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ENHANCEMENT OF BIOGAS GENERATION BY UTILIZING RAW AND MODIFIED WITH HNO_3 BIOCHAR OBTAINED FROM PYROLYSIS OF BIOMASS AND DIGESTATE

Panagiotis Basinas [1,*], Kateřina Chamrádová [1], Olga Vosnaki [2] and Jiří Rusín [1]

[1] *Institute of Environmental Technology, CEET, VSB-Technical University of Ostrava, 17. Listopadu 15/2172, Ostrava - Poruba 708 00, Czech Republic*
[2] *School of Environmental Engineering, Technical University of Crete, 73100 Chania, Crete, Greece*

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ABSTRACT
Biomass- and digestate-derived biochars were modified with nitric acid solution and examined in biochemical methane potential (BMP) tests to determine the effect of pretreatment on each of the different materials capability to improve the biogas production from the anaerobic digestion of conventional substrates such as corn silage. Methane yields from corn silage (0.308 $m^3kg_{VS}^{-1}$) were over the average value for the specific type of lignocellulosic material. Addition of digestate-derived biochar (BCD) in AD process improved the methane production 1.13-fold. However, the sawdust-derived biochar (BCS) resulted in an even greater methane release of 0.374 $m^3kg_{VS}^{-1}$. Chemical treatment reduced the pH of BCs from 10.29 and 11.54 to 3.10 and 2.81 for BCS and BCD, respectively while had a significant impact on materials composition almost removing the ash and metal elements from BCS and markedly decreasing 1.43-fold the ash fraction and by 70-75 % the minerals proportion in BCD. The presence of modified digestate-derived biochar (M-BCD) in a culture led to an enhanced methane production (0.402 m^3kgVS^{-1}) indicating that the specific additive exhibited a higher potential than all BCs to promote the efficiency of AD of a biomass feedstock. M-BCD also possessed the greatest capability to lessen an inhibition caused by H_2S retaining the concentration of the toxic gas at levels lower than 100 ppm. On the other hand, modified BCS provoked a 9% abatement in methane yields providing evidence that nitric acid could have a neutral or slightly negative effect on the capability of a BC to improve the AD process.

1. INTRODUCTION

Anaerobic digestion (AD) is the biochemical conversion of complex organic structures by microorganisms for the production of biogas in an anoxic environment. AD provides an efficient technology for the generation of renewable energy, however, faces a number of challenges including the low biodegradation efficiency, low by-products quality, long start-up times and system instability restricting its even broader application (Fagbohungbe et al., 2017). Various supporting materials such as nano-structured carbons and metals, biochar (BC), zeolites, and ore powders have been applied in AD systems to aid the process (Shen et al., 2020). BC, a carbon-rich material produced by pyrolysis of biomass, has been recognized as an AD additive capable to improve the process (Li et al., 2019; Pan et al., 2019; Salehiyoun et al., 2022) by functioning as (1) supporting media for the adhesion of microorganisms, (2) buffer for regulating system acidity, (3) adsorbent for controlling the concentration of inhibitory substances and (4) stimulator of methanogenesis assisting the direct interspecies electron transfer (DIET) (Fagbohungbe et al., 2017; Kobayashi and Kuramochi, 2022; Lü et al., 2016; Shen et al., 2020).

BCs produced from biomass have principally been reported to improve the efficiency of an AD system. Lü et al. (2016) who added fruitwood BCs (800-900°C) in a mesophilic digester noted that chars reduced the methanization lag phase by 6-24% and increased the methane production rate by 23.5-47.1%. Sunyoto et al. (2016) stated that a pine sawdust BC (650°C) enhanced the maximum production rate and yields of methane by 41.6 and 10%, respectively and concurrently shortened the lag phase of the AD of aqueous carbohydrates by 41%. Likewise, Salehiyoun et al. (2022) ascertained that a wood BC enhanced the rate and yields of methane (36.6%), controlled acidification and shortened the lag phase during AD of municipal solid waste (OFMSW).

* Corresponding author:
Panagiotis Basinas
email: panagiotis.basinas@vsb.cz

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Apart from biomass, there are several different feedstocks that could be used for the production of BC. Digestate is a by-product of AD that could be transformed into BC since it retains major part of the properties of the primary material used as substrate in AD. Transformation of digestate to BC and its subsequent use as additive in AD could provide a series of environmental and economic benefits. In a recent report (Basinas et al., 2023), BC prepared from a digestate was found to have significantly different properties than a biomass char and it was anticipated that will present a different impact on the AD of lignocellulose. However, the application of digestate biochar as support for the AD of conventional substrates such as corn silage has attracted limited attention and little information on the effect of this type of material on the AD process can be found in the literature.

BC performance in AD is prominently defined by BC properties like porous structure and the presence on its surface of oxygenated functional groups such as C=O, OH, and COOH. Biomass-derived BC presents a surface functionality that could support AD due to a sufficient porosity and surface area as well as an existence in its structure of C−O, C=O, and OH groups (Liu et al., 2015). However, modification with chemical methods could further improve the properties related to the enhancement of AD efficiency, especially the porosity since chemical agents facilitate a generation of new pores by removing fractions of carbonaceous molecules from BC structure (Kobayashi and Kuramochi, 2022; Liu et al., 2015). Zhu et al. (2018) observed a major increase in the surface area of BC as a result of a treatment with potassium carbonate. In addition to porosity growth, oxygenated functional groups like -COOH and -OH are introduced into BC with oxidation which could also aid the enhancement of a substrate's conversion in an AD system (Li et al., 2014; Liu et al., 2015). Nitric acid has been recognized as one of the most efficient agents for BC modification (Liu et al. 2015). Vu et al. (2017) reported that the number of surface carboxyl and sodium-containing functional groups of corncob-derived BC increased after its modification with HNO_3 (6 M) and NaOH (0.3 M). This caused an increase in the surface adsorption capacity of the BC and a subsequent reduction of ammonia in the system. In any case, modification of biomass-derived BC aimed at improving the surface area, pore volume and surface functional groups of BC. The same treatment could also be of relevance to increase the pore volume and functional groups of a digestate-derived BC, however no information is available about the effect of a nitric acid treatment on the properties of a digestate BC. Moreover, the influence of chemical treatment on the capability of a digestate-derived char to catalyse the AD has not been considered yet.

In the present study, BCs produced from a typical biomass and a digestate obtained from a mesophilic agricultural biogas plant were subjected to chemical treatment with nitric acid and all the materials examined for their capability to improve the efficiency of the AD of corn silage. The target of the work was to evaluate the effect of digestate derived BC on the AD process and correlate it with the case of biomass chars. Another aim was to assess the efficiency of an AD process supported by an engineered biocarbon produced using digestate-derived BC and make comparisons with the performance of systems assisted by biomass and pretreated biomass BCs.

2. MATERIALS AND METHODS

2.1 Sample collection and biochar preparation

Two different type of materials were used for production of BC. A typical biomass (sawdust) and a digestate obtained from the first stage of a mesophilic agricultural biogas plant (Pustějov II-Zemspol Studénka Ltd) operating on wet mode at 40°C with a substrate consisted of corn silage and small proportion of cattle slurry were used for the production of BC. Both materials were dried at 105°C under inert conditions (N_2), milled (IKA Tube Mill Control) and sieved to a particle size fraction between 100-300 μm.

BCs were generated in a bench-scale pyrolysis reactor operated from atmospheric temperature to 800°C with a heating rate of 10°C/min and a constant pyrolysis time of 180 min. The custom-made reactor consisted of a vertically oriented stainless-steel tube (50 mm internal diameter) placed inside an electrically heated furnace whereas the setup contained tar collection and gas cleaning systems. BCs prepared from sawdust and digestate referred to as BCS and BCD. More details about the pyrolysis reactor and procedure followed can be found in Basinas et al. (2023).

Modification of BC was carried out by soaking 50 g of material in 500 mL of a 66%vol. nitric acid solution and heating the mixture at 81°C for a total of 6 h while it was stirred at 200 rpm (Gao et al., 2021). Modified BC was washed with deionized water three times, filtered and oven dried at 105°C for 24 h. The modified BC from BCS and BCD will be referred to as M-BCS and M-BCD, respectively.

2.2 Characterization of materials and biochars

The TS content of substrate and inoculum was determined in a KERN DLB 160 3A moisture analyser and VS content by estimating the loss on ignition of material in a LECO TGA 701 thermogravimetric analyser. The same analyser was used for the proximate analysis of BCs. The mineral composition of samples was determined using Atomic Absorption Spectroscopy (HR-CS AAS contrAA 700) after dissolving the solids in aqua regia according to EN 16174:2012 standard. A LECO Truspec CHN and S628 elemental analyser was employed for the determination of the elemental composition of samples. A WTW 340i pH-meter (SenTix 410 sensor) was used for pH measurements. Carbohydrates were determined according to the ASTM D5896-96 and proteins by titration according to EN ISO 5983:1997 standard method. All analyses were performed in duplicate.

A scanning electron microscope (SEM) (Tescan Vega) equipped with a Tungsten cathode and energy-dispersive X-ray spectroscope (EDS) was used to determine the texture of materials. Micrographs were obtained using a secondary electron (SE) and backscattered electron (BSE) mode (acceleration voltage of 30 KeV) after the samples were gold sputtered (Quorum Q150R ES plus sputter) so that electron conductivity was sufficient.

2.3 Biochemical methane potential assays

2.3.1 Inoculum and substrate

Inoculum was a liquid digestate from the same mesophilic biogas plant (Pustějov II-Zemspol Studénka Ltd) obtained the digestate for the production of BC. A centrifuge (BEHO CHC-61A) operating at 25°C and 1200 rpm was employed to generate a supernatant consisting of <3%wt. of solids that was used as the inoculum for the BMP tests. Prior to the tests, the inoculum was maintained at 4°C. Corn silage which obtained by the same agricultural biogas plant with inoculum and digestate was used as the substrate for all tests.

2.3.2 Anaerobic digestion tests

BMP assays conducted at mesophilic conditions (40±0.5°C) using 1 L glass bottle reactors with a working volume of 800 mL. The impact of each different BC was examined by adding 15 g of BC together with 15 g of substrate in a reactor. Each test was performed in duplicate to account for the measurements accuracy of material's heterogeneity and were accompanied by duplicate blank runs containing merely inoculum in the same quantity with the rest of reactors to determine the background gas produced by the inoculum. The real amount of methane generated in each reactor was calculated by subtracting the average amount of methane produced from the two blank runs. The incubation period was initially selected at 40 days assuming that the degradation process would be completed. However, within that period the daily biogas production did not drop below 1%vol. of the cumulative yields for all reactors, thus the incubation period was extended to 80 days (Salehiyoun et al., 2022). Prior to tests the reactors were purged with nitrogen and during the assays the reacting mixture was stirred at 100 rpm. Biogas volume and composition were monitored on a daily basis using graduated gas-collection burettes and a gas analyser (Geotechnical Instruments Biogas5000). The details on the set-up and procedure followed are available in Basinas et al. (2022).

2.4 Statistical analysis

Analyses and experiments were performed in duplicate and the presented results are the average values. Statistical analysis was used to identify any differences and similarities in biogas, CH_4, H_2, and H_2S generation in BMP tests using the two-sample t-test analysis of Microsoft Excel.

3. RESULTS AND DISCUSSION

3.1 Influence of chemical treatment on biochar properties

3.1.1 Effect on biochar compositional and pH characteristics

Proximate analysis results and the pH values for raw and pretreated BCs are shown in Table 1. Volatile content of sawdust (6.67%wt.) and digestate (7.96%wt.) BCs was relatively low but rational for chars produced at 800°C (Luz et al., 2018b). Volatile contents between 10.30 and 18.14%wt. that can be found in the literature for chars derived from biomass like straw, wood barks, stems, paddy straw etc. are probably related to a low temperature (500-600°C) applied for their production (Lee et al., 2013). Volatile matter increased 4.8- and 4.1-fold with the chemical oxidation of sawdust and digestate BC, respectively.

Concentration of fixed carbon (FC) in the sawdust char was at 92%wt. which was expected considering results for biomass BCs produced at lower temperatures (500°C) (Lee et al., 2013). Digestate char contained a much lower FC proportion (37.75%wt.). This was presumably attributed to the fact that the feedstock for the production of the digestate contained not only corn silage but also small proportions of other additives such as cattle slurry and manure that are known to possess a low FC concentration (Basinas et al., 2023). Oxidation had a strong effect on the FC of biomass BC reducing it by 27%, whilst a much smaller influence on the FC of digestate BC which reduced only by a 4%. As a consequence of the changes caused by the oxidation of biomass BC, FC in modified material was similar to that appeared for a waste-derived BC such as poultry litter (66.40%wt.), cocopeat (67.25%wt.) and hardwood (68.66%wt.), higher than that of BCs originated from similar materials such as straw (55.37%wt.) and switchgrass (54.60%wt), but lower than that of other biomass BCs like wood stem (83.47%wt.), palm kernel shell (PKS) (80.85%wt.), bagasse (80.97%wt.), safflower seeds (80.70%wt.) and fruit cuttings (79.85%wt.) (Kambo and Dutta, 2015; Lee et al.,2013; Luz et al., 2018b).

Ash content of sawdust BC (1.36%wt.) was low compared to the values appear in the literature for the specific material mostly ranging from 7.5%wt. to 21.7%wt. for BCs produced at temperatures between 650 and 700°C (Ghanim et al., 2020; Pariyar et al, 2020). However, similar low values (2.93%wt.) of ash in a sawdust BC have been recorded (Manyuchi et al., 2021). Digestate BC contained remarkably greater ash concentration (54.72%wt.), which was also far above the ash content of similar digestate-derived (17.50%wt.) (Zhou et al., 2017) and corn-derived chars (11.37%wt) (Liao et al., 2022). Ash concentration in the digestate BC was comparable to those (55.40%wt.) of biocarbons produced from OFMSW and temperatures up to 650°C (Wen et al., 2021). Ash content decreased 1.53- and 1.43-fold with HNO_3-modification for the biomass and digestate BC, respectively.

BCs were highly alkalic as indicated by their pH values (10.29 and 11.54 for sawdust and digestate BC, respectively). Elevated pH is typical for a high-temperature BC like the ones produced at 800°C mainly for two reasons. At first is a loss of acidic groups from BC structure due to polymerisation and condensation reactions taking place during heating (Gascó et al., 2005) and the second is an enhancement of ash proportion and accumulation of cations in material occurring at high pyrolysis temperature (Monlau et al., 2016). The oxidized samples converted from alkaline to acidic showing a drastic reduction of pH from 10.29 and 11.54 to 3.10 and 2.81 for biomass- and digestate-derived BC, respectively. A similar reduction of pH from 6.85 to 2.89 and from 8 to 4 was observed when a corn stover BC and a weed-derived char, both produced at 500°C, were treated with nitric acid (Gao et al., 2021; Güzel et al., 2017).

TABLE 1: Composition characteristics and pH of raw and modified BC. Standard deviations from two replicates are shown in parentheses.

Parameter	BCS	BCD	M-BCS	M-BCD
pH	10.29 (0.03)	11.54 (0.02)	3.10 (0.01)	2.81 (0.04)
V.M.[a] ($\%wt_{TS}$)	6.67 (0.19)	7.96 (0.26)	31.97 (0.33)	32.73 (0.69)
F.C.[b] ($\%wt_{TS}$)	92.00 (1.85)	37.35 (1.12)	67.39 (1.31)	35.97 (1.02)
Ash ($\%wt_{TS}$)	1.36 (0.11)	54.72 (1.09)	0.64 (0.04)	31.31 (0.55)
Elemental Composition ($\%wt_{TS}$)				
C	95.34 (1.25)	38.87 (1.02)	77.05 (0.66)	44.24 (1.07)
H	0.95 (0.01)	0.97 (0.02)	1.67 (0.03)	1.65 (0.03)
N	0.42 (0.02)	1.04 (0.04)	1.28 (0.01)	2.73 (0.05)
S	0.00 (0.00)	0.34 (0.02)	0.00 (0.00)	0.04 (0.00)
O[c]	1.94	4.06	19.36	20.03
O/C[d]	0.02	0.08	0.19	0.34
H/C[d]	0.12	0.30	0.26	0.45

[a] volatile matter, [b] fixed carbon, [c] by subtraction, [d] molar ratios

3.1.2 Elemental composition

Elemental analysis results for the raw and pre-treated BC are included in Table 1. Carbon content of BCS was particularly high (95.34%wt.) and similar to that of biomass BCs (89.30%wt.) produced at a temperature of 700°C (Chen et al., 2016) but generally greater that the carbon contained in biomass BCs produced at low temperatures (Luz et al., 2018a). Elevated carbon content mostly derives from a dehydration and depolymerization of plant biomass occurring with heating during pyrolysis that leads to a graphitization of carbon into organized layers (Ahmad et al., 2012; Chen et al., 2008). Carbon concentration in the digestate-derived char was substantially lower (38.87%wt.) and consistent with the values reported for agricultural digestate-derived BCs (37.28-45.30%wt.) (Tayibi et al., 2021; Wei et al., 2018). In general, elemental carbon content of BCs deriving from pyrolysis of agricultural digestates that can be found in the literature is highly variable (2.25-65.90%wt.), but particularly lower than that of biomass BCs (Catenacci et al., 2022). The carbon content of M-BCS was lower than that of BCS indicating that an amount of the element removed with the treatment with HNO_3. A carbon removal was not confirmed by the results for the digestate BC where the carbon content of M-BCD (44.24%wt.) was found not to be lower but 14% higher than that of BCD (38.87%wt.).

Nitrogen concentrations were equal or lower than the unit (1.04%wt. for BCD and 0.42%wt. for BCS) which is typical for digestate- and biomass-derived BCs, respectively (Basinas et al., 2023; Luz et al., 2018b). HNO_3 treatment caused a rise of 3-fold and 2.6-fold of the nitrogen concentration of digestates. This is not surprising since modification has been proved to advance the number of structures containing N-O bonds (nitro groups and nitrate complexes) (Fernando et al., 2021; Sajjadi et al., 2018). As for nitrogen, the measured oxygen for the two high-temperature BCs was significantly low at 1.94 and 4.06%wt. for BCS and BCD, respectively. Elemental oxygen increased with the acidic treatment, 9.98-fold and 4.93-fold in M-BCS and M-BCD, respectively (Table 1). Oxidation is one of the principal reactions taking place during treatment with HNO_3 provoking a substantial number of oxygenated acidic functional groups be introduced on carbon surface (Fernando et al., 2021; Güzel et al. 2017).

Amendments in molar oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratio occurring with the acid treatment were considered in order to determine the influence of modification on the aromaticity index and polarity of BCs (Liu et al., 2020). In principle, a low O/C ratio indexes the hydrophobicity of a material whereas a low H/C ratio characterizes an aromatic material (Masebinu et al., 2019). For the two BCs, the O/C ratio was significantly small describing a hydrophobic nature for the materials. For the biomass BC, the H/C ratio was notably low showing that a high aromatization degree attained with pyrolysis at 800°C. For the digestate-derived BC, the ratio was found to be significantly higher (0.30) indicating a lower degree of aromaticity for the specific char. BCs showed enhancement of both molar O/C and H/C ratios with oxidation (Table 1). Oxidation with HNO_3 therefore allowed BCs to become less hydrophobic materials (Kobayashi and Kuramochi, 2022) with the modified digestate-derived BC displaying the greatest hydrophilicity (highest O/C ratio). Both BCs that sustained an HNO_3 treatment became also less aromatic with M-BCD exhibiting the lowest aromaticity (Shi et al., 2012).

3.1.3 Mineral composition

The main inorganic elements of raw and engineered BCs are shown in Table 2. Sawdust BC contained small amounts of minerals, mainly Ca and K, which is common for biocarbons originating from lignocellulose (Lee et al., 2013). P, Na and Si were also found in the biomass BC at proportions typical for biomass-derived chars (Lee et al., 2013; Pariyar et al., 2020). Digestate-derived BC was rich in all elements with Ca and K being the most abundant at the concentrations of 14.27 and 16.60%wt., respectively, which was in agreement with a similar digestate-derived BC produced at 600°C (Monlau et al., 2016). P, Si, Al, Mg and Na were also contained at higher concentrations than in the biomass char and at levels comparable to the results appear in the literature for similarly produced digestate chars (Basinas et al., 2023; Hung et al., 2017).

Inorganic content declined after treatment with nitric acid (Table 2). For M-BCS, the concentration of most substances approached a zero value with Ca being the most abundant at 0.38%wt. Reduction was also high for the digestate BC where modification resulted in a 70-75% decreased concentration of Ca, Al, K, and P and a complete disappearance of Mg. This was presumably ascribed to the fact that HNO_3 dissolves most inorganic substances. Nevertheless, a similar loss was not observed for Na and Si with modification of the digestate BC with HNO_3. In this case, M-BCD showed enrichment in Na and Si with Na concentration being increased 1.3-fold and Si proportion 1.9-fold (Table 2). Note that Si presence in biomass BC also remained unchanged at 0.03%wt. after treatment with HNO_3. It seems, therefore, that the Na and Si contained in digestate BC were strongly attached to the structure that despite the acid treatment they maintained and accumulated in the ash.

3.1.4 Surface morphology

BC materials are characterized by a developed porosity and high surface areas compared to the non-pyrolyzed material due to a thermal decomposition of organic matter and a release of volatiles which by being driven off the material create a network of pores in the organic structure (Monlau et al., 2016). The remaining solid is composed of highly concentrated aromatic carbon clusters forming a graphitic-like layered structure (Al-Wabel et al., 2013; Kambo and Dutta, 2015). The volatile release is more intense at high pyrolysis temperatures and therefore BCS and BCD, which produced at 800°C, were likely to show a highly-ordered porous structure. From Figures 1 (a) and (b), which show SEM images of the BCS and BCD, respectively it is seen that the surface area of both BCs contained pores at various shapes and sizes. A number of irregular folds were common on both surfaces although the two chars displayed significant differences in the other morphological characteristics. The surface of BCS was clearer than that of BCD allowing a number of thin pore walls and a uniformly distributed network of pores to be distinguished (Figure 1(a)). BCD also showed a well-developed porous structure, however, exhibited a rough surface that was characterized by a heterogeneous and pitted structure accompanied by an irregular pore arrangement (Hung et al., 2017).

The surface morphology of BCs appeared to differentiate with the acid treatment (Figure 1). Contrary to these results, Vu et al. (2017) found small differences between the surfaces of a corn-cob BC and its treated with HNO_3 counterpart. However, there are contrasting opinions about the effect of modification on the morphology of a BC. The surface of the raw biomass BC here, was smoother and more homogeneous than that of the M-BCS (Figures 1 (a) and (c)). A similar loss of smoothness and homogeneity was also observed by Li et al. (2019) for a raw and modified BC with manganese. The treatment of biomass char with HNO_3 led to a rougher and more cracked surface containing a great number of pores (Figure 1(c)). This was likely due to the activity of acid since early studies (Li et al., 2014) describe the occurrence of a partial collapse of pore walls with acid processing due to a removal of mineral matter and non-pyrolysed organics contained in BC.

In contrast to what was seen in biomass BC, the modified digestate BC presented a smoother surface than its untreated counterpart (Figure 1(d)). In this case, the bulges observed on the surface of the BCD were replaced by flatter and more compact formations of the surface of M-BCD. An extended network containing pores of all sizes was also visible. Cracking and fracture of micropores due to the introduction of oxygen functional groups in pore walls that were observed for acid-treated BCs (Cao et al., 2022; Li et al., 2014) could not be distinguished in the case of M-BCD.

3.2 AD of corn silage

3.2.1 Substrate properties

The characteristics of the corn silage and inoculum used in BMP tests are shown in Table 3. The pH value of corn silage (5.79) was close to those reported for the specific material (Tišma et al., 2018). However, the C/N ratio of 26 was rather low compared to the standards of corn biomass reported to be in the range of 32 to 45 (Şenol et al., 2020). In principle, a C/N ratio between 20 and 30, with an optimum at 25, is beneficial for AD (Panigrahi and Dubey, 2019). The C/N ratio of corn silage, therefore, implies that the material can attain a significant degree of degradability during AD.

3.2.2 Effect of biochar type on the AD of substrate

Figure 2 presents daily and cumulative biogas and biomethane generation results for the inoculum and corn silage. Daily yields present a peak early in AD indicating that the soluble organics contained in corn silage were likely consumed within the first 8-10 days of digestion. A total biogas amount of 0.526 $m^3kg_{VS}^{-1}$ was produced from the AD of the substrate, which was comparable with the average values reported for the mesophilic digestion of the specific feedstock (Tišma et al., 2018), but lower than

TABLE 2: Mineral composition of BCs before and after modification. Standard deviations from two replicates are shown in parentheses.

Sample	Element ($\%wt_{TS}$)							SUM
	Ca	Al	Mg	Na	K	P	Si	
BCS	0.68 (0.00)	0.00 (0.00)	0.00 (0.00)	0.06 (0.01)	0.30 (0.02)	0.07 (0.00)	0.03 (0.00)	1.14 (0.03)
BCD	14.27 (0.10)	1.39 (0.07)	1.60 (0.10)	1.02 (0.02)	16.60 (0.20)	4.15 (0.03)	7.00 (0.10)	46.03 (0.62)
M-BCS	0.38 (0.01)	0.00 (0.00)	0.00 (0.00)	0.02 (0.00)	0.02 (0.00)	0.07 (0.00)	0.03 (0.00)	0.52 (0.01)
M-BCD	3.78 (0.04)	0.35 (0.02)	0.00 (0.00)	1.36 (0.03)	4.94 (0.04)	1.10 (0.02)	13.48 (0.09)	25.01 (0.024)

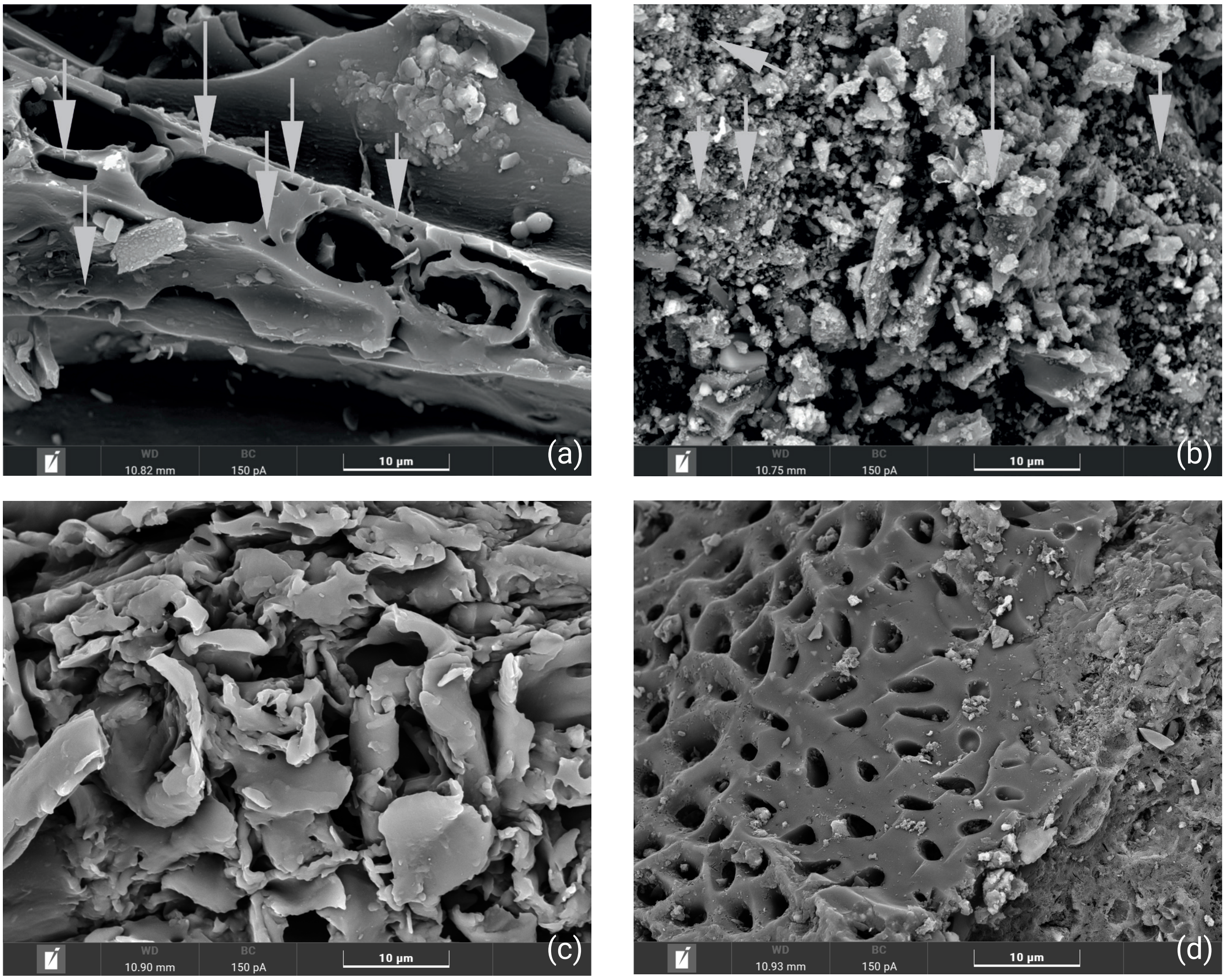

FIGURE 1: SEM images of (a) BCS, (b) BCD, (c) M-BCS and (d) M-BCD.

the biogas released from the AD of corn-derived materials (0.543-0.650 $m^3kg_{VS}^{-1}$) (Zieliński et al., 2019) and higher than that reported for other lignocelluloses such as wheat straw (0.432 $m^3kg_{VS}^{-1}$) (Yadav and Vivekanand, 2021). Total methane generation of 0.308 $m^3kg_{VS}^{-1}$ (Figure 2) was much higher than the total yields from a typical corn silage feedstock (0.153 $m^3kg_{VS}^{-1}$) (Xu et al., 2020) and also exceeded the production from other substrates like mechanically sorted-OFMSW (0.187 $m^3kg_{VS}^{-1}$), wheat (0.263 $m^3kg_{VS}^{-1}$) and rice straw (0.120 $m^3kg_{VS}^{-1}$) (Basinas et al., 2021; Mustafa et al., 2016). Lipid-rich substrates are characterized by enhanced AD performance. Besides, proteins have also positive effect on methane generation potential of a substrate (Xu et al., 2018). Corn silage contained a sufficient amount of proteins (4.26%wt_{TS}) (Table 3) that may explain the large methane production observed.

TABLE 3: Main characteristics of inoculum and substrate.

Parameter	Inoculum	Corn Silage
pH	7.97 (0.01)	5.79 (0.01)
TS (%wt.)	2.98 (0.03)	54.74 (0.14)
VS (%wt_{TS})	73.20 (0.18)	96.68 (0.21)
S (%wt_{TS})	0.49 (0.01)	0.32 (0.01)
C/N ratio	11.73	26.00
Proteins (%wt_{TS})	-	4.26 (0.16)
Carbohydrates (%wt_{TS})	-	0.30 (0.01)

TS=Total solids (105°C), VS=Loss on ignition (550°C)

To investigate the effect of BC on the AD of a lignocellulosic substrate, the biogas and methane generation potential of corn silage were determined in cultures with BCS and BCD addition. The results are shown in Figure 3. From the daily methane generation curves, a first production peak appeared on the third day of AD for all mixtures, which means that BC did not have any significant effect on the decomposition of easily degradable substances of corn. A shoulder existed at the last part of the peak extended from the fifth to twenty-fifth day. Within this period, corn silage showed a significant reduction in the daily methane yield especially on the fourth and fifth day. An extended production of VFA early in digestion and their accumulation might cause a system acidification and eventually a process inhibition. The systems containing BC showed a lower reduction in methane yields (Figure 3). BC due to its high alkalinity can relieve an acid inhibition and concurrently enhance the efficiency of microorganisms to utilize organic acids in AD protecting a system operation (Pan et al., 2019). Methane generation was not abruptly reduced regardless of the type of BC used in the reactor. For the culture containing BCD a slight increase in methane yields was observed from the twenty-fifth to the thirty-second day which was represented by a small peak on the daily methane curve (Figure 3). This peak was not observed in the case of corn silage indicating that the BCD may provoke a degradation of complex substances, such as butyric acid (Ma et al., 2018).

From Figure 3 it is evident that both BC types had a positive influence on methane generation. In particular, cumulative methane production increased from 0.308 $m^3kg_{VS}^{-1}$ provided by the raw corn to 0.374 $m^3kg_{VS}^{-1}$ provided by the culture contained BCS corresponding to an increase of 1.21-fold. The methane generation attained by the culture with BCD addition was smaller (0.347 $m^3kg_{VS}^{-1}$) representing an increment of 1.13-fold (Figure 3). The growth was greater than that appeared in other studies where an increase of 1.10-fold (Luz et al., 2018a; Sunyoto et al., 2016) and 1.12-fold (Fagbohungbe et al., 2016) were reported with addition in the AD of lignocellulosic biomass of various types of BC materials prepared at temperatures between 450-550°C. The lower methane production from the culture with BCD addition was presumably a result of the fact that BCD contained a great proportion of ash, much higher than that of BCS (Tables 1 and 2), and thus its addition in the digester likely produced a cation toxicity effect, eventually having an adverse impact on methane generation (Linville et al., 2017).

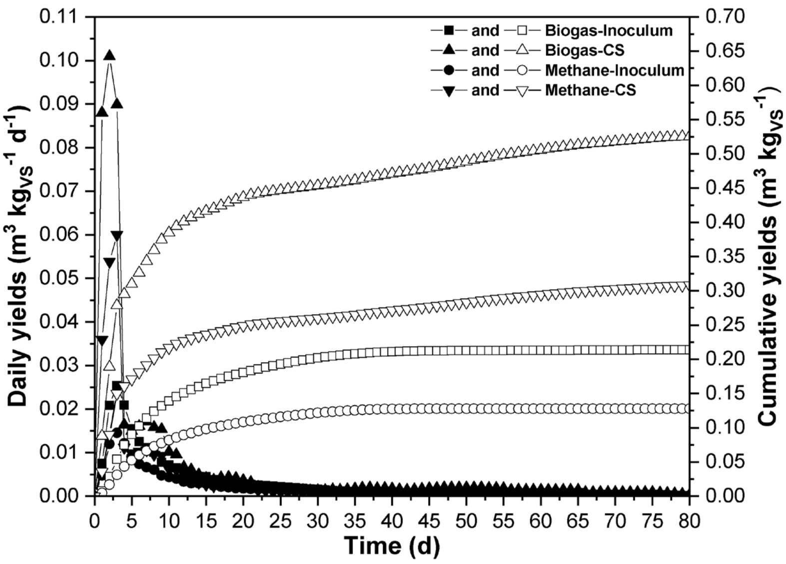

FIGURE 2: Daily (filled points) and cumulative (open points) biogas and methane production during AD of corn silage in BMP tests.

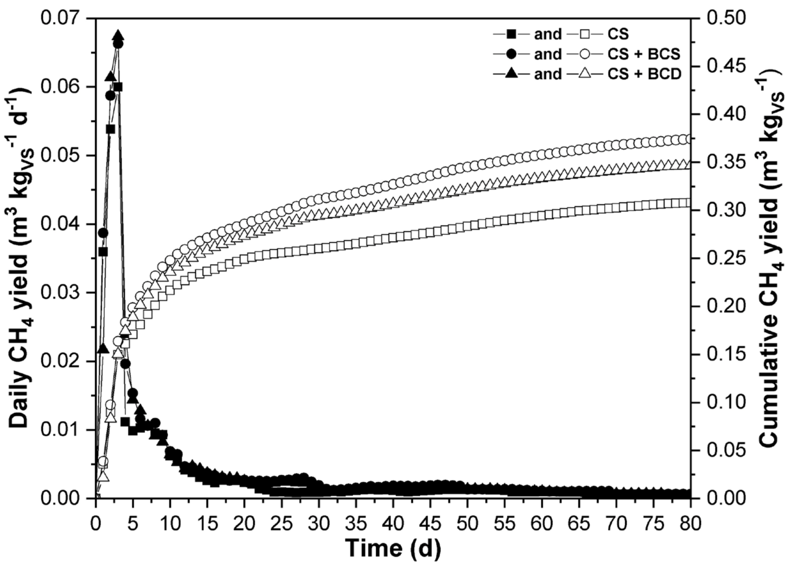

FIGURE 3: Effect of BCS and BCD on the daily (filled points) and cumulative (open points) biogas generation potential of corn silage under mesophilic AD conditions.

3.2.3 Biochar modification: Effect on the AD of corn silage

Oxidized BC can improve more than a non-pretreated BC the AD performance of a substrate (Gao et al., 2021). For this reason, BMP tests were conducted with addition of biomass-derived BC and digestate-derived BC that were previously modified with a nitric acid solution. Daily and cumulative methane generation results are shown in Figure 4. The cultures without and with M-BCS addition exhibited the highest methane generation on the third day of AD (0.060 and 0.045 $m^3 kg_{VS}^{-1} d^{-1}$, respectively) whereas the culture with M-BCD on the fourth (Figure 4). Probably, M-BCD partially inhibited the operation of methanogens. Daily release curve shows that gas yields from the culture with M-BCD addition were significantly low for the first two days providing further proof that a potential inhibition might occurred early in process due to the M-BCD addition (Figure 4). Methane yields recovered on the third day whereas showed a peak (0.031 $m^3 kg_{VS}^{-1} d^{-1}$) on the fourth day which was the maximum methane release rate attained by the specific culture. It should be emphasized here that the peak was lower by 93.6 and 45.2% than those attained by the cultures without and with M-BCS addition, respectively. It seems, therefore, that the addition of M-BCS and M-BCD led to a declined methane production rate.

A second peak that appeared for the AD of raw corn silage after the fifth day was shifted to the eighth and seventh day onwards for the cultures with M-BCS and M-BCD addition, respectively. The peak covered a period until the twenty-fifth day (Figure 4) within of which the reactor with M-BCD released the highest amount of methane followed by the reactor with M-BCS. The culture with M-BCD addition yielded daily a slightly higher amount of methane than the other two cultures during the next twenty-five days and a more significant amount of gas at around the fiftieth and sixty-fifth day of AD. This presumably means that BCD after its oxidation became more effective in promoting the conversion of persistent organic structures contained in corn silage (Kobayashi and Kuramochi, 2022).

Cumulative methane yields from the cultures with and without modified BC addition are included in Figure 4. Corn silage released gas with a high rate even by the first day. Cumulative methane production raised rapidly until the seventh day when the rate started decline and gas yields dropped below those of the culture with M-BCS addition. On the other hand, the culture with M-BCD presented significantly low yields at the initiation of AD and then a much low methane release rate. Nevertheless, the rate was stable enough that methane production became higher than that of the cultures without and with M-BCS addition after fifteen and twenty days, respectively. The two latter cultures consistently produced gas with a low and stable rate until the end of the BMP test. In contrast, methane production curve for M-BCD exhibited two points of maximum methane release rate (inflection points) during the 80 days of AD. This indicates the existence of two degradation regions which was also observed in earlier studies (Kobayashi and Kuramochi, 2022) and attributed to an effect of the BC on the degradation of easily and slowly degradable substrates. Hence, it seems that the M-BCD enabled decomposition of slowly digestible structures in corn silage (Ma et al., 2018).

Total volume of biogas and methane generated for the AD of corn silage with the addition of various types of raw and modified BCs are included in Figure 5. Methane release from the culture with M-BCS was 9% less than that from the culture with untreated BCS indicating that biomass-derived BC lost part of its capability to advance the methane generation when treated with HNO_3. Nevertheless, the two cultures (with untreated and oxidized biomass char) displayed the same total biogas generation (0.640 and 0.639 $m^3 kg_{VS}^{-1}$, respectively). This finding suggest that the M-BCS impeded mainly the total meth-

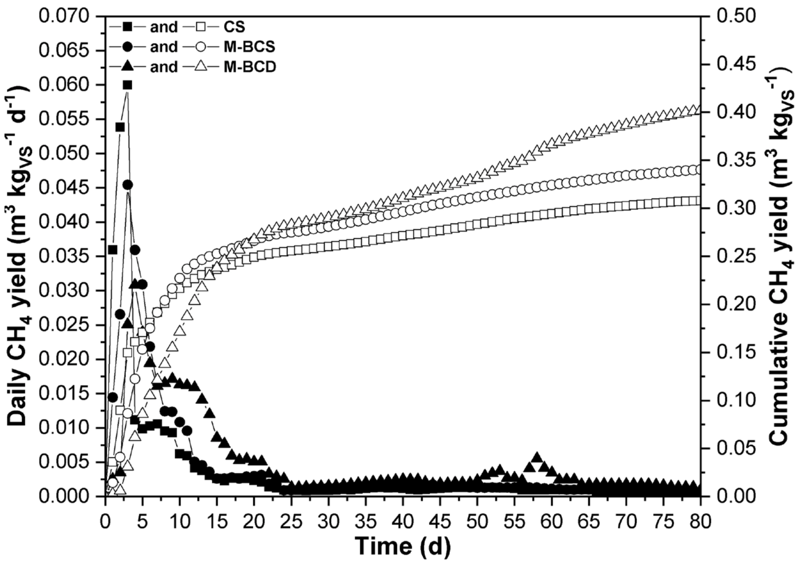

FIGURE 4: Effect of M-BCS and M-BCD on the daily (filled points) and cumulative (open points) methane generation potential of corn silage under mesophilic AD conditions.

anization of corn silage. The reason for the inhibition of methanogenesis could be likely related to the morphology characteristics of BC. As discussed above, biomass BC lost its homogeneity and smoothness of its surface with the treatment with HNO_3 obtaining a rougher and cracked morphology which may provided less support to microorganisms to develop.

Contrary to the BCS, modification of the BCD with HNO_3 led to an increased potential of the material to catalyse the AD process as indicated by the augmented total methane production attained by the culture with M-BCD addition compared to the culture with untreated BCD (Figure 5). The fact that the surface was smoothened, flattered and contained a well-developed network of pores (Figure 1) shows that BC morphology was presumably reason for the performance of the modified BC in an AD system. In addition, the cation toxicity effect of BCD on AD observed due to high proportion of minerals is also expected to be diminished due to the removal of a major part of the ash and minerals by the material with the HNO_3 oxidation (Tables 2 and 3).

Biogas and methane generation attained from the reactor with BC addition could potentially be influenced not only by the properties of BC but also by the generation of H_2S which is known to have an inhibitory effect on AD (Romero-Güiza et al., 2014). H_2S obstructs the process in two ways: competence of sulphate reducing bacteria and methanogens for the consumption of organic substances and a toxic effect that H_2S exerts on methanogenic bacteria by diffusing through their cell membrane into their cytoplasm (Chen et al., 2008). Figure 6 provides results for H_2S evolution over the 80 days of digestion. H_2S yields from most of the cultures with BC remained steadily below those from the culture without BC for the entire digestion period. This suggests that BC was capable to capture H_2S mitigating its effect on the AD, which likely explains an increment of methane and biogas yields from the reactors containing BC (Choudhury and Lansing, 2020).

As seen from Figure 6, H_2S release from the reactors with BCD and M-BCD addition did not follow the same behaviour and especially in the former case H_2S production appeared to be much greater than that from the reactor without BC addition. In particular, for the reactor containing BCD, H_2S yields abruptly increased at extremely high level (>2100 ppmv) even by the first day of digestion, remained at that level for about eight days before being dropped to around 1000 ppmv and then progressively to 300 ppmv until the end of the 80 days of digestion. Parkin et al. (1990) reported significantly hindered biogas release at H_2S concentrations higher than 100ppmv, which might explain the low methane generation observed for the culture with BCD addition. Methane release from the specific culture was higher than that from the reactor without BC and lower than that appeared for the culture with BCS addition. It can be assumed, therefore, that the advantage of an improved methane generation derived by the implementation of BC in the system was at least partially compensated by an inhibition originated from H_2S.

Figure 6 indicates that the culture with M-BCD also displayed a significant H_2S release, however, in this case the yields were at 2050 ppmv only for the initial day of digestion. The abrupt increase of H_2S during the first day coincided with a failure of the system to produce methane (Figure 3). From the second day, H_2S release fell-off to values lower than 100 ppmv where kept until the end of the BMP assay. It is interesting to note that H_2S release from the culture with M-BCD addition was permanently lower than those attained from the other cultures and concurrently the specific culture exhibited higher methane yields. Given that for all the other bioreactors, concentration of H_2S was over 100 ppmv it can be hypothesized that an inhibition in methane generation existed in all cases. It appears, therefore, that the greater methane release from the culture with M-BCD

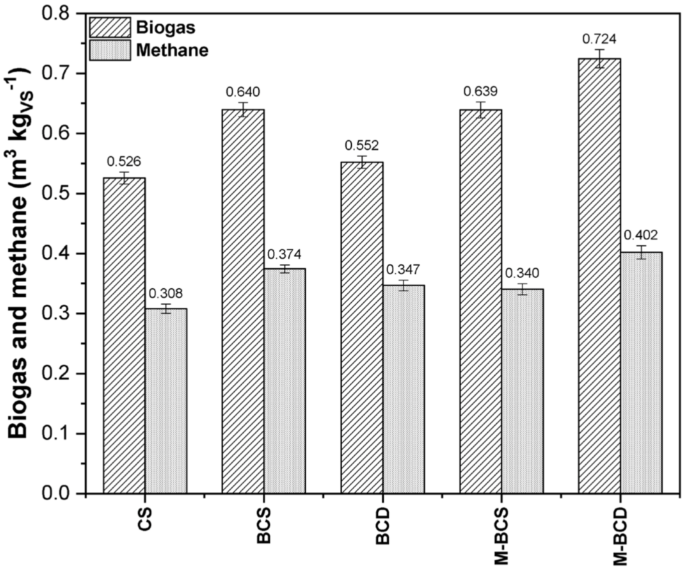

FIGURE 5: Biogas and methane generation potential of corn silage for the cultures without and with BC and modified BC. Mean values±standard deviations from two replicates are shown.

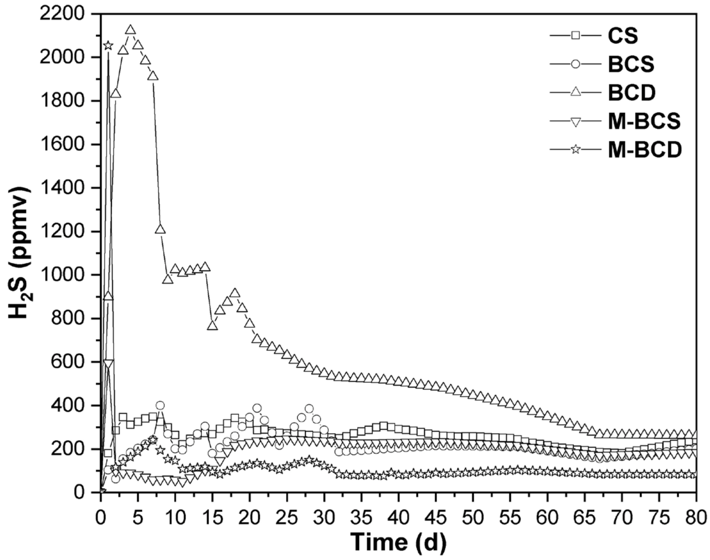

FIGURE 6: Daily hydrogen sulfide release during AD of corn silage incubated with and without BC.

addition compared to the rest of the reactors might be related to a capability of the specific BC to alleviate any inhibition induced by H_2S.

4. CONCLUSIONS

A typical biomass- and a digestate-derived BC were subjected to chemical modification with nitric acid and used as additives in the digestion of corn silage to determine the influence of oxidation on the capability of the different types of BC to improve the efficiency of the AD of biomass.

Both biomass and digestate BC had a positive effect on methane generation from the AD of corn silage. BCD addition improved methane yields from 0.308 $m^3kg_{VS}^{-1}$ released from the culture without BC to 0.347 $m^3kg_{VS}^{-1}$, whilst BCS was more efficient resulting in a total gas release of 0.374 $m^3kg_{VS}^{-1}$. Chemical modification reduced the pH of BCS from 10.29 to 3.10 and that of BCD from 11.54 to 2.8 converting BCs from alkalic to acidic, while concurrently differentiated their surface morphology. For M-BCS ash proportion was minimal at 0.64%wt_{TS} and mineral concentrations were almost nullified (<0.38%wt_{TS}), whereas for M-BCD modification reduced the ash fraction from 54.72 in BCD to 31.31%wt_{TS} in M-BCD and the concentration of each of the Ca, Al, K and P by 70-75%. The culture with M-BCS provided 9% less methane than the culture with the untreated BC, thus the chemical treatment had a slight negative impact on the catalytic activity of biomass char. In contrast, the culture with modified digestate char released the highest amount of gas (0.402 $m^3kg_{VS}^{-1}$) than all cultures. This ascertained to be a result of an increased capability of the material to assist conversion of persistent and slowly digestible organic structures contained in corn silage and to retain the H_2S yields at a level lower than 100 ppm. Therefore, M-BCD presented a higher potential to improve the efficiency of an AD system than the biomass BC (untreated and modified) and this capability could be further improved with a potential enhancement of the H_2S uptake particularly at the initiation of AD process.

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