.5	19.86	1.41	10.31 ± 0.07	8.59	7.86 ± 0.07	26.76	32.20 ± 1.4	0.59	0.75 ± 0.08
Digestate + 1% activated carbon powder	947.53 ± 74.0	25.02	1.78	10.46 ± 0.28	8.36	8.12 ± 0.05	21.80	30.54 ± 1.2	0.51	0.61 ± 0.01

The incorporation of hematite (iron (III) oxide), a source of iron, into digestate has been found to enhance the activity and growth of methanogens, which are responsible for methane production during AD, thereby increasing biomethane production [40]. Notably, the introduction of 200 mg hematite with 1% BC1 to the digestate did not result in any significant improvement in biomethane volume (813.13 NmL) compared to the digestate with hematite (885.13 NmL). This phenomenon may be attributed to several factors, such as the dependence of the optimal amount of iron supplementation on multiple variables or the presence of sufficient iron in the digestate that precludes any significant enhancement [40,41]. Consequently, further inquiry is warranted to ascertain the underlying cause of the lack of improvement in biomethane production following the addition of iron (III) oxide. Based on the results presented in Table 3, it can be observed that the addition of activated carbon powder to digestate leads to a substantial improvement in biomethane production. Specifically, the biomethane production rate increases by about 11.18% when compared to the raw digestate. Activated carbon is a highly porous material that can adsorb organic compounds, including inhibitory substances that can inhibit the growth of methanogens [42]. By removing these inhibitory substances, activated carbon can improve the activity and growth of methanogens, leading to increased biomethane production. Haut du formulaireBas du formulaire.

In addition, the study investigated the potential benefits of adding iron (III) chloride to digestate to increase biomethane production. Two different concentrations of iron chloride (0.25 g and 0.5 g) were tested, and the results showed that there was no significant improvement in biomethane production when compared to raw digestate (control). However, the addition of iron chloride did increase the VFA values (from 1.42 to 2.19 and from 134 to 2.02), while there was a significant decrease in pH (from 8.70 to 7.83 and from 8.59 to 7.86) for both concentrations tested, respectively. These observations suggest that the benefits of adding iron III chloride salt may not always be observed contrary to the findings reported in previous studies [43]. This could be explained by the high organic loading rates (OLR) in the digester that may inhibit microbial activity due to the accumulation of VFAs, resulting in a drop in pH and lower availability of iron for methanogenic microorganisms [4]. Further analysis and experimentation may be necessary to fully understand the reasons behind the lack of positive impact. Factors such as additive concentration or dosage, experimental conditions, or other variables could have influenced the results.

4. Conclusions

This paper aimed to harness digestate potential and evaluate the impact of different types of biochar on biomethane production when added to raw cattle manure digestate. The results showed that the addition of BC had varying effects on biomethane production, depending on the type of biochar used. BC 1 (PEFC-certified spruce) was found to be the most effective in enhancing biomethane production, followed by BC 2 (oak wood). However, BC 3 (cow and chicken manure digestate) showed less performance in biomethane production compared to raw digestate. Furthermore, the addition of activated carbon powder to digestate can significantly improve biomethane production, while hematite and iron chloride salt addition did not result in any positive impact on biomethane production. Moreover, the study found an overall increase in the value of COD and the VFA/CAT ratio, indicating an unstable anaerobic digestion process. In general, the results suggest that cattle manure digestate can be reused as a potential substrate for the AD process and that the addition of BC may possess a positive impact on biomethane production, yet the type of biochar used must be carefully considered to guarantee optimal results. Thus, it is imperative to conduct further research to thoroughly investigate the underlying factors and optimize the relevant conditions to enhance biomethane production from digestate.

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References

- Zouaghi, L.Y.S.K.; Djelal, H.; Salem, Z. Anaerobic co-digestion of three organic wastes under mesophilic conditions: Lab-scale and pilot-scale studies. *Environ. Dev. Sustain.* 2021, 23, 9014–9028. [CrossRef]
- Vasco-Correa, J.; Khanal, S.; Manandhar, A.; Shah, A. Anaerobic digestion for bioenergy production: Global status, environmental and techno-economic implications, and government policies. *Bioresour. Technol.* 2018, 247, 1015–1026. [CrossRef]
- Seruga, P.; Krzywonos, M.; den Boer, E.; Niedźwiecki, Ł.; Urbanowska, A.; Pawlak-Kruczek, H. Anaerobic Digestion as a Component of Circular Bioeconomy—Case Study Approach. *Energies* 2022, 16, 140. [CrossRef]
- Harirchi, S.; Wainaina, S.; Sar, T.; Nojoumi, S.A.; Parchami, M.; Parchami, M.; Varjani, S.; Khanal, S.K.; Wong, J.; Awasthi, M.K.; et al. Microbiological insights into anaerobic digestion for biogas, hydrogen or volatile fatty acids (VFAs): A review. *Bioengineered* 2022, 13, 6521–6557. [CrossRef]
- Pilli, S.; Pandey, A.K.; Katiyar, A.; Pandey, K.; Tyagi, R.D.; Pilli, S.; Pandey, A.K.; Katiyar, A.; Pandey, K.; Tyagi, R.D. Pre-Treatment Technologies to Enhance Anaerobic Digestion; IntechOpen: London, UK, 2020; ISBN 978-1-83962-707-1.
- Hajji, A.; Rhachi, M. The effect of thermochemical pretreatment on anaerobic digestion efficiency of municipal solid waste under mesophilic conditions. *Sci. Afr.* 2022, *16*, e01198. [CrossRef]
- Lee, J.; Ryu, D.-Y.; Jang, K.H.; Lee, J.W.; Kim, D. Influence of Different Pretreatment Methods and Conditions on the Anaerobic Digestion Efficiency of Spent Mushroom Substrate. *Sustainability* 2022, 14, 15854. [CrossRef]
- Singh, B.; Kovács, K.L.; Bagi, Z.; Nyári, J.; Szepesi, G.L.; Petrik, M.; Siménfalvi, Z.; Szamosi, Z. Enhancing Efficiency of Anaerobic Digestion by Optimization of Mixing Regimes Using Helical Ribbon Impeller. *Fermentation* 2021, 7, 251. [CrossRef]
- 9. Uddin, M.M.; Wright, M.M. Anaerobic digestion fundamentals, challenges, and technological advances. *Phys. Sci. Rev.* 2022. [CrossRef]
- Amalina, F.; Razak, A.S.A.; Krishnan, S.; Sulaiman, H.; Zularisam, A.W.; Nasrullah, M. Biochar production techniques utilizing biomass waste-derived materials and environmental applications—A review. J. Hazard. Mater. Adv. 2022, 7, 100134. [CrossRef]
- Mulabagal, V.; Baah, D.A.; Egiebor, N.O.; Sajjadi, B.; Chen, W.-Y.; Viticoski, R.L.; Hayworth, J.S. Biochar from Biomass: A Strategy for Carbon Dioxide Sequestration, Soil Amendment, Power Generation, CO2 Utilization, and Removal of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in the Environment. In *Handbook of Climate Change Mitigation and Adaptation*; Lackner, M., Sajjadi, B., Chen, W.-Y., Eds.; Springer International Publishing: Cham, Switzerland, 2022; pp. 1023–1085, ISBN 978-3-030-72579-2.
- Rodriguez, J.A.; Ferreira Lustosa Filho, J.; Carrijo Azevedo Melo, L.; de Assis, I.R.; Senna de Oliveira, T. Influence of pyrolysis temperature and feedstock on the properties of biochars produced from agricultural and industrial wastes. *J. Anal. Appl. Pyrolysis* 2020, 149, 104839. [CrossRef]
- 13. Kamali, M.; Sweygers, N.; Al-Salem, S.; Appels, L.; Aminabhavi, T.M.; Dewil, R. Biochar for soil applications-sustainability aspects, challenges and future prospects. *Chem. Eng. J.* 2021, 428, 131189. [CrossRef]
- 14. Ding, Y.; Liu, Y.; Liu, S.; Li, Z.; Tan, X.; Huang, X.; Zeng, G.; Zhou, L.; Zheng, B. Biochar to improve soil fertility. A review. *Agron. Sustain. Dev.* **2016**, *36*, 36. [CrossRef]
- Zeghioud, H.; Fryda, L.; Djelal, H.; Assadi, A.; Kane, A. A comprehensive review of biochar in removal of organic pollutants from wastewater: Characterization, toxicity, activation/functionalization and influencing treatment factors. *J. Water Process. Eng.* 2022, 47, 102801. [CrossRef]
- Kalu, S.; Kulmala, L.; Zrim, J.; Peltokangas, K.; Tammeorg, P.; Rasa, K.; Kitzler, B.; Pihlatie, M.; Karhu, K. Potential of Biochar to Reduce Greenhouse Gas Emissions and Increase Nitrogen Use Efficiency in Boreal Arable Soils in the Long-Term. *Front. Environ. Sci.* 2022, 10, 914766. [CrossRef]
- 17. Wang, X.; Guo, Z.; Hu, Z.; Zhang, J. Recent advances in biochar application for water and wastewater treatment: A review. *PeerJ* 2020, *8*, e9164. [CrossRef]
- 18. Xiao, L.; Lichtfouse, E.; Kumar, P.S.; Wang, Q.; Liu, F. Biochar promotes methane production during anaerobic digestion of organic waste. *Environ. Chem. Lett.* **2021**, *19*, 3557–3564. [CrossRef]
- Murtaza, G.; Ahmed, Z.; Eldin, S.M.; Ali, I.; Usman, M.; Iqbal, R.; Rizwan, M.; Abdel-Hameed, U.K.; Haider, A.A.; Tariq, A. Biochar as a Green Sorbent for Remediation of Polluted Soils and Associated Toxicity Risks: A Critical Review. *Separations* 2023, 10, 197. [CrossRef]
- Rowan, M.; Umenweke, G.C.; Epelle, E.I.; Afolabi, I.C.; Okoye, P.U.; Gunes, B.; Okolie, J.A. Anaerobic co-digestion of food waste and agricultural residues: An overview of feedstock properties and the impact of biochar addition. *Digit. Chem. Eng.* 2022, 4, 100046. [CrossRef]
- 21. Lim, J.W.; Park, T.; Tong, Y.W.; Yu, Z. The microbiome driving anaerobic digestion and microbial analysis. In *Advances in Bioenergy*; Elsevier: Amsterdam, The Netherlands, 2020; Volume 5, pp. 1–61. [CrossRef]

- Park, J.-H.; Kang, H.-J.; Park, K.-H.; Park, H.-D. Direct interspecies electron transfer via conductive materials: A perspective for anaerobic digestion applications. *Bioresour. Technol.* 2018, 254, 300–311. [CrossRef]
- Shao, L.; Li, S.; Cai, J.; He, P.; Lü, F. Ability of biochar to facilitate anaerobic digestion is restricted to stressed surroundings. J. Clean. Prod. 2019, 238, 117959. [CrossRef]
- Pan, J.; Ma, J.; Zhai, L.; Luo, T.; Mei, Z.; Liu, H. Achievements of biochar application for enhanced anaerobic digestion: A review. Bioresour. Technol. 2019, 292, 122058. [CrossRef] [PubMed]
- 25. Bin Khalid, Z.; Siddique, N.I.; Nayeem, A.; Adyel, T.M.; Bin Ismail, S.; Ibrahim, M.Z. Biochar application as sustainable precursors for enhanced anaerobic digestion: A systematic review. *J. Environ. Chem. Eng.* **2021**, *9*, 105489. [CrossRef]
- Xiang, L.; Harindintwali, J.D.; Wang, F.; Redmile-Gordon, M.; Chang, S.X.; Fu, Y.; He, C.; Muhoza, B.; Brahushi, F.; Bolan, N.; et al. Integrating Biochar, Bacteria, and Plants for Sustainable Remediation of Soils Contaminated with Organic Pollutants. *Environ. Sci. Technol.* 2022, 56, 16546–16566. [CrossRef]
- Wang, M.; Yu, X.; Weng, X.; Zeng, X.; Li, M.; Sui, X. Meta-Analysis of the Effects of Biochar Application on the Diversity of Soil Bacteria and Fungi. *Microorganisms* 2023, *11*, 641. [CrossRef]
- Chiappero, M.; Demichelis, F.; Norouzi, O.; Berruti, F.; Hu, M.; Mašek, O.; Maria, F.D.; Fiore, S. Review of Biochar Application in Anaerobic Digestion Processes. In Proceedings of the Bio-Char II: Production, Characterization and Applications 2019, Cetraro, Italy, 15–20 September 2019.
- Dutta, S.; He, M.; Xiong, X.; Tsang, D.C. Sustainable management and recycling of food waste anaerobic digestate: A review. *Bioresour. Technol.* 2021, 341, 125915. [CrossRef] [PubMed]
- 30. Tang, S.; Wang, Z.; Liu, Z.; Zhang, Y.; Si, B. The Role of Biochar to Enhance Anaerobic Digestion: A Review. J. Renew. Mater. 2020, 8, 1033–1052. [CrossRef]
- Ma, J.; Chen, F.; Xue, S.; Pan, J.; Khoshnevisan, B.; Yang, Y.; Liu, H.; Qiu, L. Improving anaerobic digestion of chicken manure under optimized biochar supplementation strategies. *Bioresour. Technol.* 2021, 325, 124697. [CrossRef]
- 32. Zhao, W.; Yang, H.; He, S.; Zhao, Q.; Wei, L. A review of biochar in anaerobic digestion to improve biogas production: Performances, mechanisms and economic assessments. *Bioresour. Technol.* **2021**, *341*, 125797. [CrossRef]
- Tomczyk, A.; Sokołowska, Z.; Boguta, P. Biochar physicochemical properties: Pyrolysis temperature and feedstock kind effects. *Rev. Environ. Sci. Biotechnol.* 2020, 19, 191–215. [CrossRef]
- 34. Mézes, L.; Biró, G.; Sulyok, E.; Petis, M.; Borbely, J.; Tamas, J. Novel Approach of the Basis of FOS/TAC Method. In Proceedings of the International Symposium "Risk Factors for Environment and Food Safety" & "Natural Resources and Sustainable Development" & "50 Years of Agriculture Research in Oradea", Oradea, Romania, 4–5 November 2011.
- 35. Luo, C.; Lü, F.; Shao, L.; He, P. Application of eco-compatible biochar in anaerobic digestion to relieve acid stress and promote the selective colonization of functional microbes. *Water Res.* 2015, *68*, 710–718. [CrossRef]
- 36. Leng, R.A.; Inthapanya, S.; Preston, T.R. Biochar Lowers Net Methane Production from Rumen Fluid in Vitro. *Livest. Res. Rural Dev.* **2012**, *24*, 1–13.
- 37. Pant, A.; Rai, J.P.N. Application of Biochar on methane production through organic solid waste and ammonia inhibition. *Environ. Chall.* **2021**, *5*, 100262. [CrossRef]
- Pandey, D.; Daverey, A.; Arunachalam, K. Biochar: Production, properties and emerging role as a support for enzyme immobilization. J. Clean. Prod. 2020, 255, 120267. [CrossRef]
- 39. Sriphirom, P.; Towprayoon, S.; Yagi, K.; Rossopa, B.; Chidthaisong, A. Changes in methane production and oxidation in rice paddy soils induced by biochar addition. *Appl. Soil Ecol.* **2022**, *179*, 104585. [CrossRef]
- Baek, G.; Kim, J.; Lee, C. A review of the effects of iron compounds on methanogenesis in anaerobic environments. *Renew. Sustain.* Energy Rev. 2019, 113, 109282. [CrossRef]
- 41. Ugwu, S.N.; Biscoff, R.K.; Enweremadu, C.C. A meta-analysis of iron-based additives on enhancements of biogas yields during anaerobic digestion of organic wastes. *J. Clean. Prod.* **2020**, *269*, 122449. [CrossRef]
- 42. Wu, F.; Xie, J.; Xin, X.; He, J. Effect of activated carbon/graphite on enhancing anaerobic digestion of waste activated sludge. *Front. Microbiol.* **2022**, *13*, 999647. [CrossRef]
- 43. François, M.; Lin, K.-S.; Rachmadona, N.; Khoo, K.S. Advancement of biochar-aided with iron chloride for contaminants removal from wastewater and biogas production: A review. *Sci. Total Environ.* **2023**, *874*, 162437. [CrossRef]

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