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AGRICULTURAL WASTE CHEMICAL PRETREATMENT WITH SODIUM HYDROXIDE AND UREA FOR THE OPTIMIZATION OF METHANE YIELD IN TWO-STAGE ANAEROBIC CODIGESTION

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ABSTRACT
This study addresses the valorization of organic agricultural waste for the energy generation. To this end, we evaluated the efficiency of chemical pretreatment of a mixture of straw (sugarcane, wheat, corn and soybean) with alkaline reagents on methane yield in anaerobic biodigestion processes. The pretreatment step was performed with two solutions, 3% sodium hydroxide and 2% sodium hydroxide/5% urea, with different contact times between substrate and reagent (24 and 48 h), compared to the sample without pretreatment (untreated wastes - UTW). In the subsequent anaerobic biodigestion step, the straw mixture was inoculated with animal manure (horse, swine and equine) and was performed under mesophilic conditions at 37°C for 37 days, in batch biodigesters (BMP - biochemical methane potential). The methane yield results indicated that the two systems with only sodium hydroxide (without addition of urea) resulted in greater methane accumulation per mass of volatile solids of residue (1.46 and 1.31 mL_{CH4}/g_{VS} for the systems pretreated only with NaOH for 24 and 48 hours, respectively). The results of low methane generation (compared to other similar studies reported in the technical literature) showed the need to optimize the biodigestion system for these substrates and inocula, especially with regard to parameters such as retention time of the biodigestion phases and nutrient content of the residue mixture.

KEY WORDS: Biodigestion, Biogas, Methanogenesis, Organic wastes.

RESUMO
O presente estudo aborda a valorização dos resíduos orgânicos da agricultura na geração de energia. Para isso, avaliou a eficiência do pré-tratamento químico de uma mistura de palhada (cana-de-açúcar, trigo, milho e soja) com reagentes alcalinos no rendimento de metano em processos de biodigestão anaerobia. A etapa de pré-tratamento foi conduzida com duas soluções, de 3% hidróxido de sódio e 2% hidróxido de sódio/5% ureia com diferentes tempos de contato entre substrato e reagente (24 e 48 h), comparativamente à amostra sem pré-tratamento (amostras não-tratadas – UTW). Na etapa subsequente, de biodigestão anaerobia, a mistura de palhada foi inoculada com dejeto animal (cavalo, suíno e equino) e conduzida sob condições mesofílicas a 37°C durante 37 dias, em biodigestores em batelada (do tipo *BMP – biochemical methane potential*). Os resultados de rendimento de metano apontaram que os dois sistemas apenas com hidróxido de sódio (sem adição de ureia) resultaram em maior acúmulo de metano por massa de sólidos voláteis de resíduo (1,46 and 1,31 mL_{CH4}/g_{VS} para os sistemas pré-tratados apenas com NaOH durante 24 e 48 horas, respectivamente). Os resultados de baixa geração de metano (comparativamente a outros trabalhos similares reportados na literature técnica) mostraram a necessidade de se otimizar o sistema de biodigestão para estes substrates e inóculos, especialmente no que se refere a parâmetros como tempo de retenção das fases de biodigestão e teor de nutrientes da mistura de resíduos.

PALAVRAS-CHAVE: Biodigestão, Biogás, Metanogênese, Resíduos orgânicos.

INTRODUCTION

Brazil is one of the largest food producers in the world regarding grain crops (maize, soybeans, wheat, rice, etc.), fruit and sugar cane. Although there is not precise data about the agricultural crop waste generation due to the different degrees of agricultural machinery used in Brazilian rural properties, data reported by Nogueira and Lora (2003) and EPE (2014) estimate the generation of 1.21 tons of soybean straw, 1.68 tons of maize waste (cob, straw and leaf), and up to 2.90 tons of wheat straw per each ton of grain produced in the country. Despite the destination of some of this waste as animal food, energy generation in boilers, and even improvement of the place where they are generated (soil moisture and nutrient control), the amount of agrowaste generated between the field and the food processing might be, on average, up to twice as much as the food harvested (EPE, 2014; NOGUEIRA and LORA, 2003), which shows that this waste destination alternatives are insufficient to meet the demands of the huge volume generated.

In such context, anaerobic digestion processes play a fundamental role as an alternative to the traditionally employed solutions of agrowaste disposal. In the last few decades, the use of agrowastes generated in the Brazilian rural properties has grown steadily. In addition to valuing the organic waste generated locally (such as biofuel in biodigesters) to produce energy, it contributes strongly to the reduction in carbon footprints in the farming sector. As a result of biodigestion, biogas and digestate appear as two relevant byproducts of the process that might be used in the same place where they are generated. Biogas is a methane-rich gaseous mixture (a compound with high heating value); while digestate is an important soil conditioner with high nutrient content (DEUBLEIN and STEINHAUSER, 2011; LOPEZ et al., 2016; MORALES-POLO et al., 2018). The efficiency of the anaerobic digestion process depends on several factors, such as the biodigested substrate composition, moisture content, pH and the medium temperature, nutrient content, volatile solids, etc.

Even being a renewable, abundant and low-cost raw material for the production of biogas, the agrowaste is a lignocellulosic biomass and, as a consequence, is not easily degraded in anaerobic conditions. Therefore, regarding agrowastes, one of the main challenges is to reduce lignin content and crystallinity of cellulose and, consequently, promote increased biodigestibility of the digested material (MANKAR et al., 2021; SCHIRMER et al., 2023).

The lignocellulosic biomass pretreatment has been widely investigated as a preliminary phase aiming to optimize methane yield in anaerobic biodigestion processes, and several pretreatment processes have been evaluated in this context (both individually and combined). Physical, chemical (with chemical reagents), and biological pretreatments are most commonly found in the technical literature applied to the delignification of the lignocellulosic substrates. As regards chemical pretreatment, acids and strong bases are the most used, such as sulfur (H_2SO_4) and hydrochloric (HCl) acids, sodium (NaOH) and potassium (KOH) hydroxides, etc. You et al. (2014) observed a reduction of up to ≈33% in the biodigestion time and increased methane yield when codigesting pretreated corn stover with swine manure: in better experimental conditions, those authors obtained 350 mL_{CH4}/g_{VS} (corn stover pretreated with 6% NaOH and 35ºC, for 3h) compared to 249 mL_{CH4}/g_{VS} obtained with untreated corn stover.

Agrowastes show characteristic low nitrogen concentrations and high carbon concentrations. Therefore, codigestion with animal manure (swine, cattle, sheep, goat, etc.) or even nitrogen supplements (adding urea, for example) might be crucial to balance carbon and nitrogen sources in the system, thus allowing optimal C/N ratio for the anaerobic biodigestion process. Some authors also evaluated the use of urea as a chemical reagent in the maize pretreatment phase and obtained positive results concerning methane yield (MOHSENZADEH et al., 2012; SHA et al., 2024; XIE et al., 2022).

Taking all that into account, this study aimed to assess the performance of chemical pretreatment of a mixture of co-digested agricultural waste with animal manure to optimize the main substrate methane yield. The pretreatment phase employed NaOH and a NaOH/urea mixture in the lignin removal from the substrate. Next, the biodigestion phase was preceded by a fermentation phase, to optimize methane generation in the following phase (methanogenic step).

MATERIAL AND METHODS

Substrates and inocula

A mixture of corn, wheat, sugarcane and soybean straw was used as the main substrate of the study. The waste was ground in a Willye knife mill, mixed in equal proportions on volatile solid basis (1 g_{VS} of each crop) and sieved in an 8-Tyler mesh sieve (2.36 mm aperture), 10-Tyler mesh sieve (1.70 mm aperture), 12-Tyler mesh sieve (1.40 mm aperture), 16-Tyler mesh sieve (1.00 mm aperture).

Swine, bovine and equine manures were used as inoculum, after being collected on rural properties and mixed together in the 3:2:1 g_{VS} bovine:horse:swine manures rate (proportion adopted as a function of the animal manure availability).

Experimental methodology

Pretreatment of the substrates

The waste straw (without inoculum) was pretreated according to the reagent concentration conditions and substrate/reagent contact time detailed below (Table 1). The straw was kept at ambient temperature throughout the pretreatment.

Table 1.Chemical pretreatment: reagent concentration and contact time. Source: the authors

Mixture	NaOH/urea concentration(2)	Pretreatment time (h)
Untreated wastes (UTW)(1)	0	0
NaOH 3-24	3%/0%	24
NaOH 3-48	3%/0%	48
NaOH/urea 24	2%/5%	24
NaOH/urea 48	2%/5%	48

(1) Untreated mixture (control) (2) Dry weight basis

Analytical methods

a) Structural analysis of pretreated substrates

The morphological structure of the pretreated and untreated mixtures (Table 1) was investigated using scanning electron microscopy – SEM (TESCAN model VEGA3 LNU), aiming to relate methane production with the degree of delignification of the substrates.

b) Characterization of the substrates

Inoculum and mixtures (pretreated and untreated) were evaluated according to the parameters listed in Table 2. The lignin and holocellulose content (sum of cellulose and hemicellulose) were evaluated before and after pretreatment to verify the action of alkaline reagents in the delignification process.

The biodigestion process was divided into two phases. When fermentation started (1st phase), pH was adjusted to 5.5 (suitable condition for the substrate hydrolysis and acidogenesis phases); while during methanogenesis (2nd phase) the initial pH was adjusted to 7.0 (a more favorable condition to the methanogenesis phase) (DEUBLEIN and STEINHAUSER, 2011; SILVA et al., 2018). The initial moisture content in the bioreactors was adjusted to ≈90% in both phases.

Table 2. Physicochemical parameters of the substrates evaluated in the experiment. Source: the authors

	Before pretreatment		After pretreatment	Methanogenesis phase						
Parameter	UTW	Inoculum	Agricultural waste3(1)	UTW +inoc.	Inoculum	NaOH 3-24	NaOH 3-24	NaOH/urea 24	NaOH/urea 48	Method or reference
Holocellulose	•	-	•	-	-	-	-	-	-	Goldschimid (1971), TAPPI (2014, 2015, 2017)
Lignin	•	-	•	-	-	-	-	-	-	
Volatile solids (VS)	•	•	-	•	•	•	•	•	•	Muffle (550°C for 2,5 h)
Total ammonia nitrogen (TAN)	-	-	-	•	•	•	•	•	•	Method 8038 USEPA (Nessler)
Chemical oxygen demand (COD)(2)	-	-	-	•	•	•	•	•	•	APHA (2017)

(•): Determined (-): Undetermined
(1) NaOH 3-24, NaOH 3-48, NaOH/urea 24 and NaOH/urea 48 (2) Soluble COD

Anaerobic digestion

Both the fermentation and the methanogenesis phases were conducted in 250-mL borosilicate flasks, adapted with accessories for monitoring and discharging the biogas generated (Figure 1).

In the fermentation phase (acidogenic), the inoculum (animal manure) mentioned in item 2.1 was added to each mixture specified in Table 1 (UTW, NaOH 3-24, NaOH 3-48, NaOH/urea 24 and NaOH/urea 48) in the substrate-inoculum ratio of 0.5 g volatile solids (0.5 g_{VS}). In the initial phase, all treatments were carried out in triplicate and remained in oven (at 37°C) for 5 days. Before sealing the biodigesters (incubation), a nitrogen gas current (N_2) was recirculated through the flask headspace to guarantee the system anaerobiosis. At this point, the fermentation phase was adopted as the inoculum adaptation phase for the methanogenesis.

In the methanogenic phase, inoculum (animal manure) was added again to each treatment (UTW, NaOH 3-24, etc.) to keep the substrate-inoculum ratio of 0.5 g volatile solids (0.5 g_{VS}) adopted in the previous phase. In this second phase, the treatments were conducted in triplicate again and kept in oven (at 37°C) until absence of biogas generation was observed (as a parameter, we adopted generation below 3% of the initial volume generated). Before sealing the biodigesters (incubation), nitrogen gas (N_2) was recirculated again through the flask headspace. Biodigesters containing only inoculum (blanks) were also monitored; the biogas volume generated in the blanks was subtracted from the volume of biogas generated in the treatments UTW, NaOH 3-24, etc.

Figure 1: Biodigesters flasks incubated at 37°C. Source: the authors

Biogas monitoring

The biogas generated in each biodigester was periodically monitored according to the pressure indicated in the system manometer (Figure 1), converted into biogas volume following the ideal gas law (SCHIRMER et al., 2023; SCHIRMER et al., 2024). The frequency of methane determination in the biogas depended on the gas generation (accumulated volume) in the biodigesters. In this study, five methane measurements were conducted throughout the 37-day biodigestion period. The biogas composition was determined using a gas analyzer, Columbus (*Columbus Instruments*), with infrared (IR) sensors to determine methane and carbon dioxide in bands from 0 to 100% (SCHIRMER et al., 2022). The methane monitoring results throughout the biodigestion period were expressed in methane volume generated per mass of substrate volatile solids (mL_{CH4}/g_{VS}).

RESULTS AND DISCUSSION

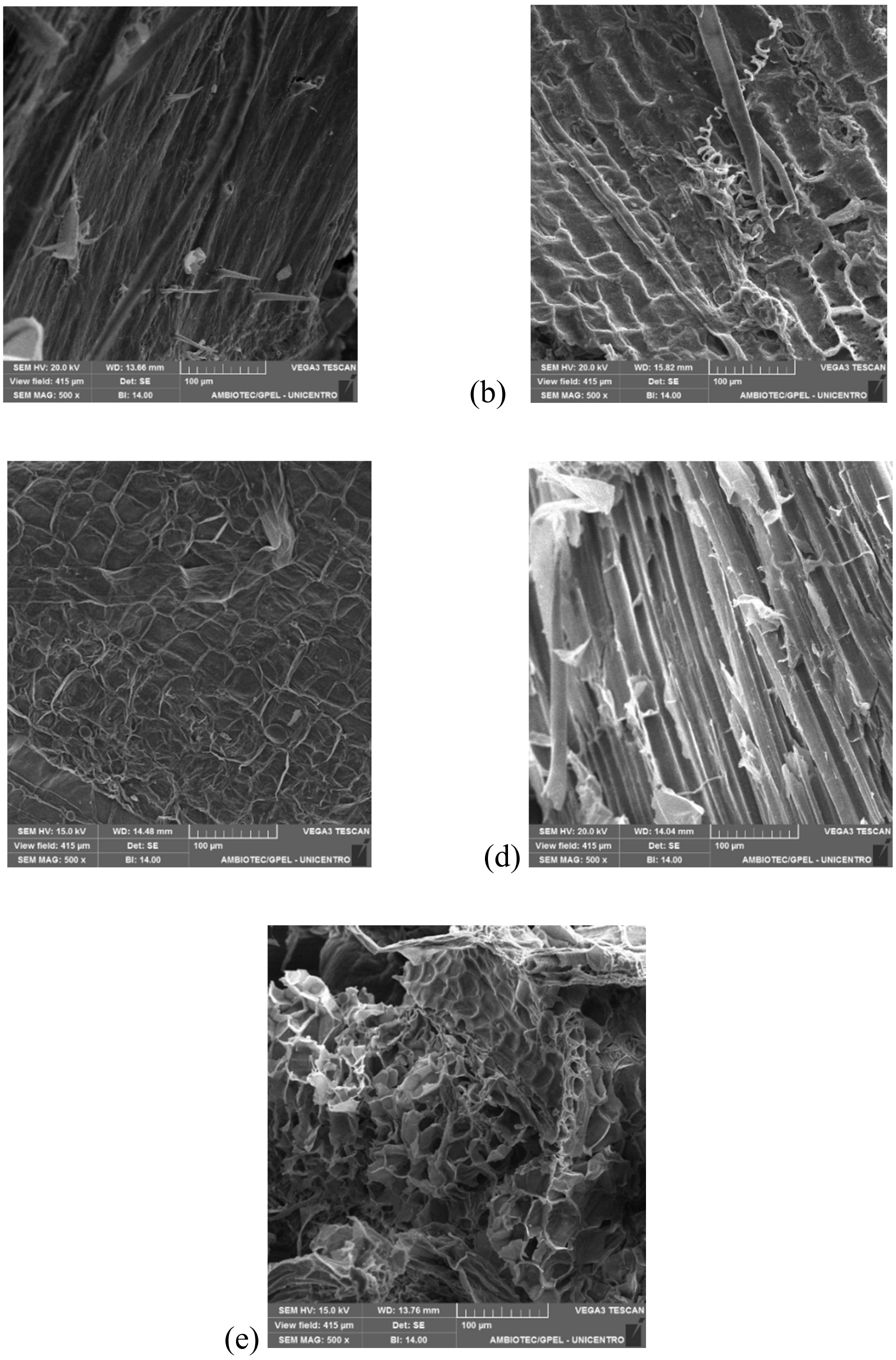
Waste pretreatment

Table 3 and Figure 2 show the pretreatment results for mixtures NaOH 3-24, NaOH 3-48, NaOH/urea 24 and NaOH/urea 48, compared to the untreated straw (UTW).

Table 3. Holocellulose and lignin content of chemically pretreated waste. Source: the authors

	Straw pretreatment condition(*)				
Substrate	UTW	NaOH 3-24	NaOH 3-48	NaOH/urea 24	NaOH/urea 48
Holocellulose	47.4	39.8	47.3	45.0	58.1
Lignin	19.6	32.0	14.4	23.4	25.8

(*) Straw mixed in equal proportion on volatile solid basis (1 g_{VS} of each crop)



(a) (b) (c) (d) (e)

Figure 2: Scanning electron microscopy (SEM) images of chemically pretreated waste: (a) UTW; (b) NaOH 3-24; (c) NaOH 3-48; (d) NaOH/urea 24; (e) NaOH/urea 48. Source: The authors.

The values obtained (Table 3) do not clarify completely the action of alkaline reagents (NaOH and urea) in the lignin removal, mainly in relation to the "UTW" and "NaOH 3-24" treatments. We also observed that the reduction in the concentration of a strong base (NaOH) and inclusion of a weak base in a higher concentration (urea) did not contribute significantly to the reduction in lignin content in the "NaOH/urea 24" and "NaOH/urea 48" treatments, while a longer time of exposure of the substrate to sodium hydroxide (from 24 to 48 h) seems to have been more efficient in this aspect. In fact, except for the NaOH/urea 24 waste, more severe treatment conditions regarding contact time between the fibers and NaOH resulted in changes in the lignocellulosic structure of the pretreated mixtures, when compared to the UTW mixture structure (with better "aligned" fibers).

Characterization of substrates and inocula

The waste (straw) segregation by means of sieving showed that most of the material remained on the bottom sieve (61,9%). The 2.33 mm, 1.7 mm, 1.4 mm and 1.0 mm sieves retained, respectively 8.8%, 8.1%, 3.2% and 17.8% mass, revealing predominance of finer particles of organic waste, therefore, highly favorable to the biodigestion process (high specific surface area). Table 4 shows the volatile solids content (VS), pH and moist of all agrowastes prior and post-mixture.

Table 4. Physicochemical characteristics of straw (substrate) and animal manure (inoculum). Source: the authors

	Before mixture							After mixture	
Parameter	WS	CS	SCS	SS	BM	SM	HM	Straw (1)	Manure (2)
Moisture content (%)	12.7	27.5	8.3	43.3	84.1	72.0	82.1	30.7	80.6
pH	-	-	-	-	-	-	-	5.8	7.6
VS (%)	93.8	90.6	87.5	91.8	82.0	67.3	84.2	93.8	84.9

(WS): wheat straw; (CS): corn straw; (SCS): sugarcane straw; (SS) soybean straw
(BM): bovine manure; (SM): swine manure; (HM): horse manure
(1) Straw mixed in equal proportion on volatile solid basis (1 g_{VS} each crop)
(2) Inoculum: different animals' manure mixed in the 3:2:1 g_{VS} bovine:horse:swine manures ratio

The pH and moisture content values confirmed the importance of adding inoculum to the substrate to keep those two parameters for the methanogenesis phase, which requires initial values close to neutrality, regarding pH (DEUBLEIN and STEINHAUSER, 2011), and above 60% concerning moisture (USEPA, 1991). The volatile solids content in the straw mixture (≈94%) revealed the substrate high potential to convert into biogas. Table 5 shows the values of physicochemical parameters of the mixtures before and after the methanogenesis phase.

Table 5. Degradation parameters of pretreated straw mixtures (with inoculum) before and after the biodigestion process. Source: the authors

	Before incubation						After incubation					
	Treatment (mixture)						Treatment (mixture)					
Parameter	Inoculum	UTW	NaOH 3-24	NaOH 3-48	NaOH/ urea 24	NaOH/ urea 48	Inoculum	UTW	NaOH 3-24	NaOH 3-48	NaOH/ urea 24	NaOH/ urea 48
M.C. (%) (1)	≈90%						ND (3)					
pH	7.2	7.1	7.1	7.1	7.1	7.1	5.8	5.5	5.1	5.7	ND (3)	5.3
VS (%)	(2)	(2)	83.5	83.5	86.6	86.2	51	45.1	38.2	41.8	ND (3)	48.7
COD ($mg.L^{-1}$)	9860	9945	10185	10310	10050	10225	327	400	429	191	ND (3)	401
TAN ($mg.L^{-1}$)	683	600	445	598	403	490	ND (3)					

(1) M.C.: Moisture content (2) Value in Table 3 (3) ND: undetermined

The determination of ammoniacal nitrogen concentrations is highly relevant in biodigestion processes in which the existing substrates might contain high nitrogen levels. In such cases, in addition to animal manure (which might contain a significant amount of urine mixed to the feces), the addition of urea to NaOH during the pretreatment phase is a factor that might contribute to the formation of ammonium nitrogen (NH_4^+) and ammonia (NH_3), two well-known inhibitors of the biodigestion process. However, the values found (Table 5) are below the necessary levels for the inhibition of the process by part of those species (YENIGÜN and DEMIREL, 2013). The soluble COD reduction was over 96% in all treatments, thus indicating good conversion of the soluble organic matter into byproducts of this process (such as biogas). However, the SV final values kept high content of biodegradable organic matter which was not consumed during the process. Finally, the pH low final values in all treatments suggest some process instability, that is, it is highly likely that the pH reduction commonly observed at the beginning of the biodigestion (formation of volatile fatty acids - VFA) was not satisfactorily buffered in the subsequent phases of the process. This might compromise the methanogenesis efficacy, thus resulting in low methane generation.

Biogas generation monitoring

Figures 3 and 4 show, respectively, the biogas total volume and the methane volume generated per substrate mass (mass of volatile solids). The data reported consider only biogas and methane net values (subtracting the biogas and methane generated in the blanks).

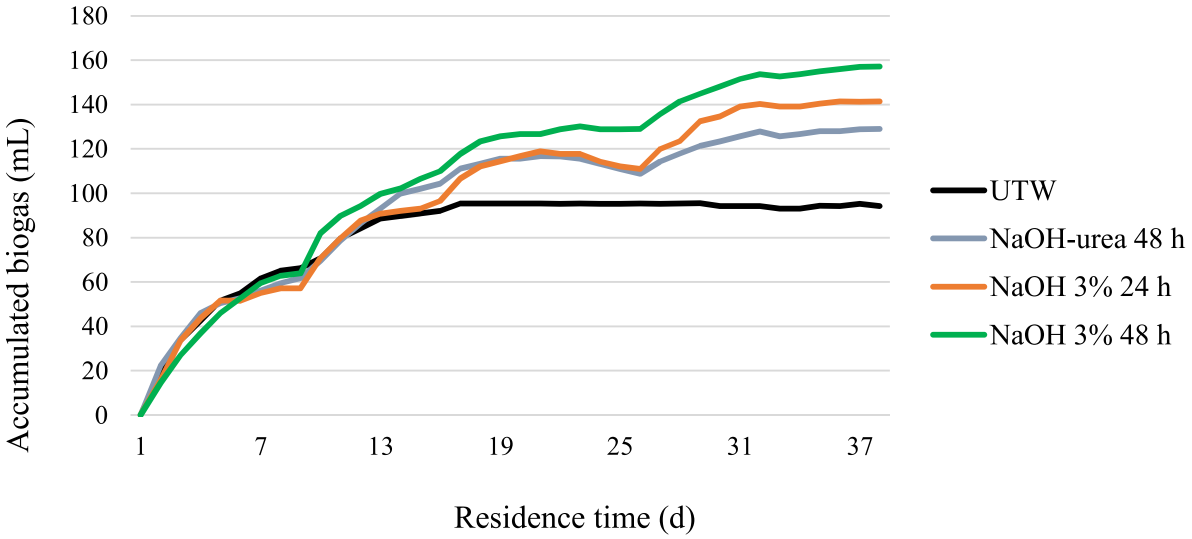


Figure 3: Biogas total volume accumulated during the incubation period. Source: the authors.

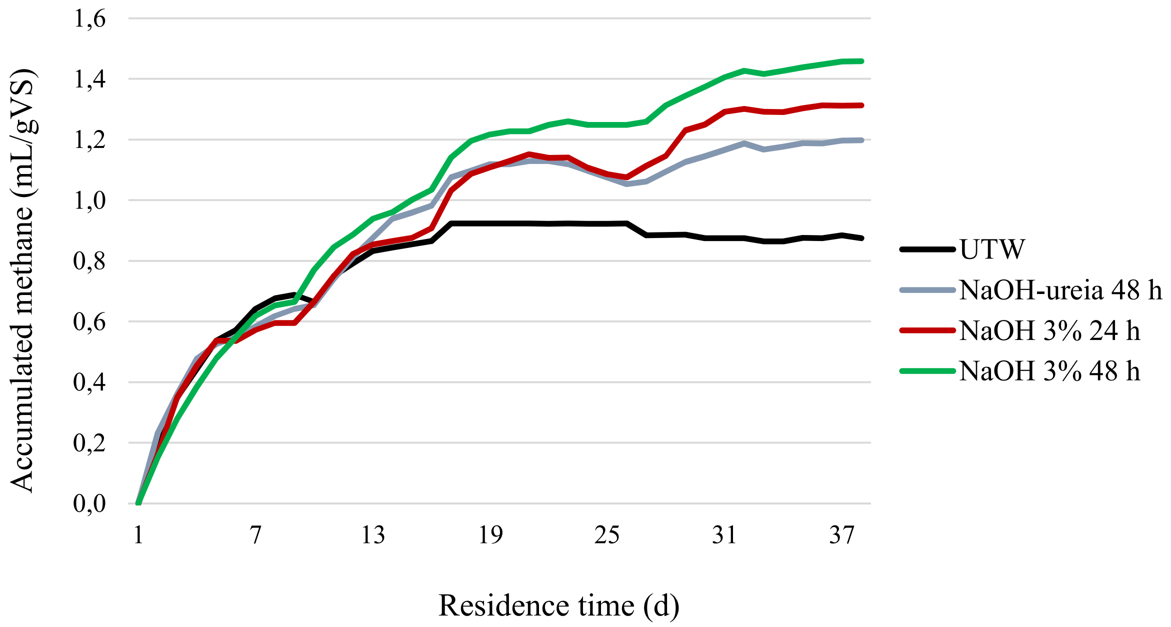


Figure 4: Methane volume accumulated per biodigested waste mass generated during the incubation process. Source: the authors.

Most of the biogas is generated in the first ten days of biodigestion. During this period, the easily degradable organic matter is consumed fast and both the anaerobiosis (set from the process start up) and the high proportion of inoculum in relation to the amount of substrate (straw) also contribute to the high biogas production in the first few days of incubation of the mixtures. The "NaOH-urea 24 h" treatment did not generate biogas from the first day of incubation. This fact might be ascribed to the poor initial anaerobiosis condition (with nitrogen gas) since the biogas generated in the "NaOH-urea 48 h" treatment rules out the possibility of souring of the digesters as a result of some urea excess. Therefore, we observed that the urea addition, originally aiming at the pretreatment improvement and supply of nutrients for the process did not contribute to biogas and methane yields. Conversely, it generated less biogas (Figure 3) and methane (Figure 4) per mass of substrate in comparison to the substrates pretreated only with sodium hydroxide ("NaOH 3% 24h" and "NaOH 3% 48h"). Considering the last two cases, the longer hydraulic detention time seems to have contributed to higher pretreatment efficiency and, therefore, to the substrate conversion into biogas and methane. This fact is confirmed by the final lower VS and COD content observed (Table 5) in the "NaOH 3% 48h" treatment. As regards the process yield, we observed low generation of both biogas and methane when compared to other studies reported in the literature using the same substrate and inoculum. The low biogas generation observed (Figure 3) is probably due to the maintenance of the process first phase; the 5 days of the fermentation phase might have exceeded the optimal residence time required by this substrate, inoculum, and the process nature (batch biodigester, organic loading rate, etc.). Even the pH final values (all below 6) confirmed some imbalance in the process in all biodigesters. Methane concentrations (included in Figure 4 values) measured on four occasions throughout the incubation period also revealed low values (all below 35%), in comparison to the theoretical 50-70% reported in the literature in ideal conditions of anaerobic biodigestion.

CONCLUSIONS

When analyzing the main physicochemical parameters of the methane generation process monitored throughout 37 days of incubation under mesophilic conditions, we concluded that both the waste pretreatment phase and the biodigestion separation into two phases (fermentation and methanogenesis) could have been optimized for this process specific conditions and as a function of the co-digested substrates. Among the process yield conditions evaluated, the waste pretreated with sodium hydroxide only for 48 hours seemed to be the most promising procedure regarding lignin removal and methane yield.
This study evaluated biogas and methane yields from a mixture of chemically pretreated agricultural waste straw under different concentration of alkaline reagent (NaOH and urea) conditions and contact time between reagents and substrate. When analyzing the main physicochemical parameters of the methane generation process monitored

throughout 37 days of incubation under mesophilic conditions, we concluded that both the waste pretreatment phase and the biodigestion separation into two phases (fermentation and methanogenesis) could have been optimized for this process specific conditions (high organic loading rate, batch biodigestion, fermentation time, etc.) and as a function of the co-digested substrates. Among the process yield conditions evaluated, the waste pretreated with sodium hydroxide only for 48 hours seems to have been the most promising regarding lignin removal and methane yield.

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