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Comparative effect of biochar and activated carbon addition on the mesophilic anaerobic digestion of piggery waste in batch mode

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Abstract

A comparative study of the batch mesophilic anaerobic digestion of piggery waste was carried out with the addition of 5% biochar and 5% activated carbon. The results obtained showed that the bioreactors amended with biochar increased cumulative methane production, the kinetic constant for methane production and the COD removal efficiency compared to the control reactors and reactors with activated carbon addition. The maximum methane production and the kinetic constant were 6.9% higher in the reactors with biochar addition compared to the controls; while the COD removal efficiency was 3% higher in the case of biochar addition. In the case of activated carbon, only a slight improvement in anaerobic digestion performance was observed compared to the control.

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KEYWORDS: biochar addition; activated carbon addition; mesophilic batch anaerobic digestion; piggery waste.

Introduction

Biochar is a material produced by the pyrolysis of waste biomass or organic waste from urban life. The utilization of biochar in the soil acts as a reservoir for carbon, thus delaying its release into the atmosphere as CO_2.[1-3] Biochar is produced through different processes such as pyrolysis (300–700 °C; in the absence of oxygen) and hydrothermal carbonization (170–250 °C; water above saturated pressure). Its use in land application has been traditionally proposed as a means for increasing the carbon storage capacity of soils, enhancing their properties and influencing the soil bacterial community and for minimizing the negative effects of heavy metals on soil. [3-5] The utilization of biochar in anaerobic digestion to improve biogas yield and process stability has been evaluated. Mumme et al.[6] assessed two types of biochars (pyrochar and hydrochar) for biogas production and to prevent ammonia inhibition in batch digesters at mesophilic temperatures. They found that both biochars prevented mild ammonia inhibition. However, for pyrolytic char, no differences were found compared to the control; whereas for hydrochar the methane yield increased by 32%. Cai et al.[7] reported that the addition of biochar (at doses of 2.5, 0.625 and 0.5 g/g of waste) in the anaerobic digestion of food waste in batch mode with inoculum-to-substrate ratios of 2, 1 and 0.8 reduced the lag phase in the ranges of 10.9-20.0%, 43.3-54.4%, and 36.3-54.0%, respectively. In the same way, Luo et al.[8] found that the addition of 0.5-1 mm biostable biochar (10 g/L) to mesophilic anaerobic digesters inoculated with crushed granules (1 g VS/L) and fed with 4, 6 and 8 g/L glucose shortened the methanogenic lag phase by 11.4%, 30.3% and 21.6% and raised the maximum methane production rate by 86.6%, 21.4% and 5.2%, respectively, compared with the controls without biochar. Capson-Tojo et al. [9] found that the addition of biochar (10-100 g/L) combined with trace elements ($FeCl_3$; 0.1–0.2 g Fe/L) favoured the digestion kinetics and improved the maximum methane production rates from 897 up to 1494 mL/day and the average daily methane production rates from 298 up to 369 mL/day. Indren et al.[10] studied biochar addition in the high-solid anaerobic digestion of poultry litter at three feedstocks (poultry litter) to inoculant (wastewater treatment plant sludge) (F/I) ratios. They found a reduction of 52% in the lag time for digesters with biochar. However, the addition of biochar could not overcome ammonia inhibition and did not significantly increase the methane yield significantly.

The research of Caivu et al. [11] determined that biochar addition had a positive effect on improving the anaerobic digestion performance of beer lees. The maximum cumulative methane production and yield with biochar were improved by 82.9 and 82.6%, respectively, under thermophilic conditions and by 47.2 and 46.8%, respectively, under mesophilic conditions when compared to the control.

Dudek et al. [12] found that biochar addition at doses of 0, 1, 3, 5, 10, 20, 30, and 50% of biochar weight related to the substrate weight (brewer spent grain) ratio in mesophilic batch anaerobic digestion increased the reaction rate constant from 1.53 d^{-1} in control reactors to 1.89 d^{-1} with biochar addition at a dose of 10%.

The research of Li et al.[13] concluded that the addition of manganese oxide-modified biochar composite (MBC) during sewage sludge anaerobic digestion improved the buffering capacity, and increased the methane production and removal of intermediate acids, hence stabilizing the process operation. They concluded that the application of MBC enhanced methane production and the cumulative methane yield by up to 121.97 %, improving metal stabilization in the digestate as compared to the control.

Yin et al.[14]applied a biochar dose of 1 g/g dry matter to microbial electrolysis cells (MECs) for methane production from waste activated sludge (WAS). Biochar accelerated methane production by 24.7% and enhanced soluble COD removal efficiency by 17.9% compared to the control group. Zhang et al.[15] evaluated the effect of nine types of biochar generated from three different feedstocks on the anaerobic digestion (AD) of sewage sludge. They found that methane production could be significantly enhanced by all types of biochar used in the test. The maximum cumulative methane yield of 218.45 L/kg VS was obtained for the culture with corn straws pyrolyzed at 600 °C, which also exhibited the largest specific surface area.

It has been found that addition of activated carbon also improves performance in anaerobic digestion processes. Zhang et al.[16] used activated carbon as an additive in the anaerobic digestion of food waste. The results showed that activated carbon accelerated the decomposition of edible oil in food waste, enhancing the conversion of food waste to methane. Pan et al. [17] suggested that granular activated carbon (GAC) could improve the methane production from mesophilic anaerobic digestion by facilitating a direct interspecies electron transfer. However, they consider that it is unclear how could enhance methane production from thermophilic anaerobic digestion and its roles in stimulating methane production have not been clarified up to now. Therefore, the effect of GAC addition on methane production from thermophilic anaerobic digestion was studied through batch experiments with sodium acetate as substrate. The results indicated that the presence of GAC may play a role in the enrichment of specific species and accelerate the newly formed pathway mediated by thermophilic microbiota. Uysal and Mut[18] compared the effect of Pectin-coated magnetite (Fe_3O_4) nanocomposite (PNC), granular activated carbon (GAC) and control anaerobic digesters. The highest biogas production was determined as 554.3 ± 0.5 mL/g-dry waste in the sample containing 2.0 g PNC/g VSS, and the percentage of methane was measured as 43.5 ± 0.3%. The highest methane production was determined as 254.2 ± 0.9 mL/g dry waste from the reactors containing these two materials at equal concentrations of 1.2 g PNC/g VSS and 1.2 g GAC/g VSS, the percentage of methane in the cumulative biogas volume was measured as 46.7 ± 0.1% in the reactor containing PNC. The highest methane content was measured as 48.2 ± 0.1% from the reactor containing 2.0 g GAC/g VSS. [18]

Zhang et al. [19] assessed the effect of activated carbon addition on methane production by comparing the anaerobic digestion performance among the anaerobic mono-digestion of food waste, co-digestion of food waste and chicken manure, and co-digestion of food waste and waste-activated sludge. The results showed that the addition of activated carbon improved methane yield by at least double through the enrichment of bacteria and archaea in the mono-digestion of food waste. The effects tended to be minimal in co-digestion of co-substrates such as chicken manure and waste-activated sludge.

Calabro et al. [20] used granular activated carbon (GAC) combined with an alkaline pre-treatment to enhance methane production during the semi-continuous anaerobic digestion of orange peel waste (OPW). Two groups of experiments, A and B, were carried out. Experiment A was performed to verify the maximum OPW loading and to assess the effect of pH and nutrients on the process. Experiment B studied the effect of alkaline pre-treatment alone and of alkaline pre-treatment aided by activated carbon addition to the process. The preliminary results showed that the OPW alkaline pre-treatment after the addition of a moderate amount of GAC can render the anaerobic digestion of OPW sustainable as long as the organic loading does not exceed 2 g VS/(L·day) and the nutrients are supplemented. The experiment in which GAC was added after alkaline pre-treatment resulted in the highest methane yield and reactor stability. Bardi and Rad [21] demonstrated that addition of 1 g of sorghum-based activated carbon (4 g TS/L) to the anaerobic co-digestion of sewage sludge and food waste stabilized the system, and reduced ammonia and TVFA concentration. In addition, the methane yield increased from 201 to 272 mL/g VS, solid retention time (SRT) reduced by 34%, and total-COD removal increased to 79.4 % in the reactor with activated carbon addition.

According to the literature reviewed, both biochar and activated carbon addition contribute to improving the anaerobic digestion process by the reduction of the lag phase time, increasing the methane yield, the maximum cumulative methane volume and the kinetic constant value. However, to the best of our knowledge, the comparative application of biochar and activated carbon in the batch anaerobic digestion of piggery waste has not been reported up to date. Therefore, the aim of the present paper was to evaluate the anaerobic digestion of piggery waste with addition of biochar and activated carbon in a comparative manner. The influence of both additions on methane production and process kinetics was also comparatively assessed.

Materials and methods

In order to carry out the experiments glass reactors of 1.5 liters operational volumes were used. Six reactors were used with only piggery waste (controls), three with piggery waste plus biochar and three with piggery waste plus activated carbon.

The reactors used as control received 833 ± 1.3 g of inoculum and 654 ± 1.1 g of piggery waste, which represents an inoculum to substrate ratio of 1.27 g/g respectively.

The reactors with biochar addition received 847.3 ± 0.1 g of inoculum and 652.78 ± 0.06 g of piggery waste, which represents a ratio of 1.30 g/g and 75 g of biochar, which represents a dose of 5% in weight. This dose was selected on the basis of previous experiments and data reported in the literature. [7, 12, 13] In the case of activated carbon, the amount of inoculum was 847.34 ± 0.01 g and 653.89 ± 0.23 g of piggery were added, which represents an inoculum-to-waste ratio of 1.3. 75 g of activated carbon were also added, which corresponds to a dose of 5% in weight of this substance. The experiments were carried out at a temperature of 37 ^{0}C, corresponding to the mesophilic range. The experiments were performed over 62 days until achieving the maximum cumulative methane production and the methane generation ceased.

The characteristics and features of the piggery waste used in the experiments are summarized in Table 1.

The biochar used in the experiments was produced from the pyrolysis of a mixture of agricultural residues (separated digestate (2/3) and care wood residues (1/3)) at a temperature around 500 °C. The physical characteristics of biochar were determined by Quantachrome Instruments, version 5.02, except for the apparent density, which was taken from the literature.[3] Table 2 shows the main physical characteristics of the biochar and activated carbon used.

Table 3 shows the chemical characteristics of the biochar and activated carbon used in the experiments.

During the experiments daily biogas production was automatically measured, samples of biogas were analyzed for the determination of CO_2 and CH_4 concentrations using a portable gas analyzer with an infrared chemical sensor BIOGAS 5000, Geotechnical Instruments (UK) Ltd. The volumes of gases were corrected under normal temperature and pressure conditions.

The Chemical analyses of total and volatile solids and chemical oxygen demand (COD) were carried out following standard methods. [22]

Data were expressed as the mean value with the standard deviation in each case. The differences concerning the variables were tested for significance with the t-Student test. A 5% significance level was considered in all cases.

3. Results and Discussion

The maximum average cumulative biogas produced for the control reactors was 4007 ± 522 mL; while for the reactors with activated carbon the value was 4093 ± 204 mL; and finally, for the reactors with biochar, the final average value was 4236 ± 149 mL. Therefore, the differences between the control reactors and the reactors with biochar and activated carbon were not significant.

The average percentages of methane in the biogas for the control reactors, reactors with biochar and with activated carbon addition were 78.6 ± 1.4%, 81.0 ± 1.1% and 75.2 ± 1.2 %, respectively. Therefore, at the end of the experiment, the reactors with biochar produced a biogas with a higher percentage of methane. This result could be due to the presence of trace metals in biochar, which can stimulate methanogenic microorganisms [5, 12] as can be appreciated in Table 3. It is well known that essential trace elements such as manganese (Mn), cobalt (Co), nickel (Ni), zinc (Zn), and iron (Fe) are very important for the methanogenesis step of anaerobic digestion, which involves the action of acetyl-CoA synthase and methyl coenzyme M reductase to catalyze key metabolic steps and requires sufficient amounts of Fe, Ni, and Co;[23] while some methanogens may require molybdenum (Mo), copper (Cu), and selenium (Se).[23] Therefore, a deficiency of these essential elements may affect the functions and activities of key enzymes, and change the environmental conditions, such as the oxidative-reductive potential for microbial growth, and result in digester failure, e.g., caused by excessive accumulation of volatile fatty acids (VFAs) and ammonia. [23] Thus, trace metal supplementation through biochar is another approach to reduce VFA accumulation during the anaerobic digestion of substrates that contains low concentrations of these metals. In the same way, it has been demonstrated that the addition of biochar also facilitates the selective enrichment of potential direct interspecies electron transfer (DIET) partners such as *Methanothrix* and *Geobacter* spp. for enhancing the DIET process.[24] Biochar also simultaneously enhanced the production and degradation of intermediate acids.[8] The fingerprint and sequencing analysis used to examine the spatial distribution and temporal evolution of microbial communities revealed that proportion of Archaea was higher in the biochar-added treatments and in the tightly-bound fractions. *Methanosarcina* located in the tightly-bound fractions on the biochar surface, and was most abundant in the larger 2-5 mm biochar particles.

Methanosaeta was enriched in the loosely-bound fractions by all-size biochar particles and within the tightly-bound fractions by small biochar particles.[8]

The explanations for the preference of those bacteria for the biochar surface, included 1) porous biochar promotes the biofilm growth, and 2) porous biochar promotes direct electron or hydrogen transfer between syntrophs and methanogens. [8]

Table 4 summarizes the average cumulative methane volume produced during the experiments for the digestion of piggery waste, piggery waste plus biochar and piggery waste plus activated carbon.

Table 4 shows that at the first 8 days the cumulative methane production from piggery waste with biochar and with activated carbon were lower compared to that of the control. However, after this time, the cumulative methane production in the reactors amended with biochar and with activated carbon was 7-10% and 4% higher respectively, than that obtained from the controls, and these differences were maintained until the end of the experiments. Similarly, Cai et al. [7] found that the addition of biochar to the batch anaerobic digestion of food waste at inoculum-to-substrate ratios of 2, 1 and 0.8 increased the maximum methane production in the ranges of 100-275%, 100-133% and 33-100%, respectively.

The average methane yield for the reactors with biochar was 341 ± 49 L/kg VS added; while for the control reactors this value was found to be 330 ± 26 L/kg VS added. Finally, for the reactors amended with activated carbon, the methane yield was 295 ±7 L/kg VS added. These results showed that there were not significant differences in the methane yield between reactors with biochar compared to the controls. On the other hand, the methane yield was lower from the digesters with activated carbon. By contrast, Gomez et al. [5] reported an increase in the methane yield from 298.7 to 395.4 L/kg VS when biochar obtained from the residual biomass of almond shell (at 550 °C) was added to anaerobic reactors treating swine manure compared to controls without biochar amendment.

The maximum methane production values (G_M) were 3088 ± 312 mL, 3304 ± 125 mL and 3176 ± 73 mL for the reactors with piggery waste (controls), the reactors with piggery waste plus biochar and the reactors with piggery waste plus activated carbon, respectively. The trend in these results coincided with that obtained by Caivu et al.[11] for anaerobic reactors with biochar addition to treat beer lees. In the same way, Gomez et al. [5] achieved a 39% improvement in methane production in reactors supplemented with biochar compared to control reactors when treating swine manure.

Figure 1 shows the variation in average cumulative methane volume with time for the control reactors, reactors with biochar and reactors with activated carbon.

Figure 1 shows typical curves of variation of the cumulative methane production as a function of the digestion time in a batch anaerobic digestion process. The curves can be divided into three periods, or stages. An initial period or lag stage of approximately 8 days, in which the inoculum was adapting to the characteristics of the substrate with low volume of methane production; a second period between day 8 and day 25, when an accelerated (exponential) production of methane was observed; and finally, a period in which methane production decreased due to the exhaustion of the organic matter in the substrate remaining with more recalcitrant compounds. A previous study revealed that the addition of biochar reduced the lag time by a greater percentage in digesters treating poultry litter with higher total solid contents.[10] There was a 17, 27 and 41% reduction lag time due to biochar addition with total solid contents of 5, 10 and 20%, respectively.[10] According to the literature reviewed [6, 25] the process kinetics follows a first-order model through the following equation:

$$G= G_M(1-e^{-kt}) \qquad (1)$$

Where G is the cumulative methane volume produced (mL) at time t (days); G_M is the maximum volume of methane accumulated (mL); t is the digestion time (days) and k is the reaction or kinetic constant (day^{-1}).

In order to determine the *k values* for each case studied, equation (1) can be linearized as follows:

$$\mathrm{Ln}[G_M/(G_M-G)]=k\cdot t \qquad (2)$$

Therefore, the plot of $\mathrm{Ln}[G_M/(G_M-G)]$ versus the digestion time (t) should give a straight line with the intercept equal to zero and the slope equal to the value of k.

The average k values for the reactors with biochar and the reactors with activated carbon were in both cases 0.062 d^{-1} with a coefficient of variation (CV) of 5 %; while for the control reactors the kinetic constant value was 0.058 d^{-1} with a CV of 5 %. Therefore, the addition of biochar and activated carbon increased the rate of methane production by 6.9% compared to the control. This increase was lower than those obtained by Luo at al.[8], Capson-Tojo et al.[9] and Zhang et al.[19] . However, in these reported results the biochar doses applied were higher than those used in the present research and the types of wastes used were also different. Kinetic constant values (0.086 d^{-1}) somewhat higher than those attained in the present research were reported by Mumme et al. [6] in the anaerobic digestion of nitrogen-rich substrates (in batch mode for 63 days at 42 °C) when pyrochar was added to the reactors; while these values decreased to 0.035 d^{-1} when hydrochar was supplemented in the reactors. For pyrochar, no clear effect on biogas production was observed; whereas hydrochar increased methane yield by 32%.[6]

It was recently reported [12] that the kinetic constant (*k*) was not improved by biochar addition in the anaerobic digestion process of brewer's spent grain, and the addition of 10 and 20% biochar even decreased *k* compared to the 0% variant (control reactor). A significant decrease in *k* was also observed for the doses of 10, 20, and 30% when compared to the 5% biochar (1.89 d^{-1}) assays.[12] On the contrary, Cheng et al. [25] observed that the first-order kinetic constant (*k*) increased from 0.029 to 0.052 d^{-1} when the dosage of biochar augmented from 2 to 10 g in the anaerobic digestion of piggery wastewater with rice straw-derived biochar addition under no ammonium stress.

The estimated average COD removal efficiencies were 50.2 ± 5%, 53.6 ± 2% and 51.6 ± 1% for control reactors, reactors with biochar and reactors with activated carbon, respectively. The highest efficiency of COD removal was found for reactors with biochar compared to the controls although the difference was only by 3%. In the case of activated carbon, the differences in COD removal efficiencies were not significant compared to that observed for the control. This trend coincided with that observed for the cumulative methane production and the maximum methane produced during the experiments. A recent study performed by Cheng et al. [26] assessed the impact of a rice straw-derived biochar on the anaerobic digestion of piggery wastewater under different ammonium stress levels. This study revealed that under no ammonium stress level, the COD removal rate was increased from 70.68 to 83.75%, and biogas production was increased from 1293 mL to 2306 mL with the increase in biochar dosage from 0 g to 15 g. When the addition of biochar increased from 0 g to 15 g, the COD removal rate was increased from 38.13 to 70.38% and the biogas yield was increased from 382 mL to 1878 mL under a high ammonium stress level. [26]

Cruz-Viggi et al. (2017) [27] claimed that the addition of electrically conductive biochar particles is an effective approach to enhance the anaerobic conversion of organic wastes by promoting syntrophic associations between acetogenic and methanogenic microorganisms. Collectively, the results of this study suggest that biochar materials specifically favoured the growth of *Methanosarcina*-like archaea over *Methanosaeta*-like archaea. Likewise, high-throughput sequencing analysis of anaerobic digesters treating food waste and sewage sludge at thermophilic temperatures using sawdust-derived biochar (SDBC) detected that SDBC considerably changed the microbial population structure, resulting in enrichment in *Tepidimicrobium* and *Methanothermobacter*-two microorganisms with the ability for extracellular electron transfer. [28]

Activated carbon has been found to promote methane production due to the absorption of inhibitive sulfide, the reduction of organic shock loading impact or the acceleration of methanogenesis during digester start-up [8]. Activated carbon can also facilitate direct interspecies electron transfer *from Geobacter metallireducens* and *Geobacter sulfurreducens* because it is highly conductive. This transfer may be beneficial in methanogenic systems. [8]

4. Conclusions

The experimental results obtained demonstrated that the addition of biochar and activated carbon at doses as low as 5% contributed to enhancing performance of the anaerobic digestion of piggery waste.

An increase in the cumulative methane production was observed in the reactors with biochar and activated carbon compared to the controls. However, the best results were obtained in the reactors amended with biochar with a higher percentage of methane in the biogas, maximum cumulative methane volume and higher COD removal efficiency compared to the controls and to reactors with activated carbon addition. It was also found that the kinetic constants in the case of biochar and activated carbon additions were similar and higher when compared to those obtained for the controls.

It can also be concluded that the best results obtained with the addition of biochar could be attributed to the presence of trace metals, which can stimulate the anaerobic digestion process.

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FIGURE CAPTIONS

Figure 1. Cumulative methane production (mL) as a function of the digestion time (*t*) with a percentage of error of 5 %.

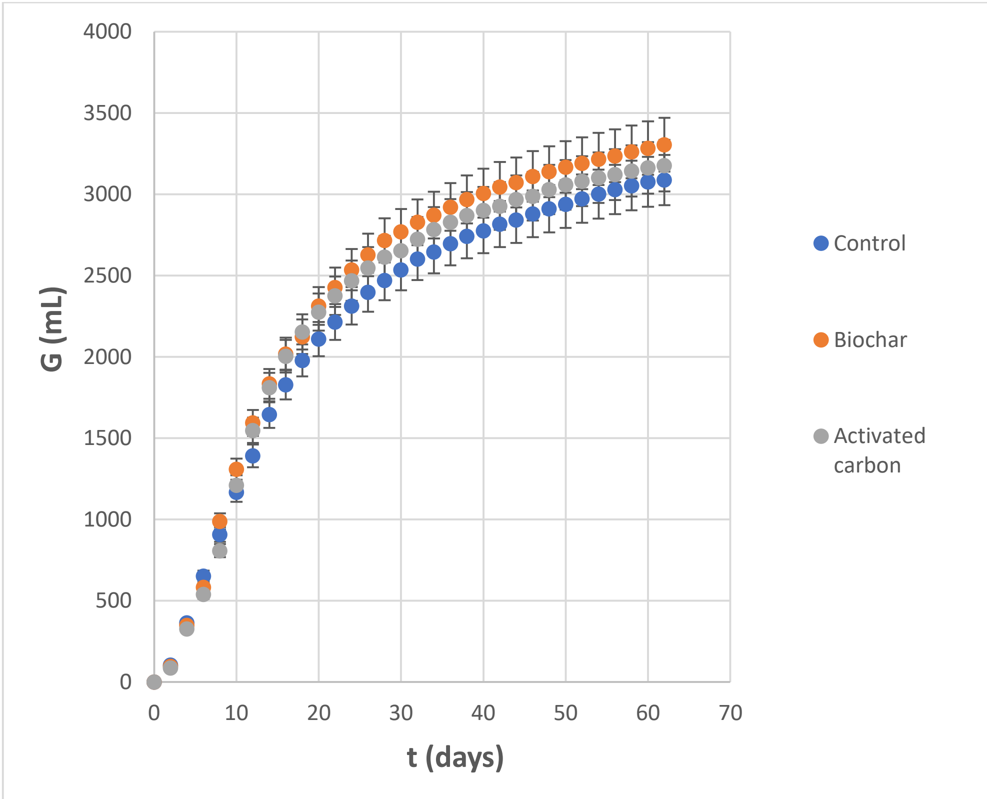
G (mL)
4000
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
t (days)
Control
Biochar
Activated carbon

Figure 1

Table 1. Characteristics and features of the piggery waste used in the experiments.

Parameter	Units	Average value	Standard deviation
Total solids (TS)	%	2.50	0.07
Volatile solids (VS)	% of TS	65.1	3.7
pH	-	7.4	0.1
$N\text{-}NH_4^+$	mg/L	1064	18
TKN	mg/L	1620	50
COD	mg/L	26834	4491

Table 2. Physical characteristics of biochar and activated carbon used in the experiments.

Parameter	Units	Biochar Average value	Activated carbon Average value
Apparent density	g/cm^3	0.30-0.43	0.44
External surface area	m^2/g	107.80	966.50
Micropore area	m^2/g	101.63	541.68
Micropore volume	cm^3/g	0.13	0.60
Micropore ratio	nm	1.68	0.88

Table 3. Chemical characteristics of biochar and activated carbon used in the experiments.

Parameter	Units	Biochar Average value	Activated carbon Average value
Total Solids	%	65.26	95.05
Volatile Solids	%	37.85	73.30
pH	-	9.02	9.18
$N\text{-}NH_4^+$	mg/kg of TS	84.50	136.30
C	% of TS	35.83	93.96
S	% of TS	0.32	0.46
H	% of TS	1.89	2.54
Al	mg/kg of TS	1184	1375
Ca	mg/kg of TS	21685	6349
Cd	mg/kg of TS	0.09	0.15
Co	mg/kg of TS	0.13	0.17
Cr	mg/kg of TS	11.91	4.18
Cu	mg/kg of TS	37.33	25.89
Fe	mg/kg of TS	2972	887
K	mg/kg of TS	10388	8134
Mg	mg/kg of TS	2136.50	239.10
Mn	mg/kg of TS	441.0	110.30
Mo	mg/kg of TS	2.65	2.78
Na	mg/kg of TS	2100	1914
Ni	mg/kg of TS	3218	9483
P	mg/kg of TS	6514	450.60
Pb	mg/kg of TS	8.33	1.94
Zn	mg/kg of TS	91.55	15.29

Table 4. Variation in the cumulative methane production with time during the experiments.

t (days)	Cumulative volume of methane (mL) Piggery waste	Piggery waste plus biochar	Piggery waste plus activated carbon
0	0	0	0
2	104	97	87
4	364	349	327
6	651	582	539
8	908	988	808
10	1166	1309	1211
12	1391	1594	1548
14	1645	1834	1811
16	1829	2018	2004
18	1979	2124	2153
20	2109	2313	2276
22	2215	2428	2376
24	2314	2536	2469
26	2398	2627	2548
28	2471	2716	2614
30	2536	2770	2654
32	2602	2828	2725
34	2645	2873	2783
36	2697	2922	2828
38	2743	2968	2871
40	2776	3006	2900
42	2817	3045	2928
44	2843	3072	2967
46	2880	3109	2989
48	2911	3139	3029
50	2940	3167	3058
52	2973	3191	3080
54	3001	3217	3102
56	3029	3237	3121
58	3053	3261	3144
60	3077	3283	3163
62	3088	3304	3176