ENHANCING THE ANAEROBIC BIOMETANIZATION OF SWINE MANURE WITH GRANULAR ACTIVATED CARBON ADDITION

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ABSTRACT

This work investigated the effect of granular activated carbon (GAC) on methane-rich biogas production in semi-dry and dry anaerobic digestion (AD) of swine manure. Adding 20 g/L GAC increased methane yield from 3 to 154-155 mL CH_4/gVS with raw and pretreated manure, respectively. Thus, no significant difference was found after pretreatment. In semi-dry AD, with pretreated manure, adding 10 g/L GAC yielded 190 mL CH_4/gVS, a value 21% higher than 20 and 30 g/L GAC. However, the kinetics were more favorable for 20 g/L GAC, according to the Modified Gompertz model, which best described the process. In dry AD, the best condition was with 30 g/L GAC (157 mL CH_4/gVS), followed by 20 and 10 g/L GAC (127 and 18 mL CH_4/gVS).

Keywords: Anaerobic digestion. Swine manure. Granular activated carbon. Pretreatment. Biogas.

1 INTRODUCTION

According to the United States Department of Agriculture, pig farming is one of the world's largest agricultural activities, with global animal protein exports totaling 12.3 million tons in 2022.[1] It is estimated that around 300 million liters of liquid pig manure are generated daily, containing a variety of pollutants, such as organic matter, nitrogen, phosphorus, heavy metals, antimicrobials, and pathogens, that can contaminate the environmental, if not managed properly.[2] Then, correctly managing organic waste is a major challenge for the livestock sector.

Since swine manure is rich in proteins, lipids, and carbohydrates, it is an excellent substrate for biogas production from anaerobic digestion (AD), a biotechnological process capable of converting organic matter into biomethane, which can be used as a source of heat and electricity, reducing dependence on fossil fuels and emissions associated with its use.[3] The AD has three classifications based on the total solids (TS) content of the system: wet (TS < 10%), semi-dry (10% ≤ TS < 15%), and dry (TS ≥ 15%). Dry and semi-dry AD have advantages, such as the possibility of execution in smaller reactors and reduced water used.[4] On the other hand, it presents biological and technological disadvantages due to the excess of solids in the reactor, such as the difficulty of mixing and homogenizing the medium, consequently affecting methane production due to the deficiency in the diffusive transport of soluble and intermediate compounds.[5]

AD is divided into four stages: hydrolysis, acetogenesis, and methanogenesis, in which bacteria carry out the first three steps, while archaea do the last. Fermentative bacteria and methanogenic archaea have complementary metabolisms, requiring syntrophy for electron exchange, which can be indirect or direct.[6] Direct Interspecies Electron Transfer (DIET) is faster and more energy efficient than indirect mechanisms, as it does not require complex enzymatic steps to produce, consume, and diffuse process redox mediators.[7] This direct mechanism can occur through conductive materials, such as granular activated carbon (GAC), a low-cost, lightweight, chemically stable conductive material that has high biocompatibility, can act as an adsorbent for toxic compounds, allows the fixation of microorganisms without forming aggregates, and can replace conductive pili during DIET, that allows the transfer of electrons from cell to cell.[8]

Therefore, this work sought to evaluate strategies to enhance the anaerobic biometanization of swine manure by adding granular activated carbon, investigating the influence of thermo-alkaline pretreatment, TS content, and GAC addition dosage.

2 MATERIAL & METHODS

Swine manure (SM) was collected in a pig farm located at the Federal University of Ceará (Fortaleza - CE), in the Department of Animal Science, by scraping the residue in the pens. The thermal-alkaline pretreatment of swine manure was carried out with 3% w/v NaOH at a proportion of 60% mass/volume and incubation in an autoclave at 121 °C for 30 minutes. The anaerobic inoculum was sludge collected from the wastewater treatment plant of a brewery located in Pacatuba, Ceará, Brazil.

The Biochemical Methane Potential (BMP) tests were carried out in batch mode and triplicate in 300 mL borosilicate bottles with a useful volume of 70 mL and 230 mL of headspace. The concentrations of TS were 10 and 15%, adjusted with the addition of deionized water. All assays were prepared with a substrate/inoculum ratio of 1 $gVS_{substrate}/gVS_{inoculum}$. Macro and micronutrients were added in appropriate concentrations, pH adjustment to 7, and addition of sodium bicarbonate (0.1g/gTS) to buffer the system. Granular activated carbon – GAC (Sigma-Aldrich, Saint Louis, MO, USA) was added in various conditions.

The conditions evaluated were sludge and raw swine manure at 10 and 15% TS (10RSM and 15RSM) and with GAC addition at a concentration of 20 g/L ($10RSM_{GAC20}$ and $15RSM_{GAC20}$); sludge and pretreated swine manure at 10 and 15% TS (10PSM and 15PSM); sludge, pretreated swine manure and nylon (20 g/L) at 10 % TS ($10PSM_N$). The other media contained sludge and pretreated manure at 10 and 15% TS with 10 g/L GAC ($10PSM_{GAC10}$ and $15PSM_{GAC10}$), 20 g/L GAC ($10PSM_{GAC20}$ and $15PSM_{GAC20}$) and 30 g/L GAC ($10PSM_{GAC30}$ and $15PSM_{GAC30}$).

The bottles were sealed with butyl rubber stoppers and purged with N_2 for 1 minute to condition in an anaerobic environment. Then, they were placed in a shaker incubator (MA-420, Marconi LTDA, Brazil) and kept under orbital agitation to promote continuous mixing at 150 rpm at a mesophilic temperature of 37 °C for 90 days until methane production stabilizes.

At the beginning and end of the experiment, the following analyses were carried out: pH, solids series, total organic carbon – COT_s, and ammonia nitrogen of the soluble fraction. Biogas quantification was carried out by measuring gauge pressure in each reactor. Biogas composition was analyzed on a gas chromatograph with discharge detection by dielectric barrier ionization (GC-BID, *gas chromatography-barrier ionization discharge*) (GC BID-2010 Plus, Shimadzu Corporation, Japan), equipped with a Select Biodiesel GC Column, (15 mx 0.32 mm) (Agilent Technologies Inc., USA).

3 RESULTS & DISCUSSION

According to the data obtained (Table 1), in semi-dry AD, the reactors with pretreated manure without additives (10PSM) and with the addition of nylon ($10PSM_N$) showed an increase of 67-93% in TOC_s, while for the reactors with GAC ($10PSM_{GAC10}$, $10PSM_{GAC20}$ and $10PSM_{GAC30}$), there was a reduction 42-66% of TOC_s. The TOC_s increase phenomenon is explained by the initial organic matter hydrolysis, which happened in all reactors. However, its reduction occurs with the conversion of organic matter into methane, which only occurs effectively in reactors with GAC addition.

Table 1 Total organic carbon soluble, biogas, and methane yields and biogas composition.

Reactors	TOC_s (mg/L)		Biogas Yield (mL/gVS)	Methane Yield (mL/gVS)	Methane composition (%)
	Initial	Final			
10RSM	5,328	11,687	69^a	3^a	5^a
$10RSM_{GAC20}$	4,684	1,664	276^b	154^b	56^b
10PSM	7,356	12,743	73^a	3^a	4^a
$10PSM_N$	6,410	12,612	76^a	3^a	4^a
$10PSM_{GAC10}$	7,460	4,405	361^c	190^c	53^b
$10PSM_{GAC20}$	6,744	2,695	276^b	155^b	56^b
$10PSM_{GAC30}$	6,388	2,168	276^b	158^b	57^b
15RSM	5,990	15,284	56^a	2^a	4^a
$15RSM_{GAC20}$	5,813	4,047	201^d	111^d	55^b
15PSM	9,195	15,327	97^a	8^a	8^a
$15PSM_{GAC10}$	6,994	15,493	72^a	18^a	25^c
$15PSM_{GAC20}$	6,323	6,393	$251^{b,d}$	127^d	51^b
$15PSM_{GAC30}$	5,989	4,182	290^b	157^b	54^b

The control group $10PSM_N$ was used to verify whether the effect of adding GAC was, in fact, due to its capacity as a conductive material or just because it is a support medium that allows biofilm formation. The biogas and methane production yield of the nylon condition ($10PSM_N$ - 76 and 3 mL/VS of biogas and CH_4) was like that of the condition without additive (10PSM - 73 and 3 mL/VS of biogas and CH_4). When adding 20g/L GAC ($10PSM_{GAC20}$), the biogas and methane yield increased to 276 and 155 mL/VS, respectively. This result demonstrates that, even when added at the same concentration, the conductive characteristics of GAC prevailed over the physical support material property also present in nylon; that is, the high biogas production and its methane content from the $10PSM_{GAC20}$ reactor is most likely due to the promotion of direct interspecies electron transfer (DIET) and previously described GAC properties.

Regarding the GAC addition dosage study, in the semi-dry AD (10 %TS) process of pretreated swine manure, the dosage of 10 g/L GAC resulted in a higher biogas production compared to dosages of 20 and 30 g/L GAC, producing on average 30% more biogas and 23% more methane. However, it is important to note in Figure 1A that, at the beginning of the experiment, $10PSM_{GAC30}$ had a cumulative methane yield slightly higher than $10PSM_{GAC20}$ and much higher when compared to $10PSM_{GAC10}$. Therefore, a higher concentration of GAC promoted faster methane production. However, around day 55, methane production in $10PSM_{GAC10}$ surpassed the others, showing that there was a greater adaptation of microorganisms over time. Therefore, a lower concentration of GAC (10 g/L) was more satisfactory considering 90 days of the experiment.

On the other hand, by increasing the TS content from 10 to 15%, using a concentration of 10 g/L GAC, there was a reduction of 80 and 90% in cumulative biogas and methane yield, respectively. Biogas composition was only 34%, a value below that expected for anaerobic digestion, usually 50 to 70%. However, the methane composition was satisfactory for 20 and 30 g/L GAC (56-63% CH4). Compared with semi-dry AD, reactors with 20 g/L GAC showed a 20% reduction in the final methane yield, while with 30 g/L GAC, there was no significant difference (Table 1). This corroborates TOC_s results, in which there was only a reduction in TOC_s (30%) for the concentration of 30 g/L GAC. In comparison, $15PSM_{GAC20}$ presented very similar initial and final TOC_s values, and $10PSM_{GAC10}$ showed a 120% increase in TOC_s at the end process, indicating that the methanogenic step was ineffective.

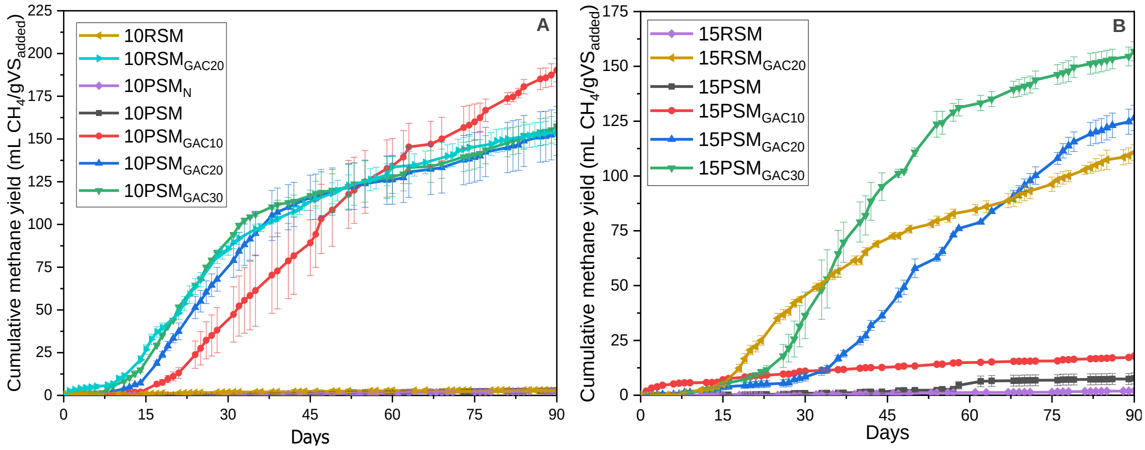

Figure 1 Cumulative methane yield of reactors at semi-dry (A) and dry (B) anaerobic digestion.

This occurs because dry AD presents limitations for substrate diffusion and negative effects on microbial metabolism due to the lower water content, and a low concentration of GAC could not offer greater resilience to the system. Thus, the mass transfer becomes more difficult, impacting intermediate product assimilation and reducing methane production efficiency.[5,9]

When raw swine manure was used in reactors without GAC addition, the TOC_s increased by 120% (10RSM) and 155% (15RSM). On the other hand, the reactors with GAC addition showed a reduction in the concentration of soluble organic matter (65% – $10RSM_{GAC20}$ and 30% – $15RSM_{GAC20}$). These results are in line with methane production (Figure 1B). The reactors without conductive material presented 56.4-68.8 mL/gVS of biogas but did not show significant methane production in the semi-dry or dry AD condition. The presence of GAC provided volumetric biogas yield of 275.6 and 201.1 mL/gVS for 10 and 15% of TS, respectively, and volumetric methane yield of 154 and 110 mL CH_4/gVS. Thus, by increasing the TS content, methane production fell by about 35%. This is due to the characteristics of swine manure combined with a high solids content (15%), meaning that the substrate is not easily digested, taking longer to be hydrolyzed and converted into methane during AD. As mentioned, the reactors only obtained significant methane production by adding GAC.

Finally, it is also noted that the pretreatment did not promote a significant difference in biogas yield, methane yield, and methane composition between reactors without GAC addition with raw and pretreated manure nor between reactors with 20g/L GAC addition with raw and pretreated manure under two conditions evaluated (10 and 15% TS). Hence, to optimize the production of methane-rich biogas, only the addition of the conductive material was necessary.

4 CONCLUSION

As a conductive material, GAC can exponentially improve methane production in AD without pretreatment. Increasing the TS content with raw manure reduced the methane yield by 35% even with GAC. For pretreated manure, the final methane production was higher at 10 g/L GAC for semi-dry and 30 g/L GAC for dry conditions. Therefore, the TS content influences the ideal GAC concentration in AD, and a higher GAC concentration makes the system more resilient to increasing TS content.

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